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Mark D. Purgett  
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POLYMERS AND COPOLYMERS FROM  $\omega$ -FUNCTIONALLY-SUBSTITUTED  $\alpha$ -OLEFINS

A Dissertation Presented

by

MARK DODD PURGETT

Submitted to the Graduate School of the  
University of Massachusetts in partial fulfillment  
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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1984

Polymer Science and Engineering

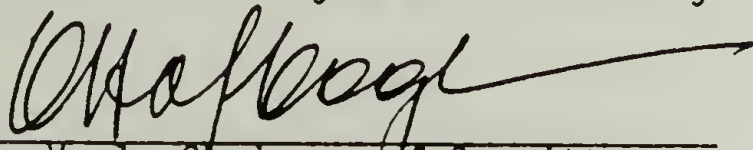
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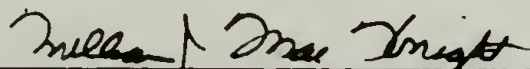
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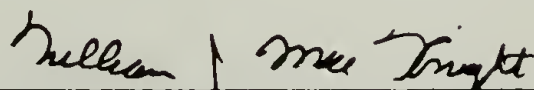
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Praise to Jesus Christ from whom all blessings flow

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Most of all I wish to thank God for the blessing of native intelligence and the opportunity to complete my formal education.

## ABSTRACT

### Polymers and Copolymers From $\omega$ -Functionally-Substituted $\alpha$ -Olefins

(February 1984)

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The polymerizability of  $\omega$ -functionally-substituted  $\alpha$ -olefins containing pendant carboxylic ester groups was investigated as a function of the (a) ester substituent group, (b) methylene spacer chain length, (c) initiator composition, (d) component stoichiometry and (e) other reaction parameters. Several high molecular weight isotactic homopolymers were prepared utilizing titanium-based Ziegler-Natta initiator systems in both solution and slurry processes. Copolymers of 2,6-dimethylphenyl 10-undecenoate with 1-dodecene, 1-hexene, propylene and ethylene were synthesized using functional monomer feed ratios of 0, 10 and 20 mole percent. Terpolymers with ethylene and propylene using titanium and vanadium-based initiators were also prepared, resulting in crystalline and amorphous products respectively.



All products were characterized by standard techniques including infrared,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, dilute solution viscometry and elemental analysis.

Representative polymers were neutralized to the corresponding sodium carboxylate salts and acidified to the polycarboxylic acid derivatives. Physical property evaluation of the parent ester-substituted polyolefins and these derivatives were performed using differential scanning calorimetry, X-ray diffraction (WAXD), thermogravimetric analysis and dynamic mechanical techniques.

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# C H A P T E R   I

## INTRODUCTION

This dissertation describes the synthesis and coordination polymerization of  $\omega$ -functionally substituted  $\alpha$ -olefins. The principal objectives of this research were the preparation and characterization of functionalized olefin polymers and copolymers containing ester, sodium carboxylate or carboxylic acid groups separated from the polymer backbone by a flexible hydrocarbon spacer chain of specified length. This study is part of a continuing investigation of functionally-substituted polymers conducted within this research group. Previous efforts have addressed the preparation and properties of poly(alkylene oxides) with similar substitution.<sup>1-4</sup>

Advances in the correlation of structure-property relationships have resulted in increased emphasis on molecular design of functional polymers for specialty applications. Interest in the functionalization of linear hydrocarbon polymers stems from the potential for enhancement of the chemical, mechanical and rheological properties of this important class of polymers.

This introductory chapter will discuss the preparation and characteristics of functionally-substituted poly( $\alpha$ -olefins). Section 1 provides an overview of the developments of coordination polymerization of ethylene and  $\alpha$ -olefins. Emphasis will be placed on evolution of stereospecific Ziegler-Natta initiation systems since their discovery thirty years ago. Section 2 will focus on application of this

technology to the homopolymerization of olefin monomers containing heteroatoms, particularly silicon, halogens, nitrogen and/or oxygen. Special consideration is placed on the effect of the functional group on the polymerizability of the monomer via an anionic coordinate insertion mechanism. Section 3 will discuss the preparation of copolymers and terpolymers from these "polar" monomers by reaction with ethylene, propylene and higher  $\alpha$ -olefins. Section 4 will deal with modification reactions of functionally-substituted polyolefins; specifically the rationale for preparation of polymers and copolymers containing pendant carboxylic acid and carboxylate salt groups. The effects of these moieties on the chemical, physical and rheological properties of the polymer, as well as subsequent applications for these ionomers and polyelectrolytes will be discussed.

#### A. Functionally-Substituted Polyolefins

##### 1. Historical perspectives on stereospecific olefin polymerization.

The earliest reported coordination polymerization was the cationic polymerization of vinyl isobutyl ether by Schildknecht in 1947.<sup>5</sup> Additional references describe the polymerization of ethylene utilizing titanium tetrachloride-aluminum-aluminum chloride, and the polymerization of styrene via phenylmagnesium bromide -  $\text{Ti}(\text{OBu})_4$ .<sup>6,7</sup>

In 1949 Ziegler and Gellert demonstrated that aluminum hydride reacts with ethylene at 60 - 80°C to yield triethylaluminum, which upon increase of the temperature to 100 - 120°C reacts with additional ethylene to give higher alkyls of aluminum.<sup>8-10</sup> At still further elevated

temperatures these alkyls were found to react with ethylene to generate olefins and triethylaluminum by means of a displacement reaction. This sequence therefore represents a catalytic process for the preparation of higher olefins from ethylene. Subsequent experiments fortuitously led to the observation that a small amount of nickel accelerated the displacement reaction, resulting in a nearly quantitative yield of 1-butene.<sup>11-12</sup> A systematic investigation was undertaken by Ziegler and his school to identify other metals that exhibited a similar catalytic effect.<sup>12-14</sup> In a key experiment utilizing zirconium acetylacetonate, a mass of polyethylene was formed rather than the anticipated lower olefins. Further work revealed that other transition metals had analogous activity to promote the polymerization of ethylene. Of the transition metals studied by Ziegler, compounds of titanium were found to be particularly effective polymerization initiators.

Ziegler and coworkers were primarily concerned with the polymerization of ethylene and its copolymerization with  $\alpha$ -olefins. Following licensing of this technology to Montedison, Natta quickly showed that these initiator systems also polymerized monosubstituted olefins including propylene, 1-butene and styrene. In addition, Natta demonstrated that these polymerization reactions were stereospecific, and prepared the sterically differentiated polymers.<sup>15-18</sup>

It had thus been demonstrated that transition metal derivatives of group IV to VIII of the periodic table, typically halides, alkoxides and acetylacetonates in an oxidation state lower than

maximum, in combination with metal alkyls or hydrides of group I to IV, result in complex initiator systems which stereospecifically polymerize  $\alpha$ -olefins. The systems are now collectively referred to as the Ziegler-Natta initiators or catalysts.

The scope of Ziegler-Natta initiators is very broad and initiator combinations and reaction conditions have been developed which also polymerize monomer types including dienes, cycloolefins, acetylenes, disubstituted ethylenes and others.<sup>19</sup> Many of these polymers are of commercial importance but are outside the scope of this study, which will be restricted to the polymerization reactions of ethylene, propylene and higher  $\alpha$ -olefins.

Polymerization with Ziegler-Natta initiators is one of the broadest based and most significant discoveries of the last 30 years of polymer science, and has been widely reviewed.<sup>10,19-33</sup> Their discovery has virtually created a new polymer industry. Independently of Ziegler and Natta, others including Vandenberg at Hercules and Baxter and coworkers at DuPont also discovered techniques for the polymerization of propylene.<sup>34-36</sup> Other initiators for the preparation of linear polyethylene was discovered by Hogan et al. for Phillips Petroleum and by Zletz et al. for Standard Oil of Indiana.<sup>37-40</sup> Examples include oxides of chromium, molybdenum, cobalt and nickel, supported on silica or alumina. These systems were found to produce linear stereoregular polypropylene, but with lower efficiency and degree of stereoregularity. The result of this burst of activity was a five-way patent interference on a composition of matter claim for crystalline



polypropylene.<sup>41</sup>

Many initiator combinations have been reported since those originally evaluated by Ziegler and Natta. Of the transition metal derivatives, the most significant are the halides, subhalides and oxyhalides of titanium, vanadium, zirconium and chromium. Others worthy of note are compounds of iron, cobalt, scandium, nickel, molybdenum and tungsten.<sup>17,18</sup> While the halide derivatives have received the most attention, other ligands including alkoxyl, phenyl, acetylacetonyl and cyclopentadienyl groups may be incorporated. The organometallic components most utilized are the alkali-metal alkyls, alkyl hydrides and alkyl halides of aluminum. The alkyls of zinc, tin, lead, cadmium and beryllium as well as Grignard reagents also demonstrate activity.<sup>42</sup>

Experimental techniques for combination of these components also vary widely, and greatly influence the form and activity of the resulting active complex. Techniques include (a) in situ combination of the organometallic with the transition metal compound in its highest valence state, such as  $\text{TiCl}_4$ <sup>43</sup>, (b) the in situ combination of an organometallic with a crystalline, reduced metal compound, such as  $\text{TiCl}_3$ <sup>44</sup>, and (c) the prereaction of the organometallic and a transition metal compound in its highest valence state in the absence of polymerizable monomer, typically in a hydrocarbon diluent. The result of this prereaction step can be a crystalline  $\text{TiCl}_3$ -containing solid, which is then combined with additional organometallic component and the monomer(s).<sup>45-47</sup> Polymerization processes for olefins utilizing the previously described components may result in homogeneous, colloidal

or heterogeneous systems, which may be conducted in the solution, slurry, fluidized bed or gas phase. The broad spectrum of initiator components, methods of combination and reaction conditions results in wide variation in the activity, efficiency and stereospecificity of the active initiator as well as the composition and morphology of the resulting polymer.

The development of these stereospecific initiators may be divided into three main periods or "generations". During the first period, research efforts concentrated on the titanium-based systems originally documented by Ziegler and Natta et al. with only slight modifications. These are now referred to as the "first generation" initiators. Forsman reported that the original Ziegler processes were based on the beta (brown) form of  $\text{TiCl}_3$ , which gave very low yields of crystalline polypropylene with most of the product being an amorphous rubber.<sup>48</sup> The early investigations of propylene polymerization by the Natta school were done with pure alpha  $\text{TiCl}_3$ , prepared by reduction of  $\text{TiCl}_4$  with  $\text{H}_2$  at elevated temperatures (500 - 800°C).<sup>49</sup> The gamma form was subsequently prepared by heating of the beta modification to 100 - 200°C, and the delta form by prolonged ball milling of the alpha or gamma forms.<sup>50-52</sup> There now exists a large number of methods for preparation of these modifications, in which  $\text{TiCl}_4$  is reduced with hydrogen, aluminum metal, aluminum alkyls and/or aluminum trichloride, under very specific conditions.<sup>53</sup>

In 1955 Vandenberg and coworkers at Hercules developed highly stereospecific initiators based on crystalline  $\text{TiCl}_3$  containing

stoichiometric amounts of aluminum trichloride, prepared by reduction of  $\text{TiCl}_4$  with aluminum metal. This modification has found major applications in the manufacture of polypropylene. Further improvements for preparation of  $\text{TiCl}_3 \cdot x \text{AlCl}_3$  systems were found and developed by Exxon, Stauffer and others.<sup>52</sup> Heterogeneous solutions of  $3\text{TiCl}_3 \cdot \text{AlCl}_3$  combined with diethylaluminum chloride are still employed, with this titanium modification referred to as  $\text{TiCl}_3\text{AA}$ , with titanium trichloride in the delta form.

Although the industrially important  $\delta\text{-TiCl}_3\text{AA}$  is highly stereospecific, its efficiency is low; 3000 - 5000 grams of polymer per gram of titanium derivative. This necessitates removal of the initiator residue via undesirable and costly purification procedures. On this basis, "second generation" systems were developed, which may be described as  $\text{TiCl}_3$ -based systems modified by the incorporation of additives or third components, generally organic in nature. Examples include Lewis bases such as esters, amines, ethers and organic phosphorus derivatives.<sup>54</sup>

The literature includes various and conflicting rationale as to the role of these donor atoms. Proposed concepts include the selective poisoning of less stereospecific centers<sup>55</sup>, complexation (and removal) of substances which act as poison to the active sites<sup>56</sup>, stabilization of active site structure<sup>57</sup> and to decrease the reducing power of the aluminum alkyl.<sup>58</sup> Use of these third components has resulted in further enhanced stereospecificity and a five-fold increase in activity. However, this level is still not sufficient to eliminate



the need for purification steps to remove metal residues.

A better understanding of the inherent limitations of generation two systems as well as the basis of a third generation may best be obtained by focusing on the nature, number and stability of the active polymerization sites. Despite the incredible amount of scientific literature detailing Ziegler-Natta polymerizations, the nature of the active site(s) and mechanism have not been fully elucidated. While full details are not yet available, the general outline appears clear. It is generally agreed that chain propagation occurs on the transition metal which has been previously complexed, alkylated and/or reduced by the organometallic component. The simplest view is that the growing chain end is a transition metal-carbon bond. Propagation occurs when the olefin coordinates at a vacant coordination site of the transition metal, followed by insertion into the Ti-C bond via a four-center addition. The general mechanism is referred to as coordinate anionic insertion, with the chain end formally considered as an anion.<sup>20</sup> Many reviews are available on this subject presenting models for stereospecific initiation. These models generally fall into two categories, differing on the structure of the active center. The structures of the active centers may be represented by the models of Cossee, and Rodriguez and van Looy, which portray the monometallic and bimetallic mechanisms respectively.<sup>59-63</sup> The complexity of the reactions which take place on the surface of the initiator as well as the instability and low concentration of active centers have made experimental confirmation of these models inconclusive. However, much is known about the



morphology of the initiator surface. X-ray crystallography reveals that  $\text{TiCl}_3$  is composed of alternating layers of titanium and chlorine atoms.<sup>30</sup> Only a small fraction of the titanium atoms are active centers, and these are thought to be located on lateral faces, edges and crystal imperfections. Estimates based on  $^{13}\text{C}$  labelling experiments place the maximum number of active sites at approximately  $1.5 \times 10^{-3}$  mole per mole of titanium derivative.<sup>64,65</sup> This accounts for the poor efficiencies of the  $\delta\text{-TiCl}_3/\text{AlR}_3$  systems, and so is the limiting factor in second generation initiators. However, it is essential to bear in mind that other experiments demonstrate that a count of the active sites at any instant is only part of the picture, since active centers can be formed and activated throughout the polymerization and as a consequence of the polymerization reaction.

Conventional  $\text{TiCl}_3$  systems may thus be viewed as "self-supported", where most of the titanium is not exposed, not active, and a source of product contamination.<sup>54</sup>

Third generation systems address this limitation by chemically bonding the titanium component onto an inert solid support including oxides, halides, hydroxides or alkoxides of magnesium, as well as silica or alumina.<sup>54</sup> An essential requirement of this approach is that the support be noncorrosive and innocuous, particularly with respect to polymer stability. By mounting the transition metal on an inert support in the proper manner, the number of active sites can be greatly increased.

While these new systems demonstrated high activity and utility

for ethylene polymerization, they were found to be quite poor for polymerization of propylene in terms of rate, yield and isotacticity index.<sup>54</sup> Modification of these supported systems to achieve the required stereospecificity without compromising activity was the next objective, which was attained by reintroduction of the now familiar Lewis base donors which found application in generation two systems.

Montedison and Mitsui Petrochemical Company received patents in 1974 for  $\text{MgCl}_2$ -supported titanium initiators suitable for propylene polymerization, as well as subsequent patents dealing with promoters to further enhance their performance.<sup>66-68</sup> A typical claim reports yields of  $2.4 \times 10^5$  g polypropylene per g of Ti, with an isotacticity index of 95%.

These high-mileage systems are prepared by complex techniques incorporating the titanium derivative, aluminum alkyl and donor molecules including organic esters (notably ethyl benzoate), alcohols and phenols. The literature includes countless examples reporting the use of additives, modifiers, third components or stereoregulators, which have been found to affect the polymerization reaction or polymer properties in a desirable manner. Most references involve the preparation of polypropylene. For example, DMF has been employed to increase molecular weight ( $\text{DMF}/\text{Al} = 0.3 - 0.6$ ).<sup>69</sup> Stereoregulators include  $(\text{Me}_2\text{CHO})_3\text{P}$ ,  $(\text{BuO})_2\text{POH}$  and  $\text{MeP}(\text{O})(\text{OPh})_2$ .<sup>70</sup> Addition of isoamyl ether and 2-methoxyethyl ether is also reported.<sup>71,72</sup> The actual function of these modifiers and promoters is the subject of current study.<sup>73-75</sup>

Recent results by Langer conclude that ethyl benzoate is

largely responsible for high stereospecificity in propylene polymerization.<sup>74</sup> The Lewis base increases tacticity by extensively deactivating the non-stereospecific sites. The net result is a decrease in activity accompanied by an increase in stereospecificity.<sup>74</sup>

Boor asserts that the driving force for isotactic propagation at a heterogeneous active center originates from steric interaction between the  $\alpha$ -olefin and ligands which form the environment of the growth center. This interaction allows the  $\alpha$ -olefin monomer to approach and complex with the metal-carbon active center in only one configuration, thereby resulting in stereospecific propagation.<sup>19</sup>

While ethylene and propylene polymers are by far the most commercially important, higher  $\alpha$ -olefins also polymerize via Ziegler-Natta initiators to stereoregular, isotactic crystalline or amorphous polymers. Examples of crystalline, limited volume commercial products are poly(1-butene) and poly(4-methyl-1-pentene).<sup>76,77</sup> Polymerization of higher olefins such as 1-hexene, 1-octene and 1-dodecene is also readily accomplished. Note that the stereoregular polymerization of the higher  $\alpha$ -olefins is slower and more dependent on the nature of the initiator. The decrease in rate becomes progressively less as the length of the pendant group increases, so that only small changes in activity are reported between 1-pentene and 1-dodecene.<sup>19</sup>

While the objective of initial research using Ziegler initiators was the preparation of stereoregular crystalline homopolymers from simple olefins, it was inevitable that emphasis would also be placed on the preparation of elastomeric copolymers. The result has



been ethylene/propylene elastomers (EPM) followed by the olefin containing terpolymers (EPDM), all of which are of commercial importance today.<sup>78</sup>

The most practical transition metal derivatives for this objective are those of titanium and vanadium, the preferred and most widely commercially used being those of vanadium. There are numerous reasons for selection of vanadium systems. Carrick and coworkers determined that the activity for copolymerization of propylene with ethylene decreased in the order  $\text{VCl}_4 > \text{VOCl}_3 > \text{TiCl}_4 > \text{ZrCl}_4 > \text{HfCl}_4$ , broadly in the order of decreasing electronegativity of the transition metal.<sup>79</sup> In addition, solid crystalline heterogeneous initiators can contain active sites of differing nature, thus resulting in copolymer compositional heterogeneity. Attempts to eliminate this constraint and at the same time increase activity led to much research on supported initiator systems. Note however, that compositional heterogeneity is also possible with homogeneous systems if more than one active species is formed. The vanadium derivatives are most often used with alkyls based on aluminum, in concert with a host of additives and methods of preparation which influence reactivity, efficiency, stability, reactivity ratios and other variables.<sup>78</sup> Amorphous, rubbery ethylene-propylene copolymers containing 20-80 mole percent propylene have been reported.<sup>78</sup>

Other combinations of  $\alpha$ -olefin monomers are also of interest. Modification in this manner permits variation of molecular structure, crystallinity and properties to meet specific needs, making available a



range of industrially important plastic and elastomeric polymers.

Terpolymerization reactions, incorporating appropriate diene monomers are also of great interest. The resulting sites of unsaturation are then available for vulcanization reactions.<sup>20</sup>

## 2. Coordination polymerization of functionally-substituted olefins.

Incorporation of polar functional groups onto polymers with a hydrocarbon backbone represents a useful method for modification of their chemical and physical properties including adhesion, dyeability, permeability, compatibility with additives and solid state morphology. Furthermore, there is currently much interest in preparation of polymers such as polyolefins or poly(alkylene oxides) containing ionic or ionizable functional groups such as carboxylates, sulfonates or phosphonates.<sup>80-82</sup> The result of this type of incorporation is significant and commercially useful modification of the physical, mechanical and rheological behavior of the polymers.<sup>83,84</sup>

Also of growing interest is the design of polymers incorporating reactive functional groups which facilitate attachment of useful moieties via substitution reactions. Many polymers have been demonstrated as useful carriers for a number of drugs and pharmaceutical preparations.<sup>85-88,89,90</sup> Grafting and crosslinking through these reactive groups is also under investigation.<sup>82</sup>

Until the mid 1960's Ziegler-Natta initiators were utilized mostly for the stereospecific polymerization of hydrocarbon monomers or for monomers containing heteroatoms such as tin or silicon that do not

strongly interact with components of the initiator system.<sup>91,92</sup>

Earlier references do report the polymerization of monomers containing donor atoms, such as vinyl ethers and vinyl chloride.<sup>93-95</sup> Vandenberg, Breslow and coworkers at Hercules studied the polymerizability of vinyl chloride, methyl methacrylate and vinyl ethers.<sup>96-98</sup>

However, in these cases, the polymerization probably proceeds by a cationic or radical mechanism with the true initiating species being secondary products resulting from reaction of the transition metal salt and organometallic component.<sup>19,91</sup> Some polar monomers are claimed to be polymerized by mechanisms involving coordination-anionic or coordination-cationic type centers, which differ from the Ziegler-Natta active center as previously described.<sup>19</sup>

The difficulty with polymerizing monomers containing donor atoms via a true Ziegler-center lies in the fact that both initiator components are Lewis acids, and as such, have the capacity to interact with heteroatoms such as nitrogen or oxygen which contain nonbonded electron pairs. The resulting coordination complexes are typically more stable than those obtained when coordination involves only the pi electrons of the double bond to be inserted. The net result is deactivation of active polymerization sites by formation of stable complexes between the initiator component(s) and the polar monomer.<sup>99</sup>

A number of approaches can be taken to minimize or eliminate this destructive interaction. In theory, the more closely the functionally-substituted monomer resembles an  $\alpha$ -olefin, the greater is the potential for it to polymerize at the same centers that are active

for simple nonpolar olefins.<sup>19</sup> In practice, this may be accomplished by: (1) insulating the double bond from the heteroatom by incorporation of a spacer group such as one or more methylene units. Physically removed in this manner, the heteroatom is less likely to electronically or sterically hinder coordination and insertion of the double bond at the active center. As will be observed, the length of the spacer chain required will be a function of the heteroatom present; (2) by increasing the steric encumbrance about the heteroatom(s); (3) by decreasing the electron donating character of the heteroatom via attachment of electron withdrawing substituents on or adjacent to it; (4) by selecting initiator components less likely to react with the donor atoms. This may be done by selection of ligands on the organometallic component which sterically or electronically limit its capacity to interact with the donor atoms, while still permitting polymerization of the double bonds; (5) by decreasing the reactivity of the organometallic component by precomplexing it with a donor molecule, such as ethyl benzoate; (6) by precomplexing the functional monomer with a Lewis acid, often the same type as will be combined with the transition metal salt to form the active centers; (7) by use of a polar solvent which complexes with the active centers, but permits entrance, coordination and polymerization of the vinyl monomer.<sup>19</sup>

If interactions resulting in deactivation can be successfully inhibited by means of one or more of the above techniques, polymerization of the functional monomer at active Ziegler sites becomes more favorable.



a. Silicon-containing monomers. The earliest report documenting the coordination polymerization of a functionally-substituted olefin was that of Natta et al in 1958.<sup>100,101</sup> Allylsilane, trimethylallylsilane and 5-trimethylsilyl-1-pentene were polymerized to isotactic product utilizing  $\text{TiCl}_4/\text{AlEt}_3$  or  $\text{TiCl}_3/\text{AlEt}_3$  initiator components. Natta reported that polymerization of these silicon containing monomers by conventional radical or ionic techniques yield only hexamer and oils respectively. Homopolymers of dimethyldiallylsilane and methylphenyldiallylsilane, as well as copolymers with propylene, were also reported by Bogomol'nyi and Nametkin respectively.<sup>102,103</sup> Longi et al. later reported the copolymerization of allylsilane with propylene and 1-hexene.<sup>104</sup>

In contrast, Carbonaro, Greco and Bassi demonstrated that placement of the silyl group directly on the double bond greatly decreases the polymerizability of vinyl ethyl silane using a  $\text{VCl}_3/\text{AlEt}_3$  initiator.<sup>105</sup> Only low molecular weight product was obtained, and with poor yield. The material was, however, isotactic. Thus it is apparent that a spacer group of a single methylene unit is sufficient to greatly enhance the polymerizability of silicon containing monomers.

b. Halogen-containing monomers. The Ziegler-initiated polymerization of 1-olefins containing halogen atoms directly attached to the polymer backbone or in a side chain has been described for a number of cases, including the polymerization of perfluoroolefins, trifluoroalkyl-substituted ethylenes, vinyl chloride, chloroprene and halostyrenes.<sup>106-113</sup> It is now believed that in most instances the mechanism is other than the true Ziegler active site as previously



described.<sup>19,114</sup> However, it must be noted that certain halogen containing molecules are routinely used in true Ziegler-initiated polymerizations without deleterious effects. Examples of such solvents include chlorobenzene and tetrachloroethylene.<sup>115</sup>

The more widely observed case is that catastrophic deactivation occurs in the presence of halo-olefins, in the form of irreversible interaction between the halide and one or both of the metallic initiator components. It is therefore necessary to suppress this interaction by selection of components which are found inactive toward halogens, or by addition of a third component.<sup>114</sup> Clark reports  $\text{TiCl}_3$ , as prepared by the aluminum sesquichloride reduction of  $\text{TiCl}_4$ , is quite inert toward many alkyl halides and presents no problem. Clark maintains that the real obstacle to polymerization of halo-olefins lay in their reactivity with most aluminum alkyls, often resulting in formation of insoluble complexes. Homo- and copolymerization reactions lead to several conclusions; that polymerization of  $\omega$ -halo-1-olefins is favored by increased size of the halogen ( $\text{I} > \text{Br} > \text{Cl}$ ), increased separation of the halogen from the vinyl group via a spacer chain, and its attachment to a primary rather than secondary or tertiary carbon atom.<sup>114</sup> The underlying principle is clearly to decrease the probability of ionic reaction of the carbon-halogen bond with the aluminum-based initiator component. In addition, the deactivating reaction appears to be suppressed in the presence of vinylic double bonds, as in the copolymerization reaction with 4-methyl-1-pentene. This suggests the formation of a labile olefin-aluminum alkyl complex.<sup>114</sup>

In 1964 Backsai developed a technique in which the reactivity of the aluminum alkyl toward the halogen was reduced by a catalytic amount of a third component; a Lewis base such as pyridine, for example. Utilizing this method with a  $\text{TiCl}_3/\text{AlEt}_3$  initiator system, Backsai has prepared co- and terpolymers of  $\omega$ -halo-1-olefins containing methylene chains with 3 to 9 units incorporating both bromine and chlorine. The comonomers included ethylene, propylene and 4-methyl-1-pentene.<sup>115</sup>

Overberger and Khattab demonstrated that fluorine containing 1-butenes and 1-pentenenes could be copolymerized with  $\text{VCl}_3/\text{Al(isoBu)}_3$  and other initiator combinations.<sup>116</sup> The polymerization and copolymerization data showed that the trifluorobutenes were less reactive than the trifluoropentenenes. This was attributed to an inductive effect of the trifluoromethyl group on the electron density of the vinyl group. In the case of the fluorobutenes, the more highly electron-deficient double bond is apparently less able to coordinate and ultimately insert into active sites. In the trifluoropentenenes, the second methyl group is sufficient to insulate the vinyl group and so permit polymerization. This concept is supported by comparison of nuclear magnetic resonance chemical shifts for these fluorolefins as compared to their  $\alpha$ -olefin counterparts which indicates an electron deficiency of the vinyl group in the case of the halogenated analogs.<sup>116</sup> Furthermore, the polymerization rates of the corresponding  $\alpha$ -olefins were not retarded by addition of organic molecules containing the trifluoromethyl group.

Vinyl chloride has probably been the most investigated of the polar monomers.<sup>117-123</sup> The preponderance of evidence indicates that the mechanism is radical in most cases.<sup>19</sup>

c. Nitrogen containing monomers. A number of vinyl monomers containing aliphatic and heterocyclic nitrogen have been polymerized using Ziegler-Natta initiators. Heller et al. polymerized carbazole-containing monomers in which the carbazole unit and the double bond were separated by a spacer chain consisting of one to five methylene units.<sup>124</sup> Polymerizability was found to increase with the length of the methylene chain, resulting in formation of crystalline, isotactic polymer. Vinyl carbazole was polymerized to both crystalline and amorphous product. However, interpretation of these results is difficult, due to the polymerizability of this monomer by various processes.<sup>19</sup> Key papers addressing polymerization of nitrogen containing monomers are those of Giannini and coworkers.<sup>91,125</sup> Of particular note are a series of tertiary amines in which the polymerizable terminal vinyl group is separated from the nitrogen atom by a methylene chain from one to nine units in length. Polymerizability of this series was evaluated as a function of: (1) length of the methylene spacer chain; (2) steric encumbrance about the heteroatom as a function of the branched alkyl substituents on the nitrogen; (3) precomplexation of the monomer with a stoichiometric amount of the same type organo-metallic component used for the initiator preparation; and (4) the effect of adjacent silicon-containing moieties on the electron density

of the nitrogen.<sup>91</sup> By application of these techniques, high polymers of unsaturated tertiary amines containing linear or branched alkyl groups attached to the nitrogen were prepared. By polymerization of the silicon derivatives and subsequent acid hydrolysis, high polymers of secondary amines were isolated.<sup>125</sup> Giannini reports that polymerization conditions were most favorable when both the heteroatom and the aluminum atom of the organo-metallic component were sterically hindered by the presence of branched alkyl groups. Amines in which the heteroatom was not sterically hindered could not be polymerized under standard conditions, but were polymerizable after precomplexing the unhindered amine with a stoichiometric amount of the aluminum alkyl.  $\delta$ -TiCl<sub>3</sub> AA was employed as the transition metal derivative in all cases.

Giannini's experiments also demonstrate that with a spacer chain of one methylene unit, no polymer is obtained. With two units, polymerization is slow, with poor yields obtained. With three or more methylene units, polymerization is rapid. It is most interesting to note that high yield and stereoregularity were obtained only with branched alkyl substituents on the organometallic component. As is the case with  $\alpha$ -olefins, stereospecificity is enhanced using aluminum dialkyl halides rather than the corresponding trialkyl aluminum. Intrinsic viscosities from 0.64 to 1.95 dL/g were obtained, with typical reaction conditions of 50-60°C for 8-140 hours. Copolymers with  $\alpha$ -olefins were also obtained.<sup>91</sup>

It is highly significant to note that only low molecular



weight polymer was obtained when these same monomers were subject to the action of radical, cationic or uncoordinated anionic initiators, thus supporting the postulated coordinate anionic Ziegler mechanism. In the former instances, formation of allylic species limits molecular weight.<sup>126</sup>

The elegant and comprehensive work of Giannini and coworkers has done much to establish and strengthen the criteria previously cited for the enhancement of the polymerizability of  $\omega$ -functionalized  $\alpha$ -olefins via Ziegler active centers.

The polymerization and copolymerization of 4-vinylpyridine (4VP) was investigated by Carlini.<sup>127</sup> The homopolymerization of 4VP, both free and precomplexed with an equimolar amount of aluminum alkyl, was studied using initiator systems combining  $\text{TiCl}_3$  "ARA" with  $\text{Al}(\text{isoBu})_2\text{Cl}$ ,  $\text{Al}(\text{isoBu})_3$  or  $\text{Zn}(\text{isoBu})_3$ . In all cases the mole ratios of  $\text{Al}(\text{or Zn})/\text{Ti} = 3.7$  and  $4\text{VP}/\text{Ti} = 15 - 20$ . The polymerizations were allowed to proceed at room temperature for 30 days. Yields of greater than 90 percent were obtained when the precomplexed 4VP adduct was introduced in combination with an aluminum alkyl initiator. However, molecular weights were very low; in the range of 1000 - 3500. The uncomplexed 4VP monomer gave only a 7 percent yield with aluminum alkyls, and 30 percent using triisobutylzinc. Carlini attributes the poor yields obtained using free 4VP to poisoning of the active sites through coordination with the nitrogen electron pair.

Copolymerizations of the free and complexed 4VP with styrene,

4-methyl-1-hexene and (R)-3,7-dimethyl-1-octene were also attempted. Reaction times of 4 days to 5 months were reported with no isotactic copolymer obtained. Using free 4VP, only poor yields of low molecular weight atactic (4VP) were obtained. When the 4VP complexed adduct was utilized, mixtures of isotactic poly( $\alpha$ -olefin) homopolymer and low molecular weight atactic poly(4VP) were isolated.

Carlini concludes that the catalytic species involved in the polymerization of 4VP, while not radical, are different from those which generate isotactic poly( $\alpha$ -olefins).<sup>127</sup>

Rodriquez and Alberola claim the stereospecific polymerization of 4-vinylpyridine to a partially crystalline product using vanadium/ $\text{AlEt}_3$  initiators. In contrast, polymerization of 2-vinylpyridine gave atactic, amorphous material.<sup>113</sup>

Gehrke and coworkers polymerized 2-methyl-5-vinylpyridine using initiators consisting of  $\text{TiCl}_4$ ,  $\text{TiCl}_3$  or  $\text{VOCl}_3$ , in combination with a dialkylaluminum chloride. Using this Ziegler-type system, high molecular weight product was obtained in contrast to low molecular weight polymer prepared by radical means.<sup>128</sup>

Yamamota reports the coordination polymerization of substituted olefins including styrene and methacrylonitrile using  $\text{Co}(\text{N}_2)\text{H}(\text{Ph}_3\text{P})_3$ . The mechanism proposed involves coordination of the monomer to a coordination site, followed by insertion into a metal-carbon or metal-hydrogen bond.<sup>129</sup>

Polymerization of acrylonitrile by a coordinate anionic mecha-

nism is claimed by Kapur, using  $\text{VOCl}_3$  or  $\text{VCl}_4/\text{AlEt}_3$ . A radical mechanism is assigned at low initiator concentration, and a coordinate anionic mechanism at higher levels.<sup>130</sup>

d. Oxygen-containing monomers. In the references previously cited, Giannini and coworkers also report polymerization of oxygen-containing olefin monomers.<sup>91,125</sup> Specifically, polymers from trimethylsiloxanic derivatives of 4-penten-1-ol and 10-undecen-1-ol were prepared using  $\text{TiCl}_3\text{AA}/\text{Al}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-\text{CH}_3)_3$ . The trimethylsilyl moiety sterically and electronically inhibited reaction of the polar monomer with the aluminum alkyl, also sterically encumbered by three isohexyl groups. The derivatized polymers were not isolated as such, but were hydrolyzed in alcoholic mineral acid solutions to generate high molecular weight crystalline poly(5-hydroxy-1-pentene) and poly(11-hydroxy-1-undecene). Polymer yields were low (20-25%) with intrinsic viscosities of from 0.6 - 1.9 dL/g.<sup>125</sup>

In perhaps the most comprehensive patent in this area to date, Holler and Youngman at Shell Oil Company<sup>131</sup> claim methods for the polymerization and copolymerization of a variety of polar-substituted  $\alpha$ -monoolefins. This study employs many of the techniques previously detailed to enhance the polymerizability of functionally-substituted  $\alpha$ -olefins. Oxygen-containing monomers reported polymerized include aliphatic esters, alkoxides, phenoxides, amides, phosphonates, phosphines and aluminum tris (alkenoxides). These monomers typically incorporate spacer chains of 6 to 9 methylene units. Reaction conditions of

20-50°C for 7-20 days are described. Yields of 11 to 100 weight percent, and inherent viscosities of 0.59 to 0.87 dL/g are reported. Copolymers of the above monomers with  $\alpha$ -olefins including 1-dodecene, 1-hexene, 4-methyl-1-pentene and propylene are claimed. In the case of higher  $\alpha$ -olefin comonomers, levels of incorporation of 4-12 weight percent and inherent viscosities of 1.1 to 2.2 dL/g are disclosed. Reaction conditions of 7 days at 50°C are recorded for these copolymerization reactions. Using 4-methyl-1-pentene as comonomer, inherent viscosities of from 3.0 to 7.2 were obtained. Block copolymers with propylene were claimed by alternately feeding propylene and a polar monomer over a period of three days, resulting in 11 to 37 percent incorporation and inherent viscosities of 5.8 to 6.4 dL/g.<sup>131</sup> For both polymerization and copolymerization reactions, the mole ratio of aluminum alkyl/transition metal derivative/polar monomer were typically 29.0/1.0/25.0.

Polymerization of vinyl phosphonic acid esters using a  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$  system was described by Sophin.<sup>132</sup> The polymerization reportedly proceeds via an active (1:1) monomer- $\text{AlEt}_2\text{Cl}$  complex.

As previously detailed early in section 2, many oxygen-containing vinyl monomers including vinyl ethers, acrylic acid and acrylic esters have been reported polymerized by Ziegler initiators, though not by the coordinate anionic insertion mechanism.<sup>96-98,133-134</sup> Details of these reactions and compete references are provided by Boor<sup>19</sup>, and are not of primary interest in this discussion.



3. Coordination copolymerization of functionally-substituted olefins with  $\alpha$ -olefins and ethylene. Random, alternating and block-like copolymers of  $\alpha$ -olefins and ethylene have been produced using Ziegler-Natta initiators, with titanium and vanadium-based initiators most employed. Extensive general and specific reviews have been presented by Lukack and Spurlin<sup>135</sup> in 1964, Boor<sup>136</sup> in 1967, Natta, Valvassori and Sartori<sup>137</sup> in 1969 and by Baldwin and Ver Strate<sup>138</sup> in 1972.

Incorporation of functional groups into polyolefins is very desirable from the standpoint of modification of their chemical and physical properties to meet the requirements for specific applications. While the characteristic inertness of polyolefins has been exploited in countless applications, this same property can lead to difficulties in some instances. For example, their lack of functionality makes surface treatments such as adhesion, dyeing or metalizing difficult or impossible without the use of special oxidation or irradiation treatments to sufficiently modify the polymer surface. In addition, the amount of additives such as stabilizers that can be accommodated in polyolefins without blooming is limited.<sup>139</sup> As a result of these and other considerations, there has been much research directed at techniques for affecting the copolymerization of olefins, particularly ethylene and propylene, with functionally-substituted vinyl monomers. An example of a successful commercial application is ethylene-acrylic acid copolymers, from which du Pont's Surlyn<sup>®</sup> ionomers are

prepared.<sup>140</sup> Copolymers of ethylene with acrylic acid or methacrylic acid prepared by radical reactions, and their carboxylate salts, will be discussed more thoroughly in section 4.

If copolymers of propylene or higher  $\alpha$ -olefins are desired, a coordination process is required to obtain high molecular weight product. However, as previously detailed for the case of homopolymerization reactions, attempts to introduce polar groups into polyolefins by copolymerizing  $\alpha$ -olefins with vinyl monomers containing polar groups have been hampered by the tendency of the polar groups to interact with, and render inactive, one or both components of the Ziegler initiator system. The methodology developed to minimize this phenomenon in order to permit homopolymerization of these monomers should also be applicable to the corresponding copolymerization reactions, since to a large extent the behavior of an olefin monomer in a copolymerization reaction can be predicted by its homopolymerization under comparable conditions.<sup>19</sup>

Many of the publications previously cited in section 2 addressing the homopolymerization of polar monomers also reported their copolymerization. For the sake of simplicity, this information was included in section 2 and may be referred to at this time. Of particular interest are the publications of Clark,<sup>114</sup> Backsai<sup>115</sup>, and Holler.<sup>131</sup> Other publications focus exclusively on the copolymerization of functional monomers, and will now be reviewed.

a. Copolymerization of oxygen containing monomers. Jasper at ICI Ltd<sup>139</sup> claimed a method for the copolymerization of  $\alpha$ -olefins with oxygen-containing  $\omega$ -substituted 1-olefins. The reported substituent groups include alcohol, carboxylic acid, amide, ester, aldehyde, ketone and sulfonic acid, as well as an aromatic nucleus bearing similar functionality. A methylene spacer chain of at least four units is a prerequisite for copolymerization. Typical Ziegler systems such as  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$  were employed. The monomer was precomplexed by heating with a stoichiometric amount of the organoaluminum compound. Copolymers of 10-undecen-1-ol and 10-undecenoic acid with 4-methyl-1-pentene are claimed with eight and four percent incorporation respectively. No information on molecular weight was given.

High molecular weight copolymers of esters of  $\omega$ -unsaturated acids with propylene and ethylene were claimed in a patent issued to Farbwerke Hoechst.<sup>141</sup> The methyl, ethyl, phenyl and 2,6-dimethylphenyl esters of 10-undecenoic acid were reportedly copolymerized using titanium, vanadium and chromium transition metal derivatives in combination with diethylaluminum chloride or triisobutyl aluminum. Levels of polar monomer incorporation varied from 0.2 to 4.5 weight percent, with highest levels (and lowest yields) obtained using vanadium-based initiators. Levels of incorporation of 0.2 to 2.1 weight percent were obtained using titanium components. Lewis base additives including di-n-butyl ether were also employed in some experiments.

Tanaka has described the preparation of olefin-alkenyl ester copolymers.<sup>142</sup> Ethylene, propylene and/or 4-methyl-1-pentene were copolymerized with 10-undecenyl acetate and 4-pentenyl acetate.  $\text{TiCl}_3$  or  $\text{VOCl}_3$  were selected for use in combination with  $\text{AlEt}_2\text{Cl}$ , with Al/ester mole ratios of at least 1.4. The acetate was precomplexed with the aluminum alkyl (1:1) before addition to the reaction. Intrinsic viscosities of 3.5 dL/g were obtained, but no information on incorporation of the polar monomer was available. Copolymerization of the free acids are also described.<sup>142</sup>

Functionally substituted terpolymers and tetrapolymers of  $\alpha$ -olefins were prepared by Collette<sup>143</sup> using  $\text{VCl}_4/\text{AlEt}_2\text{Cl}$  with hexachloropropylene as an initiator "reactivator". In this fashion tetrapolymers incorporating ethylene, 1,4-hexadiene, propylene and 5-norbornene-2-acetic acid units were reported. 2-hydroxymethyl-5-norbornene was similarly incorporated.

Pomogailo has studied the copolymerization of ethylene with methyl methacrylate (MMA) utilizing  $\text{VCl}_4/\text{Al}(\text{isoBu})_2\text{Cl}$  initiators.<sup>144</sup> Results demonstrate that the course of the reaction depends on the mode of addition of the MMA. When the free monomer was introduced, homopolymer and block copolymers of MMA were obtained by a radical mechanism. However, by precomplexation of MMA with  $\text{VCl}_4$ , copolymer was obtained with an anionic coordinate mechanism proposed.

Copolymers of 10-undecylamide with 4-methyl-1-pentene, incorporating 5-8 mole percent of the functional monomer, were described by



Clark<sup>139</sup> using a procedure in which the polar monomer was first pre-complexed with the organometallic component. A dialkylaluminum chloride was preferred.

More recently, copolymers of ethylene with acrylic acid or its derivatives were reported using  $\text{VO}(\text{OEt})_3/\text{AlEt}_2\text{Cl}$ , with 0.2 - 15% incorporation. As in previous cases, the polar monomer was pre-complexed with the aluminum alkyl.<sup>145</sup>

Copolymers of propylene with vinyl monomers containing pendant succinic, phthalic and norbornyl anhydride groups have also been claimed, using a  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$  system.<sup>146</sup>

Vulcanizable ethylene-alkenyl alkenecarboxylate copolymers such as ethylene-propylene-allyl octadecenoate were prepared using a  $\text{VC1}_3 \cdot \text{THF}/\text{AlEt}_2\text{Cl}$  initiator.<sup>147</sup> Incorporation of the functional monomer was found to be 0.8 percent.

As may be anticipated, application of supported systems to copolymerizations with functional monomers is underway. Mitsui Petrochemical claims a process utilizing a supported initiator which is prepared by reaction of  $\text{TiCl}_4$  and phenetole on  $\text{MgCl}_2$ , in combination with  $\text{AlEt}_2\text{Cl}$ .<sup>148</sup> Copolymerization of 10-undecenoic acid with propylene is reported, with up to 12.3 mole percent incorporation of the acid.

As indicated, several studies have addressed the preparation of carboxyl-substituted polyolefins by coordination techniques. Alkenoates including both aliphatic and aromatic esters were normally used, since the free carboxylic acid group is particularly active

towards reaction with the organometallic component. Derivatives of 10-undecenoic acid are commonly utilized, owing to the low cost and high purity of the parent acid.

b. Copolymerization of nitrogen-containing monomers.

Copolymers of ethylene and 2-methyl-5-vinyl pyridine have been reported by Gehrke.<sup>149</sup> Results indicate that when the molar concentration of the pyridine derivative is greater than that of the diethylaluminum chloride used in combination with  $\text{TiCl}_3$ , the yield of copolymer is small and contains greater than 30 percent of the functional monomer. However, when the ratio of aluminum alkyl/polar monomer is greater than one, the yield is increased and the resulting copolymer contains less than 5 percent of the pyridine-containing unit. Clearly, the Al/N mole ratio determined the nature and concentration of active sites. When the Al/N mole ratio is greater than one, a complex may be formed, masking the polar monomer and favoring polymerization via a coordinate mechanism.

Pomogailo et al.<sup>150</sup> copolymerized 2-vinylpyridine with ethylene by means of a technique in which the transition metal component was first precomplexed with a portion of monomer before addition of the diisobutylaluminum chloride. Copolymers containing 0.1 to 0.9% nitrogen was prepared.

Copolymers of styrene and 2-methyl-5-vinylpyridine were reported by Sakurada.<sup>151</sup> The crystallinity of isotactic polystyrene

segments decreased as the content of the polar monomer increased.

Graft terpolymers of  $\alpha$ -olefins including ethylene, propylene and 4-methyl-1-pentene with polar monomers such as 4-vinylpyridine were prepared by Yamada using a two part procedure. The  $\alpha$ -olefins were polymerized via  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$  initiators, followed by introduction of the polar monomer in the presence of  $\text{SnCl}_4$ .<sup>148</sup>

Copolymers of ethylene and acrylonitrile were claimed by Ivancheva using  $\text{VO}(\text{OEt})_3/\text{AlEt}_2\text{Cl}$  systems. A mechanism involving acrylonitrile/ $\text{AlEt}_2\text{Cl}$  complex formation was proposed. The copolymer contained 0.7 - 1.8 mole percent of the polar monomer, and demonstrated improved adhesive properties.<sup>152</sup>

c. Copolymerization of chlorine-containing monomers. The most significant publications addressing copolymerization of halogen-containing compounds are those of Clark,<sup>114</sup> Backsai<sup>115</sup> and Overberger,<sup>116</sup> previously discussed in section 2.

Mejzlik<sup>153</sup> and coworkers studied the copolymerization of propylene and vinyl chloride, and proposed that the reaction proceeds via a coordinate ionic mechanism only when the monomer feed is rich in propylene. When the charge was rich in vinyl chloride, a radical mechanism was operative.

Sophin<sup>154</sup> has described the copolymerization of ethylene with bis ( $\beta$ -chloroethyl) vinylphosphonate with  $\alpha$ - $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$ . Incorporation as high as 17.5 mole percent was claimed.

4. Modification of  $\omega$ -functionally-substituted  $\alpha$ -olefin polymers and copolymers. The preceding two sections have dealt with the homo- and copolymerization of vinyl monomers containing heteroatoms. Of particular interest are monomers incorporating ionizable groups such as carboxylate, sulfonate or phosphonate esters. As previously discussed, the ester derivatives are most often utilized to avoid catastrophic initiator deactivation observed in coordination reactions involving the free acid. Incorporation of ester functionality into a hydrocarbon backbone results in potentially useful changes in the chemical and physical properties of the polymer. While the ester-substituted polymers are themselves of interest, further modification via hydrolysis to the acid or metal salt manifests properties still farther removed from the hydrocarbon analog. Reactions of this nature, generating ionomers and polyelectrolytes, will now be addressed.

In 1964 du Pont<sup>140,155</sup> introduced a new class of  $\alpha$ -olefin based polymers, named Surlyn<sup>®</sup> ionomers, in which strong ionic interchain forces play the dominant role in controlling polymer properties. The parent ethylene-acrylic acid copolymers were prepared by radical processes, and typically contained approximately 5-10 mole percent of the acid comonomer. Hydrogen bonding occurs between these acid groups, resulting in some modification of the physical properties. However, at low levels of acid, most solid-state properties are comparable to the unsubstituted semi-crystalline polyolefin. Upon neutralization via base hydrolysis to the carboxylate salt, strong secondary forces are developed between the ionized carboxyl groups and free metal



cations, selected mainly from group I or II of the periodic table.<sup>140</sup> These ionic associations in the macromolecule behave like thermally-reversible ionic crosslinks, giving rise to unique and useful properties including high strength, toughness, puncture resistance, optical clarity (due to decrease in crystalline domain size), increased solvent resistance and decreased oil permeability. These characteristics are currently being exploited in the production of new packaging and coating materials.<sup>155</sup> Study of the structure-property relationships of ion-containing polymeric materials and the nature of these ionic interactions is an area of rapid growth and has been reviewed.<sup>155-160</sup>

When the level of acid comonomer is increased beyond that normally used in the precursor to ionomers, the polymer properties are also of commercial interest. For example, ethylene copolymers incorporating approximately 20 mole percent pendant carboxyl groups have found application in wire and cable coatings as well as hot melt adhesives. The resulting polymers demonstrate increased ultimate strength, adhesion to metals, stress-crack resistance and toughness.<sup>161</sup>

If the degree of incorporation is increased to substitution on each alternate carbon of an olefin, the result is a polyelectrolyte, which may be broadly defined as any polymeric substance in which each monomeric unit possesses ionizable units.<sup>162</sup> In contrast to simple small molecule electrolytes in which the size of the oppositely charged ions are of similar magnitude, a polyelectrolyte is composed of a macroion in which the charged groups are interconnected by chemical

bonds, together with an equivalent number of small counterions of opposite charge. Virtually all of the unique properties of polyelectrolytes result from the interaction of the interconnected ionic groups of this macroion, and in turn, from interactions of the charged macroion with its compensating counter ions.<sup>162</sup>

A large variety of synthetic polyelectrolytes have been prepared with poly(acrylic acid), first prepared by Staudinger in 1929, as the most commonly known.<sup>163</sup> Most of these compounds are prepared by radical techniques or by substitution reactions on polymers.

The well known synthetic ionomers and polyelectrolytes generally contain ionizable groups attached directly to the polymer backbone or to pendant phenyl rings. In contrast, the  $\omega$ -functionalized polyolefins discussed in sections 2 and 3 possess a spacer group, usually a methylene chain of variable length, connecting the backbone chain and the pendant ionizable group. Conversion of these polymers and copolymers to the corresponding polyelectrolytes, ionomers and polyacids, would result in a series of polymers in which the properties were a function of the spacer chain length.

Poly(alkylene oxides), containing pendant carboxylate groups separated from the main chain by a spacer group consisting of eight methylene units and prepared by coordination polymerization, have been converted to the corresponding sodium salts and polycarboxylic acids.<sup>1</sup> Ionomers and polyacids from copolymers of these functional epoxide monomers with various cyclic ethers have also been prepared.

There are many practical as well as theoretical uses for these

ion containing polymers. Examples of practical applications involve ion-exchange resins, reverse osmosis membranes, flocculants, electrostatics and bacteriocidal films. Theoretical applications include the study of chain conformations as a function of the counterion type and concentration, the mechanism of ion selectivity by ion exchange, and catalytic effect as a function of electrostatic potential and hydrophobic interaction.<sup>164</sup>

5. Conclusions. It is clear from the preceding literature review that much effort has been and currently is devoted to the polymerization of functionally-substituted  $\alpha$ -olefins using Ziegler-Natta initiator systems. Results suggest that the difficulty in polymerizing a vinyl monomer containing donor atom(s) via a coordinate-anionic mechanism generally increases with the electronegativity of the heteroatom. As previously elaborated in section 2, the more closely the functionally-substituted monomer resembles an  $\alpha$ -olefin, the greater is the potential for its polymerization at the same centers that are active for simple hydrocarbon olefins. Techniques to accomplish this are outlined in section 2.

The central problem to be addressed is the destructive interaction between the heteroatoms and the Ziegler initiator components. In addition, the presence of the polar moiety may affect the electron density of the vinyl group, thereby altering its ability to coordinate with, and ultimately insert into the transition metal-carbon active center.

The literature indicates that when the heteroatom is directly attached to the vinyl group, the polymerization mechanism is most often radical or ionic in nature, rather than coordinate-anionic. For this reason, during the course of this investigation, all monomers will incorporate a spacer chain separating the vinyl group and the donor atom(s). The polymerizability of  $\omega$ -alkenoates as a function of the spacer chain length will be determined.

Polymerization of vinyl monomers containing carboxylic ester functionality, among the most poorly tolerated in Ziegler-initiated reactions, will be investigated for a series of aliphatic and aromatic substituents employed to widely vary the steric and electronic environment of the ester group.

Commercially available titanium, vanadium and zirconium transition metal derivatives will be evaluated in combination with numerous aluminum alkyls. Literature results suggest that sterically hindered dialkyl chlorides exhibit maximum potential. If proper selection of the carboxylate and aluminum alkyl substituents do not effectively inhibit destructive interactions between these components, precomplexation techniques will be investigated. These may include a) pretreatment of the aluminum alkyl with an electron donor molecule, or b) precomplexation of the functional monomer with an equimolar amount of an aluminum alkyl.

Once polymerization is achieved, optimization of reaction components, stoichiometry and conditions will be conducted in order to obtain maximum yield, molecular weight and stereoregularity. This



technology will then be adapted for the co- and terpolymerization of  $\omega$ -alkenoates with ethylene, propylene and higher  $\alpha$ -olefins.

Representative functionally-substituted polymers and terpolymers will then be modified to generate novel polyelectrolytes and ionomers as discussed in section 4.

# CHAPTER I I

## EXPERIMENTAL SECTION

### A. Materials

The following chemicals were obtained from the sources indicated:

acetic acid	F	chloroform	F
acetic anhydride	A	chloroform-dl	SIC
acetone	F	copper(II) acetate monohydrate	A
acetonitrile	F	copper sulfate	A
aluminum sesquichloride	ET	decahydronaphthalene	F
2-amino-2-methyl-1-propanol	A	diethyl ether, anhydrous	F
argon, prepurified	L	diethylaluminum chloride	ET
azelaic acid	A	diisobutylaluminum chloride	ET
benzene	F	1,4-dioxane	F
tert-butanol	A	2,6-dimethylphenol	A
calcium chloride, anhydrous	A	2,6-diphenylphenol	GE
calcium sulfate	H	1-dodecene	A
caprolactone	A	sodium persulfate	A
1,1'-carbonyldiimidazole	SIG	sulfuric acid	McB
ethylene	M	tetrahydrofuran	F
2-ethylhexanol	A	tetramethylsilane	A

n-heptane	A	sodium bicarbonate	F
1-hexane	A	sodium hydroxide	MCB
lead tetraacetate	A	sodium sulfate	F
magnesium sulfate, anhydrous	B	thionyl chloride	A
methanol	(MCB)	titanium tetrachloride	Alpha
methyl sulfoxide	A	titanium trichloride	S
nitrogen, prepurified	M	toluene	F
1-octene	A	p-toluenesulfonic acid monohydrate	A
phenol	A	triethylaluminum	ET
phosphorus pentoxide	MCB	trifluoroacetic acid	E
propylene	M	2,2,2-trifluoroethanol	A
pyridine	F	triisobutylaluminum	ET
sebacic acid	A	10-undecenoic acid	E
silver nitrate	A	vinylacetic acid	A

Sources: A = Aldrich Chemical Co.; Alpha = Alpha Products;  
 B = J.T. Baker Chemical Co.; E = Eastman Organic Chemicals;  
 ET = Ethyl Corp.; F = Fisher Scientific Company; GE = General  
 Electric Co.; H = W.H. Hammond Drierite Co.; L = Linde Division,  
 Union Carbide Corp.; M = Matheson; MCB = MCB Manufacturing  
 Chemists, Inc.; S = Stauffer Chemical Co.; SIC = Stohler Isotope  
 Chemicals; SIG = Sigma Chemical Co.

## B. Purification of Solvents and Reagents

Solvent distillations were conducted using a 45 cm column packed with 0.5 cm sections of glass tubing. Distillations of reagents and monomers were carried out on either a 13 cm Vigreux column or a short path microdistillation apparatus. All distillations, either at atmospheric or reduced pressure, were carried out with magnetic stirring under a nitrogen atmosphere.

Tert-Butanol was dried over 4A molecular sieves before use.

$\epsilon$ -Caprolactone was distilled (54-56°C/0.12 mm) before use.

1-Dodecene was vacuum distilled before use (b.p. 80°C/1.8 mm).

n-Heptane was washed successively with concentrated sulfuric acid, distilled water, 10% aqueous sodium carbonate, distilled water and then dried over anhydrous calcium chloride. It was then distilled from phosphorus pentoxide with a center cut taken at 97°C and stored under nitrogen.

1-Hexene was distilled (b.p. 63°C) and stored under nitrogen.

1-Octene was distilled (b.p. 122°C) and stored under nitrogen.

Pyridine was distilled from sodium metal (b.p. 114.5°C) and stored under nitrogen.

Tetrahydrofuran (THF) was distilled (b.p. 62.5°C) from lithium aluminum hydride immediately before use.

Thionyl chloride was distilled (b.p. 79°C) immediately before use.

Toluene was washed in the same manner as described for n-heptane, predried over magnesium sulfate, distilled (b.p. 109.5°C)



from phosphorous pentoxide and stored under dry nitrogen.

Triethylamine was distilled (b.p. 87-88°C) from sodium and stored under nitrogen.

Trifluoroacetic anhydride was prepared by refluxing trifluoroacetic acid over phosphorous pentoxide followed by distillation (40°C) and storage under nitrogen.

Vinylacetic acid (3-butenic acid) was distilled (b.p. 164-165.5°C) and stored under nitrogen.

All other solvents and reagents were used as received.

### C. Preparation of Monomers and Intermediates

1. Methyl 10-undecenoate. A two liter, 3-neck round-bottom flask fitted with a reflux condenser, nitrogen inlet and outlet tubes, and magnetic stirring bar was charged with 10-undecenoic acid (250 g, 1.36 mol) and absolute methanol (510 ml, 13 mol). Concentrated sulfuric acid (7 mL) was then added, resulting in a mild exothermic reaction. The homogeneous mixture was heated at reflux for 1 day, and then cooled to room temperature. After cooling the yellow solution, excess methanol was removed under reduced pressure (ca. 35 mm) on a rotary evaporator. The remaining yellow oil was transferred to a large separatory funnel and 500 ml distilled water was added. Two immiscible layers formed, and after gentle shaking the lower aqueous layer was decanted and discarded. The yellow oil was then diluted with anhydrous diethyl ether (1 L) and washed with 2 x 500 mL portions of distilled

water, 5% aqueous sodium bicarbonate and distilled water. The ethereal solution was dried overnight with anhydrous magnesium sulfate and filtered. Removal of the solvent on the rotary evaporator gave a quantitative yield of crude product. Vacuum distillation (b.p. 116.5-118°C/5 mm) gave 246 g (91%) of clear, colorless methyl-10-undecenoate which was stored under nitrogen. The infrared spectrum (neat) showed absorptions at 3080  $\text{cm}^{-1}$  (C-H stretch, olefinic), 2990, 2975, 2935, 2830  $\text{cm}^{-1}$  (C-H stretch), 1745  $\text{cm}^{-1}$  (C=O stretch, ester) and 1640  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 240). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$ : 1.34 ppm ( $(\text{CH}_2)_6$ , 12H), 1.77-2.43 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2$ , 2H,  $-\text{CH}_2-\text{CO}_2-$ , 2H), 3.62 ppm ( $\text{CO}_2\text{CH}_3$ , 3H, singlet), 4.60-5.15 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.30-6.10 ppm ( $\text{CH}_2=\text{CH}-$ , 1H) (see p. 259). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 25.07 ppm ( $-\text{CH}_2\text{CH}_2\text{CO}-$ ), 29.07 and 29.31 ppm ( $=\text{CH}-\text{CH}_2(\text{CH}_2)_5$ ), 33.91 ppm ( $=\text{CH}-\text{CH}_2-$ ), 34.11 ppm ( $-\text{CH}_2\text{CO}-$ ), 51.26 ppm ( $-\text{OCH}_3$ ), 114.25 ppm ( $\text{CH}_2=$ ), 139.02 ppm ( $=\text{CH}-$ ) and 173.95 ppm ( $-\text{C}=\text{O}$ ) (see p. 269).

2. 10-Undecenoyl chloride. A 500 mL, 3-neck roundbottom flask fitted with reflux condenser, pressure-equilibrium dropper funnel, nitrogen inlet and outlet tubes and magnetic stirrer was charged with 10-undecenoic acid (157 g, 0.85 mol). Thionyl chloride (76 mL, 1.05 mol) was then added dropwise over a period of 2 hours. The reaction temperature was maintained at 25°C by means of an ice-water bath. During addition of the thionyl chloride, vigorous gas evolution and a color change from colorless to brown was observed. The hydrogen

chloride liberated was neutralized by passing through 240 mL of a 17% aqueous sodium hydroxide solution. Following the addition of the thionyl chloride the reaction was allowed to stir for 90 minutes at room temperature. The reaction mixture was then heated to 75°C until gas evolution ceased, cooled to room temperature, and stirred for 12 hours under a nitrogen atmosphere. The dark brown solution was distilled (b.p. 121-125°C/9-10 mm) to yield 141 g (82%) of 10-undecenoyl chloride which was stored under nitrogen. The infrared spectrum (neat) showed absorptions at 3060  $\text{cm}^{-1}$  (olefinic C-H stretch), 2910, 2840  $\text{cm}^{-1}$  (C-H stretch), 1795  $\text{cm}^{-1}$  (C=O stretch), and 1640  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin).

3. Tert-butyl 10-undecenoate. A one-liter, 3-neck roundbottom flask fitted with reflux condenser, pressure-equilibrium dropper funnel, magnetic stirrer, nitrogen inlet and outlet connected to a parafin oil bubbler was charged with tert-butanol (44.2 mL, 0.47 mol), tetrahydrofuran (420 mL) and triethylamine (70 mL, 0.5 mol). The reaction mixture was cooled to 0°C with an ice-water bath and a solution of 10-undecenoyl chloride (100.6 mL, 0.47 mol) in tetrahydrofuran (80 mL) was added dropwise over a period of two hours. The reaction was allowed to stir at 0°C for an additional 4 hours, and for 15 hours at room temperature. The insoluble triethylamine hydrochloride was removed by filtration and washed with THF (50 mL). The combined THF phase was reduced under vacuum to a yellow oil. The crude product was dissolved in ethyl ether, washed with distilled water (4 x 120 mL), 5%

aqueous sodium bicarbonate (2 x 250 mL), distilled water (3 x 200 mL) and dried over anhydrous magnesium sulfate. The slurry was gravity filtered, reduced under vacuum and distilled (75-76°C/0.05 mm) to yield 83 g (74%) tert-butyl 10-undecenoate. The infrared spectrum showed absorptions at 3072  $\text{cm}^{-1}$  (C-H stretch, olefin), 2980, 2860 (C-H stretch), 1735  $\text{cm}^{-1}$  (C=O stretch, ester), 1641  $\text{cm}^{-1}$  (C=C stretch, mono-substituted olefin) (see p. 240). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$ : 1.26 ppm ( $\{\text{CH}_2\}_6$ , 12H), 1.41 ppm ( $\text{C}(\text{CH}_3)_3$ , 9H, singlet), 1.70-2.43 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ , 2H,  $-\text{CH}_2-\text{CO}_2-$ , 2H), 4.50-5.05 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.26-6.03 ppm ( $\text{CH}_2=\text{CH}-$ , 1H) (see p. 259). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 25.21 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 28.16 ppm ( $\text{C}-\text{CH}_3$ ), 29.21, 29.42 ppm ( $=\text{CH}-\text{CH}_2\{\text{CH}_2\}_5$ ), 33.93 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 35.59 ppm ( $-\text{CH}_2-\text{CO}$ ), 79.58 ppm ( $\text{C}-\text{CH}_3$ ), 114.28 ppm ( $\text{CH}_2=\text{CH}-$ ), 138.92 ppm ( $\text{CH}_2=\text{CH}-$ ), 172.88 ppm ( $-\text{C}=\text{O}$ ) (see p. 269). Anal. calcd. for  $\text{C}_{15}\text{H}_{28}\text{O}_2$ : C, 74.95%; H, 11.74%. Found: C, 74.69%; H, 11.33%.

4. 2-Ethyl-1-hexyl 10-undecenoate. A 250 mL 3-neck roundbottom flask equipped with a mechanical stirrer, pressure-equilibrium dropper funnel, nitrogen inlet and outlet was charged with 2-ethyl-1-hexanol (16.2 g, 0.12 mol), THF (100 mL) and triethylamine (19.0 mL, 0.14 mol). This solution was cooled to 0°C using an ice-water bath, followed by dropwise addition of 10-undecenoyl chloride (25 g, 0.12 mol) in THF (100 mL) over a two hour period. Formation of insoluble triethylamine hydrochloride was observed during this time. The reaction was then allowed to stir for an additional 2.5 hours at 0°C, and for 14 hours at



25°C. The slurry was filtered using a pressure funnel to remove the solid white salt. The salt was washed with THF (2 x 60 mL) and the combined THF phase reduced under vacuum to a yellow oil, which was redissolved in ethyl ether. The ethereal solution was washed with distilled water (3 x 100 mL), 5% aqueous sodium carbonate (2 x 100 mL) and distilled water (4 x 100 mL), dried over magnesium sulfate and reduced under vacuum to give 37.1 g of crude product. Distillation (130-132°C/0.2 mm) yielded 28 g (74%) of 2-ethyl-1-hexyl 10-undecenoate. The infrared spectrum (neat) showed absorptions at 3072 (C-H stretch, olefinic), 3000-2860  $\text{cm}^{-1}$  (C-H stretch), 1735  $\text{cm}^{-1}$  (C=O stretch, ester) and 1641  $\text{cm}^{-1}$  (C=C stretch, mono-substituted olefin) (see p. 241). The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 0.88 ppm ( $\text{CH}_3\text{-(CH}_2)_3\text{CH-CH}_2\text{-CH}_3$ , 6H), 1.34 ppm ( $\text{CH}_2=\text{CH-CH}_2\text{-(CH}_2)_6$ , 12H,  $\text{CH}_3\text{-(CH}_2)_3\text{CH-CH}_2\text{-CH}_3$ , 9H), 1.73-2.35 ppm ( $\text{CH}_2=\text{CH-CH}_2\text{-}$ , 2H,  $\text{-CH}_2\text{-CO}_2\text{-}$ , 2H), 3.86 ppm ( $\text{-CO}_2\text{-CH}_2\text{-C-(C}_2\text{H}_5)$ , 2H, doublet), 4.50-5.02 ppm ( $\text{CH}_2=\text{CH-}$ , 2H), 5.20-5.98 ppm ( $\text{CH}_2=\text{CH-}$ , 1H) (see p. 260). The  $^{13}\text{C}$  NMR spectrum showed peaks at 11.07 ppm ( $\text{CH}_3\text{-CH}_2\text{-C(C}_4\text{H}_9\text{)-}$ ), 14.07 ppm ( $\text{CH}_3\text{-(CH}_2)_3$ ), 23.13 ppm ( $\text{CH}_3\text{-CH}_2\text{-(CH}_2)_2$ ), 24.05 ppm ( $\text{CH}_3\text{-CH}_2\text{-C(C}_4\text{H}_9\text{)-}$ ), 25.18 ppm ( $\text{CH}_2\text{-CH}_2\text{-CO-}$ ), 29.17 ppm ( $\text{-(CH}_2)_5$ ,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ ), 30.68 ppm ( $\text{CH}_3\text{-(CH}_2)_2\text{CH}_2\text{-}$ ), 33.94 ppm ( $\text{CH}_2=\text{CH-CH}_2\text{-}$ ), 34.46 ppm ( $\text{-CH}_2\text{-CO-}$ ), 39.06 ppm ( $\text{-CH}_2\text{-C(C}_4\text{H}_9\text{)-}$ ), 66.56 ppm ( $\text{-CO}_2\text{-CH}_2\text{-}$ ), 114.26 ppm ( $\text{CH}_2=\text{CH-}$ ), 138.96 ppm ( $\text{CH}_2=\text{CH-}$ ), 173.60 ppm ( $\text{-CO}_2\text{-}$ ) (see p. 270).

ANAL. calcd. for  $\text{C}_{19}\text{H}_{36}\text{O}_2$ : C, 76.96%; H, 12.24%. Found: C, 76.88%; H, 12.31%

5. 2,2,2-Trifluoroethyl 10-undecenoate. A 500 mL 3-neck round bottom flask equipped with magnetic stirrer, nitrogen inlet and outlet, Dean-Stark trap, condenser and heating mantle was charged with 10-undecenoic acid (57.1 g, 0.31 mol), benzene (300 mL) 2,2,2-trifluoroethanol (25 mL, 0.32 mol) and p-toluenesulfonic acid monohydrate (0.57 g,  $3 \times 10^{-3}$  mol). The reaction mixture was heated to reflux for 47 hours. Approximately 20 mL of benzene insoluble liquid was isolated in the Dean-Stark trap. Infrared analysis at this time indicated low conversion to the desired ester. The benzene-insoluble phase was returned to the reaction flask, along with 2,2,2-trifluoroethanol (5.0 mL, 0.06 mol) and p-toluenesulfonic acid (0.57 g,  $3 \times 10^{-3}$  mol). The flask was fitted with a continuous heavy-liquid extraction apparatus which was filled with 3A molecular sieves and the reaction was heated to reflux for 24 hours. The reaction mixture was cooled to room temperature and washed with distilled water (250 mL), 5% aqueous sodium bicarbonate (3 x 100 mL), aqueous saturated sodium chloride solution (2 x 100 mL) and distilled water (2 x 100 mL). The yellow organic phase was dried over magnesium sulfate, filtered, reduced under vacuum (10 mm) and distilled (b.p. 127-128°C/16 mm) to give 10.5 g (13%) 2,2,2-trifluoroethyl-10-undecenoate. Infrared analysis (neat) showed absorptions at  $3080\text{ cm}^{-1}$  (C-H stretch, olefinic),  $2930$ ,  $2860\text{ cm}^{-1}$  (C-H stretch),  $1760\text{ cm}^{-1}$  (C=O stretch, ester),  $1640\text{ cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 241). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 1.30 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2(\text{CH}_2)_6$ , 12H), 1.97 ppm ( $\text{CH}_2=\text{CH}_2-\text{CH}_2$ , 2H), 2.35 ppm ( $-\text{CH}_2-\text{CO}_2-\text{CH}_2-\text{CF}_3$ , 2H, triplet),

4.32 ppm ( $-\text{CO}_2-\text{CH}_2-\text{CF}_3$ , 2H, quartet), 4.59-5.07 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.3-6.07 ppm ( $\text{CH}_2=\text{CH}-$ , 1H) (see p. 260). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 24.92 ppm, ( $\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 29.18, 29.48 ppm ( $(\text{CH}_2)_5$ , 33.78 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 34.00 ppm ( $\text{CH}_2-\text{CO}_2-$ ), 59.32, 61.20 ppm ( $\text{CH}_2-\text{CF}_3$ ), 114.32 ppm ( $\text{CH}_2=\text{CH}-$ ), 116.42, 130.28 ppm ( $-\text{CH}_2-\text{CF}_3$ ), 139.21 ppm ( $\text{CH}_2=\text{CH}-$ ), 172.14 ppm ( $-\text{CO}_2-$ ) (see p. 270).

ANAL. calcd. for  $\text{C}_{13}\text{H}_{21}\text{O}_2\text{F}_3$ : C, 58.63%; H, 7.95%; F, 21.40%. Found: C, 58.35%; H, 7.72%; F, 21.77%..

6. Phenyl 10-undecenoate. A dry 250 mL 3-neck round-bottom flask equipped with magnetic stirrer, thermometer, pressure-equilibrium dropper funnel, nitrogen inlet and outlet and ice-water bath was charged with 10-undecenoic acid (40.5 mL, 0.2 mol). Trifluoroacetic anhydride (42.4 mL, 0.3 mol) was then added dropwise at a rate so that the reaction temperature did not exceed  $25^\circ\text{C}$ . Phenol (17.6 mL, 0.2 mol) was likewise added dropwise during which time the reaction changed from yellow to reddish-brown in color. This solution was allowed to stir for 90 minutes at  $25^\circ\text{C}$ , combined with benzene (200 mL) and washed with distilled water (200 mL), 5% aqueous sodium hydroxide (200 mL) and distilled water (3 x 200 mL). The organic phase was dried over sodium sulfate, gravity filtered and reduced under vacuum to give 54 g (99%) of crude product. Distillation ( $122-125^\circ\text{C}/.01\text{ mm}$ ) gave 42 g (80%) of phenyl 10-undecenoate. Infrared analysis (neat) showed absorptions at  $3070\text{ cm}^{-1}$  (C-H stretch, olefinic),  $2930$ ,  $2858\text{ cm}^{-1}$  (C-H stretch),  $1762\text{ cm}^{-1}$  (C=O stretch, ester) and  $1639\text{ cm}^{-1}$  (C=C monosubstituted olefin)



(see p. 242). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 1.34 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2(\text{CH}_2)_6$ , 12H), 1.99 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2$ , 2H), 2.43 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet), 4.66-5.07 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.35-6.05 ppm ( $\text{CH}_2=\text{CH}-$ , 1H), 6.75-7.38 ppm ( $-\text{CO}_2-\text{C}_6\text{H}_5$ , 5H) (see p. 261).

The  $^{13}\text{C}$  NMR spectrum showed peaks at 25.00 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 29.20, 29.39 ppm ( $(\text{CH}_2)_5$ ), 33.94 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 34.32 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 114.31 ppm ( $\text{CH}_2=\text{CH}-$ ), 121.66, 125.50, 129.25 and 151.12 ppm (phenyl carbons, o, p, m, and  $-\text{CO}-\text{C}$  respectively), 138.87 ppm ( $\text{CH}_2=\text{CH}-$ ) and 171.48 ppm ( $-\text{C}=\text{O}$ ) (see p. 271).

ANAL. calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_2$ : C, 78.42%; H, 9.29%. Found: C, 78.53%; H, 9.17%.

7. 2,6-Dimethylphenyl 10-undecenoate. A 500 mL, 3-neck round bottom flask equipped with pressure-equilibrium dropper funnel, thermometer, nitrogen inlet and outlet, magnetic stirrer and ice-water bath was charged with 10-undecenoic acid (101 mL, 0.5 mol). Trifluoroacetic anhydride (106 mL, 0.75 mol) was then added dropwise at a rate so that the reaction temperature did not exceed  $30^\circ\text{C}$ . 2,6-dimethylphenol (64.1 mL, 0.5 mol) was next added dropwise in the same manner. The homogeneous brown solution was allowed to stir at room temperature for 5 hours, combined with benzene (200 mL), and washed with distilled water (3 x 200 mL), 5% aqueous sodium hydroxide (1 x 200 mL) and distilled water (4 x 100 mL). The organic phase was dried over sodium sulfate, filtered and the solvent removed under vacuum to give 138 g (95%) of a clear orange oil. A second distillation (b.p.  $141-142^\circ\text{C}/.01$  mm) gave



110 g (76.2%) of 2,6-dimethylphenyl 10-undecenoate. Infrared analysis (neat) showed absorptions at  $3070\text{ cm}^{-1}$  (C-H stretch, olefinic),  $2970$ ,  $2930$ ,  $2855\text{ cm}^{-1}$  (C-H stretch),  $1758\text{ cm}^{-1}$  (C=O stretch, ester),  $1640\text{ cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 242). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ :  $1.33\text{ ppm}$  ( $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{CH}_2)_6$ , 12 H),  $1.94\text{ ppm}$  ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ , 2H),  $2.08\text{ ppm}$  ( $-\text{C}_6\text{H}_3(\text{CH}_3)_2$ , 6H),  $2.48\text{ ppm}$  ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet),  $4.70-5.16\text{ ppm}$  ( $\text{CH}_2=\text{CH}-$ , 2H),  $5.36-6.21\text{ ppm}$  ( $\text{CH}_2=\text{CH}-$ , 1H),  $6.98\text{ ppm}$  ( $\text{C}_6\text{H}_3(\text{CH}_3)_2$ , 3H, singlet) (see p. 261). The  $^{13}\text{C}$  NMR spectra showed peaks at  $16.32\text{ ppm}$  ( $-\text{C}_6\text{H}_3-(\text{CH}_3)_2$ ),  $25.17\text{ ppm}$  ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ),  $29.02$ ,  $29.16$ ,  $29.34\text{ ppm}$  ( $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{CH}_2)_5$ ),  $33.94\text{ ppm}$  ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CO}_2-$ ),  $114.28\text{ ppm}$  ( $\text{CH}_2=\text{CH}-$ ),  $125.64$ ,  $128.54$ ,  $130.04\text{ ppm}$  (phenyl carbons, p, m, o respectively),  $138.89\text{ ppm}$  ( $\text{CH}_2=\text{CH}-$ ),  $148.44\text{ ppm}$  ( $-\text{CH}_2-\text{CO}_2-\text{C}$ ),  $170.91\text{ ppm}$  ( $-\text{CO}_2-$ ) (see p. 271).

ANAL. calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_2$ : C, 79.12%; H, 9.79%. Found: C, 79.18%, H, 9.94%.

8. 2,6-Diphenylphenyl 10-undecenoate. A 250 mL 3-neck round bottom flask equipped with pressure-equilibrium dropper funnel, thermometer, nitrogen inlet and outlet, magnetic stirrer and ice-water bath was charged with 10-undecenoic acid (40.4 mL, 0.2 mol). Trifluoroacetic anhydride (42.4 mL, 0.3 mol) was added dropwise at a rate such that the reaction temperature did not exceed  $30^\circ\text{C}$ . 2,6-diphenylphenol (49.3 g, 0.2 mol) was added at a similar rate. The reaction was allowed to stir at room temperature for 17 hours followed by addition of benzene (200 mL) and washing with distilled water (200 mL), 5% aqueous sodium

hydroxide (200 mL) and distilled water (4 x 200 mL). The organic phase was dried over sodium sulfate, gravity filtered and reduced under vacuum to give 77 g (93%) of crude product. Distillation (198–201°C/0.01 mm) afforded 62 g (75%) of 2,6-diphenylphenyl 10-undecenoate. Infrared analysis (neat) showed absorptions at 3070, 3058, 3025  $\text{cm}^{-1}$  (C-H stretch, olefinic, aromatic), 2930, 2855  $\text{cm}^{-1}$  (C-H stretch) 1765  $\text{cm}^{-1}$  (C=O stretch, ester), 1635  $\text{cm}^{-1}$  (C=C stretch, mono-substituted olefin) (see p. 243). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at  $\delta$ : 1.16 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2(\underline{\text{CH}_2})_6$ , 12H), 1.93 ppm ( $\text{CH}_2=\text{CH}-\underline{\text{CH}_2}-$ , 2H,  $-\underline{\text{CH}_2}-\text{CO}_2-$ , 2H), 4.57–5.06 ppm ( $\underline{\text{CH}_2}=\text{CH}-$ , 2H), 5.30–6.03 ppm ( $\text{CH}_2=\underline{\text{CH}}-$ , 1H), 7.21 ppm (phenyl hydrogens, 13) (see p. 262). The  $^{13}\text{C}$  NMR spectrum shows peaks at 24.35 ppm ( $-\underline{\text{CH}_2}-\text{CH}_2-\text{CO}_2-$ ) 28.71, 29.13 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2(\underline{\text{CH}_2})_5$ ), 33.86 ppm ( $-\underline{\text{CH}_2}-\text{CO}_2-$ ,  $\text{CH}_2=\text{CH}-\underline{\text{CH}_2}-$ ), 114.28 ppm ( $\underline{\text{CH}_2}=\text{CH}-$ ), 126.21, 127.35, 128.12, 129.18, 130.01, 136.17, 138.12 ppm (phenyl carbons), 138.91 ppm ( $\text{CH}_2=\underline{\text{CH}}-$ ), 146.17 ppm ( $\text{CH}_2-\text{CO}_2-\underline{\text{C}}$ ), 171.17 ppm ( $\underline{\text{C}}=\text{O}$ ) (see p. 272).

ANAL. calcd. for  $\text{C}_{29}\text{H}_{32}\text{O}_2$ : C, 84.43%; H, 7.82%. Found: C, 84.50%; H, 7.56%.

9. 4,4-Dimethyl-2-oxazoline derivative of 10-undecenoic acid. A 250 mL 3-neck round-bottom flask equipped with a Dean-Stark trap, condenser, nitrogen inlet and outlet, magnetic stirrer and heating mantle was charged with 10-undecenoic acid (50 g, 0.27 mol), 2-amino-2-methyl-1-propanol (24.2 g, 0.27 mol), p-toluenesulfonic acid (0.52 g,  $2.7 \times 10^{-3}$  mol) and toluene (125 mL). This mixture was heated

to reflux for 46 hours after which time 10 mL of water had been isolated in the trap. The reaction was allowed to cool to room temperature, diluted with toluene (150 mL) and the solution washed with 2% aqueous sodium bicarbonate (50 mL), saturated aqueous sodium chloride solution (2 x 50 mL) and distilled water (2 x 50 mL). The organic phase was dried over anhydrous sodium sulfate, gravity filtered and reduced under vacuum to give 31 g (48 %) of crude product. Distillation (93-96°C/.01 mm) afforded 19.1 g (30%) of the oxazoline derivative. Infrared analysis (neat) showed absorptions at 3087  $\text{cm}^{-1}$  (C-H stretch, olefinic), 2970, 2935, 2860  $\text{cm}^{-1}$  (C-H stretch), 1675  $\text{cm}^{-1}$  (C=N stretch), 1648  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 243). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at  $\delta$ : 1.19 ppm ( $-\text{CH}_3$ , 6H, singlet), 1.29 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{CH}_2)_6$ , 12H), 2.03 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ , 2H,  $-\text{CH}_2-\text{CO}_2-$ , 2H), 3.73 ppm ( $-\text{O}-\text{CH}_2-$ , 2H, singlet), 4.57-5.13 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.28-6.02 ppm ( $\text{CH}_2=\text{CH}-$ , 1H) (see p. 262). The  $^{13}\text{C}$  NMR spectrum shows peaks at 26.07 ppm ( $-\text{CH}_2-\text{C}=\text{N}-$ ), 28.49 ppm ( $-\text{C}(\text{CH}_3)_2-$ ), 28.08, 29.15, 29.37, 30.08 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{CH}_2)_5$ ), 33.86 ppm ( $-\text{CH}_2-\text{C}=\text{N}-$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 66.88 ppm ( $-\text{C}(\text{CH}_3)_2$ ), 78.79 ppm ( $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{O}-$ ), 114.26 ppm ( $\text{CH}_2=\text{CH}-$ ), 138.76 ppm ( $\text{CH}_2=\text{CH}-$ ), 165.81 ppm ( $-\text{C}=\text{N}-$ ) (see p. 272).

ANAL. calcd. for  $\text{C}_{15}\text{H}_{27}\text{NO}$ : C, 75.89%; H, 11.47%; N, 5.90%.

Found: C, 75.90%; H, 11.68%; N, 5.90%.

10. 5-Hexenoic acid. To a pyrolysis apparatus constructed as shown in appendix D, with nitrogen stream and heated to 600-610°C was added



$\epsilon$ -caprolactone (80 g, 0.7 mol) at a rate of 0.5-0.6 g/minute. 68 g of crude pyrolyzate was obtained. The product was combined with a saturated aqueous solution of sodium bicarbonate and sodium chloride (200 mL) and stirred vigorously, followed by repeated extractions with toluene to isolate unreacted  $\epsilon$ -caprolactone. The aqueous phase was acidified with 5% aqueous hydrochloric acid, resulting in formation of a pale yellow oil. The oil was isolated, combined with toluene (200 mL) and washed with saturated aqueous sodium chloride solution (2 x 50 mL). The organic phase was dried over anhydrous magnesium sulfate, gravity filtered and reduced under vacuum. 1% hydroquinone was added to the crude product preceding vacuum distillation, (75-76°C/0.25 mm) which yielded 23.7 g (30%) of colorless 5-hexenoic acid. Infrared analysis (neat) showed absorptions at 3700-2300  $\text{cm}^{-1}$ , (OH stretch, carboxylic acid), 2980  $\text{cm}^{-1}$  (C-H stretch), 1720  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid), 1645  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 246). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at  $\delta$ : 1.15-2.78 ppm ( $(\text{CH}_2)_3$ , 6H), 4.60-5.13 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.28-6.33 ppm ( $\text{CH}_2=\text{CH}-$ , 1H), 11.5 ppm ( $-\text{CO}_2\text{H}$ , 1H, singlet) (see p. 265).  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) showed peaks at 23.99 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 33.18 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 33.49 ppm ( $-\text{CH}_2-\text{CO}_2\text{H}$ ), 115.64 ppm ( $\text{CH}_2=\text{CH}-$ ) 137.53 ppm ( $\text{CH}_2=\text{CH}-$ ), 180.42 ppm ( $-\text{CO}_2\text{H}$ ) (see p. 275).

11. Mono-2,6-dimethylphenyl sebacate. A dry one liter 3-neck round-bottom flask equipped with a rotary stirrer, claisen adapter, thermometer, pressure-equilibrium dropper funnel, nitrogen inlet and



outlet and ice-water bath was charged with sebacic acid (152 g, 0.75 mol) and benzene (200 mL). Trifluoroacetic anhydride (107 mL, 0.76 mol) was added dropwise followed by 2,6-dimethylphenol (91.6 g, 0.75 mol), added dropwise after melting with a heat gun. The reaction temperature was maintained below 25°C during these additions. The resulting solution was stirred at room temperature for 2 hours, followed by washing repeatedly with distilled water until the washings were neutral. The organic phase was dried over anhydrous magnesium sulfate, gravity filtered and reduced under vacuum to give 187 g (81%) of a yellow oil. Infrared analysis (film of chloroform soluble portion cast on a NaCl plate) showed absorptions at 3800-2400  $\text{cm}^{-1}$  ( $\text{-OH}$  stretch, carboxylic acid), 2939, 2861  $\text{cm}^{-1}$  ( $\text{C-H}$  stretch), 1761  $\text{cm}^{-1}$  ( $\text{C=O}$  stretch, ester) and 1715  $\text{cm}^{-1}$  ( $\text{C=O}$  stretch, carboxylic acid), 1480, 1370  $\text{cm}^{-1}$  ( $\text{C-H}$  bend, methylene, methyl), 1170  $\text{cm}^{-1}$  ( $\text{C-C(=O)-O}$  stretch) (see p. 245). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at  $\delta$ : 1.06-2.32 ppm ( $\text{-(CH}_2\text{)}_7$ , 14H), 2.11 ppm ( $\text{-CH}_3$ , 6H, singlet), 2.52 ppm ( $\text{-CH}_2\text{-CO}_2\text{-}$ , 2H, triplet), 6.86 ppm (phenyl, 3H, singlet), 10.78 ppm ( $\text{-CO}_2\text{H}$ , broad, 1H) (see p. 264). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at 16.36 ppm ( $\text{-C}_6\text{H}_3(\text{CH}_3)_2$ ), 24.68 ppm ( $\text{HO}_2\text{C-CH}_2\text{-CH}_2\text{-}$ ), 25.13 ppm ( $\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{-}$ ), 29.12 ppm ( $\text{HO}_2\text{C-CH}_2\text{-CH}_2\text{-(CH}_2\text{)}_4$ ), 34.06 ppm ( $\text{HO}_2\text{C-CH}_2\text{-}$ ,  $\text{-CH}_2\text{-CO}_2\text{-}$ ), 125.77, 128.59, 130.10 ppm (phenyl carbons, p, m, o respectively), 148.31 ppm ( $\text{-CH}_2\text{-CO}_2\text{-C}$ ), 171.46 ppm ( $\text{-CH}_2\text{-CO}_2\text{-}$ ), 180.21 ppm ( $\text{-CH}_2\text{-CO}_2\text{H}$ ) (see p. 247).

12. 2,6-Dimethylphenyl 3-butenolate. To a 500 mL 3-neck roundbottom flask equipped with pressure-equilibrium dropper funnel, thermometer, nitrogen inlet and outlet, magnetic stirrer and ice-water bath was charged freshly distilled (164-165°C) vinylacetic acid (25.8 g, 0.3 mol). Trifluoroacetic anhydride (63.6 mL, 0.45 mol) was then added dropwise so that the reaction temperature did not exceed 25°C. 2,6-dimethylphenol (38.5 mL, 0.3 mol) was next added dropwise at a similar rate. The resulting homogeneous solution was allowed to stir at room temperature for 5 hours followed by addition of benzene (200 mL) and washing with distilled water (3 x 200 mL), 5% aqueous sodium hydroxide (1 x 200 mL) and distilled water (4 x 100 mL). The organic phase was dried with sodium sulfate, gravity filtered and reduced under vacuum to give a quantitative yield of crude product. Distillation (77-81°C/.01 mm) produced 45 g (80%) of 2,6-dimethylphenyl 3-butenolate. Infrared analysis (neat) shows absorptions at 3080  $\text{cm}^{-1}$  (C-H stretch, olefinic), 2960, 2890  $\text{cm}^{-1}$  (C-H stretch), 1760  $\text{cm}^{-1}$  (C=O stretch, ester), 1640  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 244). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 2.06 ppm ( $-\text{CH}_3$ , 6H, singlet), 3.10, 3.22 ppm ( $-\text{CH}_2-$ , 2H, doublet), 4.86-5.30 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.49-6.02 ppm ( $\text{CH}_2=\text{CH}-$ , 1H), 6.81 ppm (phenyl, 3H) (see p. 263). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at 16.26 ppm ( $-\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 38.88 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 119.10 ppm ( $\text{CH}_2=\text{CH}-$ ), 125.88, 128.60, 129.93 ppm (phenyl carbons, p, m, o respectively), 130.09 ppm ( $\text{CH}_2-\text{CO}_2-\text{C}$ ), 148.25 ppm ( $\text{CH}_2=\text{CH}-$ ), 168.85 ppm ( $\text{CH}_2-\text{CO}_2-$ ) (see p. 273).

ANAL. calcd. for  $C_{12}H_{14}O_2$ : C, 75.76%; H, 7.42%. Found: C, 75.49%; H, 7.69%.

13. 2,6-Dimethylphenyl 5-hexenoate. A 500 mL 3-neck flask was dried at 200°C for 48 hours and fitted while hot with magnetic stir bar, three rubber septums and argon inlet and outlet needles connected to a paraffin oil bubbler. The flask was allowed to cool under argon sweep, transferred to a dry-bag purged with nitrogen and charged with 1,1'-carbonyldiimidazole (16.2 g, 0.1 mol). The flask was removed from the dry-bag, argon sweep resumed, and charged via syringe with benzene (98.3 mL, 1.1 mol) and 5-hexenoic acid (10.5 mL, 0.09 mol). The acid was added slowly dropwise, resulting in vigorous evolution of carbon dioxide. 2,6-dimethylphenol (11.6 mL, 0.09 mol) was then added using a heated syringe. A condenser was fitted to the apparatus and the reaction allowed to stir at 25°C for one hour, three hours at 65°C and for 22 hours at 25°C, under argon sweep. Benzene (100 mL) and distilled water (200 mL) were added to the reaction and the slurry allowed to stir for two minutes. The resulting two phase mixture was transferred to a 500 mL separatory funnel and the organic phase isolated and washed with distilled water (5 x 100 mL), until the wash solutions were neutral pH. The organic phase was dried for 20 hours over sodium sulfate and the solvent removed under vacuum (35 mm) to give a quantitative yield of crude product. Vacuum distillation (78°C/.03 mm) yielded 18.6 g (95%) of 2,6-dimethylphenyl 5-hexenoate. Infrared analysis (neat) showed absorptions at 3078, 3040  $cm^{-1}$  (C-H

stretch, aromatic, olefinic), 2980, 2930, 2860  $\text{cm}^{-1}$  (C-H stretch), 1765  $\text{cm}^{-1}$  (C=O stretch, ester), 1645  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin) (see p. 244). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 1.52-2.21 ppm ( $\text{CH}_2=\text{CH}(\text{CH}_2)_2$ , 4H), 2.08 ppm ( $-\text{CH}_3$ , 6H, singlet), 2.47 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet), 4.66-5.10 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.26-5.78 ppm ( $\text{CH}_2=\text{CH}-$ , 1H), 6.82 ppm (phenyl, 3H, singlet), (see p. 263). The  $^{13}\text{C}$  NMR spectrum shows peaks at 16.33 ppm ( $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 24.25 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 33.10 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 33.17 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 115.63 ppm ( $\text{CH}_2=\text{CH}-$ ), 125.72, 128.58, 130.06 ppm (phenyl carbons, p, m, o respectively), 137.49 ppm ( $\text{CH}_2-\text{CO}_2-\text{C}$ ), 148.41 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ ), 170.88 ppm ( $-\text{CH}_2-\text{CO}_2-$ ) (see p. 273).

ANAL. calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_2$ : C, 77.03%; H, 8.31%. Found: C, 76.81%; H, 8.35%.

14. 2,6-Dimethylphenyl 8-nonenoate. A dry liter 3-neck flask equipped with rubber septums was placed in a dry bag purged with nitrogen and charged with lead tetraacetate (200 g, 0.45 mol) and cupric acetate (11.2 g, 0.056 mol). The flask was then removed from the dry bag and equipped with rotary stirrer, clausen adapter, thermometer, condenser, heating mantle and argon inlet and outlet tube connected to a paraffin bubbler. To this apparatus was then charged benzene (940 mL), pyridine (27.3 mL, 0.34 mol) and mono-2,6-dimethylphenyl sebacate (86.0 g, 0.28 mol). This heterogeneous opaque green slurry was flushed with argon for 1 hour using a syringe needle positioned below the surface of the reaction mixture. The reaction was heated slowly to reflux temperature ( $81^\circ\text{C}$ ). Note that carbon dioxide evolution commenced slowly at  $65^\circ\text{C}$



and increased greatly approximately 25 minutes after reflux temperature was attained. The reaction must be carefully monitored and an ice-water bath used to cool the reaction during times of peak evolution of carbon dioxide. After this period of vigorous degassing the temperature was maintained at reflux without further danger. After a total reflux time of 1 hour, the evolution of gas diminished to a negligible level, so the reaction was allowed to cool to room temperature. Note that during the course of the reaction the color changed from green to brown, due to formation of a brown insoluble oil. The reaction slurry was extracted with distilled water (200 mL) and the organic phase washed with 3% aqueous nitric acid (2 x 400 mL), 5% aqueous sodium bicarbonate (300 mL) and distilled water (2 x 400 mL). The orange-red colored organic phase was dried over anhydrous magnesium sulfate and reduced under vacuum to give 84 g of light brown oil. Vacuum distillation (111-116°C/0.01 mm) yielded 13.1 g (18%) of 2,6-dimethylphenyl 8-nonenolate. Infrared analysis (neat) showed absorptions at 3095, 3060  $\text{cm}^{-1}$  (C-H stretch, olefinic, aromatic), 3000, 2955, 2880  $\text{cm}^{-1}$  (C-H stretch), 1755  $\text{cm}^{-1}$  (C=O stretch, ester), 1637  $\text{cm}^{-1}$  (C=C stretch, mono-substituted olefin) (see p. 245). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at  $\delta$ : 1.36 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2(\text{CH}_2)_4$ , 8H), 1.92 ppm ( $\text{CH}_2=\text{CH}-\text{CH}_2-$ , 2H), 2.11 ppm ( $-\text{CH}_3$ , 6H, singlet), 2.49 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet), 4.62-5.09 ppm ( $\text{CH}_2=\text{CH}-$ , 2H), 5.34-5.94 ppm ( $\text{CH}_2=\text{CH}-$ , 1H), 6.82 ppm (phenyl, 3H) (see p. 264). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) shows peaks at 16.35 ppm ( $-\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 25.14 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 28.82, 29.20 ppm ( $\text{CH}_2=\text{CH}_2-\text{CH}_2(\text{CH}_2)_3$ ), 33.79 ppm

(CH<sub>2</sub>=CH-CH<sub>2</sub>-), 33.99 ppm (CH<sub>2</sub>-CO<sub>2</sub>-), 114.42 ppm (CH<sub>2</sub>=CH-), 125.73, 128.57, 130.07 ppm (phenyl carbons, p, m, o respectively), 138.77 ppm (CH<sub>2</sub>-CO<sub>2</sub>-C), 148.39 ppm (CH<sub>2</sub>=CH-), 171.12 ppm (-CH<sub>2</sub>-CO<sub>2</sub>-) (see p. 274).

ANAL calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>: C, 78.42%; H, 9.29%. Found: C, 78.62%; H, 9.42%.

#### D. Coordination Polymerization of 2,6-Dimethylphenyl 10-Undecenoate

1. General procedure for polymerization with the TiCl<sub>3</sub>AA/AlR<sub>3</sub> initiator. A large (20 x 2.5 cm) polymerization tube is washed with a soap solution, rinsed with acetone and distilled water, and dried in a gravity convection oven for 48 hours at 200°C. The hot reaction tube is transferred to the ante-chamber of a Dri-Lab® (<10ppm H<sub>2</sub>O, <5ppm O<sub>2</sub>) and allowed to cool to room temperature under vacuum (10<sup>-6</sup>mm). The tube is then transferred into the dry box and charged with the specified weight (normally 0.1-0.2g) of titanium trichloride AA and equipped with a magnetic stir bar (1.3 cm) and rubber septum (\$ 24/40). The tube is removed from the dry box, safety wired and placed in a desiccator containing anhydrous calcium sulfate prior to use, normally within one hour. The reaction tube is then removed from the desiccator, Apiezon® grease (type H) applied to the septum, and fitted with nitrogen inlet needle connected to a paraffin oil bubbler. The tube is charged with the appropriate solvent, aluminum alkyl, monomer and/or monomer-aluminum alkyl complex respectively, utilizing gas-tight syringes fitted with CTFE hubbed needles. All syringes are cleaned,

rinsed with distilled water and acetone, dried at least 12 hours at 100°C and stored in an evacuated (0.01 mm) desiccator containing calcium phosphate and phosphorus pentoxide. The reactions are magnetically stirred at ambient temperature or in an oil bath at temperatures up to 65°C. For most polymerizations the nitrogen inlet needle is removed upon completion of monomer addition. Apiezon® grease is then applied to the surface of the septum.

In polymerizations with liquid titanium derivatives such as titanium tetrachloride, use of the Dri-Lab® is not required. The hot reaction tube is equipped with a magnetic stir bar, rubber septum, safety wire, nitrogen inlet and outlet needles and are carefully flamed out followed by cooling to room temperature under nitrogen flow before use. Monomer precomplexation is conducted in a reaction tube prepared in identical fashion. The prescribed amounts of solvent, aluminum alkyl and monomer are introduced using nitrogen-purged gas-tight syringes. Ageing of these precomplexation solutions is done by stirring under nitrogen flow at room temperature or in an oil bath at 65°C. After the specified reaction time, the polymerization is terminated by slow addition of 40 mL methanol to the vented reaction tube. Caution is required since vigorous degassing generally occurs. The precipitated polymer is allowed to stir in methanol for one hour and the liquid decanted. Methanol (60 mL) is then added and the polymer allowed to stir for 12 hours. The polymer is isolated by decanting the methanol solution, dried and a crude yield obtained. Homopolymers of



functionally-substituted olefins are normally reprecipitated by dissolution in toluene followed by dropwise addition of methanol.

2. Polymerization of 2,6-dimethylphenyl 10-undecenoate with  $\text{TiCl}_3\text{AA}$  1.1/ $\text{Al}(\text{isoBu})_2\text{Cl}$  initiator. A dry 20 x 2.5 cm polymerization tube fitted with magnetic stir bar and rubber septum was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.1 g, 0.5 mmole Ti) while in a nitrogen atmosphere. The reaction tube was equipped with nitrogen inlet and outlet needles, followed by addition of toluene (4.0 mL, 37.5 mmol) and diisobutylaluminum chloride (DIBAC) (0.39 mL, 2.0 mmol) utilizing nitrogen-purged gas-tight syringes. To this heterogeneous mixture was added a solution consisting of toluene (4.0 mL, 37.5 mmol), DIBAC (0.97 mL, 5.0 mmol) and 2,6-dimethylphenyl 10-undecenoate (DMPU) (1.47 mL, 5.0 mmol) which had been charged to a similarly equipped reaction tube. The resulting purple-colored mixture was stirred at 25°C for 7 days, during which time the viscosity of the reaction increased to form a plug. The polymerization was terminated by slowly adding (caution-vigorous degassing) 30 mL of methanol to the vented tube. During this addition the color of the plug changed from dark purple-brown to ivory. The contents of the polymerization tube were added to a beaker containing methanol (200 mL) and allowed to stir for 12 hours. The polymer was isolated by decanting the methanol solution and was dried by evacuation at 0.01 mm for 48 hours. 1.27 g (88%) of poly(2,6-dimethylphenyl 10-undecenoate) was obtained. The polymer was dissolved in toluene (40 mL) and reprecipitated by dropwise addition of methanol. The resulting polymer was



white, opaque, non tacky and non elastomeric. The inherent viscosity of the polymer (0.5 % in benzene, 30°C) was 2.9 dL/g; this corresponds to average molecular weights  $\bar{M}_n = 3.06 \times 10^5$  and  $\bar{M}_w = 2.59 \times 10^6$  (based on polystyrene calibration standards) as determined by gel permeation chromatographic analysis of poly (DMPU) in THF solution (0.15 w/v%). The infrared spectrum (thin film cast from toluene) showed absorptions centered at 3040  $\text{cm}^{-1}$  (C-H stretch, aromatic), 2938, 2860  $\text{cm}^{-1}$  (C-H stretch), 1762  $\text{cm}^{-1}$  (C=O stretch, ester), 1470, 1375  $\text{cm}^{-1}$  (C-H bend, methylene and methyl respectively), 768  $\text{cm}^{-1}$  (see p. 247). The  $^1\text{H}$  NMR showed peaks at  $\delta$ : 0.50 - 2.18 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-$ , 17H), 2.04 ppm ( $-\text{CH}_3$ , 6H, singlet), 2.45 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet), 6.83 ppm (phenyl hydrogens, 3H, singlet) (see p. 266). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 16.34 ppm ( $-\text{CH}_3$ ), 25.28 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 26.83 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.54, 29.87, 30.50 ppm ( $-\text{CH}_2-$ ), 32.41 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 34.08 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 35.06 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-$ ), 40.14 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 125.75, 128.60, 130.11, 148.42 ppm (phenyl carbons, p, m, o,  $-\text{CO}_2-\text{C}-$ , respectively), 171.13 ppm (C=O) (see p. 277).

ANAL. calcd. for  $(\text{C}_{19}\text{H}_{28}\text{O}_2)_n$ : C, 79.12%; H, 9.79%. Found: C, 78.76%; H, 9.71%.

#### E. Polymerization of 10-Undecenoates Using the

##### $\text{TiCl}_3\text{AA}$ 1.1/ $\text{AlEt}_2\text{Cl}$ Initiator

#### 1. General procedure for polymerization of the 10-undecenoate series.

Reaction apparatus, preparation and polymerization techniques as

described in experimental section D-1 were utilized for this polymerization series. Sixteen reaction tubes were cleaned, dried and equipped with magnetic stir bars, rubber septums and safety wires. Eight tubes, designated as initiator tubes were charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol  $\text{TiCl}_3$ ), toluene (10.0 mL, 94 mmol), and diethylaluminum chloride (DEAC) (0.5 mL, 4.0 mmol). The eight remaining tubes, designated as precomplexation tubes, were charged with one of the eight prescribed 10-undecenoates (10.0 mmol), toluene (6.0 mL, 56 mmol), and DEAC (1.25 mL, 10.0 mmol). The solutions in the complexation tubes (9-16) were then transferred to the initiator tubes (1-8) using nitrogen-purged gas-tight syringes. The eight polymerizations were then stirred at 65°C for 10 days, allowed to cool and terminated by slow addition of acidic methanol (5% HCl) (5 mL) to the vented tubes. The contents of the tubes were transferred to beakers containing methanol (200 mL) and allowed to stir for 12 hours. The polymers were then isolated by decanting or suction filtration with a scintered glass funnel. The solvent was removed by evacuation in a desiccator to constant weight at 0.01 mm /25°C. The polymers were reprecipitated by dissolving in toluene (30 mL) and dropwise addition of methanol. The polymers were again dried under vacuum.

a. Polymerization of 2,6-diphenylphenyl 10-undecenoate. A dry 20 x 2.5 cm reaction tube, designated as the initiator tube, was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol) in a nitrogen atmosphere and equipped with a magnetic stir bar, rubber septum and safety wire. Toluene (10.0 mL, 94.1 mmol) and diethylaluminum chloride (DEAC) (0.5

mL, 4.0 mmol) were then introduced using nitrogen-purged gas-tight syringes. A second reaction tube, designated the precomplexation tube, was equipped in identical fashion and charged with toluene (6.0 mL, 57 mmol), diphenylphenyl 10-undecenoate (4.0 mL, 10.0 mmol), and DEAC (1.25 mL, 10.0 mmol). The contents of the precomplexation tube were then transferred to the initiator tube, which was stirred at 65°C for 10 days. During this time the color changed from brown to greenish-black, and the viscosity increased but did not form a plug. The reaction was allowed to cool and was terminated by slow addition of acidic methanol (10 mL methanol, 0.5 mL conc. hydrochloric acid). The contents of the polymerization tube were transferred to a beaker containing methanol (200 mL) and allowed to stir for 12 hours. The solvent was decanted and the polymer dried for 48 hours at 0.01 mm and room temperature over calcium phosphate. Yield of the ivory-colored slightly elastic poly(2,6-diphenylphenyl-10-undecenoate) was 3.2 g (77%). The polymer was reprecipitated by dissolving in toluene (20 mL) and dropwise addition of methanol. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.8 dL/g. The infrared spectrum (thin film from toluene) showed absorptions centered at 3053  $\text{cm}^{-1}$  (C-H stretch, aromatic), 2920, 2850  $\text{cm}^{-1}$  (C-H stretch), 1950, 1885, 1805  $\text{cm}^{-1}$  (overtone or combination bands), 1762  $\text{cm}^{-1}$  (C=O, ester), 1598, 1500  $\text{cm}^{-1}$  (C-C ring stretch), 1463  $\text{cm}^{-1}$  (C-H bend, methylene) (see p. 247). The  $^1\text{H}$  NMR spectrum showed peaks centered at  $\delta$ : 1.03 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}(\text{CH}_2)_7$ , 17H), 1.85 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H), 7.14 ppm (phenyl hydrogens, 13H), (see p. 266). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed



peaks at 24.40 ppm ( $-\underline{\text{CH}}_2-\text{CH}_2-\text{CO}_2-$ ), 26.67 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-\underline{\text{CH}}_2-$ ), 28.83 ppm, 29.40 ppm, 29.64 ppm, 30.47 ppm, ( $\text{-(CH}_2)_4$ ), 32.43 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 33.85 ppm ( $-\underline{\text{CH}}_2-\text{CO}_2-$ ), 35.15 ppm ( $\text{CH}_2-\overset{|}{\text{CH}}-\underline{\text{CH}}_2-$ ), 40.85 ppm ( $-\underline{\text{CH}}_2-\overset{|}{\text{CH}}$ ), 126.28 ppm, 127.35 ppm, 127.75 ppm, 128.12 ppm, 129.12 ppm, 130.02 ppm, 130.51 ppm, 136.03 ppm and 138.02 ppm, phenyl carbons), 145.22 ppm ( $\text{CH}_2-\text{CO}_2-\underline{\text{C}}$ ), 171.27 ppm ( $\text{C=O}$ ) (see p. 279).

ANAL. calcd. for  $\text{(C}_{29}\text{H}_{32}\text{O}_2)_n$ : C, 84.43; H, 7.82. Found: C, 83.95; H, 7.89; ash 0.2%.

b. Polymerization of phenyl 10-undecenoate. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8.0 mL, 75 mmol) and diisobutylaluminum chloride (DIBAC) (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8.0 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol) and phenyl 10-undecenoate (2.6 mL, 10.0 mmol). The contents of the pre-complexation tube were transferred to the polymerization tube and the resulting homogeneous slurry was allowed to stir at 25°C for 7 days.

c. Polymerization of the 4,4-dimethyl-2-oxazoline derivative of 10-undecenoic acid. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2g, 1.0 mmol), toluene (14.0 mL, 130 mmol), and DEAC (0.5 mL, 4.0 mmol). The precomplexation tube was charged with toluene (6.0 mL, 56 mmol), DEAC (1.25 mL, 10 mmol) and the oxazoline derivative, (2.7 mL, 8.85 mmol). The contents of the precomplexation tube were transferred to the initiation tube and the reaction allowed to stir at 25°C for 7 days. The inherent viscosity ( $\text{H}_2\text{O}$ , 30°C) of the



product was 0.24 dL/g. The infrared spectra (film cast from methanol) showed absorptions at 3500-2800, 2070  $\text{cm}^{-1}$ , N-H stretch and combination band, 2950  $\text{cm}^{-1}$ , 2870  $\text{cm}^{-1}$  (C-H stretch), 1740  $\text{cm}^{-1}$  (C=O stretch, ester), 1600  $\text{cm}^{-1}$ , 1505  $\text{cm}^{-1}$  (NH band, asymmetric and symmetric), 1390  $\text{cm}^{-1}$ , 1372  $\text{cm}^{-1}$  (gem-dimethyl C-H band). The  $^{13}\text{C}$  NMR spectrum ( $\text{D}_2\text{O}$ , 60°C) showed peaks at 175.39, 69.70, 55.25, 35.14, 30.95, 30.65, 29.92, 26.16 and 23.83 ppm.

F. Polymerization of  $\omega$ -Alkenoates with Variation  
of the Methylene Chain Length.

1. General procedure for polymerization. All apparatus was cleaned, dried and set up according to the procedure previously detailed in experimental section D-1. The four polymerizations were conducted simultaneously and allowed to react for 7 days at 25°C.
2. Polymerization of 2,6-dimethylphenyl 10-undecenoate. The dry initiator/polymerization tube (20 x 2.5 cm) was equipped with magnetic stir bar and rubber septum, and charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol) and diisobutylaluminum chloride (DIBAC) (0.78 mL, 4.0 mmol). The precomplexation tube was similarly equipped and charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol) and DMPU (2.94 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube and the resulting purple heterogeneous slurry allowed to stir at 25°C for 7 days. 2.8 g (94%) of polymer was obtained. The inherent viscosity (0.5% in benzene, 30°C) was 2.88 dL/g. The infrared spectrum (film from

toluene) was identical to that described in section D-2. The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) was identical to that described in section D-2.

3. Polymerization of 2,6-dimethylphenyl 8-nonenoate. The dry initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol) and DIBAC (0.78 mL, 4.0 mmol). The pre-complexation tube was charged with toluene, (8 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol) and 2,6-dimethylphenyl 8-nonenoate (2.65 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube and the resulting heterogeneous slurry allowed to stir at  $25^\circ\text{C}$  for 7 days. 1.5 g (57%) of polymer was obtained. The inherent viscosity (0.5% in benzene,  $30^\circ\text{C}$ ) was 2.84 dL/g. The infrared spectrum showed absorptions at  $3030\text{ cm}^{-1}$  (C-H stretch, aromatic),  $2922$ ,  $2858\text{ cm}^{-1}$  (C-H stretch, aliphatic),  $1760\text{ cm}^{-1}$  (C=O stretch, ester),  $1479$  (C-H bend) (see p. 246). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 16.34 ppm ( $-\text{CH}_3$ ), 25.27 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 26.58 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.54 ppm, 30.12 ppm ( $\{\text{CH}_2\}_2$ ), 32.15 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 33.96 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 34.92 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-\text{CH}_2-$ ), 40.07 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 125.73 ppm, 128.54 ppm, 130.00 ppm (phenyl carbons, p, m, o respectively), 148.21 ppm ( $\text{CH}_2-\text{CO}_2-\text{C}$ ), 171.21 ppm ( $\text{C}=\text{O}$ ) (see p. 278).

ANAL. calcd. for  $\{\text{C}_{17}\text{H}_{24}\text{O}_2\}$ : C, 78.42%; H, 9.29%. Found: C, 78.22%; H, 9.36%; % ash < 0.1%.

4. Attempted polymerization of 2,6-dimethylphenyl 5-hexenoate. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8 mL, 75 mmol), DIBAC

(1.94 mL, 10.0 mmol) and 2,6-dimethylphenyl 5-hexenoate (2.22 mL, 10.0 mmol). The contents of the polymerization tube were transferred to the polymerization tube and the resulting slurry allowed to stir for 7 days at 25°C. No polymer was obtained.

5. Attempted polymerization of 2,6-dimethylphenyl 3-butenate. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2g, 1.0 mmol), toluene (8 mL, 75 mmol) and DIBAC (0.78 mL, 4.0 mmol). The pre-complexation tube was charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10 mmol) and 2,6-dimethylphenyl 3-butenate (1.94 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube and the resulting heterogeneous slurry allowed to stir at 25°C for 7 days. No polymer was obtained.

#### G. Copolymerization of 2,6-Dimethylphenyl 10-Undecenoate

##### (DMPU) with $\alpha$ -Olefins and Ethylene

1. General procedure for copolymerization. The reaction apparatus, preparation and polymerization techniques as detailed in experimental section D-1 were adapted for the copolymerization reactions to follow. 2,6-dimethylphenyl 10-undecenoate was copolymerized with 1-dodecene, 1-hexene, propylene and ethylene. Terpolymerization with ethylene and propylene was also conducted. In each of the reaction series a set of tubes designated as initiator/polymerization tubes were charged with  $\text{TiCl}_3\text{AA}$  in a dry box with a nitrogen atmosphere, and each equipped with magnetic stir bar, rubber septum and safety wire. Specified amounts of



solvent and aluminum alkyl were then added with nitrogen-purged gas-tight syringes. An equal number of tubes designated as precomplexation tubes, were similarly equipped and charged with the appropriate solvent, DMPU and aluminum alkyl (mole ratio Al/DMPU=1.0). In the case of liquid olefin comonomers including 1-dodecene and 1-hexene, the olefin was charged to the initiator tube prior to addition of the contents of the precomplexation tube. When addition of all components was complete, the polymerization tubes were allowed to stir at room temperature for 48 hours. For copolymerizations of ethylene and/or propylene, the monomer gas feed was regulated via Brooks® flowmeters and delivered through 18 gauge steel syringe needles positioned below the level of the polymerization slurry. The monomer gas feed was introduced into the polymerization tube for approximately 30 seconds, followed by addition of the contents of the precomplexation tube. The gas feed was maintained at a gentle rate for periods ranging from 15 minutes to 4 hours. The gas flow was introduced at a rate so that a very slight positive pressure was maintained as evidenced by a paraffin oil bubbler connected to the reaction tube vent needles. The copolymerizations were continued until a plug of polymer had formed in the reaction tube. All reactions were then immediately terminated by slow addition of methanol (30 mL) to the vented tube. The contents of each reaction tube was transferred to a beaker containing methanol (200 mL) and the resulting slurry allowed to stir for 12 hours.

Solid polymers were isolated by decanting the methanol, and powders by suction filtration through a scintered glass funnel. All



polymers were dried to constant weight at 0.01 mm and 25°C, and the yield determined. Most polymers were reprecipitated by dissolution in toluene (30 mL) and dropwise addition of methanol. For each copolymer series, homopolymerization of the  $\alpha$ -olefin monomer was simultaneously conducted as a reference reaction. Monomer feed ratios of 10 and 20 mole-percent DMPU comonomer were carried out for both 1-dodecene and 1-hexene, with both toluene and heptane solvents utilized. Detailed information on these copolymerization series is found in Tables 16-20. The information to follow is in a highly condensed form adopted in order to minimize repetition.

## 2. Copolymerization of 1-dodecene and 2,6-dimethylphenyl 10-undecenoate (DMPU).

a. Polymerization of 1-dodecene. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (20 mL, 188 mmol), diisobutylaluminum chloride (DIBAC), (0.78 mL, 4.0 mmol), and 1-dodecene (8.88 mL, 40.0 mmol). Reaction conditions: 2 days at 25°C; yield: 6.48 g (97%). The inherent viscosity (0.5% in benzene, 30°C) was 3.78 dL/g. The infrared spectrum (thin film from toluene) showed absorptions at 2962 (C-H stretch, methyl), 2930, 2860  $\text{cm}^{-1}$  (C-H stretch, methylene), 1470, 1380 (C-H bend, methylene and methyl respectively) 720  $\text{cm}^{-1}$  (C-H rock) (see p. 248). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 14.14 ppm ( $-\underline{\text{CH}}_3$ ), 22.79 ppm ( $-\underline{\text{CH}}_2-\text{CH}_3$ ), 26.70 ppm ( $-\text{CH}_2-\overset{\text{I}}{\text{CH}}-\text{CH}_2-\underline{\text{CH}}_2-$ ), 29.58 ppm, 30.00 ppm, 30.45

ppm ( $\overline{\text{CH}_2}$ ), 32.10 ppm ( $\text{--CH}_2\text{--CH}_2\text{--CH}_3$ ), 32.54 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--}$ ), 35.18 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--CH}_2\text{--}$ ), 40.46 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--}$ ) (see p. 279).

b. Copolymerization of 1-dodecene with DMPU (80/20 feed mole ratio). The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (20 mL, 188 mmol) and diisobutylaluminum chloride (DIBAC) (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (5 mL, 47 mmol), 2,6-dimethyphenyl 10-undecenoate (DMPU) (2.94 mL, 10 mmol), and DIBAC (1.94 mL, 10 mmol). 1-dodecene (8.9 mL, 40 mmol) was charged to the polymerization tube, followed by the contents of the precomplexation tube. Reaction conditions: 2 days, 25°C; yield: 8.5 g (89%). The inherent viscosity (0.5% in benzene, 30°C) was 4.25 dL/g. The infrared spectrum (thin film from toluene) showed absorptions at 2960, 2930, 2860  $\text{cm}^{-1}$  (C-H stretch), 1762  $\text{cm}^{-1}$  (C=O stretch, ester), 1470, 1379  $\text{cm}^{-1}$  (C-H bend, methylene and methyl) 1168  $\text{cm}^{-1}$  (C-C(=O)-O stretch), 719  $\text{cm}^{-1}$  ( $\text{CH}_2$  rock), 765  $\text{cm}^{-1}$  (see p. 248). The  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) showed peaks at 14.08 ppm ( $\text{--CH}_3$ ), 16.32 ppm ( $\text{--C}_6\text{H}_3(\text{CH}_3)_2$ ), 22.76 ppm ( $\text{--CH}_2\text{--CH}_3$ ), 25.30 ppm ( $\text{--CH}_2\text{--CH}_2\text{--CO}_2\text{--}$ ), 26.73 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--CH}_2\text{--CH}_2\text{--}$ ), 29.53 ppm, 29.94 ppm, 30.45 ppm ( $\overline{\text{CH}_2}$ ), 32.06 ppm ( $\text{--CH}_2\text{--CH}_2\text{--CH}_3$ ), 32.69 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--}$ ), 34.12 ppm ( $\text{--CH}_2\text{--CO}_2\text{--}$ ), 35.29 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--CH}_2\text{--}$ ), 40.57 ppm ( $\text{--CH}_2\text{--}\overline{\text{CH}}\text{--}$ ), 125.76 ppm, 128.62 ppm, 130.14 ppm (phenyl carbons, p, m, o respectively), 148.41 ppm ( $\text{--CO}_2\text{--}\overline{\text{C}}$ ), 171.14 ppm ( $\text{C=O}$ ) (see p. 279).

The relative composition of the copolymer was 18 mole-% DMPU and 82 mole-% DOD.

ANAL. calcd. for  $(C_{11}H_{22})_{.82} (C_{19}H_{28}O_2)_{.18}$ : C, 83.73%; H, 13.04%; O, 3.23%. Found: C, 83.30%; H, 13.46%; O, 3.2%.

C. Copolymerization of 1-dodecene with DMPU (90/10 feed mole ratio).

The initiator/polymerization tube was charged with  $TiCl_3AA$  1.1 (0.2 g, 1.0 mmol), toluene (20 mL, 188 mmol) and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (3 mL, 28 mmol), DMPU (1.3 mL, 4.4 mmol) and DIBAC (0.85 mL, 4.4 mmol). 1-dodecene (8.9 mL, 40 mmol) was charged to the polymerization tube, followed by the contents of the precomplexation tube. Reaction conditions: 25°C, 2 days; yield: 7.8 g (97%). The inherent viscosity (0.5% in benzene, 30°C) was 3.81 dL/g. The infrared spectrum shows absorptions identical to those previously listed for the polymer obtained with 80/20 feed mole ratio described in part 2b. The  $^{13}C$  NMR ( $CDCl_3$ ) spectrum shows peaks identical to those listed in part 2b.

The relative composition of the copolymer was 8 mole-% DMPU and 92 mole-% DOD.

3. Copolymerization of 1-hexene and 2,6-dimethylphenyl 10-undecenoate (DMPU).

a. Polymerization of 1-hexene. The initiator/polymerization tube was charged with  $TiCl_3AA$  1.1 (0.2 g, 1.0 mmol), toluene (25 mL, 235 mmol), DIBAC (0.78 mL, 4.0 mmol) and 1-hexene (6.25 mL, 50 mmol). Reaction conditions: 25°C, 2 days; yield: 4.2 g (99%). The inherent viscosity (0.5% in benzene, 30°C) was 2.79 dL/g. The infrared spectrum



showed absorptions at 2963, 2935, 2862  $\text{cm}^{-1}$  (C-H stretch), 1460  $\text{cm}^{-1}$  (C-H bend, methylene), 1380  $\text{cm}^{-1}$  (C-H bend, methyl) (see p. 249). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 14.21 ppm ( $-\underline{\text{CH}}_3$ ), 23.33 ppm ( $-\underline{\text{CH}}_2-\text{CH}_3$ ), 28.86 ppm ( $-\underline{\text{CH}}_2-\text{CH}_2-\text{CH}_3$ ), 32.58 ppm ( $-\text{CH}_2-\underline{\text{CH}}-$ ), 34.77 ppm ( $-\text{CH}_2-\underline{\text{CH}}-\underline{\text{CH}}_2-$ ), 40.44 ppm, ( $-\underline{\text{CH}}_2-\underline{\text{CH}}-$ ) (see p. 280).

b. Copolymerization of 1-hexene and DMPU (80/20 feed mole ratio). The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (25 mL, 235 mmol) and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (6.9 mL, 65 mmol), DMPU (3.68 g, 12.5 mmol) and DIBAC (0.54 mL, 12.5 mmol). 1-hexene (6.25 mL, 50 mmol) charged to polymerization tube, followed by contents of the precomplexation tube. Reaction conditions: 25°C, 2 days; yield toluene soluble fraction: 6.28 g (80%). The inherent viscosity (0.5% in benzene, 30°C) was 3.40 dL/g. The infrared spectrum showed absorptions at 2955, 2930, 2860  $\text{cm}^{-1}$  (C-H stretch), 1762  $\text{cm}^{-1}$  (C=O stretch, ester), 1470, 1381  $\text{cm}^{-1}$  (C-H bend, methylene, methyl respectively), 1170  $\text{cm}^{-1}$  (C-C(=O)-O stretch), 768  $\text{cm}^{-1}$  (see p. 249). The  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) showed peaks at 14.19 ppm ( $-\underline{\text{CH}}_3$ ), 16.34 ppm ( $-\text{C}_6\text{H}_3(\underline{\text{CH}}_3)_2$ ), 23.27 ppm ( $-\underline{\text{CH}}_2-\text{CH}_3$ ), 25.24 ppm ( $-\underline{\text{CH}}_2-\text{CH}_2-\text{CO}_2-$ ), 26.73 ppm ( $-\text{CH}_2-\underline{\text{CH}}-\text{CH}_2-\underline{\text{CH}}_2-$ ), 28.77 ppm ( $-\text{CH}_2-\underline{\text{CH}}-\text{CH}_2-\underline{\text{CH}}_2-\text{CH}_2-\text{CH}_3$ ), 29.47 ppm, 29.76 ppm, 30.15 ppm, 30.41 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 32.48 ppm ( $-\text{CH}_2-\underline{\text{CH}}-$ ), 34.09 ppm ( $-\underline{\text{CH}}_2-\text{CO}_2-$ ), 34.69 ppm ( $-\text{CH}_2-\underline{\text{CH}}-\underline{\text{CH}}_2-(\text{CH}_2)_2-\text{CH}_3$ ), 40.36 ppm ( $-\underline{\text{CH}}_2-\underline{\text{CH}}-$ ), 125.75 ppm, 128.56 ppm, 130.07 ppm (phenyl carbons, p, m, o respectively). 148.29 ppm ( $-\text{CO}_2-\underline{\text{C}}$ ), 171.29 ppm ( $\text{C}=\text{O}$ ) (see p. 280).



The relative composition of the copolymer was 14 mole-% DMPU and 86 mole-% HEX.

ANAL. calcd. for  $(C_6H_{12})_{.86}(C_{19}H_{28}O_2)_{.14}$ : C, 83.86%; H, 12.77%; O, 3.87%. Found: C, 83.12%; H, 13.02%; O, 4.2%.

c. Copolymerization of 1-hexene with DMPU (90/10 feed mole ratio). The initiator/polymerization tube was charged with  $TiCl_3AA$  1.1 (0.2 g, 1.0 mmol), toluene (25 mL, 235 mmol) and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (3.1 mL, 29.2 mmol) DIBAC (1.08 mL, 5.6 mmol) and DMPU (1.63 mL, 5.6 mmol). 1-hexene (6.25 mL, 50 mmol) was charged to the polymerization tube, followed by the contents of the precomplexation tube. Reaction conditions: 25°C, 2 days; yield: 5.7 g (98%). The inherent viscosity (0.5% in benzene, 30°C) was 3.22 dL/g. The infrared spectrum showed absorptions at identical to those previously listed in part 3b. The  $^{13}C$  NMR ( $CDCl_3$ ) showed peaks identical to those previously listed in part 3b.

The relative composition of the copolymer was 6 mole-% DMPU and 94 mole-% HEX.

#### 4. Terpolymerization of ethylene, propylene and DMPU.

a. Copolymerization of ethylene and propylene using  $TiCl_3AA/AlEt_2Cl$  initiators. The initiator/polymerization tube was charged with  $TiCl_3AA$  1.1 (0.2 g, 1.0 mmol), toluene (16 mL, 150 mmol) and diethylaluminum chloride (DEAC) (0.46 mL, 3.7 mmol). A monomer feed consisting of propylene and ethylene (9:1 ratio by volume) was introduced into the polymerization tube by means of an 18 gauge syringe

needle positioned below the level of the reaction mixture. A gentle flow was maintained for 70 minutes at room temperature. The reaction was mildly exothermic and polymer began to precipitate immediately. The yield was 1.54 g of a white crumbly powder. The inherent viscosity of the copolymer (0.5% in decalin, 135°C) was 2.91 dL/g. The infrared spectrum (thin film cast from decalin) showed absorptions at 2950, 2918, 2845  $\text{cm}^{-1}$  (C-H stretch, methyl, methylene), 1460  $\text{cm}^{-1}$  (C-H bend, methylene), 1373  $\text{cm}^{-1}$  (C-H bend, methyl), 1258, 796, 725, 715  $\text{cm}^{-1}$  (see p. 256). The  $^{13}\text{C}$  NMR (1,2,4-trichlorobenzene/benzene- $\text{d}_6$ , 3/1 by volume, 120°C) showed peaks at 21.74 ppm ( $-\text{CH}_3$ ), 28.97 ppm ( $\text{CH}_2-\overset{\text{I}}{\text{CH}}$ ), 29.92 ( $\text{CH}_2-\text{CH}_2$ ), 46.57 ppm, ( $\overset{\text{I}}{\text{CH}_2}-\text{CH}$ ), (see p. 282).

b. Terpolymerization of ethylene, propylene and DMPU using

$\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$  initiators. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (5.92 mL, 55.7 mmol) and DEAC (0.46 mL, 3.7 mmol). The precomplexation tube was charged with toluene (10.0 mL, 94.1 mmol), DEAC (1.24 mL, 10.0 mmol) and DMPU (2.94 mL, 10.0 mmol). A monomer feed consisting of propylene and ethylene (9/1 by volume) was introduced into the polymerization mixture by means of an 18 gauge syringe needle. A gentle flow was maintained at a rate which insured slight positive pressure as indicated by a paraffin oil bubbler connected to the polymerization tube vent. Reaction conditions: 25°C, 70 minutes; yield: 2.64 g of a white, slightly tacky, tough elastic solid. The inherent viscosity of

the terpolymer (0.5% in decalin, 135°C) was 2.34 dL/g. The infrared spectrum (thin film cast from decalin) showed absorptions at 2950, 2925, 2850  $\text{cm}^{-1}$  (C-H stretch), 1762  $\text{cm}^{-1}$  (C=O stretch, ester), 1460  $\text{cm}^{-1}$  (C-H bend, methylene), 1378  $\text{cm}^{-1}$  (C-H bend, methyl), 1168  $\text{cm}^{-1}$  (C-C(=O)-O stretch), 764  $\text{cm}^{-1}$  (see p. 256). The  $^{13}\text{C}$  NMR spectrum (trichlorobenzene, benzene- $\text{d}_6$ , 3/1, 120°C) showed peaks at 16.22 ppm ( $-\text{CO}_2-\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 19.88, 20.62, 21.72 ppm ( $\text{CH}_2-\text{CH}(\text{CH}_3)$ ), 25.37 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 28.93 ppm ( $\text{CH}_2-\text{CH}(\text{CH}_3)$ ), 29.58 ppm ( $\text{CH}_2$ ), 29.89 ppm ( $\text{CH}_2-\text{CH}_2$ ), 34.14 ppm ( $-\text{CH}_2-\text{CO}_2-\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 46.54 ppm ( $\text{CH}_2-\text{CH}(\text{CH}_3)$ ), (see p. 282).

The relative composition of the terpolymer was approximately 6 mole-% DMPU, 47 mole-% propylene and 47 mole-% ethylene.

ANAL. calcd. for  $\text{C}_2\text{H}_4 \cdot 47\text{C}_3\text{H}_6 \cdot 47\text{C}_{19}\text{H}_{28}\text{O}_2 \cdot 06$ : C, 83.22%; H, 12.96%. Found: C, 83.28%; H, 12.70%.

c. Copolymerization of ethylene and propylene using  $\text{VOCl}_3/\text{AlEt}_2\text{Cl}$  initiators. The polymerization tube was charged with toluene (16 mL, 150 mmol),  $\text{VOCl}_3$  (0.094 mL, 1.0 mmol) and diethylaluminum chloride (DEAC) (0.5 mL, 4.0 mmol). A monomer feed consisting of propylene and ethylene (9:1 volume ratio) was introduced into the polymerization tube by means of an 18 gauge syringe needle positioned below the level of the homogeneous reaction solution. A gentle bubble rate was maintained for 70 minutes at 25°C. The yield was 0.23 g of a white rubbery polymer. The infrared spectrum (film cast from decalin) showed

absorptions at  $2960\text{ cm}^{-1}$ ,  $2869\text{ cm}^{-1}$  (C-H stretch, methyl),  $2920\text{ cm}^{-1}$ ,  $2842\text{ cm}^{-1}$ , (C-H stretch, methylene),  $1460\text{ cm}^{-1}$  (C-H bend, methylene),  $1380\text{ cm}^{-1}$  (C-H bend, methylene),  $1380\text{ cm}^{-1}$  (C-H bend, methyl),  $1155\text{ cm}^{-1}$ ,  $970\text{ cm}^{-1}$  (see p. 257). The  $^{13}\text{C}$  NMR spectrum (trichlorobenzene,  $80^\circ\text{C}$ ) showed peaks at 20.02, 20.74 and 20.85 ppm ( $-\underline{\text{C}}\text{H}_3$ ), 28.23 ppm ( $\underline{\text{C}}\text{H}_2-\text{CH}(\text{CH}_3)$ ) 28.54 ppm ( $\underline{\text{C}}\text{H}_2-\text{CH}_2$ ), and 46.28 ppm ( $(\underline{\text{C}}\text{H}_2-\text{CH}(\text{CH}_3))$ ), see p. 284).

d. Terpolymerization of ethylene, propylene and DMPU using  $\text{VOCl}_3/\text{AlEt}_2\text{Cl}$  initiator. The initiator/polymerization tube was charged with toluene (8.0 mL, 75 mmol),  $\text{VOCl}_3$  (0.094 mL, 1.0 mmol) and DEAC (0.5 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8.0 mL, 75 mmol), DEAC (1.24 mL, 10.0 mmol) and DMPU (2.94 mL, 10.0 mmol). A monomer feed consisting of propylene and ethylene (10:1 volume ratio) was initiated into the polymerization tube for 30 seconds followed by addition of the contents of the precomplexation tube. Monomer gas flow was maintained for 60 minutes at  $25^\circ\text{C}$ , and for 80 minutes at a reaction temperature gradually increasing from 30 to  $60^\circ\text{C}$ . 0.08 g of a white rubbery polymer was obtained. The infrared spectrum (film cast from decalin) showed absorptions at  $2940\text{ cm}^{-1}$ ,  $2915\text{ cm}^{-1}$  and  $2840\text{ cm}^{-1}$  (C-H stretch),  $1758\text{ cm}^{-1}$  (C=O stretch, aromatic ester),  $1455\text{ cm}^{-1}$  (C-H bend, methylene),  $1372\text{ cm}^{-1}$  (C-H bend, methyl) and  $1165\text{ cm}^{-1}$  (C-C(=O)-O stretch) (see p. 257).



5. Copolymerization of propylene with DMPU.

a. Polymerization of propylene. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (16.0 mL, 150 mmol) and DIBAC (2.71 mL, 10 mmol). Propylene gas was introduced below the surface of the polymerization mixture by means of an 18 gauge syringe needle. A gentle flow rate was maintained for 4 hours, at 25°C. The yield was 2.5 g of a white powder. The inherent viscosity (0.5% in decalin, 135°C) was 2.93 dL/g. The infrared spectra (thin film from decalin) showed absorptions at 2960, 2875  $\text{cm}^{-1}$  (C-H stretch, methyl), 2930, 2850  $\text{cm}^{-1}$  (C-H stretch, methylene), 1458  $\text{cm}^{-1}$  (C-H bend, methyl and methylene), 1380  $\text{cm}^{-1}$  (C-H bend, methyl), 1169  $\text{cm}^{-1}$  ( $\text{CH}_2$  twist) and 998, 972  $\text{cm}^{-1}$  (see p. 251). The  $^{13}\text{C}$  NMR spectrum (1,2,4-trichlorobenzene, 120°C) showed peaks at 46.53 ppm ( $-\text{CH}_2-$ ); 28.95 ppm ( $-\text{CH}-$ ); and 21.73 ppm ( $-\text{CH}_3$ ) (see p. 283).

b. Copolymerization of propylene with DMPU. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8.0 mL, 75 mmol) and DEAC (0.5 mL, 4 mmol). The pre-complexation tube was charged with toluene (8.0 mL, 75 mmol), DEAC (1.24 mL, 10.0 mmol) and DMPU (2.94 mL, 10.0 mmol). Propylene feed was introduced into the polymerization tube followed by the contents of the precomplexation tube. Propylene feed was maintained for 4 hours at a rate so that very slight positive pressure was maintained as indicated by a paraffin oil bubbler connected to the polymerization tube vent.

3.61 g of a white flocculent powder was obtained. The inherent viscosity (0.5% in decalin, 135°C) was 2.85 dL/g. The infrared spectrum (thin film from decalin) showed absorptions at 2960, 2870  $\text{cm}^{-1}$  (C-H stretch, methyl), 2925, 2848  $\text{cm}^{-1}$  (C-H stretch, methylene), 1765  $\text{cm}^{-1}$  (C=O stretch, ester), 1460, 1380 (C-H bend), 1170  $\text{cm}^{-1}$  (C-C(=O)-O stretch), and 998, 972  $\text{cm}^{-1}$  (see p. 251). The  $^{13}\text{C}$  NMR spectrum (trichlorobenzene, benzene  $d_6$ , 3/1, 120°C) showed peaks at 16.28 ppm, ( $-\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$ ), 21.74 ppm, ( $\text{-(CH}_2\text{-CH(CH}_3\text{))}_n$ ), 25.40 ppm, ( $-\text{CH}_2\text{-CH}_2\text{-CO}_2-$ ), 28.97 ppm ( $\text{-(CH}_2\text{-CH(CH}_3\text{))}_n$ ), 29.61, 29.80, 29.87 ppm, ( $\text{-(CH}_2\text{)}_4$ ), 34.14 ppm ( $-\text{CH}_2\text{-CO}_2\text{-C}_6\text{H}_3(\text{CH}_3)_2$ ), 46.56 ppm ( $\text{-(CH}_2\text{-CH(CH}_3\text{))}_n$ ), (see p. 283).

The relative composition of the copolymer was 5 mole-% DMPU and 95 mole-% propylene.

ANAL. calcd. for  $\text{-(C}_3\text{H}_6\text{)}_{0.95}\text{-(C}_{19}\text{H}_{28}\text{O}_2\text{)}_{0.05}$ : C, 83.90%; H, 13.16%; 2.94%. Found: C, 83.65%; H, 13.18%; O, 3.0%.

## 6. Copolymerization of ethylene with DMPU.

a. Polymerization of ethylene. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2g, 1.0 mmol), toluene (16.0 mL, 150 mmol) and DEAC (1.74 mL, 14 mmol). Ethylene feed was introduced at a very slow rate for 4 hours at 25°C. 3.0 g of a white powder was obtained. The inherent viscosity (0.5% in decalin, 135°C) was 5.67 dL/g. The infrared spectrum (thin film cast from decalin) showed absorptions at 2925, 2860  $\text{cm}^{-1}$  (C-H stretch), 1462  $\text{cm}^{-1}$  (C-H bend,

methylene), and 720, 730  $\text{cm}^{-1}$  ( $\text{CH}_2$  rock, methylene) (see p. 252) . The  $^{13}\text{C}$  NMR spectrum (1,2,4-trichlorobenzene,  $120^\circ\text{C}$ ) showed a single peak at 28.89 ppm ( $-\text{CH}_2-$ ).

b. Copolymerization of ethylene with DMPU. The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2g, 1.0 mmol), toluene (8.0 mL, 75 mmol) and DEAC (0.5 mL, 4.0 mmol). The pre-complexation tube was charged with toluene (8.0 mL, 75 mmol), DEAC (1.24 mL, 10.0 mmol) and DMPU (2.94 mL, 10.0 mmol). Ethylene was introduced below the surface of the polymerization mixture via syringe needle, followed by transfer of the contents of the precomplexation tube. The ethylene feed was applied at a very gentle rate intermittently (30 second introduction at 10 minute intervals) for 4 hours. The yield was 4.4 g of a white powder. The inherent viscosity (0.5% in decalin,  $135^\circ\text{C}$ ) was 5.61 dL/g. The infrared spectrum (thin film from decalin) showed absorptions at 2930, 2860  $\text{cm}^{-1}$  (C-H stretch), 1762  $\text{cm}^{-1}$  (C=O stretch, ester), 1468  $\text{cm}^{-1}$  (C-H bend), 1169  $\text{cm}^{-1}$  ( $-\text{C}-\text{C}(=\text{O})-\text{O}-$  stretch), 720, 730  $\text{cm}^{-1}$  ( $\text{CH}_2$  rock) (see p. 252).

The relative composition of the copolymer was 3 mole-% DMPU and 97 mole-% ethylene.

ANAL. calcd. for  $(\text{C}_2\text{H}_4)_{.97}(\text{C}_{19}\text{H}_{28}\text{O}_2)_{.03}$ : C, 84.05%; H, 13.27%; O, 2.68%. Found: C, 84.23%, H, 13.47%; O, 2.6%.

## H. Modifications of $\omega$ -Functionally-Substituted Polyolefins.

### 1. Preparation of polyolefin ionomers and polyelectrolytes.

#### a. Saponification of poly(2,6-dimethylphenyl 10-undecenoate).

A 3-neck 500 mL roundbottom flask equipped with oil bath, magnetic stirrer, condenser, thermometer and argon inlet and outlet needles connected to an oil bubbler, was charged with poly (DMPU) (1.42 g, 4.9 mmol) and purified 1,4-dioxane (250 mL). This solution was heated gently at 85°C until all polymer dissolved, resulting in a translucent solution. A 4N aqueous sodium hydroxide solution (0.6 g sodium hydroxide in 3.7 mL distilled water) was then added rapidly dropwise, resulting in formation of a lower immiscible phase which rapidly turned yellow in color. This slurry was stirred under argon sweep at 85°C for one hour, followed by addition of distilled water (4.5 mL) and 4N aqueous sodium hydroxide solution (0.6 g sodium hydroxide in 3.7 mL distilled water). After 10 minutes the viscosity of the solution greatly increased. After an additional 30 minutes reaction time, gel formation was observed and the viscosity decreased. This slurry was allowed to stir at 85°C for 12 hours during which time the amount of gel diminished and a granular powder formed. The reaction was allowed to cool and the granular product was collected by filtration. The polymer was washed repeatedly with methanol until the washings were completely neutral. The solid was dried for one day at 0.01 mm over phosphorous pentoxide. The yield was 1.0 g (99%) of a fine ivory



powder. To insure total conversion to the carboxylate salt, the product was charged to an apparatus identical to that previously described along with distilled water (200 mL) and sodium hydroxide (0.67 g, 16.8 mmol). The polymer readily dissolved and the resulting solution was stirred for 3 hours at 70°C and for 12 hours at 25°C under argon sweep. The resulting viscous solution was suction filtered through a 50  $\mu$  fritted glass filter and divided into two equal portions. One portion was set aside for conversion to the polyacid derivative as described in section 2a. The second portion was precipitated by addition of 1,4-dioxane (180 mL). The product was isolated by filtration and washed numerous times with methanol until the washings were completely neutral. The product was dried for 1 day at 0.01 mm over phosphorous pentoxide. 0.45 g (90%) of a white free flowing powder was obtained. The inherent viscosity of the polymer (0.5% in water, 30°C) was 0.48 dL/g. The infrared spectra (KBr) showed absorptions at 2925  $\text{cm}^{-1}$ , 2855  $\text{cm}^{-1}$  (C-H stretch), 1560  $\text{cm}^{-1}$ , 1415  $\text{cm}^{-1}$  ( $\text{CO}_2^-$  stretch, carboxylate anion) (see p. 253). The  $^{13}\text{C}$  NMR spectrum ( $\text{D}_2\text{O}$ ), 60°C) showed peaks at 27.73 ppm ( $-\underline{\text{CH}}_2-\text{CH}_2-\text{COO}^-\text{Na}^+$ ), 30.39, 30.61, 30.98 and 31.12 ppm ( $\text{CH}_2$ )<sub>4</sub>, 34.95 ppm ( $-\text{CH}_2-\overset{|}{\text{CH}}-$ ), 36.18 ppm ( $-\text{CH}_2-\text{CH}-\underline{\text{CH}}_2-$ ), 39.23 ppm ( $-\underline{\text{CH}}_2-\text{COO}^-\text{Na}^+$ ), 42.57 ppm ( $\text{CH}_2-\overset{|}{\text{CH}}$ ), 184.39 ppm ( $-\underline{\text{COO}}^-\text{Na}^+$ ) (see p. 284).

ANAL. calcd. for  $(\text{C}_{11}\text{H}_{19}\text{O}_2\text{Na}\cdot 4\text{H}_2\text{O})_n$ : C, 47.47%; H, 9.78%; Na, 8.26%. Found: C, 47.38%; H, 7.32%; Na, 8.7%.

b. Saponification of poly(ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate). A 3-neck 100 mL roundbottom flask equipped with oil bath, magnetic stirrer, condenser, thermometer and nitrogen inlet and outlets (via rubber septum and syringe needles) connected to an oil bubbler was charged with poly(ethylene-co-propylene-co-2,6-dimethyl 10-undecenoate) (0.48 g), and 1,4-dioxane (25 mL). This mixture was allowed to stir at room temperature for 8 hours and for 1 hour at 85°C, followed by addition of 4N aqueous sodium hydroxide solution (0.2 g, 5 mmol) sodium hydroxide in 0.7 mL distilled water). The resulting slurry was then heated at 85°C for 3 hours, allowed to cool and filtered through a scintered glass funnel. The solid was washed with an ether/methanol solution (4/1 by volume) (200 mL), transferred to a beaker and allowed to stir for 1 day in a fresh ether/methanol solution of the same proportions and volume. The liquid was decanted and replaced by an identical solution and again allowed to stir at room temperature for 1 day. The tan powder was isolated by filtration and dried at 0.01 mm /100°C for 48 hours to yield 0.40 g, (84%) of light tan powder. The infrared spectrum (KBr) showed absorptions at 2910  $\text{cm}^{-1}$ , 2850  $\text{cm}^{-1}$  (C-H stretch), 1565  $\text{cm}^{-1}$ , 1420  $\text{cm}^{-1}$  ( $\text{CO}_2$ -stretch, carboxylate anion), 1460  $\text{cm}^{-1}$ , 1376  $\text{cm}^{-1}$  (C-H bend) (see p. 255).

ANAL. calcd. for  $(\text{C}_2\text{H}_4)_{.47}(\text{C}_3\text{H}_6)_{.47}(\text{C}_{11}\text{H}_{19}\text{O}_2\text{Na}\cdot\text{H}_2\text{O})_{.06}$ : C, 77.88%; H, 12.94%; Na, 2.97%. Found: C, 77.08%; H, 13.08%; Na, 3.01%.

## 2. Preparation of polyolefin carboxylic acids.

a. Poly(10-undecenoic acid). A 3-neck 500 mL roundbottom flask equipped with magnetic stirrer, oil bath, condenser, thermometer, septum stoppers and argon inlet and outlet needles connected to an oil bubbler was charged with a previously prepared solution consisting of poly(10-undecenoic acid sodium salt) (0.8 g, 3.9 mmol), sodium hydroxide (0.34 g, 8.4 mmol) and distilled water (115 mL). Glacial acetic acid (3 mL, 52.0 mmol) was added dropwise over a period of 30 minutes, and the resulting solution stirred at 25°C for 3 hours. The polymer product was isolated by filtration and washed thoroughly with distilled water (5 x 50 mL) and acetone (2 x 50 mL). The powder was dried for 2 days at 100°C and 0.005 mm over phosphorous pentoxide. The yield was 0.54 g (76%). The infrared spectrum (film cast from 1,4-dioxane) showed absorptions at 3400 - 2400  $\text{cm}^{-1}$  (-OH stretch, carboxylic acid), 2930  $\text{cm}^{-1}$ , 2853  $\text{cm}^{-1}$  (C-H stretch), 1708  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid), 1440  $\text{cm}^{-1}$  (C-OH bend), 1290  $\text{cm}^{-1}$  (C-O stretch) (see p. 254).

ANAL. calcd. for  $\text{(C}_{11}\text{H}_{20}\text{O}_2\text{)}$ : C, 71.70%; H, 10.94%. Found: C, 70.32%; H, 11.30; Na, <0.1%.

b. Poly(ethylene-co-propylene-co-10-undecenoic acid). A 3-neck 100 mL roundbottom flask equipped with magnetic stirrer, septum stoppers and nitrogen inlet and outlet needles connected to an oil bubbler was charged with poly(ethylene-co-propylene-co-10-undecenoic

acid, sodium salt) (0.5 g), 1,4-dioxane (50 mL) distilled water (21.0 mL) and glacial acetic acid (6.0 mL). This mixture was allowed to stir for 1 day at 25°C. The polymer was then isolated by filtration, washed by stirring in distilled water for 2 hours and dried for 2 days at 100°C and 0.01 mm over phosphorous pentoxide. The yield was 0.4 g (82%) of a white, rubbery polymer. The infrared spectrum (film cast from decalin) showed absorptions at 3400 - 2500  $\text{cm}^{-1}$  (-OH stretch, carboxylic acid), 2955  $\text{cm}^{-1}$ , 2920  $\text{cm}^{-1}$ , 2855  $\text{cm}^{-1}$  (C-H stretch), 1715  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid), 1465  $\text{cm}^{-1}$ , 1380  $\text{cm}^{-1}$  (C-H bend) (see p. 255).

ANAL. calcd. for  $(\text{C}_2\text{H}_4)_{0.47}(\text{C}_3\text{H}_6)_{0.47}(\text{C}_{11}\text{H}_{20}\text{O}_2)_{0.06}$ : C, 82.13%; H, 13.51%. Found: C, 82.05%; H, 14.08%; Na, <0.1%.

## I. Measurements

1. General Methods and Procedures. Infrared spectra were recorded on Perkin-Elmer Models 727 and 783 spectrophotometers. Liquid samples were measured as neat films between NaCl plates and solid samples as films cast from onto NaCl plates from chloroform, toluene or decahydro-naphthalene solutions. KBr pellets and Fluorolube® mulls were prepared from insoluble solid samples. Peak assignments were recorded to within 5  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectra of monomers, intermediates and selected polymers were obtained on a 60 MHz T-60 or 90MHz R-32 Perkin-Elmer NMR



### Spectrometers.

The  $^{13}\text{C}$  NMR spectra were recorded on a Varian CFT-20 Fourier-Transform spectrometer operating at 22.6 MHz. Sample concentrations were typically 20-40 w/v % in  $\text{CDCl}_3$  benzene- $\text{d}_6$ , or 1,2,4-trichlorobenzene, benzene  $\text{d}_6$  (3/1 by volume). Several hundred transients were accumulated for low molecular weight samples while at least 20,000 transients were obtained for polymer samples. Typical instrument parameters include a pulse width (PW) of 5 to 15 microseconds, a pulse delay (PD) of 0 to 15 seconds and an aquisition time of 1.023 seconds.

Inherent viscosity measurements were run at 30°C in benzene and 135°C in decalin, using ostwald-type viscometers. Solution concentrations were 0.5 g/dL and reported values are the average of at least three trials.

Gel permeation chromatography was conducted on a Waters Associates Model 210 liquid chromatograph, utilizing a set of 5 MicroStyragel® columns (nominal pore size 500,  $10^3$  (two),  $10^4$  and  $10^5$  Å). Tetrahydrofuran was used as solvent, with a flow rate of 1.47 mL per minute. Solutions were 0.15% (w/v) in THF. The instrument was calibrated using a set of four narrow-distribution polystyrenes supplied by Pressure Chemicals and Waters Associates.

The glass transition temperatures ( $T_g$ ) and melting temperatures ( $T_m$ ) for polymer samples were determined on a Perkin-Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of

20°C/minute. The instrument was calibrated for low temperature using a cyclohexane standard exhibiting a crystal-crystal transition at 186.1 K and a melting point of 279.7 K. For high temperature measurements the instrument was calibrated with indium which melts at 429.8 K.

Thermogravimetric analysis (TGA) of polymers was conducted on a Perkin-Elmer TSG-2 Thermogravimetric Analyzer, with a heating rate of 20°C/min in a nitrogen atmosphere.

Wide-angle x-ray diffraction (WAXD) measurements on bulk polymer samples were obtained using a Siemens Model D-500 Diffractometer. A copper cathode radiation source was employed; the wavelength of Cu-K $\alpha$  radiation was 1.5418Å. The x-rays were fitted by a monochromator located before the detector. Diffraction patterns were obtained using a Statton camera.

Dynamic mechanical properties of polymers were analyzed using a Polymer Laboratories DMTA, in shear mode with a frequency of 1 Hz and 5°C/min heating rate.

Gas chromatography (GC) analyses were performed on Varian Aerograph Models 1420 and 920, using helium as the carrier gas.

Microanalyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Massachusetts.

## C H A P T E R     I I I

### RESULTS AND DISCUSSION

#### A. Objectives

The objectives of this research were: (1) to investigate the polymerizability of  $\omega$ -functionally substituted  $\alpha$ -olefins, containing pendant carboxylic ester groups separated from the vinyl group by a hydrocarbon spacer chain, as a function of (a) ester substituent group, (b) length of methylene spacer chain, (c) initiator composition, (d) stoichiometry and (e) reaction parameters; (2) to prepare co- and terpolymers with ethylene, propylene and higher  $\alpha$ -olefins; (3) to convert representative polymers to the corresponding polyolefin ionomers, polyelectrolytes and polyacids; and (4) to conduct characterization and analysis of the resulting polymers.

In order to fulfill these objectives a series of  $\omega$ -substituted alkenoate monomers was synthesized containing numerous aliphatic and aromatic ester substituents, and spacer chains consisting of 1, 3, 6 or 8 methylene units. Selected titanium, vanadium and zirconium transition metal derivatives and aluminum alkyl initiator components were evaluated and reaction variables optimized for homopolymerization reactions. Co- and terpolymerizations of 2,6-dimethylphenyl 10-undecenoate with 1-dodecene, 1-hexene, propylene and ethylene were performed at several monomer feed ratios, using both titanium and vanadium based initiator systems. Selected polymers and terpolymers were

hydrolyzed to the corresponding sodium carboxylate salts and polycarboxylic acids. Monomers and polymers were characterized by standard techniques, including infrared,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy, elemental analysis and dilute solution viscometry. Selected samples were analyzed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), X-ray diffraction (WAXD), thermal gravimetric analysis (TGA) and dynamic mechanical testing (DMTA).

### B. Synthesis of Monomers and Intermediates

Several synthetic routes were necessary to prepare the required<sup>14</sup> monomers and intermediates. Preparation of the starting  $\omega$ -alkenoic acids will first be discussed, followed by details of the esterification procedures. Yield and boiling points for all monomers and intermediates are recorded in Tables 1 and 2. Summaries of the infrared and  $^{13}\text{C}$  NMR assignments for these monomers are included in Tables 3 and 4.

1. 10-Undecenoic acid. This popular starting material, a pyrolysis product of castor oil,<sup>165</sup> was purchased in high purity (99%) and used as received.

2. 8-Nonenoic acid. Synthesis of 8-nonenoic acid was attempted by means of a method developed by Ogibin et al.<sup>166,167</sup> Starting with sebacic acid, Ogibin reports an 80% yield of the desired  $\omega$ -alkenoic acid. The dicarboxylic acid is oxidatively decarboxylated to the 7-carboxyheptyl radical, by the action of an equimolar amount of



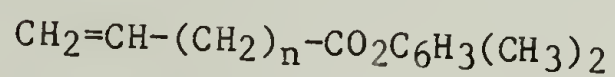
TABLE 1  
SYNTHESIS OF 10-UNDECENOATES  
 $\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{CO}_2\text{R}$

R	B.P. (°C/mm)	YIELD (%)
-CH <sub>3</sub>	117-118/5	91
-Cl <sup>a</sup>	121-125/9-10	82
-tertC <sub>4</sub> H <sub>9</sub>	75-76/0.01	74
-CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>	130-132/0.2	74
-CH <sub>2</sub> CF <sub>3</sub>	127-128/16	13
-C <sub>6</sub> H <sub>5</sub>	122-125/0.01	80
-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	145/0.05	76
-C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	198-201/0.01	75
$\begin{array}{c} \text{N} \quad \text{CH}_3^{\text{b}} \\   \quad   \\ -\text{C} \quad \text{O} \quad \text{CH}_3 \end{array}$	93-96/0.01	30

<sup>a</sup>acid chloride derivative of 10-undecenoic acid

<sup>b</sup>oxazoline derivative

TABLE 2

SYNTHESIS OF 2,6-DIMETHYLPHENYL  $\omega$ -ALKENOATES AND INTERMEDIATES

Monomer/Intermediate	B.P. ( $^{\circ}\text{C}/\text{mm Hg}$ )	% Yield
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	77-81/0.01	80
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$	75-76/0.25	39
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	78/0.03	98
$\text{HO}_2\text{C}-(\text{CH}_2)_8-\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	192/0.01	81
$\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	116-117/0.01	18
$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	145/0.05	76

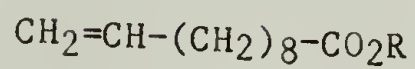
TABLE 3

 $^{13}\text{C}$  NMR CHEMICAL SHIFT DATA FOR 10-UNDECENOATES<sup>a</sup>

R	$\overline{\text{CH}_2}=\text{CH}-$	$\text{CH}_2=\overline{\text{CH}}-$	$\text{C}=\overline{\text{O}}$	$-\overline{\text{CH}_2}-\text{CO}_2\text{R}$	$-\overline{\text{CH}_2}-\text{CH}_2-\text{CO}_2\text{R}$	$\text{CH}_2=\text{CH}-\overline{\text{CH}_2}-$
-H	114.27	138.98	180.62	34.23	24.79	33.94
-CH <sub>3</sub>	114.25	139.02	173.95	34.11	25.07	33.91
-tertC <sub>4</sub> H <sub>9</sub>	114.28	139.92	172.88	35.59	25.21	33.93
-CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>	114.26	138.96	173.60	34.46	25.18	33.94
-CH <sub>2</sub> CF <sub>3</sub>	114.32	139.21	172.14	34.00	24.92	33.78
-C <sub>6</sub> H <sub>5</sub>	114.31	138.87	171.48	34.32	25.00	33.94
-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	114.28	138.89	170.91	33.94	25.17	33.94
-C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	114.28	138.91	171.17	33.86	24.35	33.86
Oxazoline derivative	114.26	138.76	165.81 <sup>b</sup>	33.86	26.07	33.86

<sup>a</sup>In ppm downfield from TMS (CDCl<sub>3</sub>)<sup>b</sup>-C=N-stretch

TABLE 4  
INFRARED DATA FOR 10-UNDECENOATES



R	$\nu\text{C}=\text{O}$ , ( $\text{cm}^{-1}$ )	$\nu\text{C}=\text{C}$ , ( $\text{cm}^{-1}$ )
-CH <sub>3</sub>	1745	1640
-Cl <sup>a</sup>	1795	1640
-tertC <sub>4</sub> H <sub>9</sub>	1735	1641
-CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>	1735	1641
-CH <sub>2</sub> CF <sub>3</sub>	1760	1640
-C <sub>6</sub> H <sub>5</sub>	1762	1639
-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	1758	1640
-C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1765	1635
-Oxazoline	1675 <sup>b</sup>	1648

<sup>a</sup>acid chloride

<sup>b</sup> -C=N- stretch



$\text{Na}_2\text{S}_2\text{O}_8$  in the presence of  $\text{AgNO}_3$  and  $\text{CuSO}_4$ . Formation of an alkylcopper complex inhibits inter- or intra-molecular radical transfer (to form the saturated acid or lactone) and permits  $\beta$ -deprotonation to generate 8-nonenoic acid.

Two attempts in this laboratory to prepare 8-nonenoic acid via the Ogibin method were not successful. The experimental procedure calls for dissolution of the dicarboxylic acid,  $\text{AgNO}_3$  and  $\text{CuSO}_4$  in water at  $60^\circ\text{C}$ , followed by addition of an aqueous  $\text{Na}_2\text{S}_2\text{O}_8$  solution. However, this experimenter found that sebacic acid was insoluble in water at the specified temperature. The aqueous  $\text{Na}_2\text{S}_2\text{O}_8$  was therefore added to the slurry, resulting in limited  $\text{CO}_2$  evolution. After stirring for 1 hour at  $70^\circ\text{C}$  and 12 hours at  $25^\circ\text{C}$ , the reaction consisted of an aqua colored liquid phase and a large amount of tan solid, found to be insoluble in the ether extraction prescribed by Ogibin. Thus it appears that Ogibin's procedure may be acceptable for shorter chain acids such as adipic acid, in which case the dicarboxylic acid is water soluble at  $60^\circ\text{C}$ , and the resulting 4-pentenoic acid is ether soluble, but is not suitable as written for longer chain acids where the starting material and product solubility are considerably different.

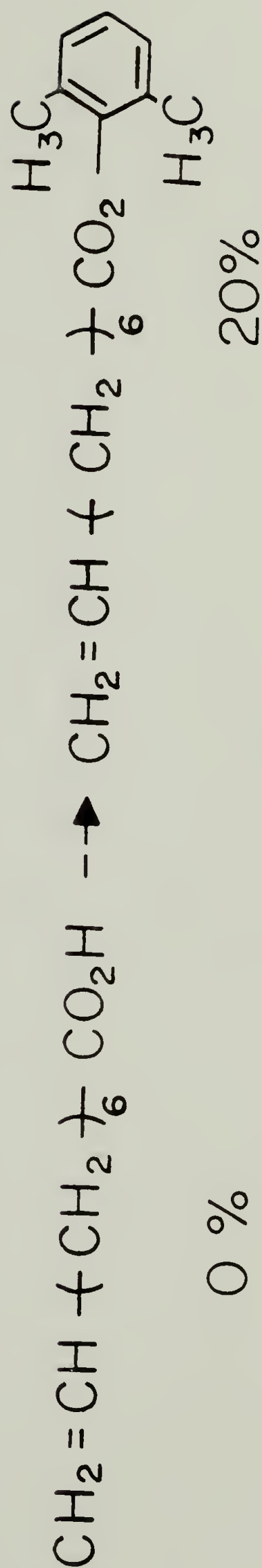
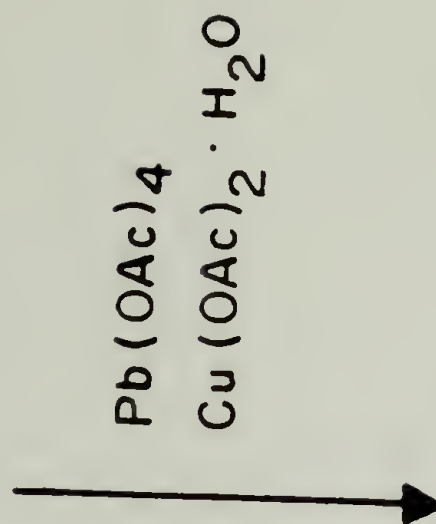
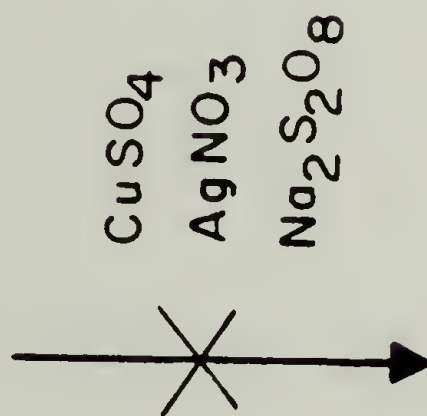
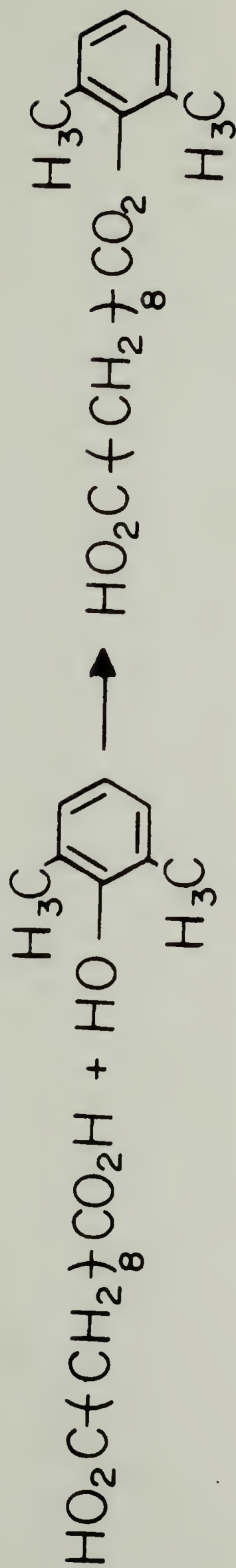
Ogibin also reports a modified procedure in which the monosodium salt of the dicarboxylic acid, in the presence of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and acetonitrile, is reacted with aqueous  $\text{Na}_2\text{S}_2\text{O}_8$ , followed by

ether extraction of the product. However, the monosodium salt of sebacic acid was heated to 70°C but also did not form a homogeneous solution. Upon addition of the  $\text{Na}_2\text{S}_2\text{O}_8$ , no  $\text{CO}_2$  evolution was observed. Infrared analysis of the product revealed that it was unreacted sebacic acid, with no evidence of unsaturated material present.

An alternate route for the preparation of 2,6-dimethylphenyl 8-nonenoate based on a procedure by Kochi and Bacha<sup>168</sup> was then successfully carried out, as will be described (see Equation 1). Kochi also reports a procedure for the decarboxylation of  $\alpha$ ,  $\omega$ -dibasic acids to the corresponding unsaturated acids, catalyzed by lead tetraacetate and cupric acetate.<sup>168</sup> This procedure would have been investigated had the preparation of 2,6-dimethylphenyl-8-nonenoate via decarboxylation of the half-ester been unsuccessful. For further discussion of the Ogibin method, see the attempted preparation of 7-octenoic acid.

3. 7-Octenoic acid. Synthesis of 7-octenoic acid via the Ogibin<sup>166,167</sup> method was unsuccessfully attempted. Following the previously described failure to prepare 8-nonenoic acid by this technique, reaction of azelaic acid was then selected, on the basis of its solubility in hot water. The azelaic acid was allowed to dissolve completely at 70°C, followed by addition of  $\text{CuSO}_4$ , resulting in a clear blue solution.  $\text{AgNO}_3$  was then added, resulting in formation of a large amount of a white precipitate. The specified amount of  $\text{Na}_2\text{S}_2\text{O}_8$  was added last, resulting in vigorous generation of  $\text{CO}_2$  gas. Simultaneously, the white solid disappeared and a brown oil formed.

Equation 1. Synthesis of 2,6-Dimethyl 8-Nonenoate.





Upon cooling a tan solid appeared. This slurry was extracted with ether and the product analyzed by infrared spectroscopy. The absence of a C=C stretch absorption at  $\sim 1640\text{ cm}^{-1}$  demonstrated that no 7-octenoic acid was isolated.

4. 5-Hexenoic acid. The synthesis of 5-hexenoic acid was prepared by pyrolysis of  $\epsilon$ -caprolactone at  $610^\circ\text{C}$ , with a feed rate of  $0.5\text{g/min}$  as indicated in Equation 2. Bailey<sup>200</sup> et al. demonstrated that pyrolysis of lactones with at least a seven-membered ring produced  $\omega$ -unsaturated acids in good yields. A crude yield of 39% was obtained in this laboratory, compared to 53% reported by Bailey. Approximately 50% of the pyrolyzate product was unreacted lactone, so that recycling would improve the efficiency of this method. The purification of 5-hexenoic acid was complicated by the proximity of its boiling point to that of the starting  $\epsilon$ -caprolactone. Purification by extraction with sodium bicarbonate followed by acidification and traditional vacuum distillation appeared more efficient than direct distillation under reduced pressure in a spinning band column. One percent hydroquinone was added to the distillation to retard polymerization. Note that the purified acid appeared stable during storage at ambient temperature. The final yield of 5-hexenoic acid was 29.8%.

5. 3-Butenoic acid. 3-Butenoic acid (vinylacetic acid) was purchased in 90% purity from Aldrich and purified by vacuum distillation. The

Equation 2. Synthesis of 2,6-Dimethylphenyl 5-Hexenoate.



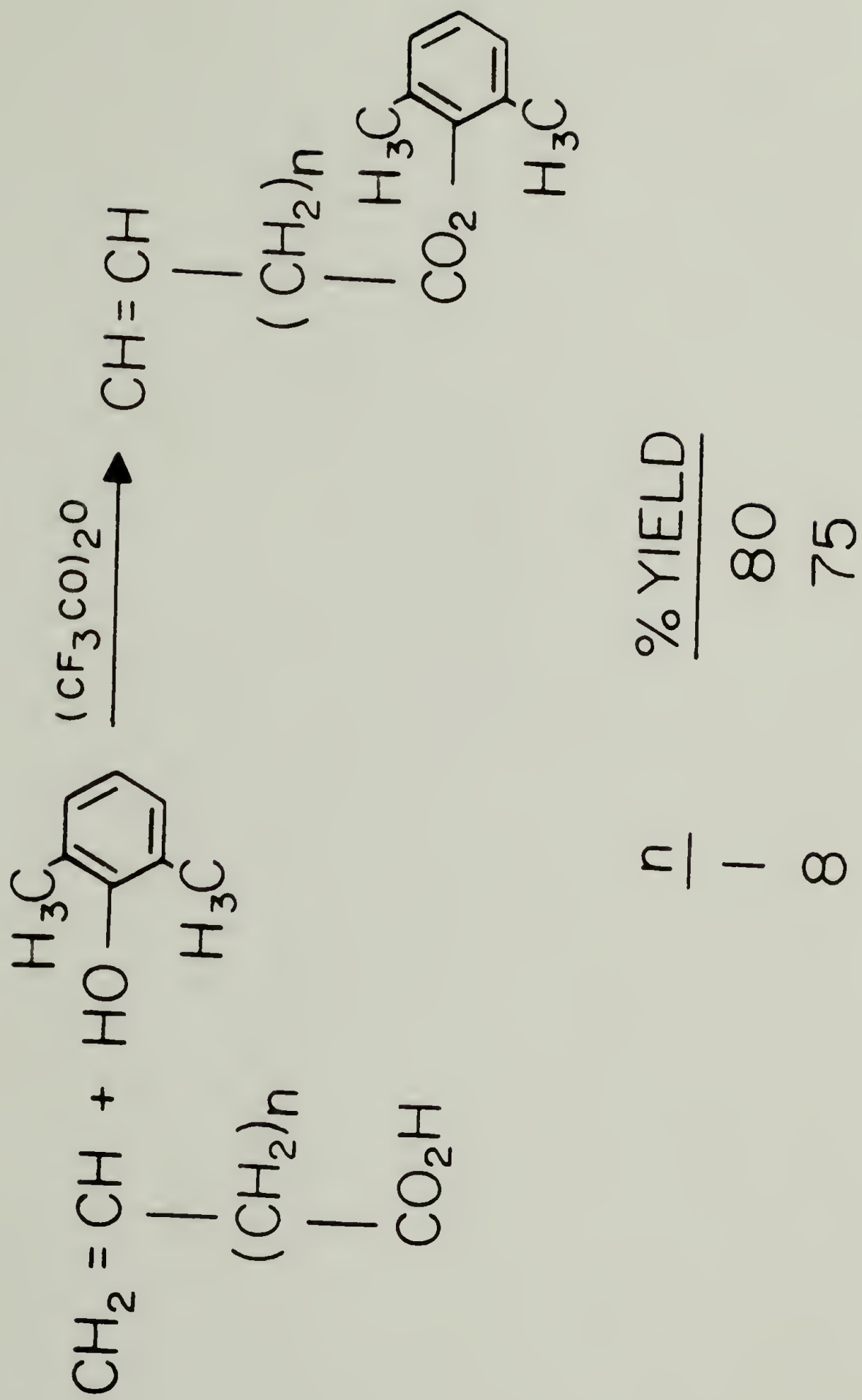
purified 3-butenic acid was isolated in 84% yield.

6. 2,6-Dimethylphenyl 3-butenate. The method developed by Tedder<sup>169</sup> for the synthesis of esters from carboxylic acids and hindered phenols was adapted for the preparation of this monomer. Equimolar amounts of 3-butenic acid and trifluoroacetic anhydride are first reacted to prepare the mixed anhydride, which was then combined with 2,6-dimethyl phenol. This esterification reaction is rapid and essentially complete after an hour at 25°C. Trifluoroacetic acid by-product is removed by extraction of the organic phase with water. Utilizing this procedure, yields of 75-80% were consistently obtained. Esterification by this technique is fast, convenient and affords crude product of high purity. Additional modifications and discussion of this method are found in the literature<sup>170-172</sup> (see Equation 3).

7. 2,6-Dimethylphenyl 5-hexenoate. The esterification procedure adapted from that of Tedder<sup>169</sup> was applicable to the preparation of the 2,6-dimethylphenyl esters of 10-undecenoic acid and 3-butenic acid, but was not suitable for the preparation of 2,6-dimethylphenyl 5-hexenoate. 5-hexenoic acid was allowed to react with trifluoroacetic anhydride and 2,6-dimethylphenol as previously described. However, during dropwise addition of trifluoroacetic anhydride, the reaction temperature rose from 0°C to 75°C, in a manner not previously observed, which indicated that a reaction other than formation of the mixed



Equation 3. Synthesis of 2,6-Dimethylphenyl 10-Undecenoate (DMPU) and 2,6-Dimethylphenyl 3-Butenoate.



anhydride had occurred. The product isolated was not the desired ester, but rather found to be 2-cyclohexene-1-one. Subsequent review of the literature revealed this to be a known cyclization reaction.<sup>171</sup> Reaction of 5-hexenoic acid with 2,6-dimethylphenol in the presence of 5 mole percent sulfuric acid was then conducted. Again ring closure occurred as indicated by a change in the infrared absorption for C=C from  $1645\text{ cm}^{-1}$  to  $1595\text{ cm}^{-1}$ .

The third attempt to esterify 5-hexenoic acid employed an esterification procedure of Staab<sup>173</sup> utilizing the dehydrating agent N,N'-carbonyldiimidazole (CDI). 5-hexenoic acid and a slight molar excess of CDI were reacted to form the imidazolide intermediate and  $\text{CO}_2$  as shown in Equation 2. 2,6-dimethylphenol was then added and the solution gently heated ( $70^\circ\text{C}$ ) for 2 hours, resulting in a quantitative yield of very pure ester product.

8. 2,6-Dimethylphenyl-8-nonenoate. Since the synthesis of 8-nonenoic acid according to Ogibin<sup>166,167</sup> could not be reproduced in this laboratory, an alternate route to this ester had to be developed. The resulting two step procedure is detailed in Equation 1. Equimolar quantities of sebacic acid, trifluoroacetic anhydride and 2,6-dimethylphenol were reacted by the now-familiar adaptation of the procedure by Tedder<sup>169</sup>, to provide the half ester mono-2,6-dimethylphenyl sebacate in 80% crude yield. In step two, the monoester was decarboxylated according to a procedure by Bacha and Kochi<sup>168</sup>. The  $\omega$ -alkenoate was generated by thermal oxidative decarboxylation of the

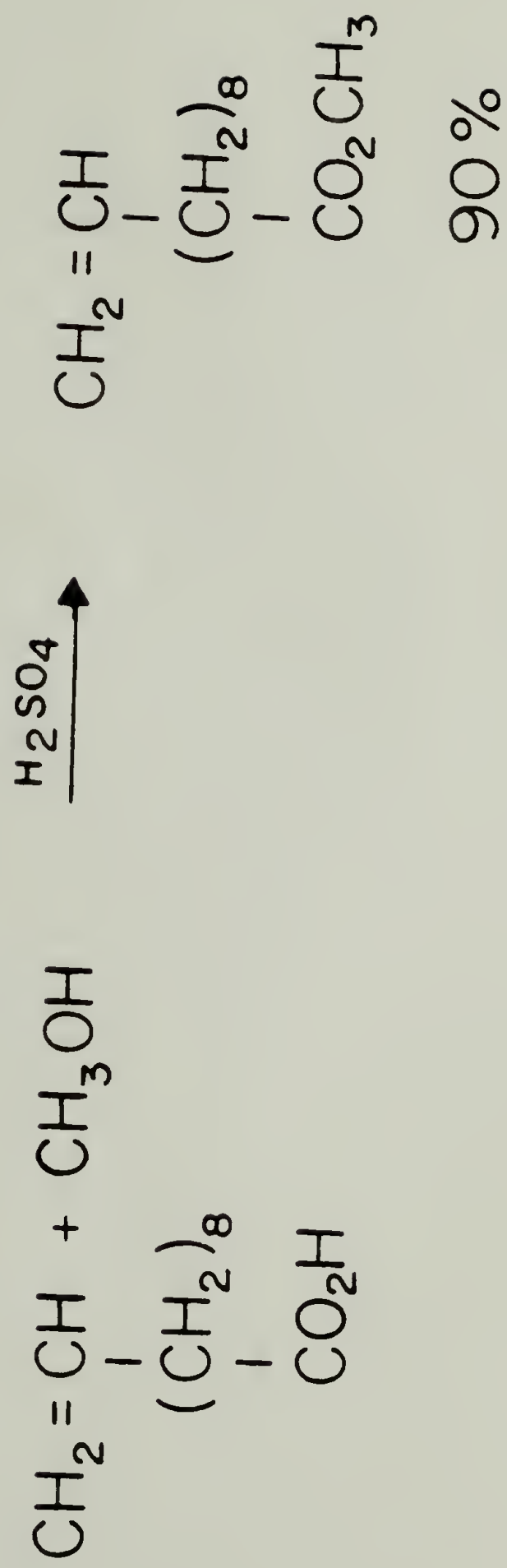
half ester in the presence of lead tetraacetate and cupric acetate. The reaction mixture was heated slowly to 80°C and must be very carefully monitored, since CO<sub>2</sub> evolution vigorously begins after an induction period of approximately 25 minutes. Removal of the heating mantle and cooling with an ice-water bath is required to prevent runaway decarboxylation. Also note that the volume of the reaction should be no more than one third the capacity of the reaction flask. Following work up and vacuum distillation, infrared analysis indicated that the desired  $\omega$ -alkenoate had been prepared but was contaminated with residue acid functionality. Purified product was obtained in a 20% yield after extraction with saturated aqueous sodium bicarbonate and a second distillation.

9. 2,6,-Dimethylphenyl 10-undecenoate. This key monomer was prepared by adaptation of the procedure of Tedder<sup>169</sup>, previously detailed for the synthesis of 2,6-dimethylphenyl 3-butenate. 10-undecenoic acid was used as received from Aldrich. The yield after two distillations was 75% (see Equation 3).

10. Methyl 10-undecenoate. The methyl ester of 10-undecenoic acid was prepared as previously described by Bansleben.<sup>1</sup> A yield of over 90% was obtained via sulfuric acid-catalyzed esterification of 10-undecenoic acid in a 10-fold excess of methanol, as indicated in Equation 4.



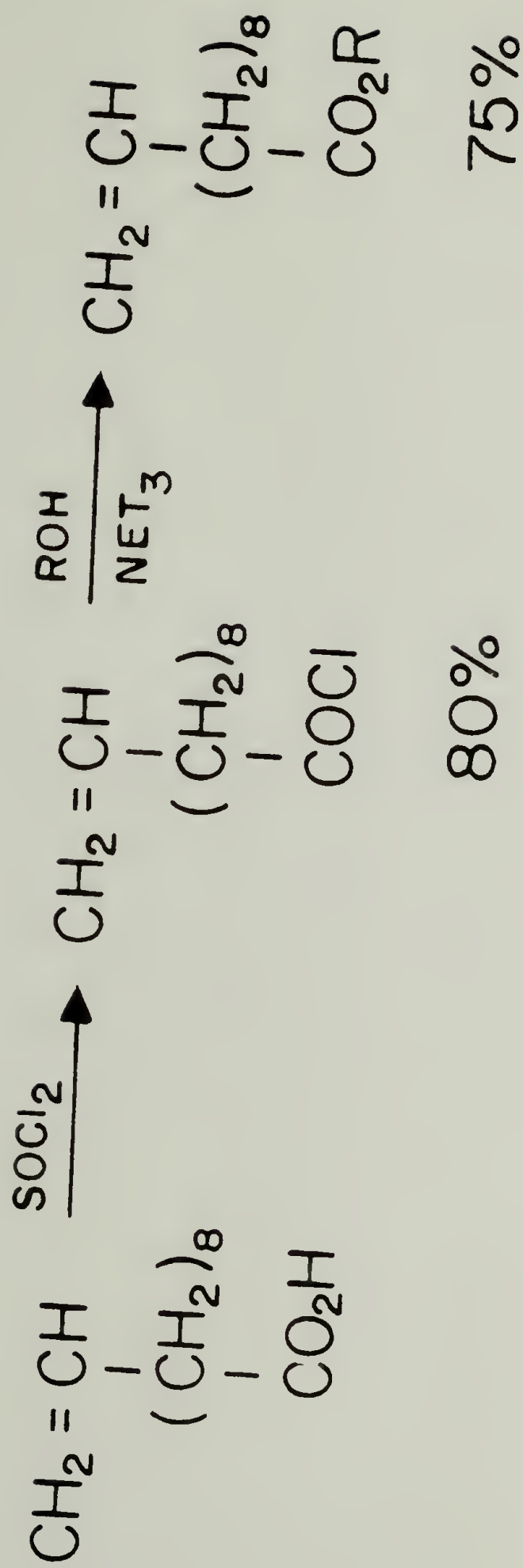
Equation 4. Synthesis of Methyl 10-Undecenoate.



11. Tert-butyl 10-undecenoate. The ter-butyl ester of 10-undecenoic acid was accomplished in two steps, as illustrated in Equation 5. In practice, esters are usually prepared from the acid chloride derivative rather than from the carboxylic acid directly. Both the preparation of the acid chloride and its reaction with an alcohol are rapid and essentially irreversible. Thus it is more convenient to carry out these two steps than the single slow, reversible reaction of the acid and alcohol.<sup>174</sup> Among the reagents commonly used for the preparation of acid chlorides, thionyl chloride is particularly convenient, since both by-products are gases (HCl and SO<sub>2</sub>) and are easily separated from the acid chloride product. In addition, any excess of thionyl chloride is readily removed by distillation.<sup>175</sup> Using this technique, 10-undecenoyl chloride was obtained in 82% yield. As indicated in Equation 5 the second step is reaction of the acid chloride with tert-butanol in the presence of triethylamine, which may function as both acid-acceptor and catalyst. A yield of 75% was obtained.
12. 2-Ethyl-1-hexyl 10-undecenoate. This aliphatic ester of 10-undecenoic acid was prepared in 74% yield using a two-step procedure analogous to that described for tert-butyl 10-undecenoate, as detailed in Equation 5.
13. 2,2,2-Trifluoroethyl 10-undecenoate. Preparation of this fluorinated ester was first attempted by the classical sulfuric acid catalyzed reaction of 10-undecenoic acid with a 1.5 molar excess of

Equation 5. Synthesis of Tert-Butyl 10-Undecenoate and  
2-Ethyl-1-Hexyl 10-Undecenoate.

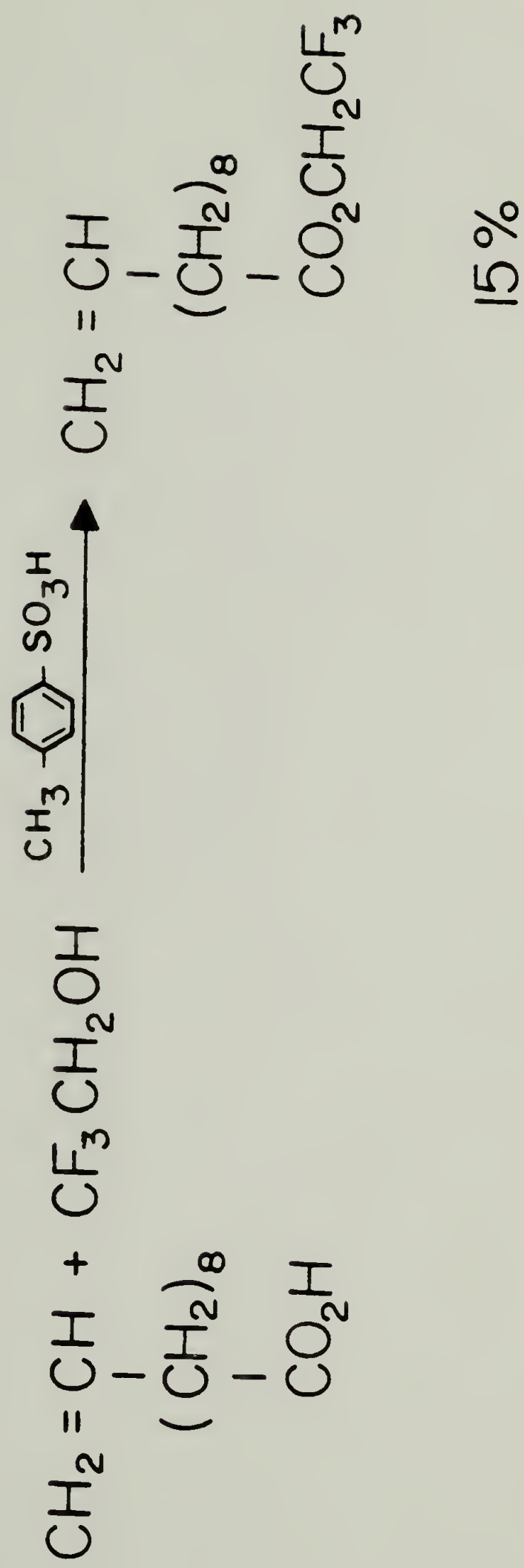




2,2,2-trifluoroethanol. Infrared analysis of the product revealed that absorptions characteristic of a terminal olefin were no longer present. Absorptions at  $3150\text{ cm}^{-1}$  (C-H stretch olefinic),  $1645\text{ cm}^{-1}$  (C=C stretch, monosubstituted olefin), and  $900\text{ cm}^{-1}$  (C-H out of plane bend) were totally absent and the absorption at  $960\text{ cm}^{-1}$  had increased in magnitude. This suggests that isomerization of the terminal olefin to a trans internal olefin had occurred. The C=C stretch absorption for a disubstituted trans configuration is normally at  $1678\text{--}1668\text{ cm}^{-1}$ , but may be extremely weak or absent. The appearance of a strong absorption at  $960\text{ cm}^{-1}$  (C-H out of plane bend for a trans disubstituted olefin) also indicates isomerization had taken place. However, the esterification was successful as evidenced by the carbonyl absorptions at  $1760\text{ cm}^{-1}$  and the lack of a carboxylic acid hydroxyl stretch. The isomerized product was isolated in 13% yield with elemental analysis results supporting the structure.

The second reaction of 10-undecenoic acid and 2,2,2-trifluoroethanol in the presence of 1% p-toluenesulfonic acid with benzene solvent resulted in a 15% yield of the desired terminally-unsaturated ester (see Equation 6). The Dean-Stark azeotropic distillation technique was employed to remove water produced during the esterification reaction. Following distillation GC analysis showed only one component present. However, infrared analysis indicated an impurity absorption at  $1700\text{ cm}^{-1}$  which could not be removed.

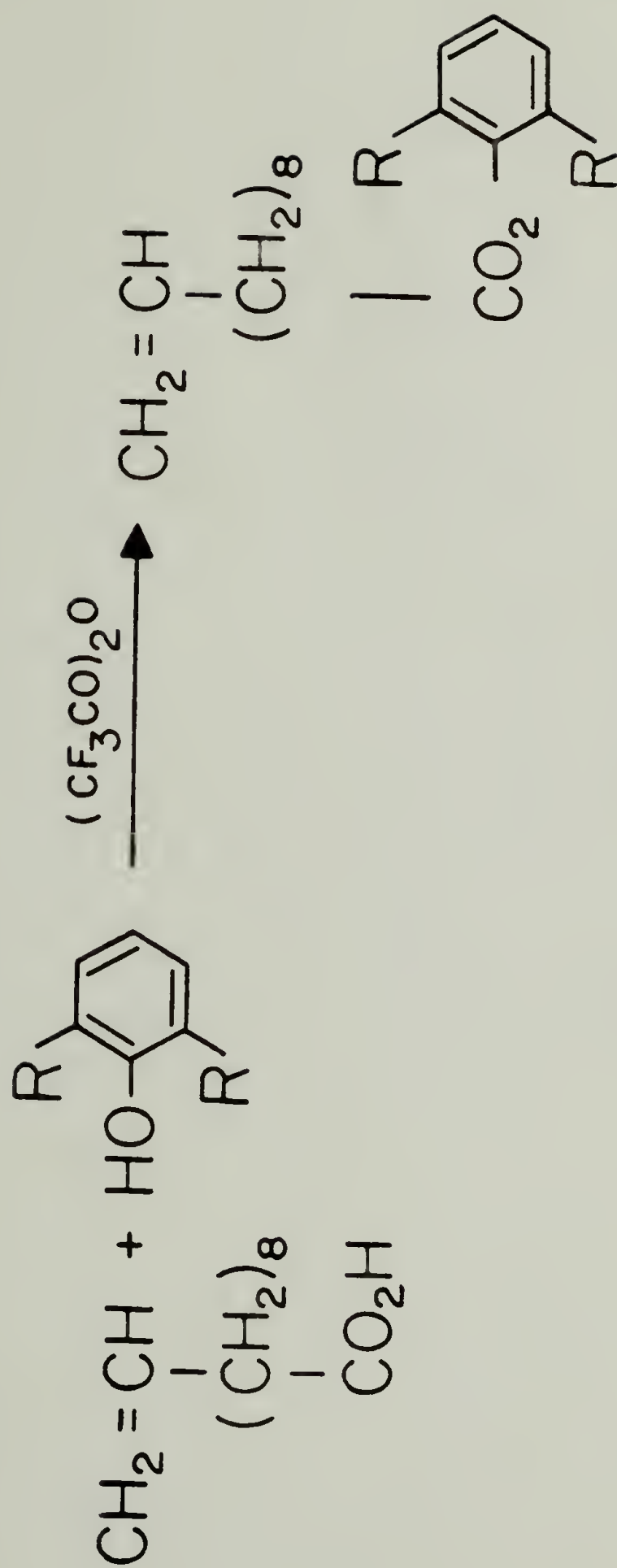
Equation 6. Synthesis of 2,2,2-Trifluoroethyl 10-Undecenoate.





14. Phenyl 10-undecenoate. The phenyl ester of 10-undecenoic acid was prepared by adaptation of the Tedder<sup>169</sup> procedure for the synthesis of esters from carboxylic acids and hindered alcohols. Comments are analogous to those included in the discussion of 2,6-dimethylphenyl 3-butenate. The product was obtained in 80% yield (see Equation 7).
15. 2,6-diphenylphenyl 10-undecenoate. Tedder's<sup>169</sup> procedure was likewise used for the preparation of this ester from 10-undecenoic acid and 2,6-diphenylphenol. A 75% yield was obtained (see Equation 7).
16. 4,4-Dimethyl-2-oxazoline derivative of 10-undecenoic acid. The preparation of carboxyl-protected 10-undecenoic acid was conducted according to the procedure of Meyers and Temple,<sup>176</sup> as illustrated in equation 8. Use of the 2-oxazoline protecting group is well known<sup>177</sup> and derivatives are readily prepared.<sup>175,178</sup> The 2-substituted 4,4-dimethyl-2-oxazoline system is of particular interest due to its ease of formation<sup>178</sup>, ready availability of starting materials and stability towards a variety of temperatures and reagents. When desired, the carboxylic acid may be regenerated by acid hydrolysis of the oxazoline at 95°C. To prepare this derivative, 10-undecenoic acid, 2-amino-2-methyl-1-propanol and p-toluenesulfonic acid were refluxed in toluene, with the water by-product isolated using a Dear-Stark trap. Infrared analysis confirmed the proposed structure by presence of the C=N stretch at 1675 cm<sup>-1</sup> and absence of the carboxylic acid absorptions. A 30% yield was recorded (see Equation 8).

Equation 7. Synthesis of the Phenyl Esters of 10-Undecenoic  
Acid.



$\text{R}$	% YIELD
H	80
$\text{CH}_3$	75
$\text{C}_6\text{H}_5$	75

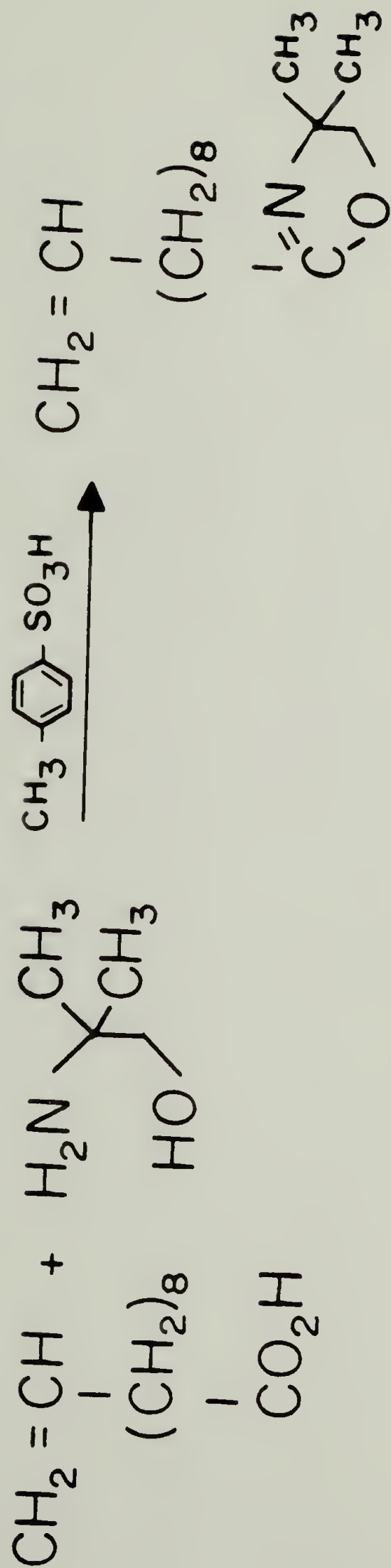
C. Polymerization of 2,6-Dimethylphenyl  
10-Undecenoate: Initiator Development

As illustrated by the literature citations reviewed in Chapter 1, the nature and properties of polymers obtained using Ziegler-Natta initiators are a function of a great number of interrelated variables. The crystallinity, stereoregularity, yield, molecular weight, molecular weight distribution, copolymer composition, nascent morphology and other physical properties are strongly influenced by the selection, stoichiometry and techniques for the introduction and reaction of initiator components and monomers. Specifically, the following factors must be considered: transition metal derivative; choice of metal, valence, ligands and crystal modification, organometallic component; choice of metal, alkyl or halogen substituents, selection of third component(s), inert gas and solvent, stoichiometry of the preceding components, use of ageing and heat treatments for initiators and monomer precomplexes, reaction conditions; time, temperature, method and sequence of component addition, stirring technique and polymer work up. In addition, preparative and purification techniques must be optimized and scrupulously maintained to insure experimental repeatability.

1. Variation of the transition metal derivative. The role of the transition metal component in coordination polymerization has been extensively examined.<sup>19</sup> While individual factors including choice of metal, ligand, valence, mode of reaction, etc., are extremely

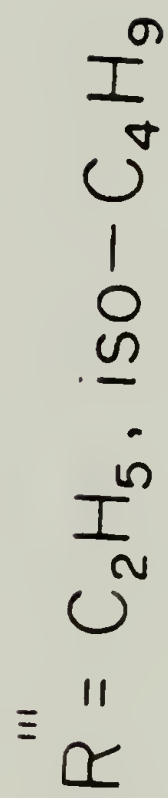
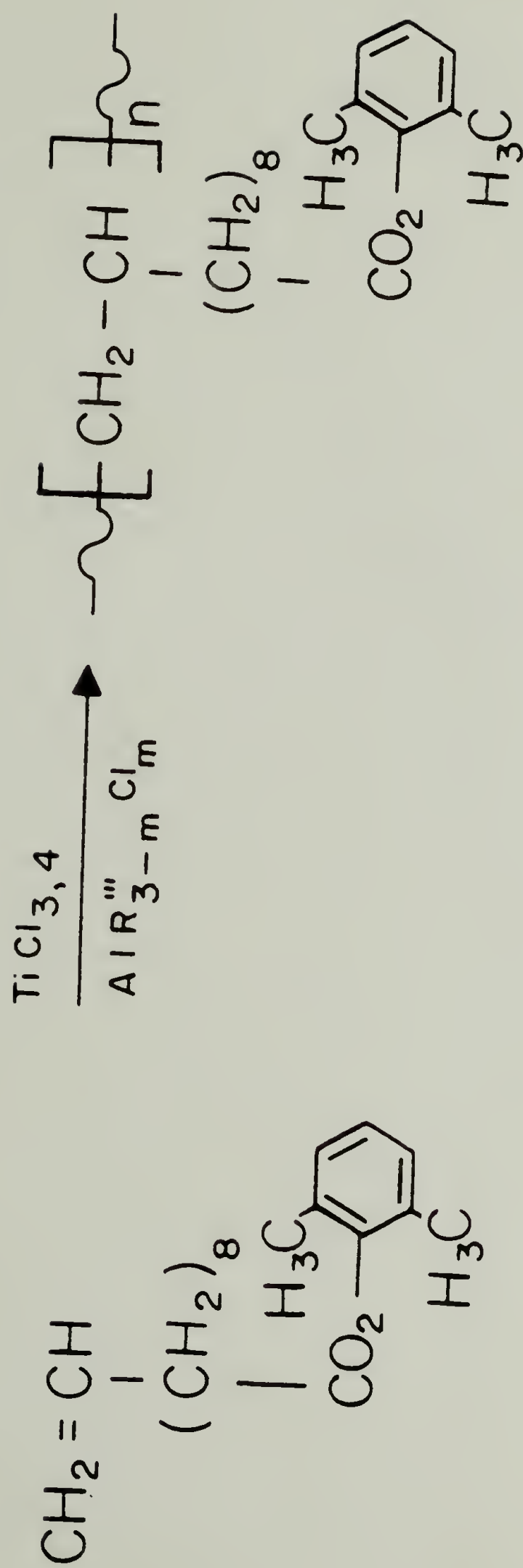


Equation 8. Synthesis of Oxazoline Derivative of  
10-Undecenoic Acid.



30 %

Equation 9. Polymerization of 2,6-Dimethylphenyl  
10-Undecenoate (DMPU).





important, Natta<sup>179</sup> recognized early that it is the combined effects of these factors which ultimately determines the contribution of the transition metal salt.<sup>19</sup> While nearly all of the transition metals have been shown to form active metal salts for one or more monomers, the commercially important results have been obtained with only a small number of metals. The early extensive use of titanium derivatives was certainly a result of the ready availability of  $\text{TiCl}_4$  at low cost and high purity. The same holds true for the extensive use of the aluminum-based alkyls. In due course, other transition derivatives of scandium, vanadium, chromium, niobium, zirconium and tungsten have been evaluated and are available. Salts of vanadium including  $\text{VCl}_4$ ,  $\text{VCl}_3$  and  $\text{VOCl}_3$  have received much attention owing to their ability to generate random copolymers as compared to the blocky products obtained using titanium systems.

The variation in reported ligand structure is great, including halogen, oxychloride, acetylacetonate, alkoxyl, cyclopentadienyl, oxides, phosphate, sulfate and others. Note that exchange with the aluminum alkyl is possible, so that the ligand structure of the active center may be different from the starting salt. Choices for both metal and ligand become restricted when discussion turns from ethylene to propylene and to higher  $\alpha$ -olefins, due to differences in activity and steric restrictions. As shown in Chapter 1, the majority of research on the polymerization of functional monomers report use of halogen-substituted titanium, specifically  $\text{TiCl}_3$  forms prepared by reduction of

$\text{TiCl}_4$ . In addition, as discussed in Chapter 1, of the unsupported systems, the  $\delta$  form of  $\text{TiCl}_3$  demonstrates the highest activity and stereospecificity. On this basis, several commercially available  $\text{TiCl}_4$  and  $\text{TiCl}_3$  products were selected for initial screening. Since random co- and terpolymers with ethylene and propylene were also an objective, vanadium oxychloride was selected. Zirconium tetrachloride was also evaluated. Table 5 includes the results from homopolymerizations of 2,6-dimethylphenyl 10-undecenoate. As indicated, good yields were obtained only in experiments utilizing  $\text{TiCl}_3\text{AA}$  ( $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$ ) commercially available from Stauffer Chemical Co., prepared by aluminum metal reduction of  $\text{TiCl}_4$  under specific conditions followed by ball milling to increase active site concentration per unit surface area. Three grades were evaluated, with comparable results.  $\text{TiCl}_3\text{AA}$  1.1 and 1.2 differ only in crystallite size, which is closely related to activity, the smaller size reported as more active due to higher surface area and so a higher concentration of active sites.  $\text{TiCl}_3\text{AA}$  1.3 has been treated with a low molecular weight polar molecule, probably camphor. Note that no polymer was obtained with  $\text{TiCl}_3$  prepared by hydrogen reduction of  $\text{TiCl}_4$ , or with  $\text{ZrCl}_4$ , and only an oily oligomer was obtained using  $\text{TiCl}_4$  directly. Also note that no oligomer or polymer was formed in the presence of aluminum alkyl in the absence of a transition metal salt.

2. Variation of the aluminum alkyl. Not all metals in groups I to III of the periodic table form active metal alkyls as claimed in patent

TABLE 5

POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE (DMPU)<sup>a</sup>

WITH VARIATION OF THE TRANSITION METAL DERIVATIVE (TMD)

Experiment	Charged Monomer in g	Solvent	TMD	Mole Ratio <sup>b</sup> Al/Ti/Monomer	Reaction Temperature in °C	Polymer Yield in %
1	1.4	heptane	TiCl <sub>4</sub>	3.7+11.4/1.0/11.4	45	Oligomer
2	3.0	heptane	TiCl <sub>4</sub>	30.0/1.0/25	45	Oligomer
3	2.9	toluene	TiCl <sub>3</sub> <sup>b</sup>	4.0+10.0/1.0/10.0	25	0
4	2.9	toluene	ZrCl <sub>4</sub>	4.0+10.0/1.0/10.0	25	0
5	2.9	toluene	TiCl <sub>3</sub> AA <sup>c</sup> 1.1	4.0+10.0/1.0/10.0	65	76 <sup>d</sup>
6	2.9	toluene	TiCl <sub>3</sub> AA1.2	4.0+10.0/1.0/10.0	65	78 <sup>d</sup>
7	2.9	toluene	TiCl <sub>3</sub> AA1.3	4.0+10.0/1.0/10.0	65	62 <sup>d</sup>
8	2.9	toluene	none	4.0+10.0/0.0/10.0	65	0

<sup>a</sup>Reaction conditions: 25-65°C, 10 days; AlR<sub>2</sub>Cl=AlEt<sub>2</sub>Cl; mole ratio Ti/solvent=1.0/150.

<sup>b</sup>TiCl<sub>3</sub>, hydrogen reduced; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl.

<sup>c</sup>TiCl<sub>3</sub>AA=TiCl<sub>3</sub>•1/3AlCl<sub>3</sub>.

<sup>d</sup>Yield after reprecipitation.

literature. Active systems have been prepared from lithium, sodium and potassium of group I, beryllium, magnesium, zinc and cadmium of group II, and aluminum and gallium of group III.<sup>19</sup> Most of the group I alkyls have only limited solubility in hydrocarbon solvents routinely used with Ziegler-Natta initiators. Zinc is the most widely used of the group II metals, and is useful for the polymerization of propylene and 1-butene. The aluminum alkyls have been by far the most extensively studied, due to availability, cost, ease of handling, toxicity and solubility properties. The most widely used aluminum alkyls are triethylaluminum (TEA), triisobutylaluminum (TIBA), diethylaluminum dichloride (DEAC).

Substitution of one or two alkyl groups by halogens generally alters the activity and stereoregulating ability of the aluminum alkyl. Danusso<sup>180</sup> demonstrated that this substitution consistently results in decreased activity and increased stereospecificity. As detailed in Chapter 1, the loss in activity can be restored by addition of electron donor molecules. As shown in Table 6, TEA, TIBA, DEAC and diisobutylaluminum chloride (DIBAC) were evaluated for the polymerization of  $\omega$ -alkenoates. As indicated, low yields were obtained using TEA and TIBA. In contrast, very good yields (80%) were achieved using both DEAC and DIBAC. Table 10 later demonstrates that much higher molecular weights were obtained using DIBAC. This will be discussed in more detail in section 6 to follow.



3. Variation of the aluminum/titanium mole ratio. Alkylation of the transition metal derivative by the base metal alkyl results in the formation of active centers. The literature contains reports of these components being combined in mole ratios from less than one to thirty and higher. It is now recognized that the mole ratio of the organometallic component to the transition metal derivative is a most important variable in Ziegler-Natta polymerization, and affects the polymer reaction rate, yield, stereospecificity and molecular weight.<sup>10</sup> For most nonpolar hydrocarbon monomers the optimum Al/Ti mole ratio for maximum yield falls in the range from 1 to 3 for heterogeneous systems, but can be as high as 10. It is important to note that the Al/Ti mole ratio that gives the best yield does not necessarily result in the optimum stereoregularity.<sup>181</sup> Quite the opposite has been demonstrated for a system polymerizing 1-butene.<sup>182</sup> In addition, different initiator combinations result in different optimum Al/Ti mole ratios for the same monomer.

The literature indicates that polymerizations involving monomers containing heteroatoms invariably require significantly higher Al/Ti mole ratios. In many cases, the monomer is precomplexed with an equimolar amount of the aluminum alkyl before addition to an initiator prepared using more conventional mole ratios in the range of 3-4. In other publications, Al/Ti mole ratios of as high as 30 are reported, with subsequent addition of the functional monomer. It appears probable to this experimenter that in this case also, the result is a 1:1

TABLE 6

POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE (DMPU)  
WITH VARIATION OF THE ALUMINUM ALKYL<sup>a</sup>

Experiment	Charged Monomer in g	Type AlR <sub>3</sub>	Mole Ratio <sup>b</sup> Al/Ti/Monomer	Polymer Yield in %	$\eta_{inh}^c$ in dL/g
1	2.9	None	0/1.0/10.0	0	-
2	2.9	AlEt <sub>3</sub>	3.7+10.0/1.0/10.0	4	-
3	2.9	Al(isoBu) <sub>3</sub>	3.7+10.0/1.0/10.0	7	-
4	2.9	AlEt <sub>2</sub> Cl	3.7+10.0/1.0/10.0	78	d
5	2.9	Al(isoBu) <sub>2</sub> Cl	3.7+10.0/1.0/10.0	82	d

<sup>a</sup>Reaction conditions: Ti=TiCl<sub>3</sub>AA 1.1, solvent=toluene, 60°C/10 days.

<sup>b</sup>Mole ratio Ti/solvent = 1.0/150; monomer precomplexed with aluminium alkyl, 1:1.

<sup>c</sup>0.5% solution in benzene, 30°C.

<sup>d</sup>Major portion of product is insoluble.

complexation of the monomer, with sufficient uncomplexed aluminum alkyl remaining to initiate polymerization, if alkylation has not already occurred before monomer addition.

It is also important to recall that metal alkyls can act as terminators of chain growth and under suitable circumstances, act as true chain transfer agents. Natta and Pasquon<sup>183</sup> first realized this for the polymerization of propylene with  $\text{TiCl}_3/\text{AlEt}_3$ . Natta et al.<sup>184</sup> later demonstrated that  $\text{ZnEt}_2$  was a considerably effective transfer agent, resulting in a convenient method for controlling molecular weight. Thus it is apparent that excess organometallic component is undesirable.

Given this information, the homopolymerization of 2,6-dimethylphenyl 10-undecenoate (DMPU) was conducted using various Al/Ti mole ratios, as detailed in Table 7. With no aluminum alkyl present, no polymerization was observed. With a mole ratio of 3.6, a yield of 5% was obtained. By precomplexing the DMPU with an equimolar amount of DEAC, the yield dramatically increased to 93%. In experiments 4 and 5, further increase did not adversely affect the polymer yield, but did result in decreased molecular weight, as evidenced by loss of integrity of the products, which were tacky flowing solids. Note that molecular weight estimation via dilute solution viscometry were attempted but were not successful due to insolubility of the bulk of the polymer product. This problem was remedied by conducting the

TABLE 7

## POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE

WITH VARIATION OF THE MOLE RATIO Al/Ti<sup>a</sup>

Experiment	Charged Monomer in g	Type AlR <sub>3</sub>	Mole Ratio <sup>b</sup> Al/Ti	Polymer Yield in %	$\eta_{inh}^c$ in dL/g
1	2.9	AlEt <sub>2</sub> Cl	0/1.0	0	-
2	2.9	AlEt <sub>2</sub> Cl	3.6/1.0	5	-
3	2.9	AlEt <sub>2</sub> Cl	3.6+10.0/1.0	93	d
4	2.9	AlEt <sub>2</sub> Cl	7.4+10.0/1.0	89	d
5	2.9	AlEt <sub>2</sub> Cl	11.1+10.0/1.0	95	d

<sup>a</sup>Reaction conditions: 60°C/10 days, Ti=TiCl<sub>3</sub>AA 1.1, solvent=toluene.<sup>b</sup>Mole ratio Ti/solvent = 1.0/150.<sup>c</sup>0.5% solution in benzene, 30°C.<sup>d</sup>Major portion of product is insoluble.



polymerizations at 25°C rather than 65°C. Further discussion of this point is included in section 6.

4. Variation of the monomer/titanium mole ratio. As discussed in chapter 1, the efficiency of the initiator system is of great concern for commercial polymer production, and has been the driving force for development of each successive generation, from the unsupported to the supported systems utilizing third components, which eliminate the need for removal of initiator residues. Supported systems for the polymerization of propylene conducted in a solvent are typically 15 to 50 times more efficient than the nonsupported  $\delta$   $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$  based initiators. Processes involving liquid monomer or gas phase reactions boast yields per gram of titanium that are 80 times greater.<sup>54</sup> Initiator performance for gaseous monomers including ethylene and propylene are normally reported in g polymer/g Ti/hour at a specified pressure and temperature. Reports of g polymer/g Ti for a specified reaction time are also common. For unsupported systems, polypropylene yields of 8-20 g/g Ti/hour are typical, compared to 300 g/g Ti/ hour for  $\text{MgCl}_2$  supported systems.<sup>51,185</sup> For polypropylene prepared with an unsupported system, this translates into a monomer/Ti mole ratio of approximately 110-280 or higher.

Literature reports of homopolymerization reactions of monomers containing heteroatoms claim monomer/Ti mole ratios considerably lower than those reported for nonpolar hydrocarbon systems. For example, key

papers and patents discussed in Chapter 1 report the following monomer/Ti mole ratios: Giannini,<sup>91,92</sup> polymerization of monomers containing nitrogen and oxygen, monomer/Ti = 11.4; Clark,<sup>114</sup> polymerization of halogen containing monomers, monomer/Ti=20; Carlini,<sup>127</sup> polymerization of vinyl pyridines, monomer/Ti=20; Holler and Youngman,<sup>131</sup> polymerization of nitrogen, phosphorous and oxygen containing monomers, monomer/Ti=25-50.

On the basis of these findings, the polymerization of 2,6-dimethylphenyl 10-undecenoate was conducted using monomer/Ti mole ratios from 10 to 40. Results are found in Table 8. It is clear that best results were obtained with a mole ratio of 10, which gave a very high yield (97%) and an inherent viscosity of 2.86 dL/g. Increase of the monomer/Ti mole ratio to 20 resulted in a significant drop in the yield (65%) but did not significantly affect the molecular weight. Further increase in the mole ratio to 40 continued the trend resulting in a 42% yield of polymer with a moderate decrease in inherent viscosity measurements.

As the monomer/Ti mole ratio is increased, the weight percent of transition metal component, and so the number of potentially active sites, is decreased. It follows that the yield would decrease, but not the molecular weight.

It is apparent that these results are in general agreement with previous findings. Note however, that the inherent viscosities of the polymers prepared in the course of this study are considerably

TABLE 8  
 POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE WITH  
 VARIATION OF THE MONOMER/Ti MOLE RATIO<sup>a</sup>

Experiment	Mole Ratio Monomer/Ti	% wt Ti in reaction	Polymer yield in %	$\eta_{inh}^b$ in dL/g
1	10.0/1.0	1.03	97	2.86
2	20.0/1.0	0.53	65	2.77
3	40.0/1.0	0.33	42	2.27

<sup>a</sup>Reaction conditions: 25°C, 7 days; Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl;  
 solvent=toluene.

<sup>b</sup>0.5% solution in benzene, 30°C.

higher than those of the previously cited efforts. Also note that optimized reaction conditions include use of DIBAC aluminum alkyl and reaction at 25°C rather than 65°C.

5. Variation of reaction solvent. In theory, any solvent that does not react with the initiator components in a deleterious manner can be used for Ziegler-Natta polymerization. The proper choice depends on the initiator system and conditions to be utilized.<sup>19</sup> Solubility of the monomer and polymer, boiling point and purity must be considered. Aliphatic and aromatic hydrocarbons are primarily employed in laboratory studies as well as in industrial processes.

In general, polymerization of monoolefins is carried out in aliphatic hydrocarbons, including the range from propane to octane, higher alkanes and cyclohexane. Aromatic solvents such as benzene and toluene are also used to a lesser extent. Polyolefins are normally synthesized in particulate form, making the aliphatic solvents more desirable. Halogenated solvents such as chloroethane have been used, in instances when reaction with the aluminum alkyl will not occur. For the present study, reaction conditions from 25 - 90°C were anticipated. Toluene (bp 111°C) and n-heptane (98°C) were selected on the basis of their boiling points, and the fact that they would provide a solvating and nonsolvating medium respectively, for homopolymerization of the  $\omega$ -alkenoates. Tables 8 and 9 provide data for comparison of the polymerizability of 2,6-dimethylphenyl 10-undecenoate in toluene and



TABLE 9

POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE IN n-HEPTANE<sup>a</sup>

Experiment	Charged Monomer in g	Type AlR <sub>2</sub> Cl	Reaction Temperature in °C	Mole Ratio <sup>b</sup> Al/Ti	Polymer Yield in %	$\eta_{inh}$ in dL/g
1	2.9	AlEt <sub>2</sub> Cl	60	2.0+10/1.0	28	
2	2.9	AlEt <sub>2</sub> Cl	60	4.0+10/1.0	36	1.09
3	2.9	AlEt <sub>2</sub> Cl	60	20.0+10/1.0	39	
4	1.5	Al(isoBu) <sub>2</sub> Cl	25	4.0+10/1.0	58	2.94

<sup>a</sup>Reaction conditions: 6 days; Ti=TiCl<sub>3</sub>AA 1.1.

<sup>b</sup>Mole ratio Ti/monomer/solvent = 1.0/10.0/100.

<sup>c</sup>0.5% solution in benzene, 30°C.

n-heptane. Using the heterogeneous  $\text{TiCl}_3\text{AA}/\text{AlR}_2\text{Cl}$  systems, the polymerization reactions prepared with both toluene and n-heptane were deep purple slurries at the start of the reaction. However, after only a few minutes the appearance of the tubes varied as a function of the solvent. Agglomerates of dark colored particulate appeared in the experiment conducted using n-heptane, which soon settled out, resulting in a two-phase system which stirred poorly. Upon further reaction, a dark purple plug appeared on the bottom of the polymerization vessel, with a clear, non-viscous upper phase, assumed to be solvent and residue monomer. The size of this plug increased over the course of the reaction while the solvent phase remained non-viscous. It is clear that in those experiments using n-heptane, poly(DMPU) is insoluble and precipitates out of solution resulting in a plug, which may limit further diffusion of monomer to the active sites, accounting for the decreased yields (28-58%) using n-heptane. In contrast, the experiments using toluene solvent remained as a uniform purple-colored slurry, which stirred well until increased viscosity of the single phase resulted in plug formation. Consistently high yields (74-97%) were obtained using toluene. The experimental series conducted in heptane also demonstrate that use of DIBAC aluminum alkyl and a reaction temperature of 25°C results in optimum yield and molecular weight (see Table 9). Results also indicate that while the use of heptane adversely affects the yield, the molecular weight obtained is comparable to that obtained in experiments using toluene as solvent. For further

discussion of solvent effects in copolymerization reactions, see section F.

6. Variation of reaction temperature and monomer/aluminum alkyl pre-complexation techniques. Reaction temperatures from  $-90^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  have been reported for use with Ziegler-Natta initiators. In the case of polypropylene, syndiotactic polymerizations are most favorable at  $-78$  to  $-45^{\circ}\text{C}$ ; and isotactic polymerizations from  $25^{\circ}\text{C}$  to  $90^{\circ}\text{C}$  for a slurry process, and from  $110^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  for a solution process.

Boor<sup>19</sup> reports that the polymerization temperature can affect the rate, stereoregularity and molecular weight, in ways that are not always predictable, and are best experimentally established for a particular system. Combs and coworkers<sup>186</sup> showed that stereoregularity varied with temperature, and that the molecular weight distribution can become more narrow as the reaction temperature is increased. However, Novokshonova<sup>187</sup> et al. demonstrated that for polypropylene, the molecular weights decreased greatly by increasing the temperature from  $30$  to  $60^{\circ}\text{C}$ . For example, an intrinsic viscosity of  $9.5$  dL/g was obtained at  $30^{\circ}\text{C}$  compared to a value of  $4.5$  at  $60^{\circ}\text{C}$ . Similar results are documented for other systems.<sup>188</sup>

The polymerizations and copolymerizations conducted in the course of this study were conducted either at  $25^{\circ}\text{C}$  or  $65^{\circ}\text{C}$ . Initial homopolymerizations were all conducted at  $65^{\circ}\text{C}$ , resulting in yields of  $80\%$  and better. However, while the polymers were found to swell highly

in toluene or benzene and form a micro-gel, a significant portion of the polymer did not dissolve. As a result, molecular weight estimates via dilute solution viscometry could not be obtained. Variation in the work-up procedures, including treatments with aqueous or alcoholic acid solutions did not improve the solubility in most cases. Poly(DMPU) samples prepared at 65°C as described in Table 10 were elastic solids with little toughness and slight surface-tack. However, when the identical reaction was conducted at 25°C, the resulting polymer was totally soluble in benzene and toluene, and had a tough rubber-like appearance with no tackiness. It is evident that for this initiator system and monomer, the lower temperature is preferred.

Many of the literature references addressing the polymerization of functional monomers utilize precomplexation, ageing and/or heat treatments of the initiator components or monomer with the aluminum alkyl. Modifications of this type were investigated in the present study, as detailed in Table 10. Four variations were evaluated utilizing initiator systems consisting of  $\text{TiCl}_3\text{AA}/\text{Al}(\text{isoBu})_2\text{Cl}$  and  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$ , resulting in a total of eight experiments. In all cases, the monomer was precomplexed with an equimolar amount of the appropriate aluminum alkyl. In variation 1, the monomer precomplex was prepared and allowed to stir at 22°C for 20 minutes, which was the time required to prepare the initiator slurry. The precomplex and initiator tubes were then combined and the resulting mixture was allowed to react at 22°C. Variation 2 called for preparation of the monomer precomplex



TABLE 10  
POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE  
WITH VARIATION OF THE ALUMINUM ALKYL, REACTION AND  
PRECOMPLEXATION TEMPERATURE<sup>a</sup>

Experiment	Type AlR <sub>3</sub>	Reaction Temperature in °C	Precomplex Ageing in °C/min	Polymer Yield in %	$\eta_{inh}^b$ in dL/g
1	AlEt <sub>2</sub> Cl	22	22/20	84	1.21
2	"	60	22/20	90	c
3	"	22	60/45	74	0.89
4	"	60	60/45	79	c
5	Al(isoBu) <sub>2</sub> Cl	22	22/20	88	2.51
6	"	60	22/20	88	c
7	"	22	60/45	89	2.86
8	"	60	60/45	74	c

<sup>a</sup>Reaction conditions: Ti= TiCl<sub>3</sub>AA 1.1; mole ratio Al/Ti/monomer/solvent= 4.0+10/1.0/10.0/150, reaction time=7 days, solvent=toluene.

<sup>b</sup>0.5% solution in benzene, 30°C.

<sup>c</sup>Major portion of product is insoluble.

as previously described, followed by transfer to the initiator tube and reaction at 60°C. Variation 3 involved preparation of the monomer/aluminum alkyl precomplex followed by ageing at 60°C for 45 minutes prior to combination with the initiator tube and reaction at 22°C. Variation 4 required similar ageing of the precomplex at 60°C for 45 minutes, followed by polymerization at 60°C.

The yields for all eight polymerizations were good; in the range of 74 - 90%. However, important variations in product solubility and molecular weights were observed. Those four reactions conducted at 60°C, regardless of the precomplex ageing technique, produced polymer that was mostly insoluble in toluene, as previously discussed in section 6. In contrast, the four polymerizations run at 22°C, regardless of the precomplex ageing temperature, produced toluene soluble polymer. Comparison of both yield and inherent viscosity data demonstrate that best results are obtained using diisobutylaluminum chloride (DIBAC) aluminum alkyl, and a polymerization temperature of approximately 25°C.

Comparison of experiments 1 and 3, run at 22°C and using DEAC, indicates that heat ageing the monomer precomplex results in a decrease in the molecular weight. However, comparison of experiments 5 and 7, run at 22°C with DIBAC, suggest a slight increase in molecular weight with heat treatment. In either case, the differences are not great enough for conclusions to be drawn on the effects of heat ageing without further experimentation.

7. Variation of reaction time. Batch-type polymerizations of ethylene or propylene are normally conducted over a period of 1 to 7 hours, with times of 1 to 3 hours most typical. Longer times, up to 10 days have been reported in the literature. Higher  $\alpha$ -olefins are less reactive and generally require longer reaction times. A review of the key papers dealing with polymerization of functional monomers suggests that reaction times on the order of days rather than hours are required for monomers containing heteroatoms. The homopolymerizations of Giannini,<sup>91,92</sup> Carlini<sup>127</sup> and Holler<sup>131</sup> were conducted for 4-10 days, 6-30 days, and 7-20 days respectively. Given this information, initial polymerizations performed in this study were reacted for 7-10 days. Subsequently, a series was conducted, using the  $\text{TiCl}_3\text{AA}/\text{Al}(\text{isoBu})_2\text{Cl}$  initiator system at  $25^\circ\text{C}$ , in which the reaction time was varied from 1 to 10 days. The results are included in Table 11. After only 1 day, a yield 50% was obtained. Over the course of the next nine days, the yield slowly increased to a maximum of 98%. A plot of polymer yield in percent vs. time in days is presented in Figure 1. As might be expected, the molecular weights as reflected by inherent viscosity measurements were high after only one day and further reaction resulted in only a slight increase.

#### D. Polymerization of 10-Undecenoates

Chapter 1 included a detailed discussion on the necessity and means of "masking" the carboxylate group to prevent undesirable

Figure 1. Yield of Poly(DMPU) as a Function of Reaction Time.



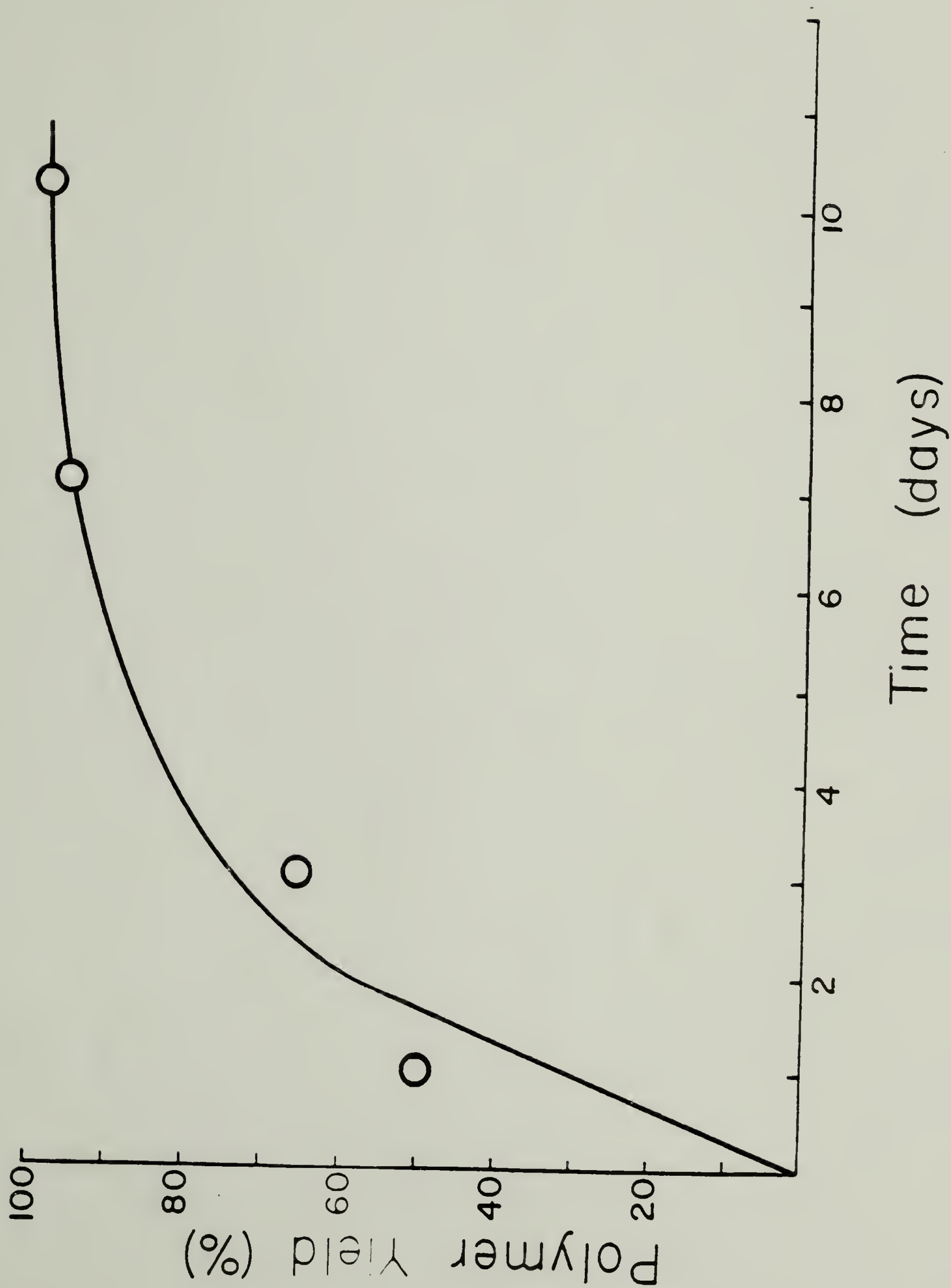


TABLE 11  
 POLYMERIZATION OF 2,6-DIMETHYLPHENYL 10-UNDECENOATE  
 WITH VARIATION OF REACTION TIME<sup>a</sup>

Experiment	Monomer Charge in g	Reaction Time in Days	Polymer Yield in %	$\eta_{inh}^b$ in dL/g
1	1.5	1	49	2.58
2	1.5	2	59	
3	1.5	3	65	2.79
4	1.5	7	94	
5	1.5	10	98	2.88

<sup>a</sup>Reaction conditions: 25°C; Ti= TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl;  
 solvent=toluene; mole ratio Al/Ti/monomer/solvent=4.0+10/1.0/10/150.

<sup>b</sup>0.5% solution in benzene, 30°C.

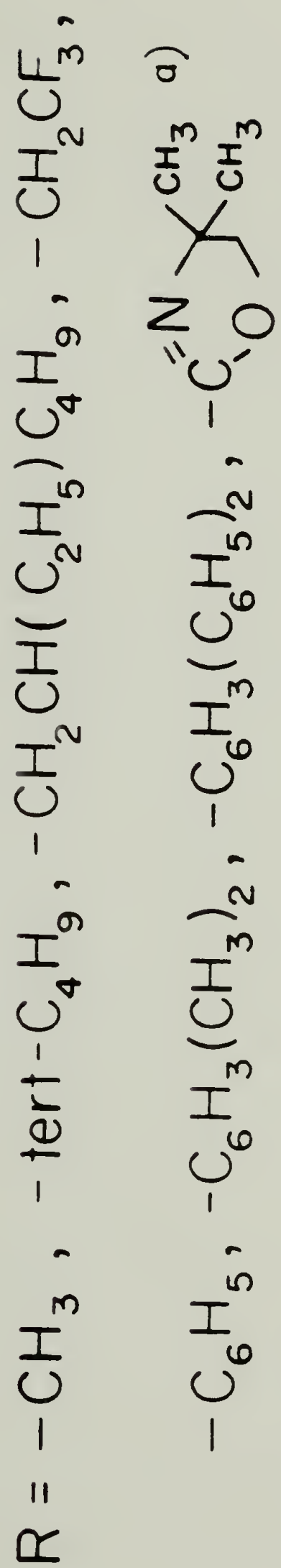
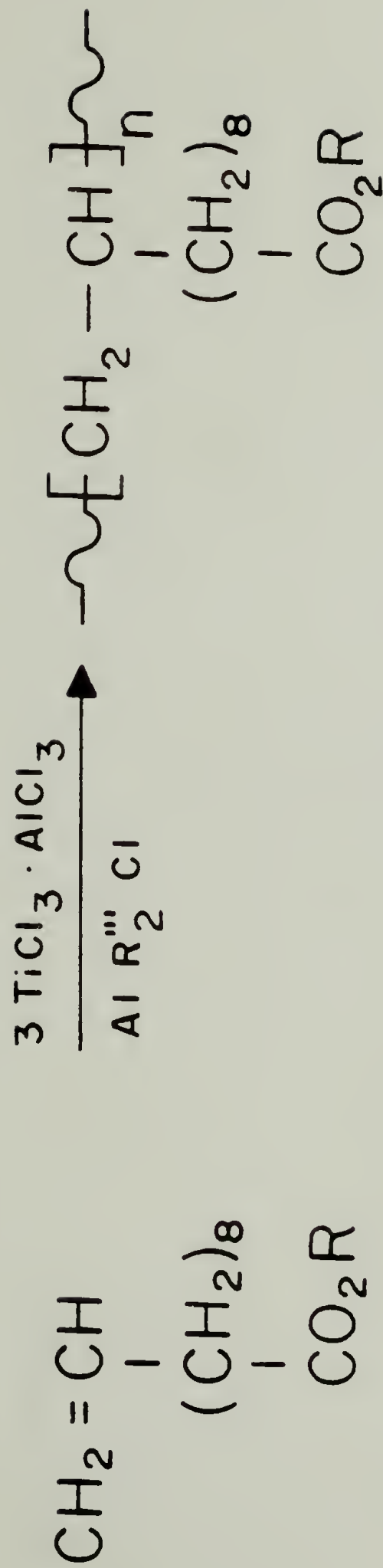
interaction with the initiator components and the active centers. This section will address the affect of the nature of the ester substituent on the polymerizability of a series of 10-undecenoates. As recorded in Table 12 and illustrated in equation 10, 8 different ester substituents and derivatives, possessing widely different electronic and steric environments were evaluated. Two reaction series were conducted. The first series employed DEAC aluminum alkyl, toluene solvent, and a reaction temperature of 65°C. The yields for the most of the  $\omega$ -alkenoates, including the methyl, tert-butyl, 2-ethyl-1-hexyl, trifluoroethyl and the phenyl ester were very poor; in the range from 2 - 6%. Note that in the case of the tert-butyl ester, a gaseous product, possibly isobutylene, vigorously evolved upon initial heating of the reaction tube.

In contrast, good yields (75%) were obtained for the 2,6-dimethylphenyl and 2,6-diphenylphenyl substituted  $\omega$ -alkenoates.

The 4,4-dimethyl-2-oxazoline derivative of 10-undecenoic acid behaved in a manner far different from that exhibited by the 10-alkenoates. The other seven polymerization reactions initially appeared as deep purple colored slurries which remained a single phase while the viscosity increased. However, the reaction containing the 2-oxazoline derivative behaved in a manner previously described in section 5, when n-heptane solvent was used. That is, a black agglomerate formed early in the reaction which reduced stirring efficiency. Over the course of 24 hours, two phases were formed, a dark solid plug and a

Equation 10. Polymerization of 10-Undecenoates.





$\text{R}^{\text{'''}} = \text{iso-C}_4\text{H}_9, -\text{C}_2\text{H}_5$ 
a) oxazoline derivative

TABLE 12

POLYMERIZATION OF 10-UNDECENOATES<sup>a</sup>

Experiment	R	Monomer Charge in g	Type AlR <sub>2</sub> Cl	Reaction Temperature in °C	Polymer Yield in mol-%	$\eta_{inh}$ in dL/g
1	-CH <sub>3</sub>	2.0	AlEt <sub>2</sub> Cl	65	2	
2	-CH <sub>3</sub>	2.0	Al(isoBu) <sub>2</sub> Cl	25	8	
3	-tertC <sub>4</sub> H <sub>9</sub>	2.4	AlEt <sub>2</sub> Cl	65	2	
4	-CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>	3.0	AlEt <sub>2</sub> Cl	65	5	
5	-CH <sub>2</sub> CF <sub>3</sub>	2.7	AlEt <sub>2</sub> Cl	65	2	
6	-C <sub>6</sub> H <sub>5</sub>	2.6	AlEt <sub>2</sub> Cl	65	6	
7	-C <sub>6</sub> H <sub>5</sub>	2.6	Al(isoBu) <sub>2</sub> Cl	25	54	d
8	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.9	AlEt <sub>2</sub> Cl	65	79	1.84
9	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.9	Al(isoBu) <sub>2</sub> Cl	25	97	2.86
10	-C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	4.1	AlEt <sub>2</sub> Cl	65	77	0.80
11	-Oxazoline	2.8	AlEt <sub>2</sub> Cl	25	e	0.24 <sup>c</sup>

<sup>a</sup>Reaction conditions: 7 days; Ti=TiCl<sub>3</sub>AA 1.1; solvent=toluene; mole ratio

Al/Ti/monomer/solvent=4.0+10.0/1.0/10.0/150.      <sup>b</sup>0.5% solution in benzene, 30°C.

<sup>c</sup>0.5% solution in H<sub>2</sub>O, 30°C.      <sup>d</sup>Major portion of product is insoluble.      <sup>e</sup>Crude yield in excess of theoretical amount.

water-thin clear liquid, probably toluene solvent. The reaction product was therefore insoluble in toluene, which was unexpected. Work up in the usual fashion by precipitation into methanol afforded no polymer product, since the plug formed proved to be soluble in both methanol and water, but not in aromatic hydrocarbons at ambient temperatures. The product was isolated by evaporation of the methanol, resulting in a brittle nontacky film. Solubility testing revealed that the material was soluble in methanol and water, but totally insoluble in toluene, chloroform and 1,4-dioxane. The film was redissolved in water and precipitated into chloroform to form a polymer-like flowing mass. Infrared analysis of the product indicated that the vinyl absorption at  $1645\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretch) was absent, as was the  $-\text{C}=\text{N}$  stretch at  $1680\text{ cm}^{-1}$ . The  $^{13}\text{C}$  NMR spectra confirmed the above results and also showed evidence for the presence of ester functionality and the four carbons initially comprising the oxazoline group. Thus it appears that polymerization did occur, and that the oxazoline nitrogen formed a toluene-insoluble complex by reaction with the aluminum alkyl. Upon work up, decomposition of the oxazoline group to form the 2-amino-2,2-dimethylethyl ester derivative appears likely. The existence of the amine as a salt rather than the free primary amine is suggested by the solubility characteristics and infrared absorptions at  $1600\text{ cm}^{-1}$  and  $1505\text{ cm}^{-1}$  ( $\text{NH}_3^+$  asymmetric and symmetric bends respectively). The inherent viscosity in  $\text{H}_2\text{O}$  was  $0.24\text{ dL/g}$ , approximately half that of the sodium

salt of poly(DMPU).

Subsequent polymerizations of DMPU demonstrated that DIBAC aluminum alkyl and a reaction temperature of 25°C resulted in higher yields and molecular weight (compare Tables 10 and 8). The methyl and phenyl esters and the oxazoline derivative were then polymerized in a second series, using the optimized conditions. In the case of the phenyl ester, the yield increase from 6 to 54%. The methyl ester was obtained in an only slightly improved yield of 8%. The oxazoline derivative generated a quantitative yield of a water soluble material that behaved very much like a polymer when precipitated into chloroform. Note that the poly(phenyl 10-undecenoate) was highly swollen in organic solvents but would not dissolve. This same insolubility was observed for poly(DMPU) samples prepared at 65°C, and may be due to crosslinking via friedel-crafts alkylation of the phenyl rings.

On the basis of yield, inherent viscosity measurements and solubility, 2,6-dimethylphenyl 10-undecenoate was selected for further detailed characterization and reactions including copolymerization and polymer modifications.

#### E. Polymerization of 2,6-Dimethylphenyl $\omega$ -Alkenoates

As stated earlier in this chapter, one of the objectives of this effort was to study the polymerizability of  $\omega$ -alkenoates as a function of methylene spacer chain length. Interaction between the ester substituent and vinyl group, specifically inductive effects, must



be addressed. It is known that variation in the electron density of a vinyl group can alter its affinity toward coordination with active centers, which is requisite to the insertion reaction. It is therefore necessary to "insulate" the vinyl group from the carboxylate function, in this case by a hydrocarbon chain consisting of methylene units.

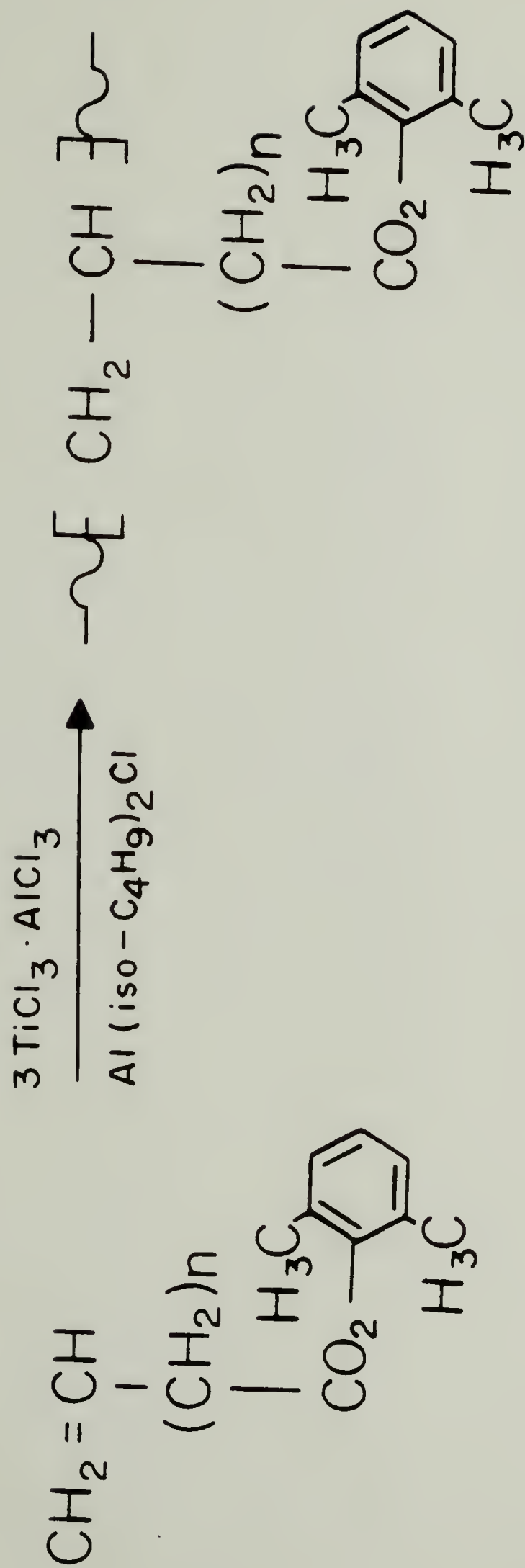
In order to study the insulating ability of the hydrocarbon chain, a series of  $\omega$ -alkenoates containing the 2,6-dimethylphenyl ester substituent and methylene chains of 1,3,6 and 8 units were prepared. Two of the starting acids, 3-butenic acid ( $n=1$ ) and 10-undecenoic acid ( $n=8$ ) were commercially available. 5-hexenoic acid ( $n=3$ ) and 8-nonenoic acid ( $n=6$ ) were not available and synthetic routes were designed as detailed in section B. 5-hexenoic acid was prepared in fair yield (30%) by pyrolysis of  $\epsilon$ -caprolactone. Attempts to prepare 8-nonenoic acid and 7-octenoic acid via oxidative decarboxylation according to Ogibin<sup>166,167</sup> were unsuccessful. An alternate route to 2,6-dimethylphenyl-8-nonenoate was then conceived and successfully conducted. The starting sebacic acid was converted to the mono-2,6-dimethylphenyl ester, which was oxidatively decarboxylated by adaptation of a procedure by Kochi and Bacha.<sup>168</sup> The 2,6-dimethylphenyl esters of 10-undecenoic acid and 3-butenic acid were then prepared using a method developed by Tedder.<sup>169</sup> Esterification of 5-hexenoic acid by this method, and by classical acid catalyzed esterification techniques were not successful, and produced the cyclic product 2-cyclohexene-1-one. The third attempt, using

N,N'-carbonyldiimidazole (CDI) gave a quantitative yield of 2,6-dimethylphenyl 5-hexenoate.

As illustrated in eqn. 11, the four monomers were polymerized using  $\text{TiCl}_3\text{AA}/\text{Al}(\text{isoBu})_2\text{Cl}$  in toluene at  $25^\circ\text{C}$ . Results are recorded in Table 13. As previously demonstrated, the  $n=8$  ester polymerized in high yield (95%). A good yield of the  $n=6$  ester (57%) was likewise obtained. The inherent viscosities of these two polymers were very similar, approximately 2.9 dL/g. No polymer or oligomer was obtained for the  $n=1$  or  $n=3$  esters. This indicates that a spacer chain of greater than 3, and less than or equal to 6 units are required to insulate the double bond from the electronic and steric effects of the ester substituent. A quantitative estimate of the electronic effects of the ester functionality on the double bond may be found in the  $^{13}\text{C}$  NMR chemical shift data for the vinyl methylene and methine carbons, recorded in Table 14. The chemical shift of the methylene carbon is known to be related to the electron density of the carbon-carbon double bond. Electron deficiency of the vinyl group is reflected in an increase in the chemical shift (downfield movement). This is clearly demonstrated in Table 14, with a range from 114.28 ppm to 119.10 ppm as the insulating spacer chain decreases from 8 to 1 unit in length. The cut off for polymerizability is apparently between 114.42 ppm and 115.63 ppm.

Key infrared absorptions for these  $\omega$ -alkenoates are included in Table 15. As noted by Muggee for a series of methyl  $\omega$ -alkenoates,

Equation 11. Polymerization of 2,6-Dimethyl  $\omega$ -Alkenoates with  
Variation of Methylene Chain Length.



% YIELD

n    1    3    6    8

—    —    60    95



TABLE 13  
 POLYMERIZATION OF 2,6-DIMETHYLPHENYL  $\omega$ -ALKENOATES  
 WITH VARIATION OF THE METHYLENE CHAIN LENGTH<sup>a</sup>

Experiment	n	Monomer Charge in ml	Polymer Yield in mole-%	$\eta_{inh}$ <sup>b</sup> in dL/g
1	1	1.94	-	-
2	3	2.22	-	-
3	6	2.65	57	2.84
4	8	2.94	94	2.88

<sup>a</sup>Reaction conditions: 25°C, 10 days; Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl;  
 solvent=toluene; mole ratio Al/Ti/monomer/solvent=4.0+10/1.0/10/150.

<sup>b</sup>0.5% solution in benzene, 30°C.

the frequency of the lower vinyl C-H out of plane bending vibration was observed to decrease as the spacer group length increased.<sup>3</sup> This observation is consistent with established correlations between functional group electron density and infrared absorption frequency.<sup>189</sup>

The conclusion that a spacer group of greater than 3 methylene units is required to insulate the vinyl group is in general agreement with the findings of other studies of functional monomers discussed in Chapter 1. Recall that a spacer group of only one methylene unit was sufficient to insulate the effects of the less electronegative silicon atom.<sup>100,101</sup> Giannini reported that in the case of a series of N,N'-diisopropylamines, no polymerization occurred when n=1 methylene unit. For n=2, polymerization proceeded very slowly in low yields, and for n=3, polymerization readily occurred. For polymerizations and copolymerizations involving oxygen containing monomers, at least 3 and preferably 4 carbons were required.<sup>131,139</sup>

Recent work by Muggee<sup>2,3</sup> within this laboratory demonstrated that rates for the coordination polymerization of methyl  $\omega$ -epoxyalkenoates reached a constant value when a spacer group of more than 3 carbons was incorporated.

#### F. Copolymerization of 2,6-Dimethylphenyl 10-Undecenoate (DMPU) with $\alpha$ -Olefins and Ethylene

1. Copolymerization of DMPU with 1-dodecene. The polymerization and copolymerization of 1-dodecene was readily accomplished as described in

TABLE 14

<sup>13</sup>C NMR CHEMICAL SHIFT DATA FOR 2,6-DIMETHYLPHENYL ω-ALKENOATES AND ω-ALKENOIC ACIDS<sup>a</sup>



COMPOUND	n	CH <sub>2</sub> =CH-		C=O	CARBON ATOMS OF SPACER GROUP <sup>b</sup>							
		CH <sub>2</sub> =CH-	CH <sub>2</sub> =CH-		1	2	3	4	5	6	7	8
2,6-Dimethylphenyl 3-butenate	1	119.10	129.93	168.85	38.88							
2,6-Dimethylphenyl 5-hexenoate	3	115.63	137.49	170.88	33.10	24.25	33.17					
2,6-Dimethylphenyl 8-nonenate	6	114.42	138.77	171.12	33.79	29.20	29.20	28.82	25.14	33.99		
2,6-Dimethylphenyl 10-undecenoate	8	114.28	138.89	170.91	33.94	29.34	29.16	29.16	29.34	29.02	25.17	33.94
3-Butenoic acid	1	119.04	129.73	178.56	38.96							
5-Hexenoic acid	3	115.64	137.53	180.42	33.18	23.99	33.49					
10-Undecenoic acid	8	114.27	138.98	180.62	33.94	29.38	29.38	29.38	29.38	29.23	24.79	34.23

<sup>a</sup>In ppm downfield from TMS (CDCl<sub>3</sub>).

<sup>b</sup>Carbon atom nearest olefin designated atom 1 of spacer group.

TABLE 15  
INFRARED DATA FOR 2,6-DIMETHYLPHENYL  $\omega$ -ALKENOATES  
 $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CO}_2-\text{C}_6\text{H}_3(\text{CH}_3)_2$

Compound	n	$\nu_{\text{C=O}}, (\text{cm}^{-1})$	$\nu_{\text{C=C}}, (\text{cm}^{-1})$	$=\text{C-H}, (\text{cm}^{-1})$
2,6-Dimethylphenyl 3-butenate	1	1764	1640	989, 920
2,6-Dimethylphenyl 5-hexenoate	3	1765	1645	994, 915
2,6-Dimethylphenyl 8-nonenate	6	1762	1640	994, 910
2,6-Dimethylphenyl 10-undecenoate	8	1760	1640	989, 907

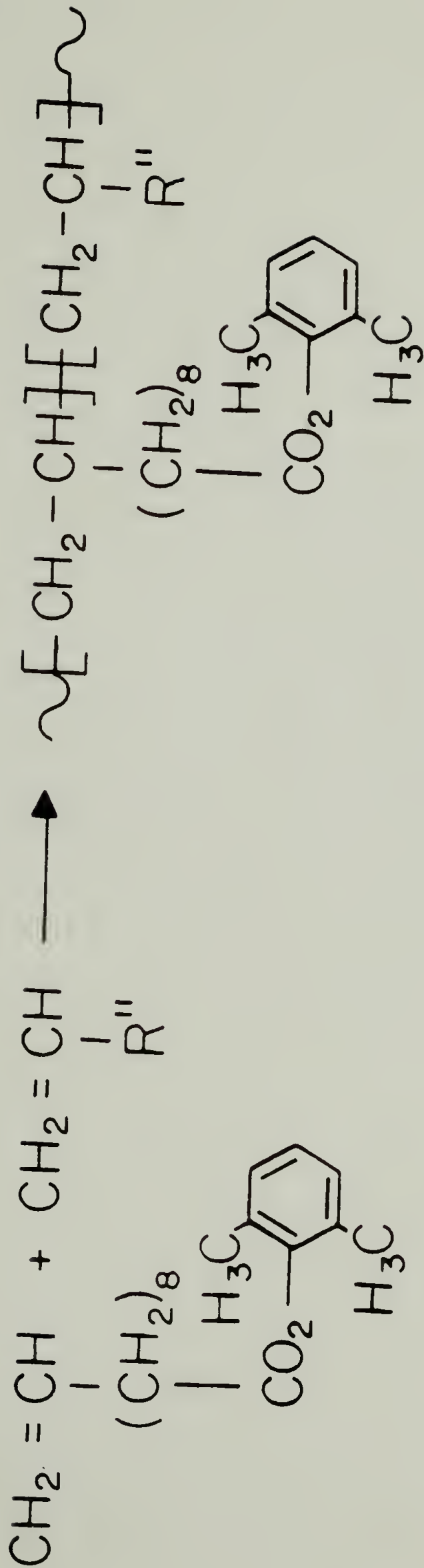


Chapter 2, section G.2, and shown in Equation 12. Note that the pre-complex and initiator tubes were prepared, and 1-dodecene added to the initiator tube, followed immediately by the contents of the pre-complexation tube. Polymerizations containing mole ratios of 20, 10 and 0 percent DMPU were conducted at 25°C for 48 hours. All reactions were slightly exothermic and formed single phase viscous plugs after less than an hour. Toluene solvent was utilized in all but one reaction, which contained n-heptane and was considerably slower, exhibited no noticeable exotherm, and formed a plug in 2 hours. The yields in all polymerizations were very good; in excess of 90 percent, with inherent viscosities ranging from 3.8 - 4.3 dL/g. The copolymers were white, nontacky, tough, rubbery materials. Percent incorporation of the functional monomer was determined using  $^1\text{H}$  NMR integration and/or elemental analysis. As indicated in Table 16, 80-90 percent of the DMPU monomer feed was incorporated into the copolymers.

Note that presence of the DMPU comonomer did not result in a significant change in the polymer yield, and in fact the inherent viscosities appeared to increase as the incorporation of DMPU increased (see Table 16). All polymers were totally soluble in toluene and benzene.

2. Copolymerization of DMPU with 1-hexene. Copolymerizations of DMPU and 1-hexene were also readily accomplished as detailed in Chapter 2, section G.3. and summarized in Table 17. DMPU monomer feeds of 20, 10 and 0 mole percent were again selected, resulting in 60-70 percent

Equation 12. Copolymerization of DMPU with  $\alpha$ -Olefins and Ethylene.



incorporation as indicated by  $^1\text{H}$ NMR integration and/or elemental analysis. All reactions were conducted at 25°C for 48 hours.

Reactions utilizing toluene solvents were exothermic and formed single phase plugs within 30 minutes. A reaction utilizing n-heptane solvent was not noticeably exothermic and formed a two phase system, resulting in a plug after 2 hours. The copolymers were white, very tough, elastic materials exhibiting surface tackiness. Yields were very good (80-99%) with inherent viscosities ranging from 2.8 to 3.4 dL/g. As in the case of 1-dodecene copolymers, the viscosities increased with the incorporation of DMPU.

3. Copolymerization of DMPU with propylene. Copolymerization with a gaseous monomer required modification of reaction procedure, as detailed in Chapter 2, section G.5. Use of 12", 18 gauge syringe needles worked moderately well for the delivery of propylene, but became clogged occasionally. As may be anticipated, incorporation of DMPU with propylene was much more difficult than for the higher  $\alpha$ -olefins, 1-dodecene and 1-hexene. As indicated in Table 18, polypropylene homopolymer was obtained in all early experiments. Polymer products were screened by infrared analysis, with the presence of absorptions at  $1765\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretch, aromatic ester) and  $1170\text{ cm}^{-1}$  ( $-\text{C}-\text{C}(=\text{O})-\text{O}$  stretch) denoting DMPU incorporation. As illustrated in Table 18, numerous combinations of aluminum alkyl, solvent, stoichiometry, and reaction temperature were utilized without



TABLE 16

COPOLYMERIZATION OF 1-DODECENE(DOD) AND 2,6-DIMETHYLPHENYL 10-UNDECENOATE (DMPU)<sup>a</sup>

Experiment	DOD		DMPU		mole-% in comonomer feed	Mole ratio Al/Ti/DMPU	Polymer Comonomer <sup>c</sup> Yield units, in in % mole-%	$\eta_{inh}$ in dL/g	
	in g	in mmol	in g	in mmol					
1	6.7	40	0.0	0.0	0.0	4.0/1.0/0.0	96	0	3.78
2	6.7	40	1.3	4.4	10.0	4.0+4.8/1.0/4.8	97	8	3.81
3	6.7	40	2.5	8.9	20.0	4.0+8.9/1.0/8.9	89	18	4.25

<sup>a</sup>Reaction conditions: 25°C, 2 days; Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl; solvent=toluene.

<sup>b</sup>0.5% solution in benzene, 30°C.

<sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy and/or elemental analysis.

TABLE 17

COPOLYMERIZATION OF 1-HEXENE (HEX) AND 2,6-DIMETHYLPHENYL 10-UNDECENOATE (DMPU)<sup>a</sup>

Experiment	HEX		DMPU		Mole ratio Al/Ti/DMPU	Polymer Yield in %	Comonomer <sup>c</sup> units, in mole-%	$\eta_{inh}^b$ in dL/g
	in g	in mmol	in g	in mmol				
1	4.2	50	0.0	0.0	4.0/1.0/0.0	99	0	2.79
2	4.2	50	1.6	5.5	4.0+5.5/1.0/5.5	98	6	3.22
3	4.2	50	3.6	11.0	4.0+11.0/1.0/11.0	80 <sup>d</sup>	14	3.40

<sup>a</sup>Reaction conditions: 25°C/48 Hrs; Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl=Al(isoBu)<sub>2</sub>Cl.

<sup>b</sup>0.5% solution in benzene, 30°C.

<sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy and/or elemental analysis.

<sup>d</sup>Toluene soluble fraction.

incorporation. Copolymer containing 5 mole percent DMPU (as determined by elemental analysis of carbon, hydrogen and oxygen) was successfully obtained using diethylaluminum chloride (DEAC), increased concentration of DMPU, toluene solvent and reaction at 25°C for 4 hours (followed by immediate work-up). Note that identical reactions substituting diisobutylaluminum chloride (DIBAC) for DEAC generated only polypropylene homopolymer. It appears that for copolymerization reactions, DEAC is preferred. In contrast, Tables 9 and 10 indicate that DIBAC was preferred for the homopolymerization of DMPU. Since the propylene feed was not quantified, no information on polymer yield was obtained. Inherent viscosities were conducted in decalin at 135°C in a silicon oil bath, and values for both homopolymer and copolymer were approximately 2.9 g/dL. The polymer was an off-white free flowing powder. Continuous extraction of the polymer product with toluene did not remove the infrared absorptions previously cited, indicating that the product was in fact a copolymer, rather than a mixture of homopolymers or polypropylene contaminated with residue DMPU monomer or oligomer.

4. Copolymerization of DMPU with ethylene. On the basis of the results previously reported for the copolymerization with propylene, copolymerization with ethylene was attempted using  $\text{TiCl}_3\text{AA}/\text{DEAC}$  in toluene at 25°C. Ethylene gas was fed into the polymerization reaction very slowly and intermittently over a period of 4 hours, followed by immediate termination and work-up. Infrared analysis of the copolymerization reaction demonstrated the presence of the ester substituent by

TABLE 18

COPOLYMERIZATION OF PROPYLENE WITH 2,6-DIMETHYLPHENYL 10-UNDECENOATE<sup>a</sup>

Experiment	Solvent	AlR <sub>3</sub>	Mole Ratio Al/Ti/DMPU	DMPU in g	Reaction Temp/Time in °C/min	Polymer Yield in g	DMPU <sup>b</sup> incorp in mole %	$\eta_{inhc}$ in dL/g
1	heptane	AlEt <sub>2</sub> Cl	1.3/1.0/1.8	2.0	25/15	2.5	0	
2	heptane	AlEt <sub>2</sub> Cl	1.3/1.0/2.2	2.0	65/390	2.6	0	
3	toluene	Al(isoBu) <sub>2</sub> Cl	4.0/1.0/0.0	0.0	25/150	3.2	-	
4	heptane	Al(isoBu) <sub>2</sub> Cl	4.0/1.0/0.0	0.0	25/150	1.9	-	
5	toluene	Al(isoBu) <sub>2</sub> Cl	4.0+1.2/1.0/1.2	0.33	25/150	3.0	0	
6	toluene	AlEt <sub>2</sub> Cl	4.0+1.2/1.0/1.2	0.33	25/150	8.2	0	
7	toluene	Al(isoBu) <sub>2</sub> Cl	4.0+2.3/1.0/2.3	0.67	25/150	3.0	0	
8	heptane	Al(isoBu) <sub>2</sub> Cl	4.0+1.2/1.0/1.2	0.33	25/150	3.9	0	
9	toluene	Al(isoBu) <sub>2</sub> Cl	4.0+10.0/1.0/0.0	0.0	25/240	2.4	-	2.93
10	toluene	Al(isoBu) <sub>2</sub> Cl	4.0+10.0/1.0/10.0	2.9	25/240	3.0	0	
11	toluene	AlEt <sub>2</sub> Cl	4.0+10.0/1.0/10.0	2.9	25/240	3.6	5b	2.85

<sup>a</sup>Reaction conditions: Ti = TiCl<sub>3</sub>AA 1.1. <sup>b</sup>Determined by elemental analysis. c0.5% solution in decalin, 135°C.



characteristic absorptions at  $1762\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretch, aromatic ester) and  $1169\text{ cm}^{-1}$  ( $-\text{C}-(\text{C}=\text{O})-\text{O}$  stretch). Carbon, hydrogen and oxygen elemental analysis indicated 3 mole percent incorporation of the DMPU unit. As detailed in Table 19, the inherent viscosities, conducted in decalin at  $135^\circ\text{C}$ , were approximately  $5.6\text{ dL/g}$ .

G. Terpolymerization of 2,6-Dimethylphenyl 10-Undecenoate  
with Propylene and Ethylene

Terpolymerizations of DMPU with ethylene and propylene were also conducted. Both titanium and vanadium-based initiator systems were evaluated, with copolymerization of ethylene and propylene conducted as reference reactions.

1. Copolymerization of ethylene and propylene using  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$ .

The details of these copolymerizations are included in Chapter 2, section G.4.a. As shown in Table 20, the reaction were conducted using toluene and n-heptane solvents, with a slightly higher yield consistently obtained in toluene. Also note that infrared analysis indicated higher propylene incorporation using toluene solvent. A comonomer gas flow of approximately 10:1 propylene/ethylene by volume was fed to the reactions, using a pair of Brooks® flowmeters, and again using syringe needles for delivery. The resulting polymers were white, flocculent, rubbery nontacky particulates, with inherent viscosities of approximately  $2.9\text{ dL/g}$ . The infrared spectra also contained a pair of absorptions of equal magnitude at  $725$  and  $715\text{ cm}^{-1}$ , indicative of polyethylene crystallinity. Analysis of ethylene-propylene copolymers

TABLE 19

## COPOLYMERIZATION OF ETHYLENE AND 2,6-DIMETHYLPHENYL 10-UNDECENOATE

Experiment	DMPU		solvent <sup>b</sup>	mole ratio Al/Ti/DMPU	Polymer Yield in g	DMPUC incorp in mole-%	$\eta_{inh}$ in dL/g
	in g	in mmol					
1	0.0	0.0	toluene	14.0/1.0/0.0	3.0	-	5.67
2	2.9	10.0	toluene	4.0+10.0/1.0/10.0	4.4	3	5.61

<sup>a</sup>Reaction conditions; 25°C/3 hours, Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>3</sub>=AlEt<sub>2</sub>Cl.

<sup>b</sup>16 mL.

<sup>c</sup>Determined by elemental analysis.

<sup>d</sup>0.5% solution in decalin, 135°C.

TABLE 20

TERPOLYMERIZATION OF ETHYLENE, PROPYLENE AND 2,6-DIMETHYLPHENYL 10-UNDECENOATE<sup>a</sup>

Experiment	DMPU		Solvent <sup>b</sup>	Mole Ratio Al/Ti/DMPU	Polymer Yield in g	Comonomer <sup>c</sup> units, in mole-%	$\eta_{inh}^d$ in dL/g
	in g	in mmol					
1	0.0	0.0	toluene	3.7/1.0/0.0	1.5	-	2.91
2	0.0	0.0	heptane	3.7/1.0/0.0	1.2	-	
3	2.9	10.0	toluene	3.7+10/1.0/10.0	2.6	6	2.34
4	2.9	10.0	heptane	3.7+10/1.0/10.0	2.4	6	

<sup>a</sup>Reaction conditions: 25°C/70 minutes; Ti=TiCl<sub>3</sub>AA 1.1; AlR<sub>3</sub>=AlEt<sub>2</sub>Cl; 90/10 propylene/ethylene feed by volume.

<sup>b</sup>20 mL.

<sup>c</sup>Determined by elemental analysis.

<sup>d</sup>0.5% solution in decalin, 135°C.

by DSC and  $^{13}\text{C}$  NMR is discussed in section H.

2. Copolymerization of ethylene and propylene using  $\text{VOCl}_3/\text{AlEt}_2\text{Cl}$ .

This copolymerization is described in detail in Chapter 2, section G.4.c. Two copolymerizations were conducted, differing only in the Al/V mole ratios of 4.0 and 14.0. The reactions were allowed to proceed with a propylene/ethylene volume feed ratio of 10:1 for a period of 140 minutes. The temperature was initially  $25^\circ\text{C}$ , but was slowly increased to  $60^\circ\text{C}$  over the course of the reaction. The yield for both copolymerizations was very poor; approximately 0.2 g in both reactions, slightly better for Al/V = 4.0. Recall that the yields utilizing  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$  were much higher. The products were white, soft rubbery, tacky solids. Infrared analysis indicated presence of both propylene and ethylene, and absence of the absorption band at  $725\text{ cm}^{-1}$  which was present in the copolymer prepared using  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$ , and is used to evaluate the degree of crystallinity in polyethylenes. Thermal analysis by DSC revealed a sharp transition at  $-26^\circ\text{C}$  (see Table 24) and the absence of significant melting transitions characteristic of ethylene and propylene, indicating that the copolymer is primarily amorphous in nature (see Figure 8).

3. Terpolymerization of DMPU, propylene and ethylene using

$\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$ . As documented in Table 20, two terpolymerizations using  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$  were conducted at  $25^\circ\text{C}$  for 70 minutes; one in



toluene and the other in n-heptane solvent. A slightly better yield was obtained using toluene, as was previously observed for the copolymerization of ethylene with propylene. Infrared analysis indicated that the relative proportions of DMPU, propylene and ethylene were very similar in the two samples. Approximately 6 mole percent DMPU is incorporated, estimated by carbon, hydrogen elemental analysis. The mole ratios of ethylene and propylene were estimated on the basis of the relative size of crystalline melting transitions obtained by DSC analysis. Inherent viscosities of 2.3 dL/g were obtained. The polymers were white, slightly tacky, tough elastic polymer solids. Thermal analysis by DSC is discussed in section H to follow.

4. Terpolymerization of DMPU, propylene and ethylene using  $\text{VOCl}_3/\text{AlEt}_2\text{Cl}$ . This terpolymerization is described in detail in Chapter 2, section G.4.d. The reaction was allowed to proceed for 140 minutes, with the temperature gradually increased from 25°C to 60°C. The yield was very poor; less than 0.1g. The product was a translucent, rubbery, tacky solid. Infrared analysis revealed the ethylene/propylene mole ratio comparable to those obtained using titanium-based initiators, and improved incorporation of DMPU as evidenced by a stronger absorption at 1758  $\text{cm}^{-1}$  (C=O stretch, aromatic ester). Thermal analysis by DSC was also conducted, revealing a sharp glass transition at -43°C and an absence of characteristic melting transitions, indicating that the terpolymer is essentially amorphous,

as typified by products of vanadium-based systems (see Table 24 and Figure 8).

#### H. Modification Reactions of Polyolefin

##### Pendant Reactive Groups and Product Characterization

As previously stated, one of the objectives of this research was the conversion of selected functionally-substituted polymers and copolymers to the corresponding polyolefin ionomers, polyacids and polyelectrolytes. The parent compounds selected for modification were poly(2,6-dimethylphenyl 10-undecenoate) and the terpolymer poly(ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate), which contained approximately 6 mole percent of the carboxylate-containing unit. Both polymers were hydrolyzed under alkaline conditions to the sodium carboxylate salts, followed by acidification to liberate the carboxylic acid derivatives. All members of the resulting series were analyzed by infrared and  $^{13}\text{C}$  NMR spectroscopy, elemental analysis and DSC, and selected members by WAXD, TGA and DMTA.

##### 1. Modification reactions of poly(2,6-dimethylphenyl 10-undecenoate).

As described in Chapter 1, olefin polymers containing ester or acid functionality, such as ethylene-acrylic acid copolymers, are readily neutralized to carboxylate salts by base hydrolysis.<sup>155,197</sup>

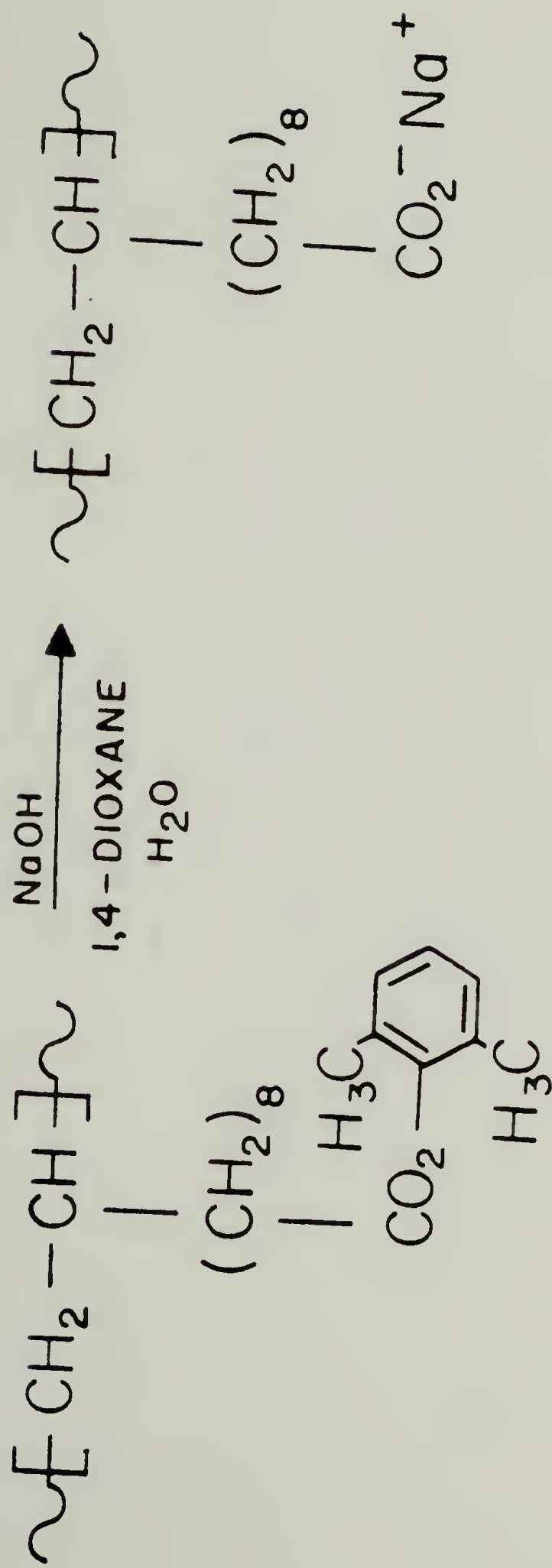
Preparation of poly(alkylene oxide) ionomers by Bansleben<sup>1</sup> in this laboratory utilized comparable procedures.

The experimental procedure for the base hydrolysis of

poly(DMPU) is detailed in Chapter 2, section H.1, and shown in Figure 13. The parent homopolymer was a white, nontacky, flexible solid with an inherent viscosity of approximately 2.9 dL/g, and was found to be totally soluble in 1,4-dioxane with gently heating over a period of 4 hours. Upon addition of 4N aqueous sodium hydroxide solution, a second lower phase was formed which rapidly turned yellow in color and later formed a granular paste. After approximately 70 minutes at 85°C, the viscosity of the solution greatly increased. Note that initial experiments using greater than the specified 0.6% (w/v) solution of poly(DMPU) in 1,4-dioxane resulted in unstirrable gels. Over the course of 12 hours at 85°C, a granular product precipitated and the viscosity decreased to the original level. A quantitative yield of the poly(10-undecenoic acid sodium salt) was obtained. Infrared analysis of the products of initial reactions indicated the presence of residue ester functionality, as is commonly the case.<sup>197</sup> It is clear that product solubility limits the degree of neutralization. To insure total conversion, the product was dissolved (or swollen) in water and further treated with base, followed by reprecipitation by addition of 1,4-dioxane. The resulting white free-flowing fine powder was dried over P<sub>2</sub>O<sub>5</sub> for 48 hours at 100°C/0.01mm. After two reactions, the yield was still in excess of 90%. Infrared analysis by both KBr disc and Fluorolube® mull indicated total conversion of the ester to the sodium salt as evidenced by a shift in the carbonyl stretch absorption from 1760 cm<sup>-1</sup> to 1542 cm<sup>-1</sup> (see Figure 2). <sup>13</sup>C NMR analysis also confirmed

Equation 13. Preparation of Poly(10-Undecenoic Acid Sodium Salt) from Poly(DMPU).

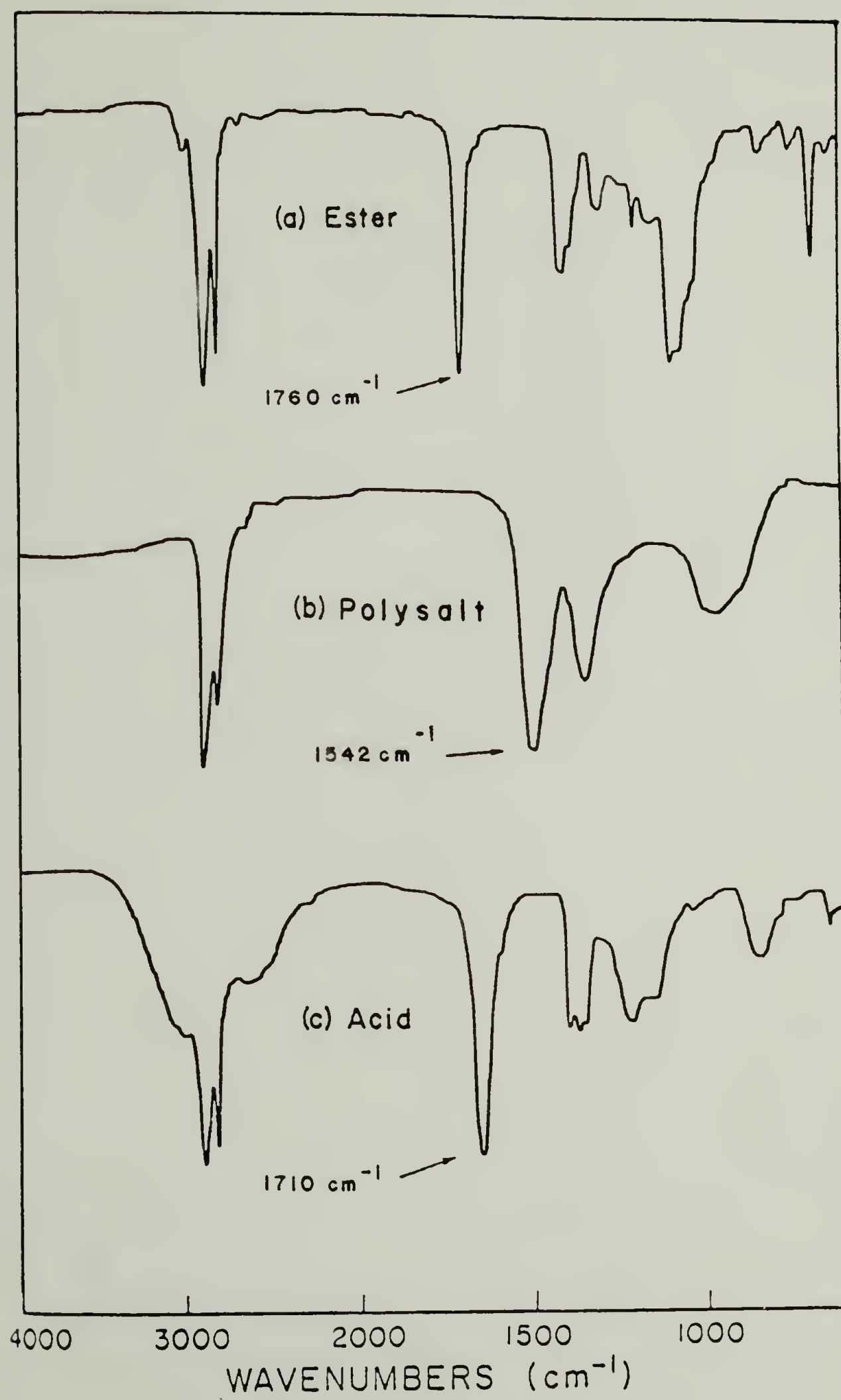




total conversion to the salt. However, the IR analysis revealed that presence of an -OH stretch, suggesting that residue water remained bound in the polymeric salt. Further attempts to dry the sample decreased but did not eliminate the absorption. Attempts to remove the water by azeotropic distillation from benzene were not successful, possibly due to the total insolubility of the polysalt in benzene, and the affinity of the salt group to bind the water molecule(s). Elemental analysis results further suggest the presence of bound water, since the data obtained for samples dried at varying degrees more closely agrees with the tetra- or dihydrate rather than the anhydrous carboxylate salt. A study of water uptake for styrene and ethylene ionomers has been conducted by Eisenberg<sup>190</sup>, demonstrating that for copolymers of styrene-sodium methacrylate with up to 6 mole-% sodium methacrylate incorporation, 1 water molecule is absorbed per ion pair. Above this level of incorporation (7-10 mole%), 3-5 water molecules are absorbed per ion pair. In contrast, ethylene ionomers are found to absorb more than one molecule per ion pair, even at low levels of incorporation of acrylic or methacrylic acid. Analogous to the current experimental observations, Breslow and Kutner<sup>191</sup> reported that salts of the homopolymer poly(ethylenesulfonic acid) did not lose absorbed water even upon heating at greater than 100°C under vacuum.

Note that while the starting material, poly(DMPU) was a tough, flexible solid, the poly(10-undecenoic acid sodium salt) was a fine, free flowing powder, with totally different solubility properties.

Figure 2. Comparison of Infrared Spectra of Functionally Substituted Polyolefins: (a) Poly(DMPU), (b) Poly(10-Undecenoic Acid Sodium Salt), (c) Poly(10-Undecenoic Acid).

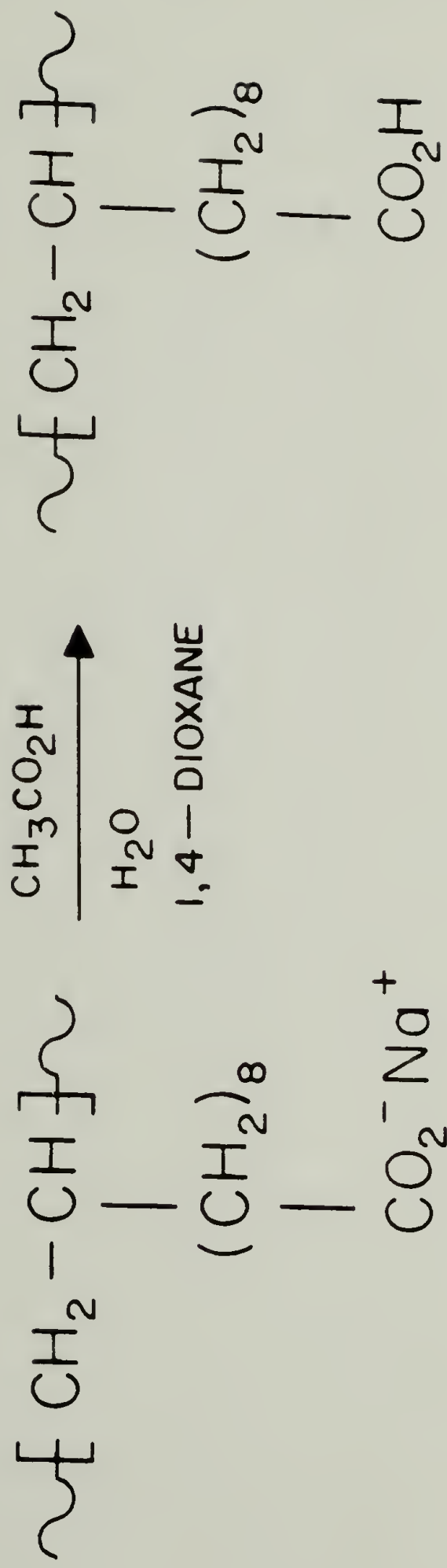




While poly(DMPU) is totally soluble in 1,4-dioxane and unswellable in water, the reverse was true of the polysalt. Gentle heating was required to completely dissolve the polysalt in water, resulting in an inherent viscosity of 0.48 dL/g, which is much lower than that of the starting poly(DMPU) in benzene at equal concentration. The relationship between ionic group concentration and dilute solution properties is of great interest, as briefly discussed in Chapter 1. Although not an objective of the current effort, the dilute solution characteristics of these polymers, particularly effects due to the presence of the hydrocarbon spacer chain, should be studied.

Poly(10-undecenoic acid) was readily prepared as described in Chapter 2, section H.2.a, and shown in Equation 14. The sodium salt was completely dissolved in distilled water at room temperature and treated with glacial acetic acid. After 3 hours, the resulting fine powder was isolated by filtration and repeatedly washed with distilled water. After drying for 48 hours at 100°C/0.01 mm, a 76% yield of white powder was obtained. As shown in Figure 2, the infrared spectra contained strong absorptions at 3400-2400  $\text{cm}^{-1}$  (OH stretch, carboxylic acid) and 1708  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid). The sodium analysis indicated less than 0.1% residue sodium. A second step in which the polyacid was swollen in 1,4-dioxane and treated with additional acetic acid/distilled water was conducted to insure total conversion to the polycarboxylic acid, but was shown to be unnecessary in this case by the low sodium analysis after a single reaction. Note that the

Equation 14. Preparation of Poly(10-Undecenoic Acid) from Poly(10-Undecenoic Acid Sodium Salt).



infrared spectra contained a weak absorption at  $1585\text{ cm}^{-1}$ , initially believed to be residue carboxylate stretching (seen at  $1560\text{ cm}^{-1}$  in the homosalt). However, a second treatment of the polymer with acetic acid did not decrease the intensity of this band, and the sodium analysis of both products was  $<0.1\%$ . The absorption at  $1585\text{ cm}^{-1}$  was then tentatively assigned as an overtone band.

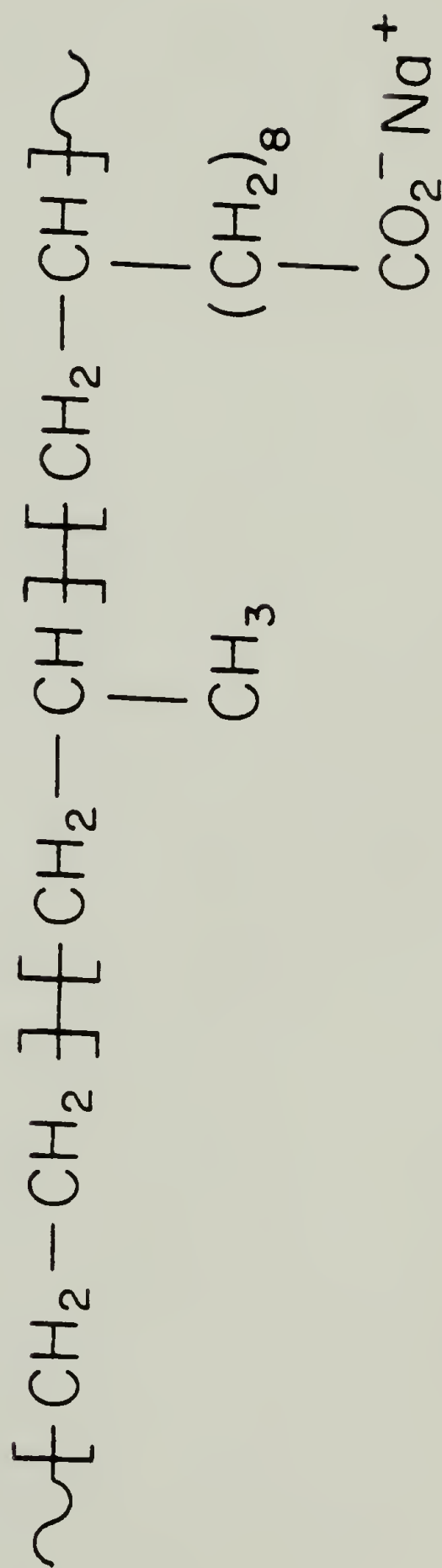
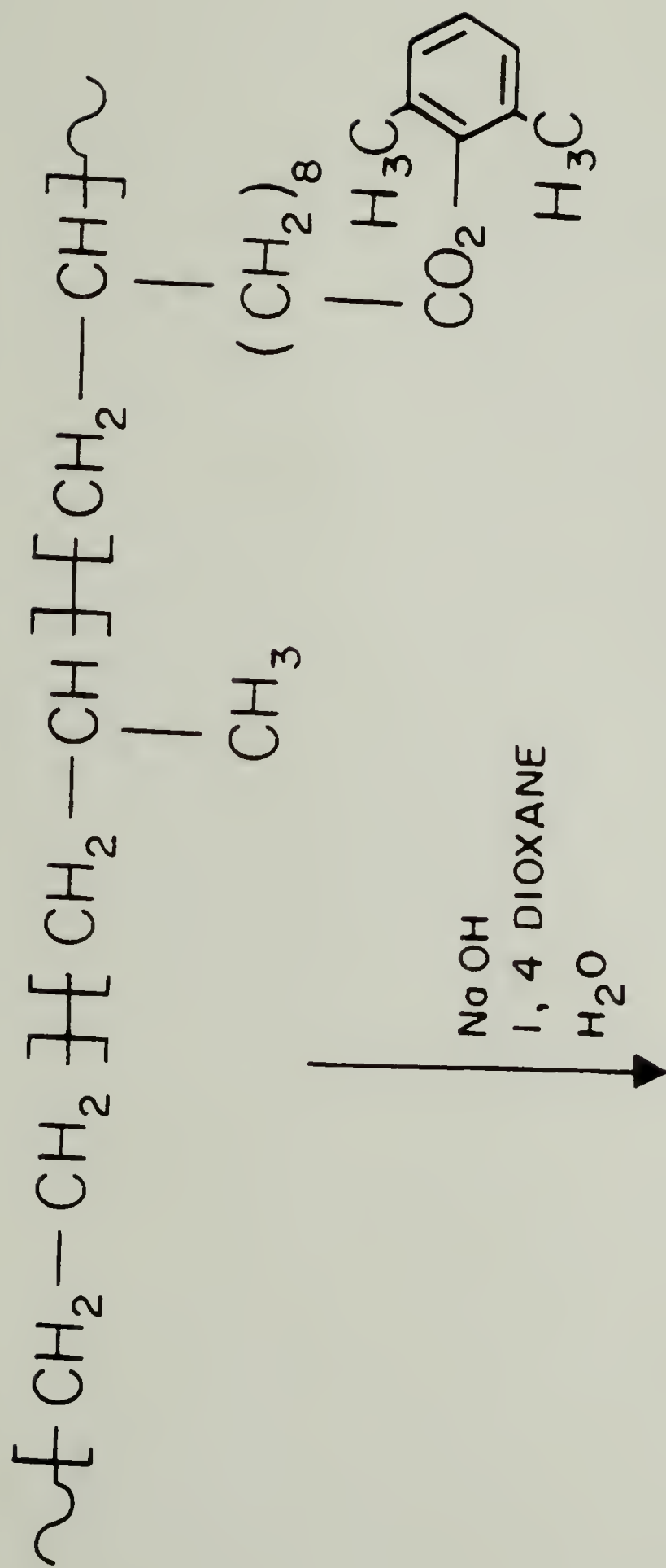
The elemental analysis of poly(10-undecenoic acid) was also in poor agreement with the theoretical values for the anhydrous acid, although not as dramatically as in the case of the polysalt previously described. The carbon analysis was low and the hydrogen slightly high, suggesting the presence of residue water. Note that analyses for samples initially dried for 48 hours at  $25^{\circ}\text{C}/0.01\text{mm}$  were in closer agreement after an additional 48 hours drying at  $100^{\circ}\text{C}/0.01\text{mm}$ .

2. Modification reactions of poly(ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate). Base hydrolysis was again employed for the preparation of the terpolymer sodium salt. However, the procedure previously described for neutralization of poly(DMPU) could not be directly applied, due to differences in solubility of both the starting ester-substituted terpolymer and the desired sodium carboxylate-containing terpolymer.

The E/P/DMPU terpolymer was not soluble in 1,4-dioxane but formed a flocculent suspension after stirring for 8 hours at  $25^{\circ}\text{C}$  and for 1 hour at  $85^{\circ}\text{C}$  under argon sweep. This slurry was treated with 4N aqueous sodium hydroxide, stirred at  $85^{\circ}\text{C}$  for 3 hours, and the product



Equation 15. Preparation of Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid Sodium Salt) from Poly(Ethylene-co-Propylene-co-DMPU).



isolated by filtration. Note that the washing procedure for this polymer is most critical. The polymer must be rinsed to remove residue base, however, water must not be used since excess water will result in a shift to the right of the salt-acid equilibrium, resulting in formation of carboxylic acid functionality and sodium hydroxide. The end result is a polymer with a sodium analysis far lower than predicted. A washing procedure reported by Bansleben<sup>1</sup> was successfully adapted, which calls for stirring the polymer in ether/methanol (4/1 by volume) solutions for 2 days. After drying, 84% of a light tan powder was obtained. The infrared spectrum as shown in Figure 3 demonstrates the anticipated shift of the carbonyl stretch from  $1762\text{ cm}^{-1}$  (C=O stretch, aromatic ester) to  $1565\text{ cm}^{-1}$  (C=O stretch, carboxylate salt).

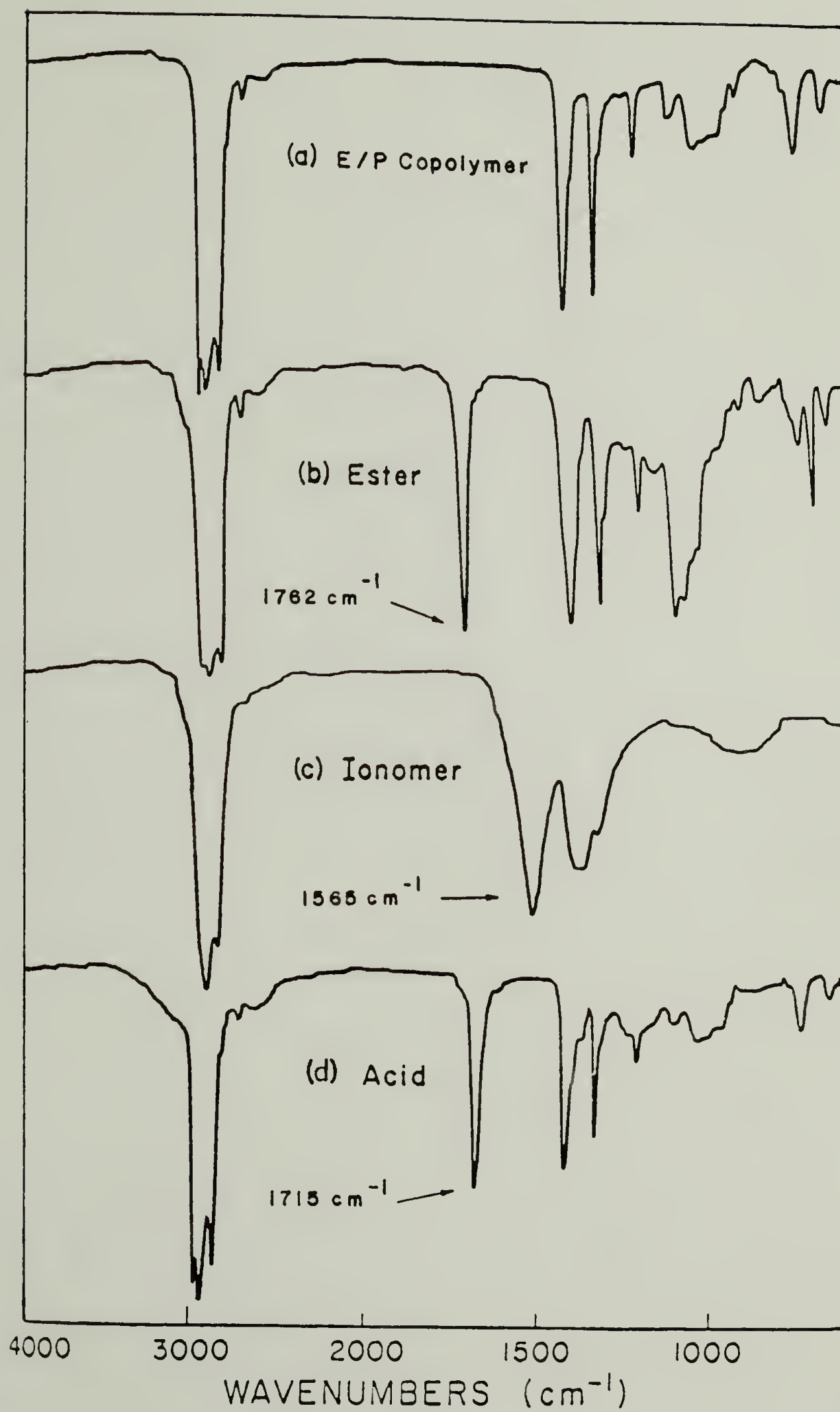
Note that while the E/P/DMPU terpolymer was soluble in hot decalin, the terpolymer salt  $\text{E/P/U}^-\text{Na}^+$  was not, confirming incorporation of the DMPU into the bulk polyolefin product.

In the case of this sodium carboxylate-containing terpolymer as well, the elemental analysis indicates presence of bound water not removable by conventional drying techniques.

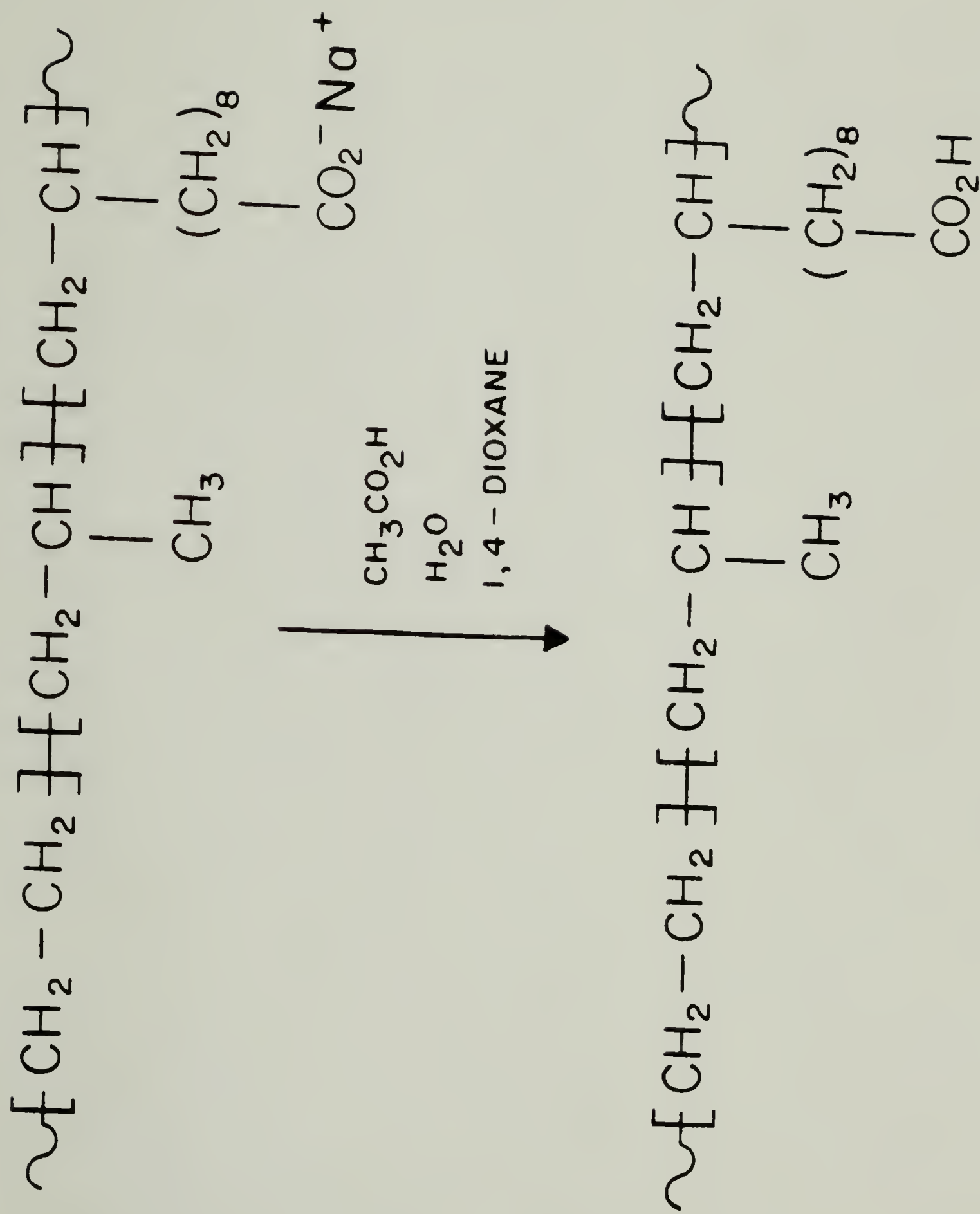
Poly(ethylene-co-propylene-co-10-undecenoic acid) was easily prepared as shown in Equation 16, by treating the terpolymer salt with acetic acid in a 1,4-dioxane/water solution at  $25^\circ\text{C}$  for 1 day. The polymer was isolated by filtration, stirred in excess water for 2 hours to remove residue acetic acid, and dried over  $\text{P}_2\text{O}_5$  for 48 hours at  $100^\circ\text{C}/0.01\text{mm}$ . 82% of a white, rubbery particulate was obtained.

Figure 3. Comparison of Infrared Spectra of Functionally Substituted Polyolefin Terpolymer: (a) Poly(Ethylene-co-Propylene-co-DMPU), (b) Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid Sodium Salt), (c) Poly Ethylene-co-Propylene-co-10-Undecenoic Acid).





Equation 16. Preparation of Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid) from Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid Sodium Salt).



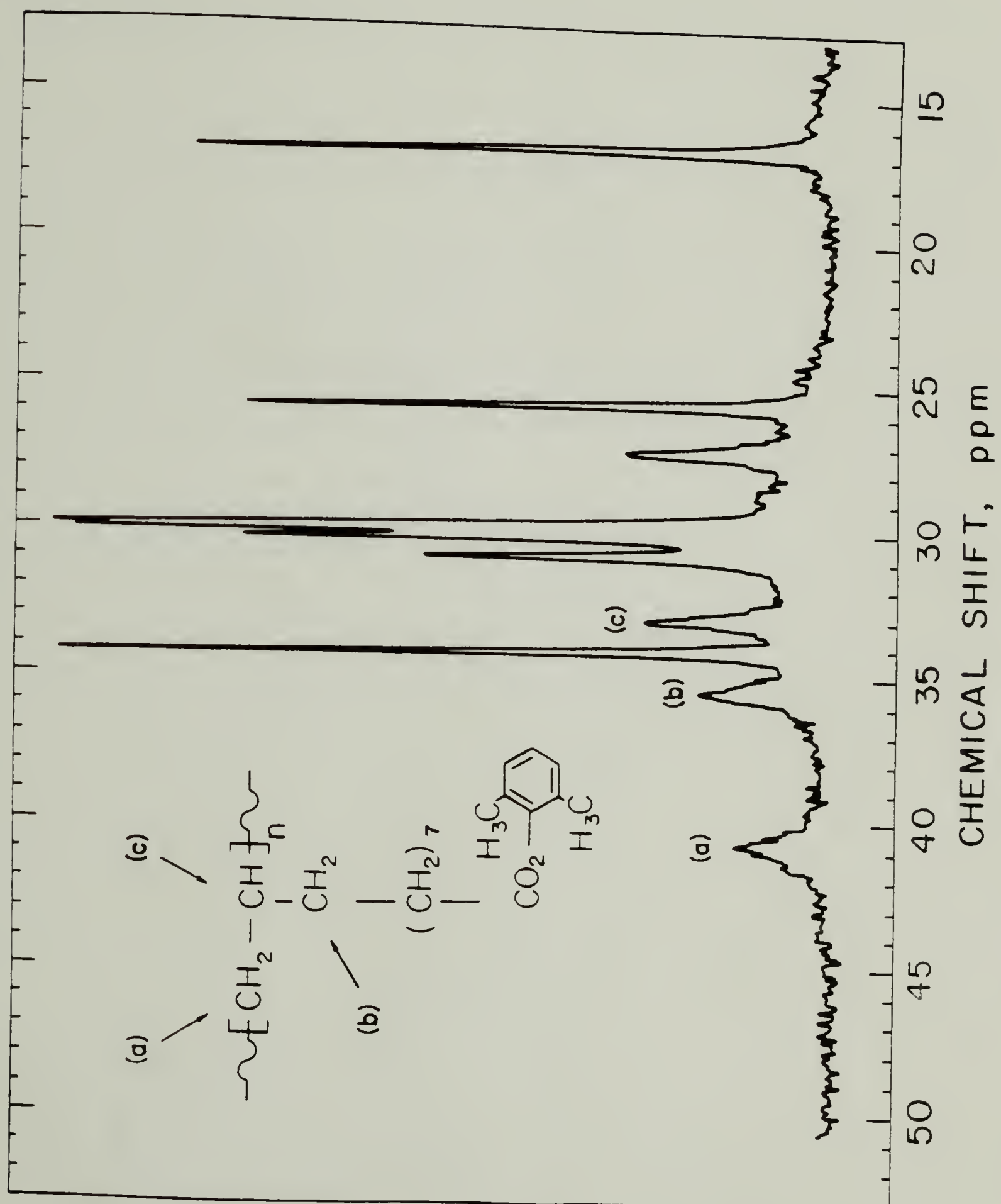
Infrared analysis (see Figure 3) indicated total conversion to the polycarboxylic acid as demonstrated by a shift in the carbonyl absorption from  $1565\text{ cm}^{-1}$  (C=O stretch, carboxylate salt) to  $1715\text{ cm}^{-1}$  (C=O stretch, carboxylic acid). The elemental analysis of the dried sample was in good agreement with the calculated values for the carboxylic acid-containing terpolymer.

## I. Analysis of $\omega$ -Functionally-Substituted Polyolefins

1. Analysis of poly(DMPU), poly(10-undecenoic acid sodium salt) and poly(10-undecenoic acid). The homopolymer poly (2,6-dimethylphenyl 10-undecenoate), referred to as poly (DMPU), was selected for further detailed analyses and modification reactions on the basis of product yield, inherent viscosity and solubility. The proposed polymer structure was confirmed by infrared,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and elemental analysis. The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) is included in Appendix C and the chemical shift assignments are recorded in section D.2 of chapter 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonance spectroscopy have become powerful tools for the study of polymer tacticity, specifically for the differentiation between isotactic and syndiotactic structures. For polypropylene or higher poly( $\alpha$ -olefins), the chemical shifts of the methylene and methine carbons of the polymer backbone and the methylene carbon (methyl in the case of propylene) of the side chain are readily differentiated and useful for the determination of tacticity. The chemical shifts observed reflect the sum of the relative local stereochemistry at each carbon along the polymer chain. A detailed explanation



Figure 4.  $^{13}\text{C}$  NMR Spectrum of Poly (DMPU) Backbone Carbon Atoms (Expanded Scale).



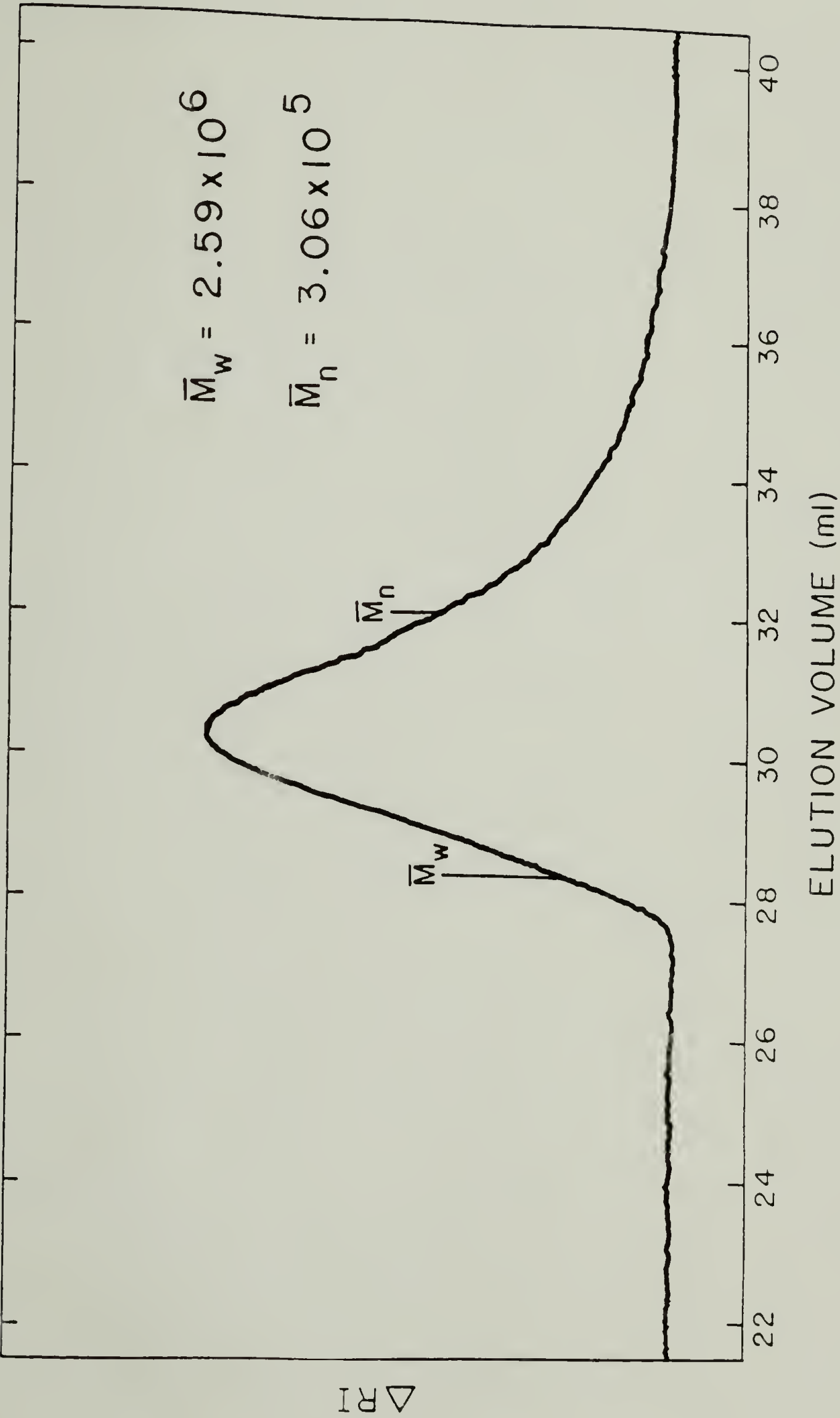
of the treatment of microtacticity is presented by Levy.<sup>192</sup> An expanded scale  $^{13}\text{C}$  NMR spectrum of poly(DMPU) is found in Figure 4. The key peaks for the backbone methylene and methine carbons, and the side chain methylene carbon are assigned to 40.14, 32.41 and 35.06 ppm respectively. Examination of comparable polymer systems indicate that when both isotactic and syndiotactic sequences are present, multiplicity of these peaks is observed, with variations in chemical shift from 0.5 to 2.0 ppm. Since splitting of this nature is not observed in the expanded spectra of poly(DMPU), a highly tactic structure is confirmed. Since the titanium initiator systems and reaction conditions utilized during the course of this study are known to generate primarily isotactic product,<sup>19</sup> an isotactic structure is assigned to poly(DMPU).

Relative number-average ( $\overline{M}_n$ ) and weight-average ( $\overline{M}_w$ ) molecular weights were obtained by gel permeation chromatography (GPC) for a poly(DMPU) sample with an inherent viscosity (0.5% in benzene, 30°C) of 2.9 dL/g. The GPC curve is shown in Figure 5. Relative to polystyrene calibration standards, the molecular weight averages obtained were:  $\overline{M}_n = 3.06 \times 10^5$  and  $\overline{M}_w = 2.59 \times 10^6$ . The molecular weight distribution was 8.47, which is consistent with that expected for the reprecipitated product of a solution polymerization.

Preparation of the parent ester-substituted homopolymer poly(DMPU), the sodium carboxylate salt, poly( $\text{UA}^-\text{Na}^+$ ), and the polycarboxylic acid, poly(UA) has been discussed in section H.1 of this chapter. During development of the synthetic procedures for conversion to the polysalt and polyacid, infrared analysis was utilized to monitor

Figure 5. Gel permeation chromatogram of poly(DMPU),  
 $\eta_{0.5\%} = 2.9 \text{ dL/g}$ .





reaction progress and ultimate degree of conversion. The infrared spectra of poly(DMPU), poly(UA<sup>-</sup>NA<sup>+</sup>) and poly (UA) as illustrated in Figure 2 demonstrate that essentially complete conversion to each derivative was achieved.

Thermal analysis by means of differential scanning calorimetry was then conducted on members of this homopolymer series. Samples of approximately  $10 \pm 0.5$  mg were scanned from  $-150^{\circ}\text{C}$  to  $77^{\circ}\text{C}$ , and from 7 to  $287^{\circ}\text{C}$ . The low temperature scans were heated at  $20^{\circ}\text{C}/\text{min}$ , quenched and a second run conducted. The high temperature scans were then conducted at  $20^{\circ}\text{C}/\text{min}$ , followed by quenching and a second scan. The samples were then cooled at  $20^{\circ}\text{C}/\text{min}$  and a third scan performed. Figure 6 displays the results of the initial scans, with all thermal transitions recorded in Table 21. Unless otherwise specified, glass transition onset values will be used for the purpose of this discussion.

The transitions obtained for poly(DMPU) were found to be a function of the recent thermal history of the sample. For example, sample dried in the abderhalden pistol at  $100^{\circ}\text{C}/0.01$  mm for 48 hours, allowed to cool to  $25^{\circ}\text{C}$  and run the same day showed a glass transition at  $-28^{\circ}\text{C}$ , with no melting transition observed. However, when the polymer was allowed to stand at  $25^{\circ}\text{C}$  for 2 days after drying, a strong melting transition at  $64^{\circ}\text{C}$  (melting range  $22$ - $75^{\circ}\text{C}$ ) was recorded. Note that a second run after cooling at  $10^{\circ}\text{C}/\text{min}$  gave only a glass transition. A closer examination of the sample upon removal from the drying apparatus reveals that the sample was very flexible with significant surface tackiness. After standing for approximately 2 days,

Figure 6. DSC Scans of (a) Poly(DMPU), (b) Poly-(10-Undecenoic Acid Sodium Salt) and (c) Poly(10-Undecenoic Acid).

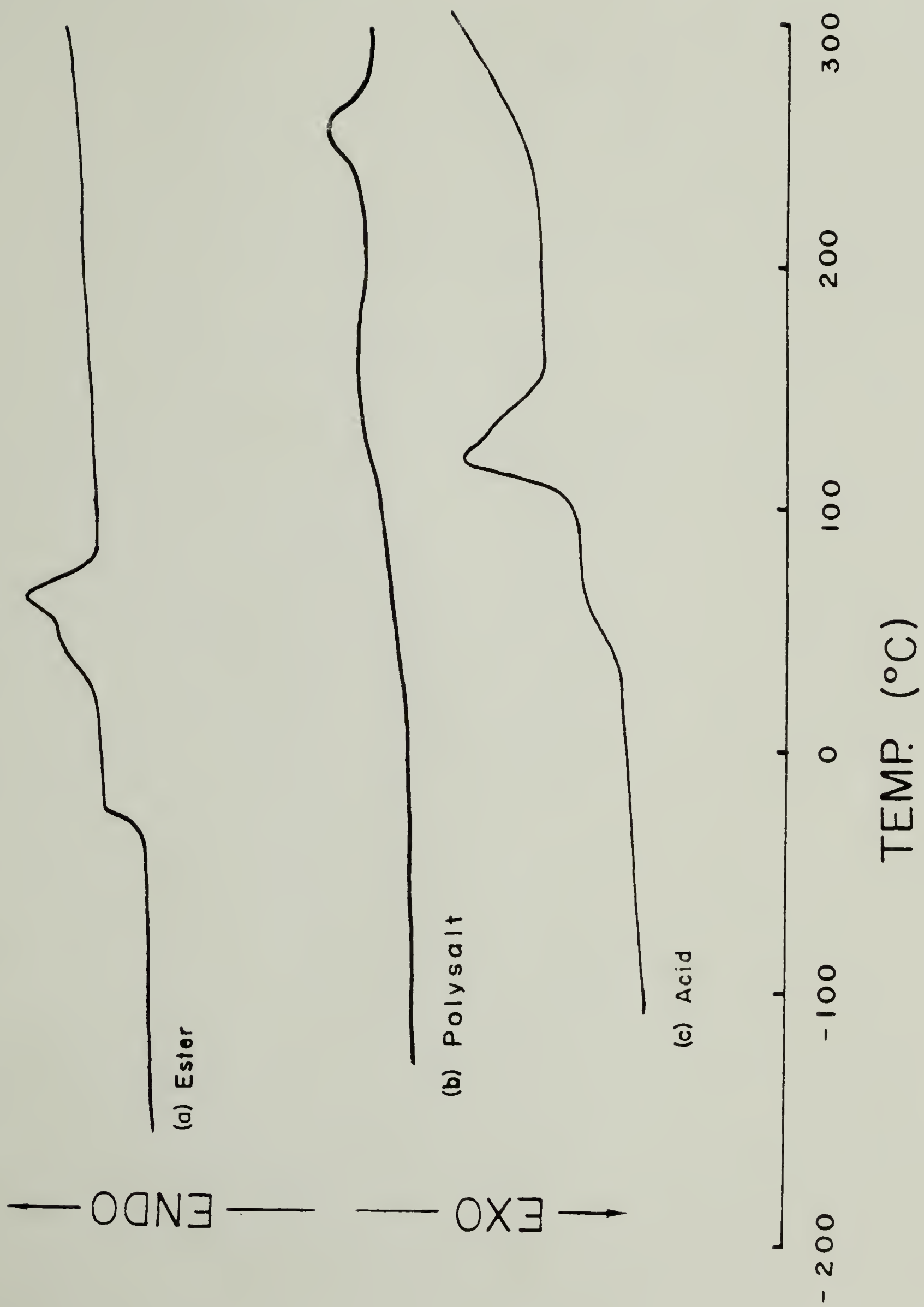
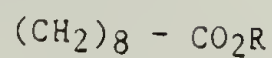
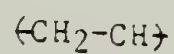


TABLE 21  
THERMAL TRANSITION TEMPERATURES OF FUNCTIONALLY-  
SUBSTITUTED POLY( $\omega$ -ALKENOATE) HOMOPOLYMERS<sup>a</sup>



Polymer	R	T <sub>g</sub> in °C <sup>b</sup>	T <sub>g</sub> in °C <sup>c</sup>	T <sub>m</sub> in °C
Poly(DMPU)	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	-28	-27	64 <sup>d</sup>
Poly(UA <sup>-</sup> Na <sup>+</sup> )	Na <sup>+</sup>	30 <sup>d</sup>	107 <sup>d</sup>	248 <sup>d</sup> , 252
Poly(UA)	H	36 <sup>e</sup>	54 <sup>e</sup>	119 <sup>d</sup> , 132

<sup>a</sup>Determined by DSC, heating rate 20°C/min, run 1 of 2.

<sup>b</sup>Transition onset.

<sup>c</sup>Transition midpoint.

<sup>d</sup>Observed in initial scan only.

<sup>e</sup>Transition strongest in initial scan.



the sample was a rigid plastic in appearance, with no surface tackiness. These results indicate that the sample is effectively annealed upon standing at ambient temperatures, resulting in the formation of crystallinity.

X-Ray analysis (WAXD) confirms the presence of crystallinity, as shown in Table 22, and will be discussed.

The dynamic mechanical behavior of poly(DMPU) was also investigated in shear mode at a frequency of 1 Hz over a temperature range of -50 to 135°C. The plot of loss modulus as a function of temperature as illustrated in Figure 8 indicates two low temperature relaxations at -28°C, possibly a phenyl ring rotation or other sub-T<sub>g</sub> motion, and -7°C which was assigned as the glass transition. Plots of shear modulus and  $\tan \delta$  as a function of temperature are included in Figure 7. Two relaxations are observed; the glass transition at -7°C and a melting transition at 63°C. Due to frequency dependence, this value for the glass transition is higher than that obtained by DSC. The melting transitions obtained by DSC and dynamic mechanical analysis are in good agreement.

DSC analysis of the acid homopolymer poly (UA) revealed a glass transition at 36°C, which was broader and 64° higher than that observed for the parent ester-substituted polyolefin. In addition, a melting transition at 119°C (melting range 102-155°C) was recorded. After quenching at 320°/min a second scan revealed a much weaker glass transition and a sharper melting transition at 132°C.

The behavior of this sample is most interesting. Note the

Figure 7. Dynamic Mechanical Analysis of Poly(DMPU); Shear Modulus and  $\tan \delta$  as a Function of Temperature.

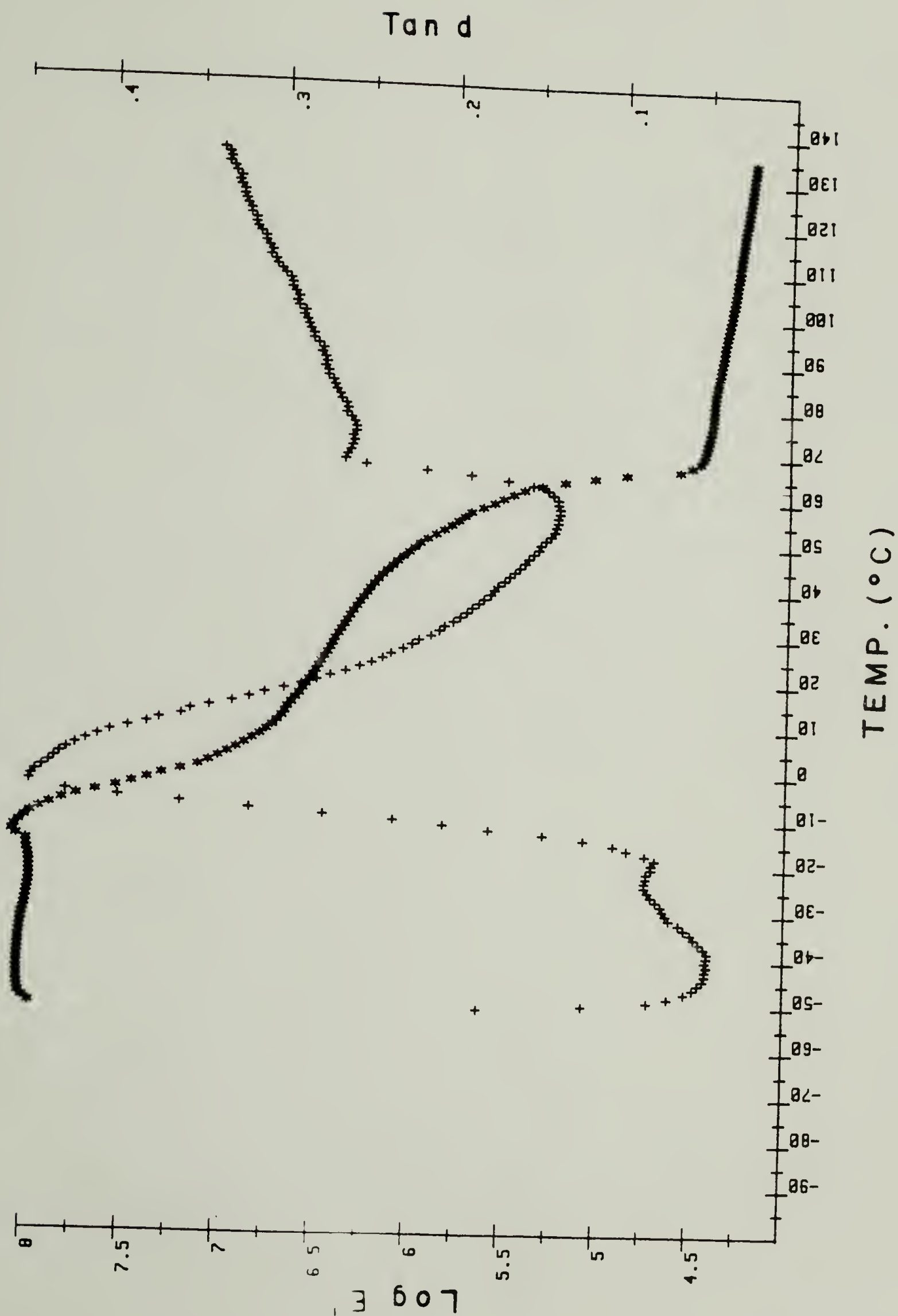
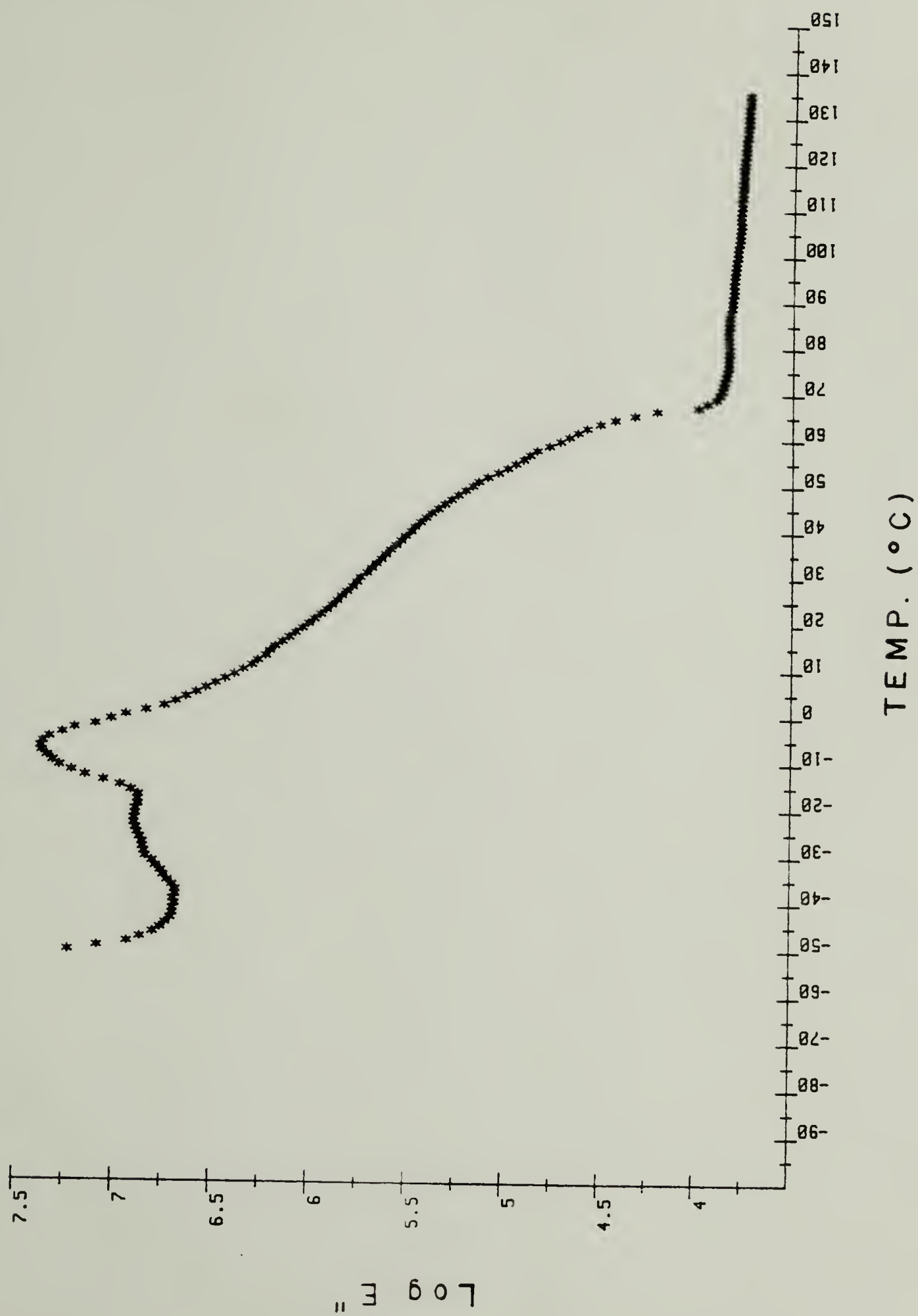


Figure 8. Dynamic Mechanical Analysis of Poly(DMPU); Loss Modulus as a Function of Temperature.





magnitude of the difference ( $60^\circ$ ) in the glass transition from that of the parent homoester, and the behavior of the transition upon quenching. A review of the literature reveals that for conventional ion-containing systems at a given concentration, the nature of the pendant group (ester, salt or acid) does not greatly affect the value of the glass transition.<sup>83</sup> For example, Holliday<sup>156</sup> reports that for a series of styrene-methacrylic acid copolymers, containing from 0 to 40 mole-% incorporation of the polar monomer, the glass transitions of the acid and salt vary from only 3 to  $10^\circ\text{C}$  respectively. However, results in this laboratory for carboxylate-substituted poly(alkenoates) demonstrate a variation of at least  $50^\circ\text{C}$  between the ester and acid derivatives.<sup>1</sup>

The observation that upon quenching of the poly(acid), the second scan shows a diminished glass transition and a sharper, higher melting transition is also significant. It has been established that the glass transition temperature is related to segment mobility, which in turn is related to inter-chain forces.<sup>156</sup> In the case of the poly(acid), it appears that the increase in the glass transition as a result of hydrogen bonding is very substantial. In addition, the results suggest that upon melting the sample during the initial scan, order within the system due to hydrogen bonding is increased, so that the second scan after quenching exhibited a diminished glass transition and an enhanced melting transition. If this were the case, a similar but even more dramatic effect may be anticipated for the case of the polysalt, which is found to be the case. As shown in Figure 6 and

Table 21, the initial scan for poly (UA<sup>-</sup>Na<sup>+</sup>) reveals a broad glass transition at 80°C (transition midpoint at 107°C) which is totally absent in the second scan after quenching. The initial scan of the polysalt also contains a melting transition at 248°C, which sharpens and increases to 252°C in the second scan. Upon cooling the sample at 20°C/min, an exotherm centered at 177°C was recorded. Note that the assignment of this peak to an impurity or reaction by-product was ruled out, since sodium 2,6-dimethylphenoxide, the only other reaction product, has a melting point of 45°C.<sup>193</sup> In addition, no phenyl carbons were identified in the <sup>13</sup>C NMR spectra of poly (UA<sup>-</sup>Na<sup>+</sup>).

In the case of the homopolymer salt, the glass transition is over 100°C higher than that of the parent ester-substituted polymer, and the melting transition is much higher than that exhibited for main-chain or side-chain crystallinity in simple polyolefins. Thus it is evident that electrostatic forces between the bound ions in the polymer chains and the counter ions dramatically reduce configurational entropy and so increase the glass transition. The disappearance of the glass transition following the initial scan indicates further enhancement of the ionic interaction, so that the thermal behavior resembles that of highly crosslinked carbon polymer systems, in which there is no indication of a glass transition below the decomposition temperature of the polymer.<sup>156</sup> Thermal analysis of sodium carboxylate-substituted poly(alkylene oxide) homopolymers prepared in this lab<sup>1</sup> show no glass transition or melting transition between -120 to 225°C (third scan reported). This experimenter suggests that a melting transition at

approximately 252°C would have been observed had the scan continued.

Thus it appears that by conversion of the pendant carboxylate ester to the carboxylic acid and the sodium carboxylate salt, the crystallinity and segment mobility is greatly altered by the formation of hydrogen bonding and ionic crosslinks respectively, which is manifested in an increase and/or loss of the glass transition, loss of conventional crystallinity and high melting transitions signifying thermal disruption of these strong interchain interactions.

Note that the most important characteristic difference between these polymers (and copolymers) and conventional polyelectrolyte derivatives (and ionomers) is the incorporation of a flexible hydrocarbon spacer chain consisting of 8 methylene units. The presence of this spacer group may be expected to enhance the mobility of the carboxylate groups compared to systems in which the ionizable group is directly attached to the polymer backbone chain, in which case mobility of the carboxylate group is limited by entanglements and other factors which restrict backbone chain movement and limit the number of ion pairs that may participate in multiplet formation. The result of this improved mobility will certainly be enhancement of those physical properties known to result from the hydrogen bonding and ionic interactions.

X-Ray diffraction measurements have been very useful in the analysis of ion-containing polymers. Reports by Rees and Vaughn,<sup>197</sup> Wilson<sup>194</sup> et al. and MacKnight<sup>195</sup> confirm the presence of a strong peak at low diffraction angles which is not observed in the parent unionized polymer. The behavior of this peak is correlatable

to compositional variables and so is particularly significant in describing the solid state structure of ion-containing polymers.<sup>156</sup> This peak reportedly occurs in the vicinity of  $2\theta = 4.5^\circ$  which suggests the presence of a structural motif that repeats with a translation of approximately  $20\text{\AA}$ .

The wide angle diffraction pattern obtained for poly ( $\text{UA}^-\text{Na}^+$ ) is consistent with the above findings. As illustrated in Figure 9 and recorded in Table 22, the poly(10-undecenoic acid sodium salt) produced two sharp peaks at  $2\theta = 3.26$  and  $6.63$ , corresponding to spacings of  $25.5$  and  $12.9 \text{ \AA}$  respectively. The presence of these integral higher order peaks, and the absence of higher angle (crystal lattice) reflections suggest the presence of alternating lamellar ionic and hydrocarbon domains, with little or no main or side-chain crystallinity.<sup>196,202</sup>

Much emphasis has been placed on determination of the distribution of salt groups in ion-containing systems. A review of the models put forth to correlate experimental and theoretical results has been prepared by MacKnight.<sup>155</sup> The homopolymer carboxylate discussed differs from conventional ionomer systems by virtue of the high concentration of carboxylate groups, and the flexible spacer chain separating them from the backbone chain. Any models subsequently proposed to elucidate the detailed structure of these polymers must consider these features, as well as the fact that the salt groups retain bound water molecules and exist as the di- or tetrahydrates, as explained in section H of this chapter.



Figure 9. Wide Angle X-Ray Diffraction (WAXD) Scans of Poly-(10-Undecenoic Acid Sodium Salt).



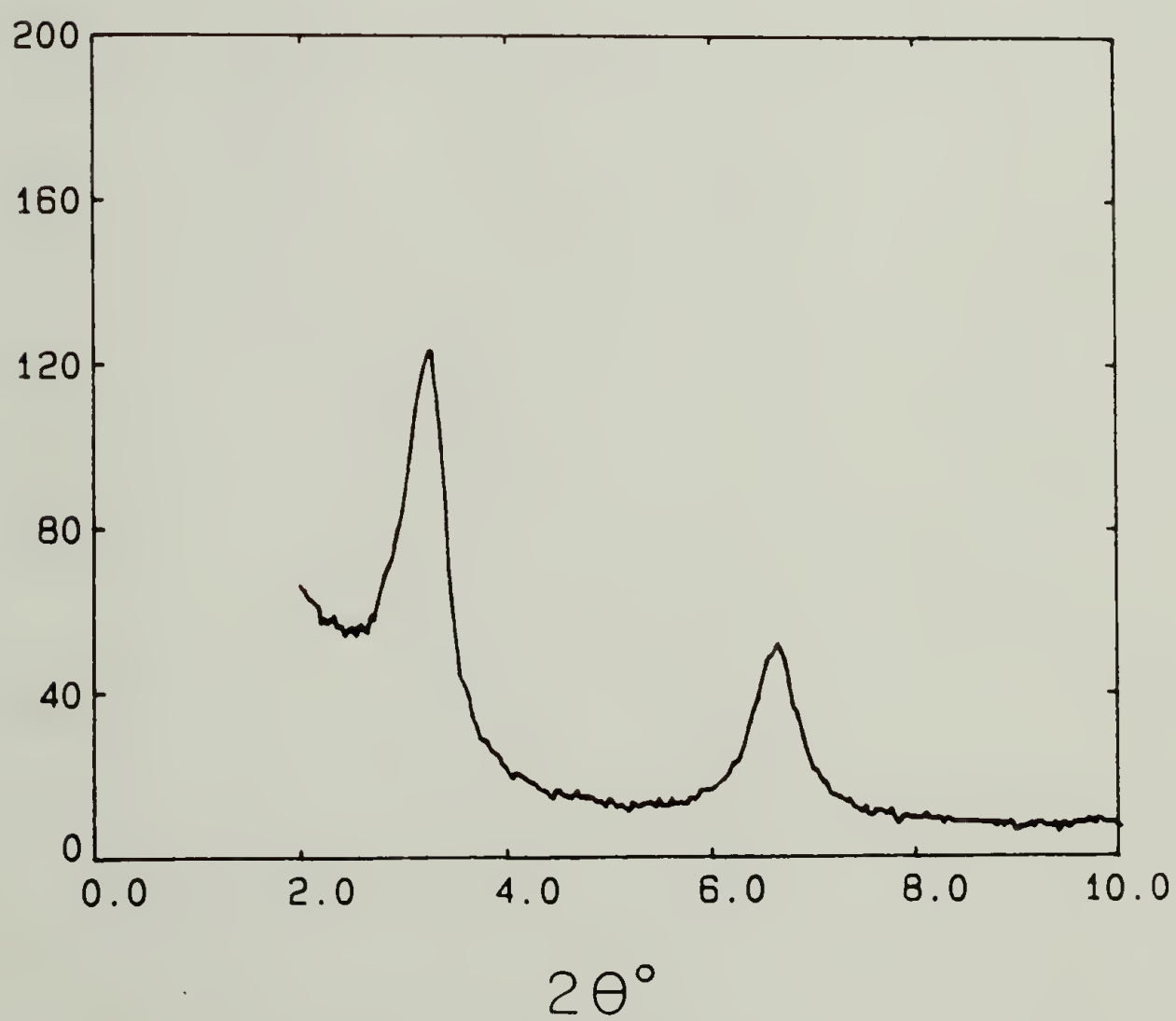
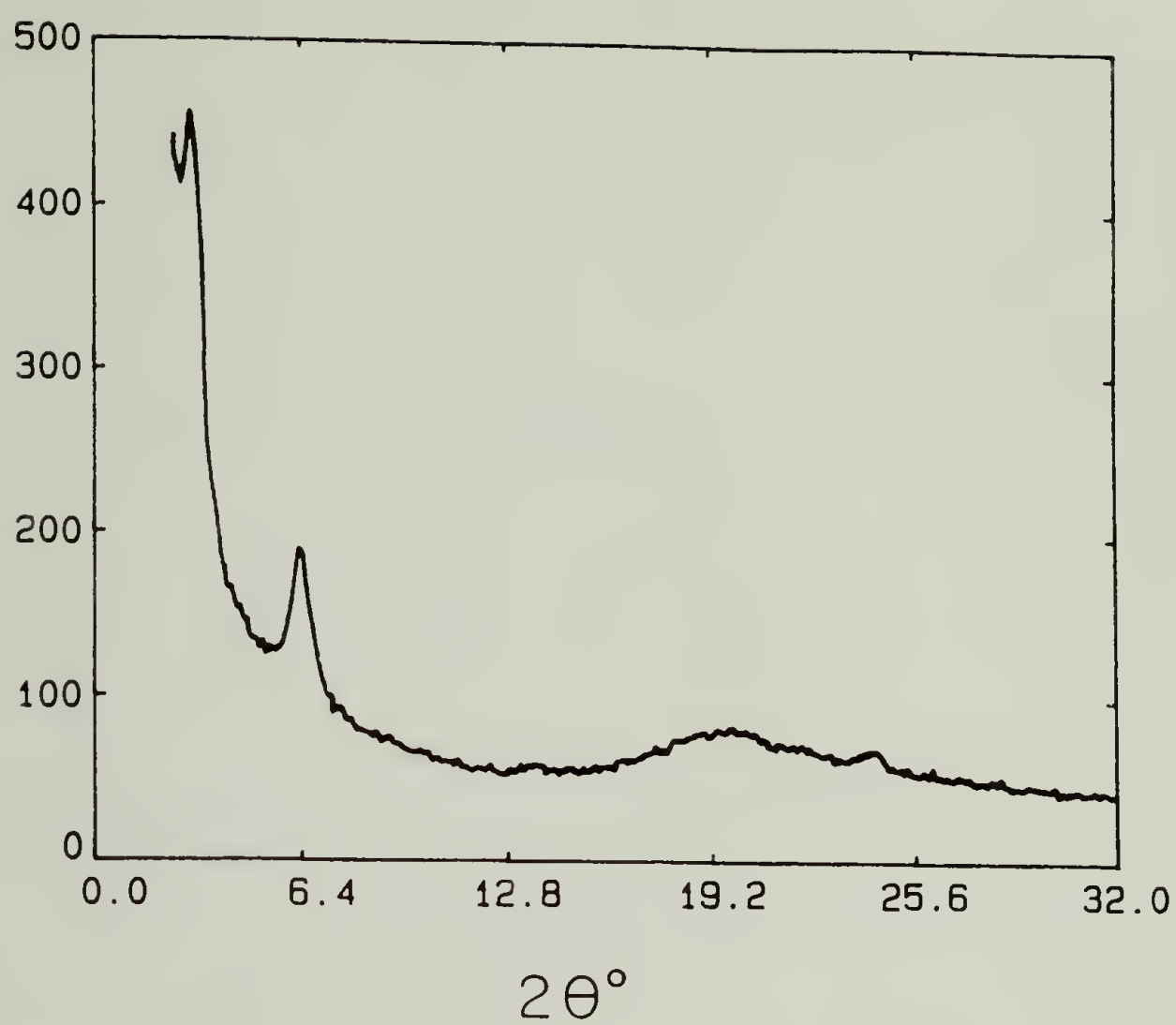


TABLE 22

WIDE ANGLE X-RAY DIFFRACTION MAXIMA OF FUNCTIONALLY-SUBSTITUTED  
 $\alpha$ -OLEFIN POLYMERS AND TERPOLYMERS

Polymer	Mole-% Functionality and Type	Angular Position of Peak (in degrees $2\theta$ )	Spacings (Å)
Poly (DMPU)	100, 2,6-dimethyl- phenyl ester	3.9*, 8.0, 10.0, 11.8*, 13.4, 14.5, 16.5, 20.1*, 21.6, 23.4, 33.5*	22.5, 11.1, 8.9, 7.5, 6.6, 6.1, 5.4, 4.4, 4.1, 3.8, 2.7
Poly (UA <sup>-</sup> Na <sup>+</sup> )	100, sodium carboxylate	3.3*, 6.6*	25.5, 12.9
Poly (UA)	100, carboxylic acid	3.5*, 7.1*	25.5, 12.4
Poly (E/P/UA <sup>-</sup> Na <sup>+</sup> )	6, sodium carboxylate	6.6, 14.0*, 16.9, 18.4, 21.4*, 23.7, 34.3	13.5, 6.3, 5.3, 4.8, 4.2, 3.8, 2.6

\*Denotes major peaks in WAXD scan.

Diffraction patterns for poly (10-undecenoic acid) obtained with the Statton camera exhibited comparable maxima at  $2\theta = 3.46$  and  $7.11$ , corresponding to a periodicity of  $25.5$  and  $12.4$  Å. A similar lamellar structure of alternating hydrocarbon and polar domains is proposed.

The diffraction pattern for a poly(DMPU) sample allowed to anneal for several days at room temperature exhibited maxima and corresponding spacings as recorded in Table 22. The degree and variety of order demonstrated by this sample is unexpected and will require further analysis to definitively assign the complex scattering pattern obtained. However, tentative assignments may be proposed at this time. The spacing of  $2.7$ ,  $3.8$  and  $4.1$  Å may be due to imperfect polyethylene side-chain crystallinity, while those of  $4.4$ ,  $5.4$ ,  $6.1$  and  $6.6$  Å may be attributed to distorted main-chain crystallinity. The larger spacings at  $11.1$  and  $22.5$  Å suggest order resulting from ester group interaction. Further experiments, including analysis of oriented samples should be conducted.

The scattering maxima and corresponding spacings obtained for the terpolymer salt poly(ethylene-co-propylene-co-10-undecenoic acid sodium salt) are also recorded in Table 22. Note the existence of the ionic peak at  $2\theta = 6.6^\circ$ , which correlates to a domain spacing of  $13$  Å, and is in good agreement with that observed by Bansleben<sup>1</sup> for poly (alkylene oxides) with identical spacer chain and sodium carboxylate incorporation. The spacings  $2.6$ ,  $3.8$  and  $4.2$  Å, and at  $4.8$ ,  $5.3$  and  $6.3$  Å are assigned to crystallinity from polyethylene and polypropylene

blocks respectively. In the case of this terpolymer carboxylate salt, a core-shell ionic domain structure in concert with considerable main-chain crystallinity is proposed.

Thermogravimetric analysis of the homopolymer series including poly (DMPU), poly ( $\text{UA}^-\text{Na}^+$ ) and poly (UA) was conducted at a heating rate of  $20^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. The degradation curves are presented in Figure 10 and the transition temperatures recorded in Table 23. The primary objective of these analyses was to further characterize the melting transition at  $252^\circ\text{C}$  observed in the DSC analysis of the poly (10-undecenoic acid sodium salt). Potential explanations for this transition included the liberation of bound water molecules, or possibly the onset of degradation, both of which would be readily detected by TGA analysis. The curve shown in Figure 10 for poly ( $\text{UA}^-\text{Na}$ ) demonstrates that no weight loss occurs below  $470^\circ\text{C}$ , thus eliminating both of the aforementioned explanations for the DSC peaks at  $252^\circ\text{C}$ .

Figure 10 also illustrates that the ester-substituted parent poly (DMPU) exhibits greater stability (weight loss onset at  $355^\circ\text{C}$ ) than the corresponding carboxylic acid derivative (weight loss onset  $250^\circ\text{C}$ ), possibly due to anhydride formation and loss of water.

2. Analysis of poly(ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate), poly(ethylene-co-propylene-co-10-undecenoic acid sodium salt) and poly(ethylene-co-propylene-co-10-undecenoic acid).

Discussion of the synthesis of poly (E/P/DMPU), the sodium salt, poly

Figure 10. Thermogravimetric Analysis Curves for (a) Poly(DMPU), (b) Poly(10-Undecenoic Acid Sodium Salt and (c) Poly(10-Undecenoic Acid).



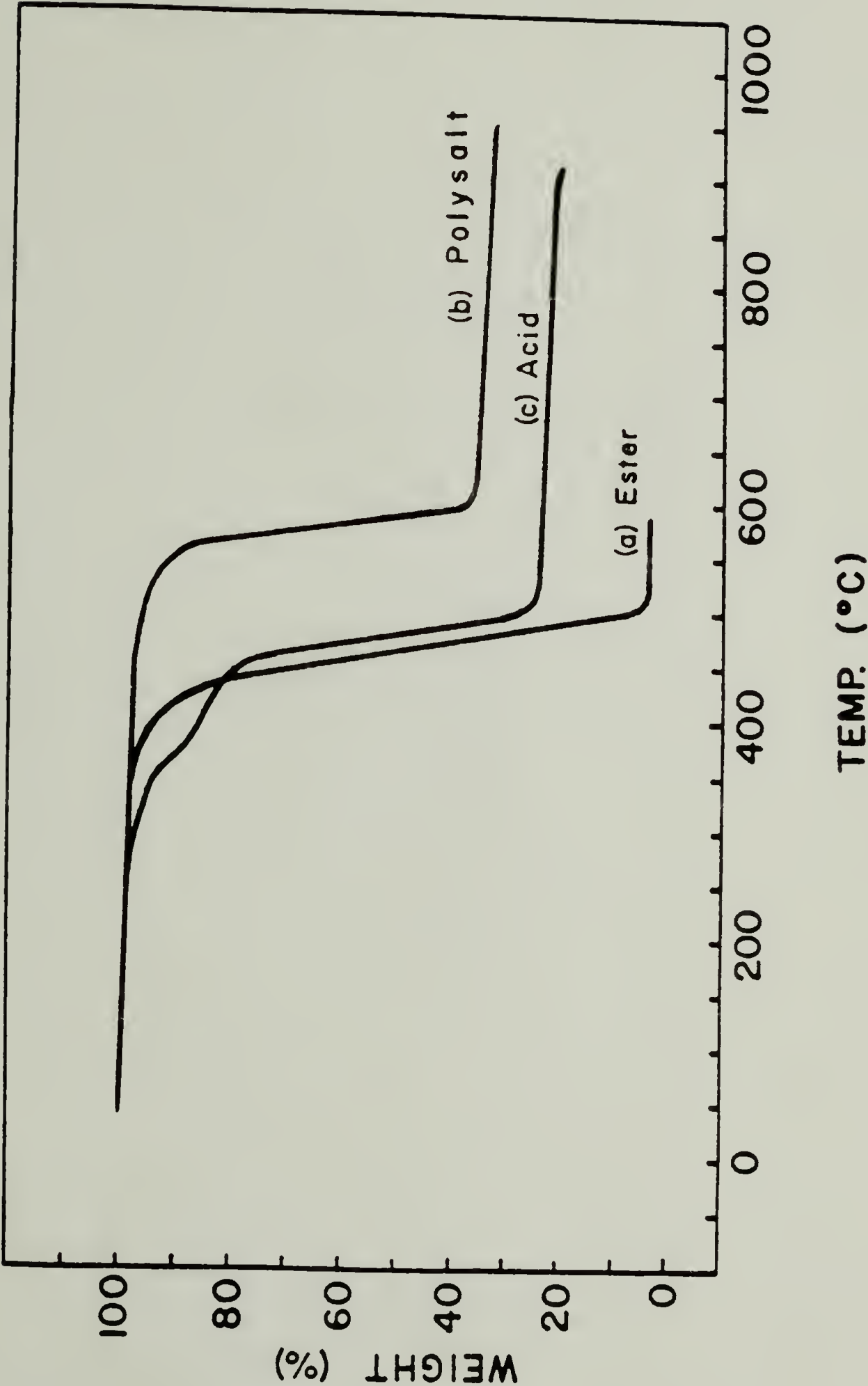
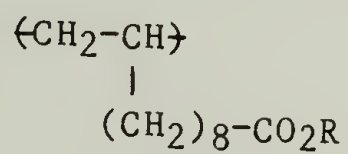


TABLE 23

THERMOGRAVIMETRIC ANALYSIS TRANSITION TEMPERATURES FOR  
FUNCTIONALLY-SUBSTITUTED POLY( $\omega$ -ALKENOATE) HOMOPOLYMERS<sup>a</sup>



Polymer	R	Transition Onset in °C	Transition Midpoint in °C
Poly(DMPU)	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	355	473
Poly(UA <sup>-</sup> Na <sup>+</sup> )	Na <sup>+</sup>	470	568
Poly(UA)	H	250	473

<sup>a</sup>Determined by TGA, heating rate 20°C/min.

(E/P/UA<sup>-</sup>Na<sup>+</sup>) and the carboxylic acid derivative poly (E/P/UA) are included in sections G.3 and H.2. As in the case of the homopolymer series derived from poly (DMPU), infrared analysis was employed to monitor the extent of conversion of the ester-substituted polyolefin to the terpolymer salt and carboxylic acid derivatives. Figure 3 compared the infrared spectras of these three compounds with that of an ethylene/propylene reference copolymer.

DSC analysis was also conducted on the four members of this co- and terpolymer series, as detailed in Table 24 and Figures 11 and 12. The reference copolymer prepared using the TiCl<sub>3</sub>AA/AlEt<sub>2</sub>Cl initiator system produced a broad glass transition at -55°C (-30°C, transition midpoint) compared to a literature value of -20°C<sup>203</sup> for isotactic polypropylene, indicating incorporation of ethylene in the amorphous phase. Melting transitions at 122 and 152°C were also observed, as compared to literature values of 138°C and 175°C for linear polyethylene and isotactic polypropylene respectively.<sup>199</sup> These results demonstrate that the copolymer is not random, but rather contains crystalline blocks of polyethylene and polypropylene, as may be anticipated when titanium based initiators are employed.<sup>78</sup>

The terpolymer poly (E/P/DMPU) prepared using TiCl<sub>3</sub>AA/AlEt<sub>2</sub>Cl (under conditions identical to those of the reference copolymer) showed a glass transition at -43°C and a melting transition at 101, 123 and 146°C. The position and character of these transitions suggest that incorporation of the ester-substituted monomer has partially inhibited the formation and crystallization of blocky domains.

Figure 11. DSC Scans of (a) Poly(Ethylene-co-Propylene-co-DMPU), (b) Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid Sodium Salt) and (c) Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid).

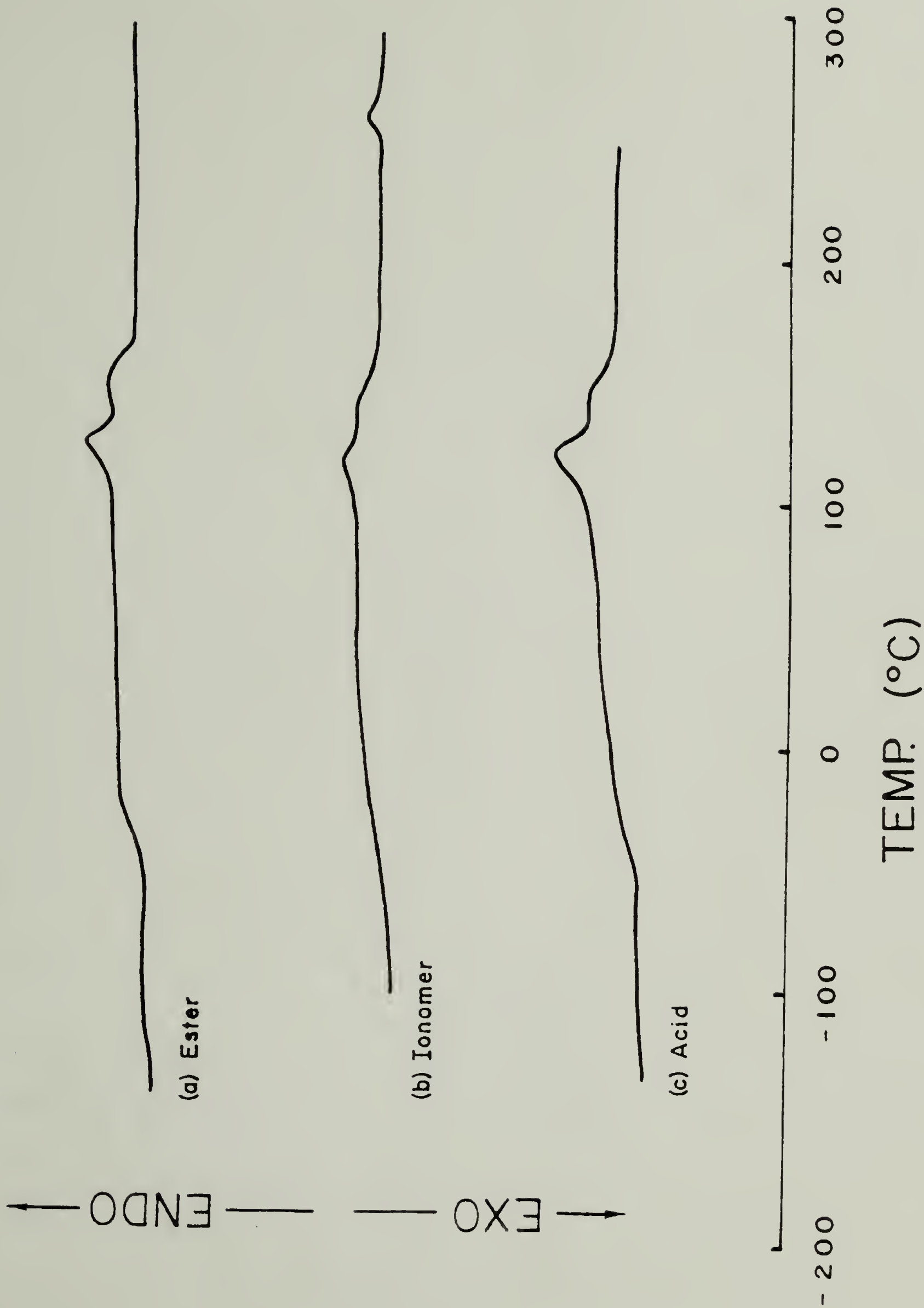




Figure 12. DSC Scans of (a) Poly(Ethylene-co-Propylene) via  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$ , (b) Poly(Ethylene-co-Propylene) via  $\text{VOCl}_3/\text{AlEt}_2\text{Cl}$ , and (c) Poly(Ethylene-co-Propylene-co-2,6-Dimethylphenyl 10-Undecenoate).

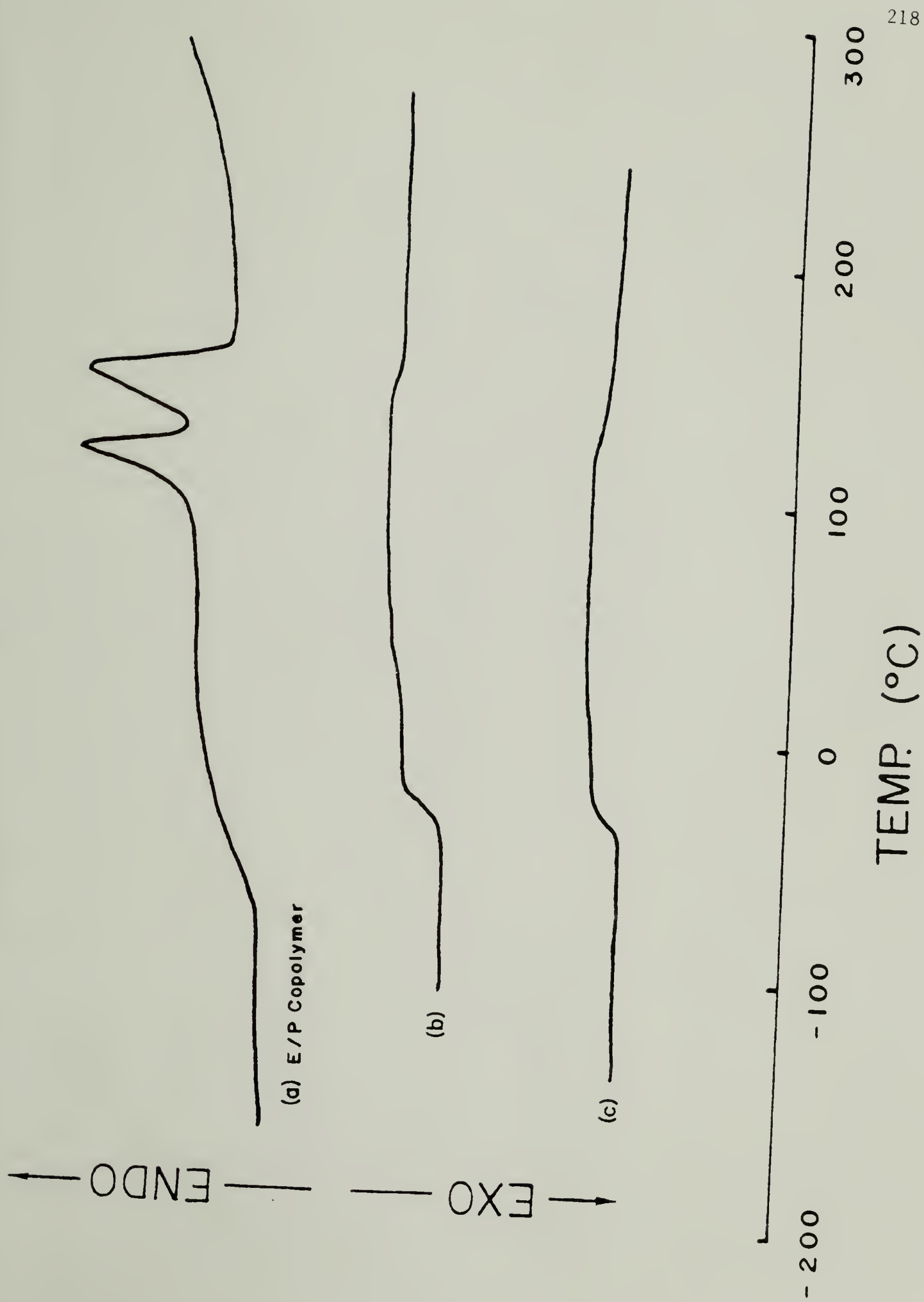
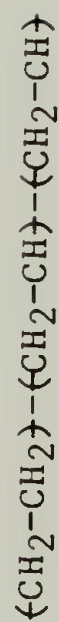


TABLE 24

THERMAL TRANSITION TEMPERATURES OF FUNCTIONALLY-SUBSTITUTED  $\alpha$ -OLEFIN TERPOLYMERS<sup>a</sup>

Co/terpolymer	TMD	R	T <sub>g</sub> in °C <sup>b</sup>	T <sub>g</sub> in °C <sup>c</sup>	T <sub>m</sub> in °C
E/P	TiCl <sub>3</sub> AA 1.1	-	-55	-30	122, 152
E/P	VOC13	-	-26	-22	-
E/P/DMPU	TiCl <sub>3</sub> AA 1.1	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	-43	-33	101 <sup>d</sup> , 123, 146
E/P/DMPU	VOC13	-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	-31	-26	-
E/P/UA <sup>-</sup> Na <sup>+</sup>	TiCl <sub>3</sub> AA 1.1	Na <sup>+</sup>	-51	-11	120, 131, 252
E/P/UA	TiCl <sub>3</sub> AA 1.1	H	-51	-1	122, 141

<sup>a</sup>Determined by DSC, heating rate 20°C/min, run 2 of 3.<sup>b</sup>Transition onset.<sup>c</sup>Transition midpoint.<sup>d</sup>Observed in initial scan only.

The terpolymer salt, poly (E/P/UA<sup>-</sup>Na<sup>+</sup>) exhibits a broadening and increase in the glass transition, accompanied by a decrease in the degree of crystallinity of the blocky domains and the appearance of a higher melting transition at 252°C. This transition corresponds exactly to that observed in the homopolymer sodium salt displayed in Figure 6. This peak, characteristic of both the homopolymer and terpolymer salts, is most interesting.

The terpolymer acid, poly (E/P/UA), shows a glass transition similar to that of the salt as well as melting transitions at 122 and 141°C.

Thus there is crystallinity due to polyethylene and polypropylene blocks in all four co- and terpolymers, with the relative degree of crystallinity (for samples of identical weight) appearing to decrease in the order poly (E/P) > poly (E/P/DMPU) ≈ poly (E/P/UA) > poly (E/P/UA<sup>-</sup>Na<sup>+</sup>). The most notable observation in this series is the reappearance of the melting transition at 252°C in the terpolymer salt, previously observed in the homosalt, and apparently accompanying thermal disruption of ionic interactions. Note that upon cooling the terpolymer salt at 20°C/min, an exotherm at 244°C was recorded.

3. Analysis of poly(ethylene-co-propylene) and poly(ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate) prepared using VOCl<sub>3</sub>/AlEt<sub>2</sub>Cl initiator. The ethylene-propylene copolymer and ester substituted-terpolymer prepared using the VOCl<sub>3</sub>/AlEt<sub>2</sub>Cl initiator system as discussed in sections G.2 and 4 were both rubbery, flexible

materials. The DSC analysis of these polymers is illustrated in Figure 12, with thermal transitions recorded in Table 24. Both poly (E/P) and poly (E/P/DMPU) had very sharp glass transitions, at  $-26^{\circ}$  and  $-31^{\circ}\text{C}$  respectively, suggesting a more uniform amorphous phase than was observed in copolymers prepared using titanium-based initiators. In addition, both polymers exhibit only extremely weak melting transitions in the region from  $117$  to  $142^{\circ}\text{C}$ , indicating very low crystallinity, such as would be expected from a random co- or terpolymer prepared using a vanadium-based initiator system.

#### J. Conclusions and Future Work

The objectives originally set forth at the start of this project have been successfully accomplished. The polymerizability of  $\omega$ -functionally-substituted  $\alpha$ -olefins containing pendant carboxylic ester groups has been investigated as a function of the ester substituent group, initiator composition, stoichiometry, reaction parameters and spacer chain length. High molecular weight isotactic homopolymers were obtained for several  $\omega$ -alkenoates using  $\text{TiCl}_3\text{AA}/\text{Al}(\text{isoBu})_2\text{Cl}$  initiator systems. Results demonstrate that a methylene spacer chain of greater than 3 and less than or equal to 6 units is required to insulate the vinyl group from the ester substituent.

Copolymers of 2,6-dimethylphenyl 10-undecenoate with 1-dodecene, 1-hexene, propylene and ethylene were prepared using  $\text{TiCl}_3\text{AA}/\text{AlEt}_2\text{Cl}$  initiators. Terpolymers of this  $\omega$ -alkenoate with ethylene and propylene were also prepared, using both titanium-based



initiators, resulting in blocky semicrystalline terpolymers and vanadium-base initiators, generating amorphous terpolymer.

Poly (2,6-dimethylphenyl 10-undecenoate) and poly (ethylene-co-propylene-co-2,6-dimethylphenyl 10-undecenoate) were neutralized and acidified to the corresponding sodium carboxylate salts and polycarboxylic acid derivatives. Physical property analyses by DSC, X-ray diffraction (WAXD), TGA and DMTA were conducted on all or selected members of the homo- and terpolymer series.

The current study represents the initial effort from this laboratory in the synthesis, polymerization and analysis of  $\omega$ -functionally-substituted  $\alpha$ -olefins. Subsequent research can conceivably be directed in three areas; additional synthetic development, modification and application of the polymers currently reported, and detailed investigation of the physical properties of these homopolymers and copolymers.

The most interesting and significant future effort would be the indepth analysis of the physical properties, specifically relaxation and rheological behavior, of the carboxylate and carboxylic acid derivatives of poly (DMPU) and poly (E/P/DMPU). The unexpected melting transition at 252°C observed in both the homo- and terpolymer sodium carboxylate salts should be the subject of further study. If possible, additional DSC and X-ray analysis of the similarly substituted poly (alkylene oxide) homo- and copolymers should be conducted and results correlated with the current study.

Future polymer modifications envisioned include attachment of functional groups to the polycarboxylic acid derivatives via displacement reactions. Use of esterification or amidation reactions employing the dehydrating agent 1,1'-carbonyldiimidazole (CDI) as discussed in Chapters 2 and 3 are particularly recommended. In this fashion, moieties with biological activity, stabilizers or other exploitable functionality could be readily attached to the hydrogen backbone.

Additional synthetic work could take several directions. Of particular interest to this experimenter would be the evaluation of hindered aluminum alkyls (not commercially available) prepared by Langer.<sup>185</sup> Also of interest is the further optimization of the vanadium-based terpolymerization reactions to provide noncrystalline ethylene,  $\alpha$ -olefin and  $\omega$ -alkenoate terpolymers.

Carboxylate salts of poly (UA) and poly (E/P/UA) could also be prepared using divalent metals, and their physical properties compared to those of the sodium salts.

The homopolymerizations of  $\omega$ -alkenoates having hydrocarbon spacer chains of 1, 3, 6 and 8 methylene units were investigated during the course of this study. While high molecular weight polymer was obtained when  $n = 6$  and 8, no polymer or oligomer was obtained when  $n = 1$  and 3. Thus a spacer chain of greater than 3, and 6 or less methylene units is a requisite for polymerization by these Ziegler-Natta techniques, for reasons previously elaborated. Preparation and polymerization of  $\omega$ -alkenoates in which  $n = 4$  and 5 would more precisely define the limits of this system. Esters of heptenoic acid ( $n=4$ ) and

octenoic acid ( $n=5$ ) could be prepared using the two step procedure previously developed for the preparation of 2,6-dimethylphenyl-8-nonenoate ( $n=6$ ).

The synthesis and copolymerization of vinyl hindered-phenol derivatives such as 2,6-Di-t-butyl-4-vinylphenol by radical techniques, to generate polymeric antioxidants, has recently been investigated in this laboratory.<sup>198</sup> Since these vinyl monomers were readily available, copolymerization and homopolymerization reactions were conducted using the Ziegler-Natta initiators and techniques developed in the current study. Preliminary results not presented in this dissertation demonstrate that homopolymerization was achieved and that copolymerizations with propylene were not deactivated by presence of these polar monomers. Thus it appears that the techniques developed during the course of this study for  $\omega$ -alkenoates could readily be adapted to the polymerization of other functionally-substituted vinyl monomers.

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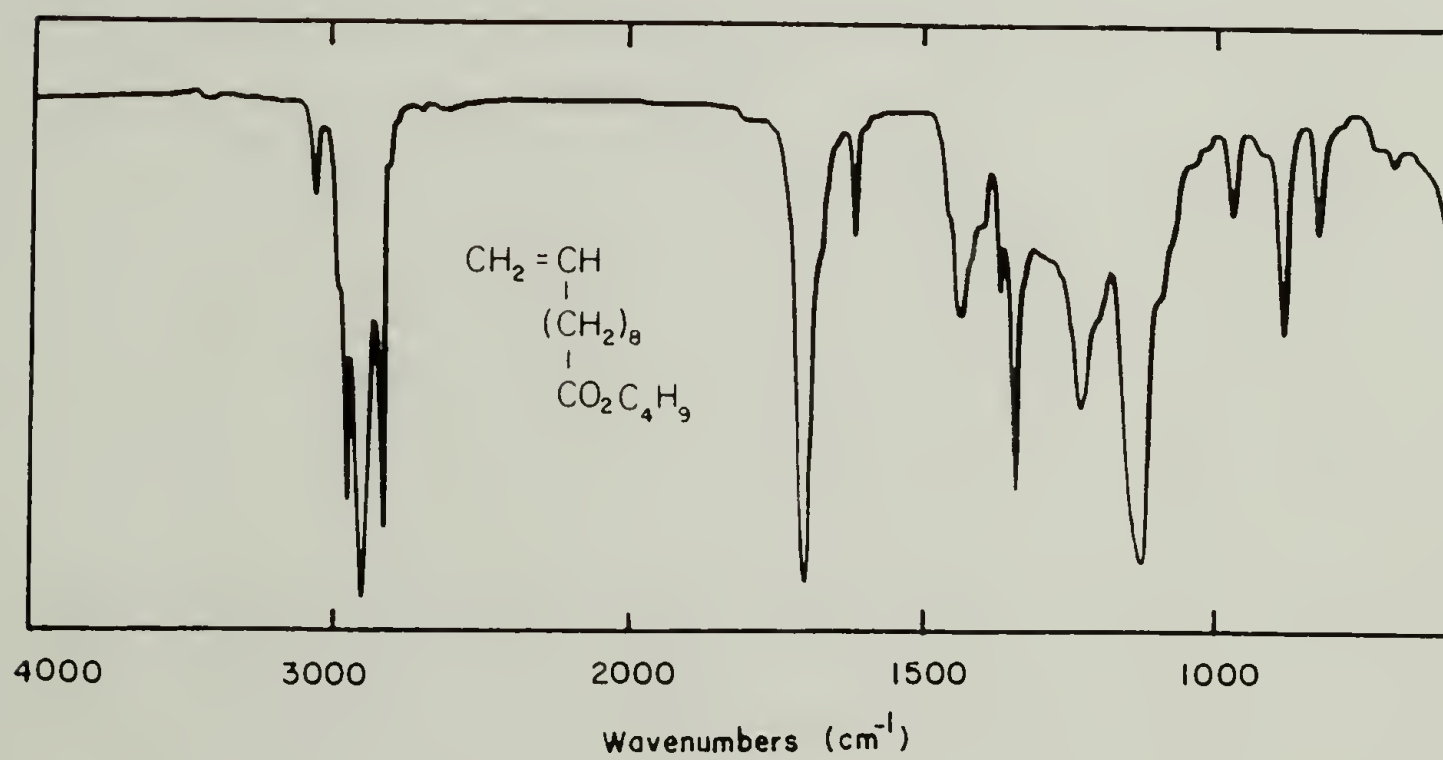
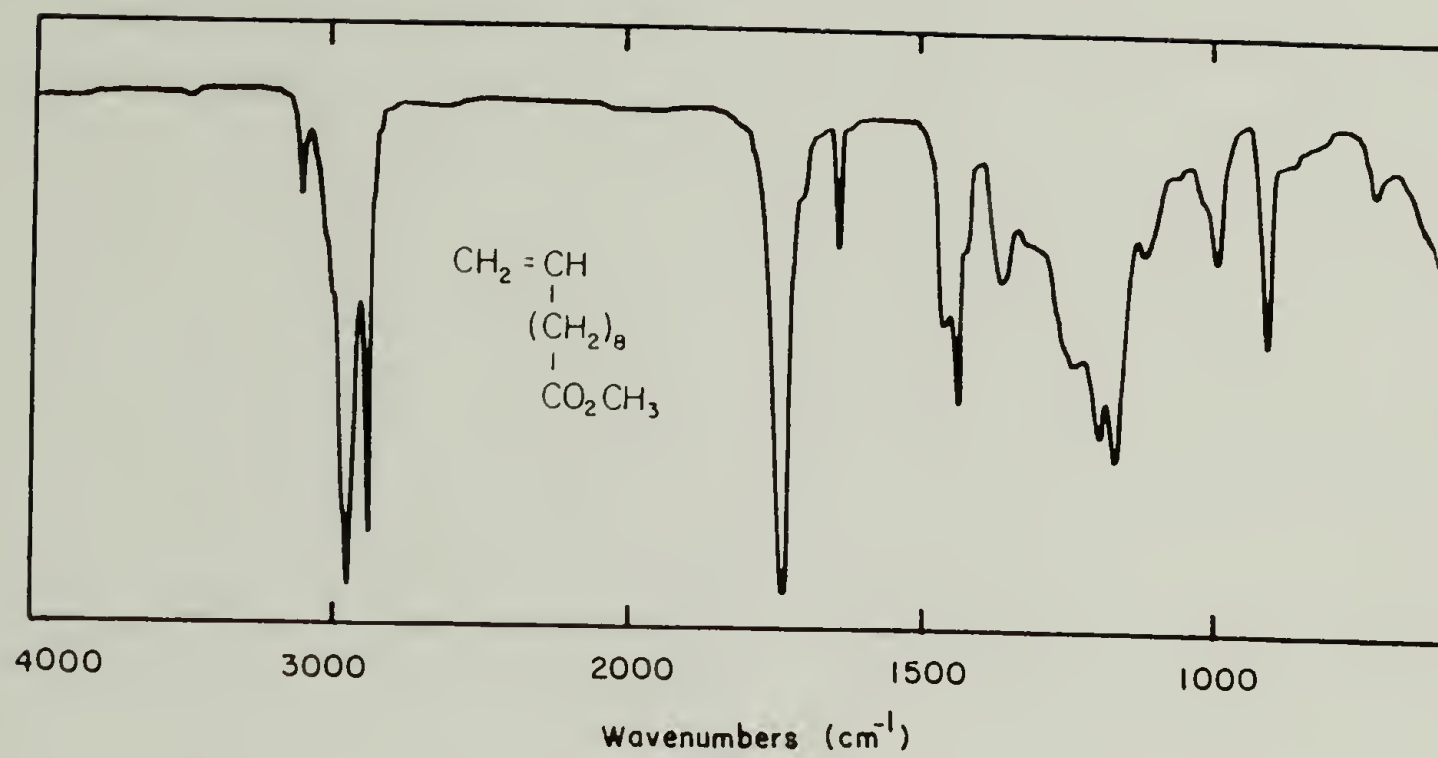
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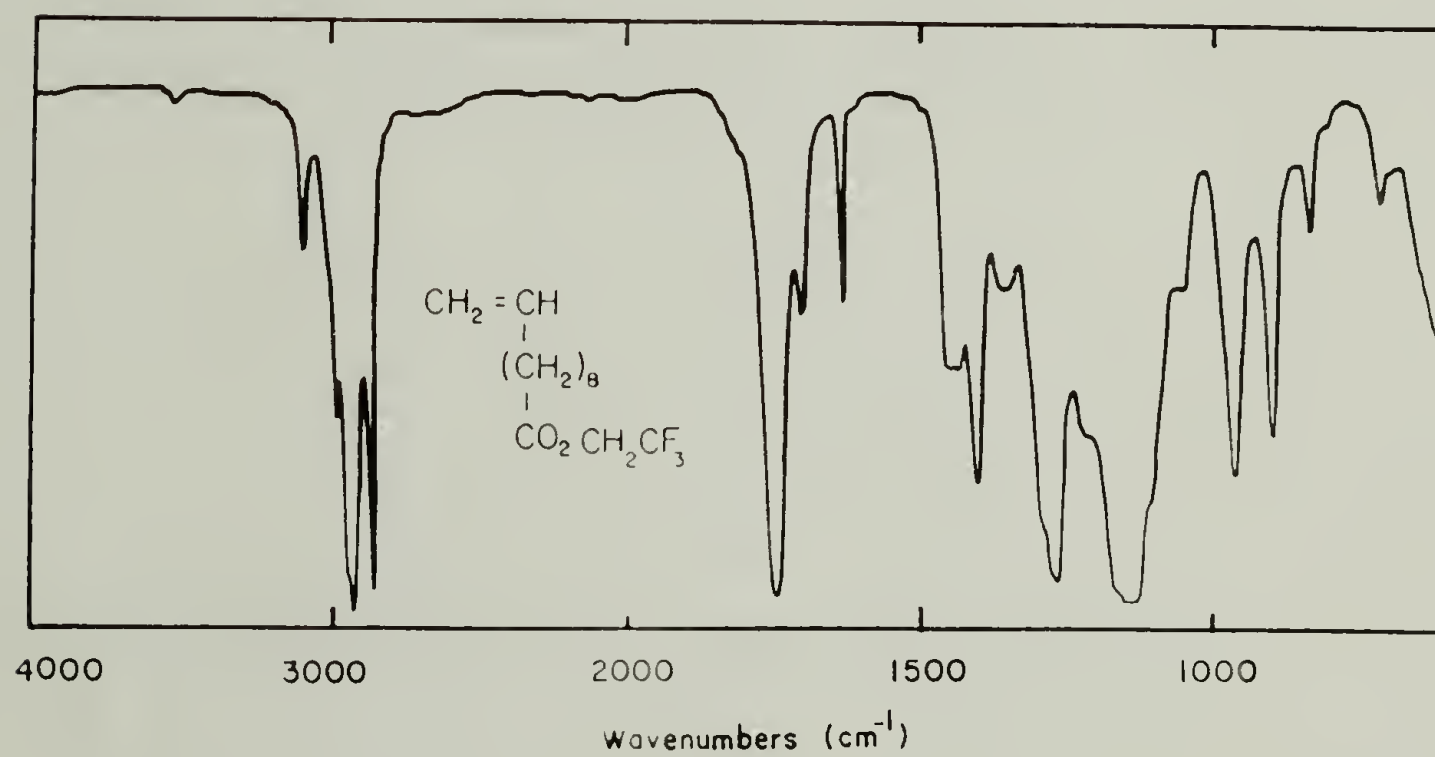
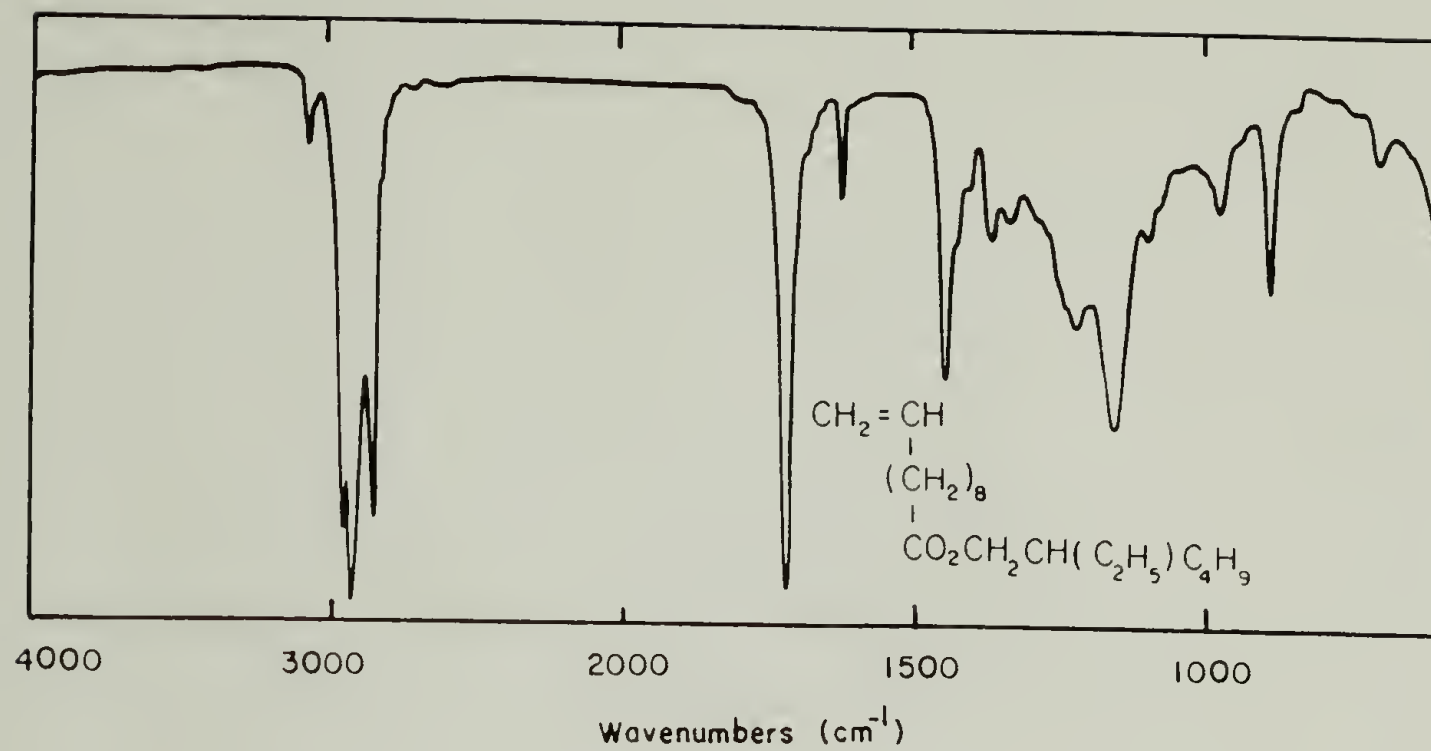


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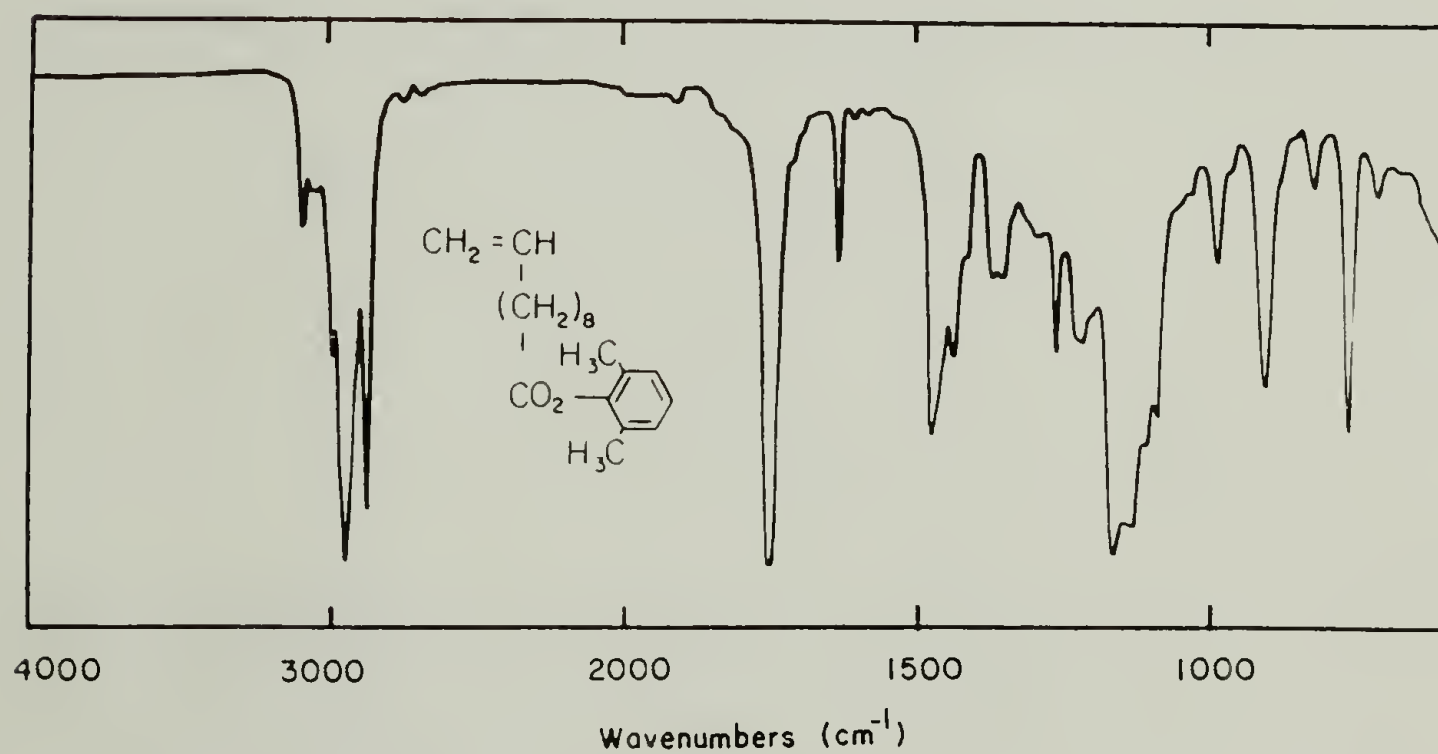
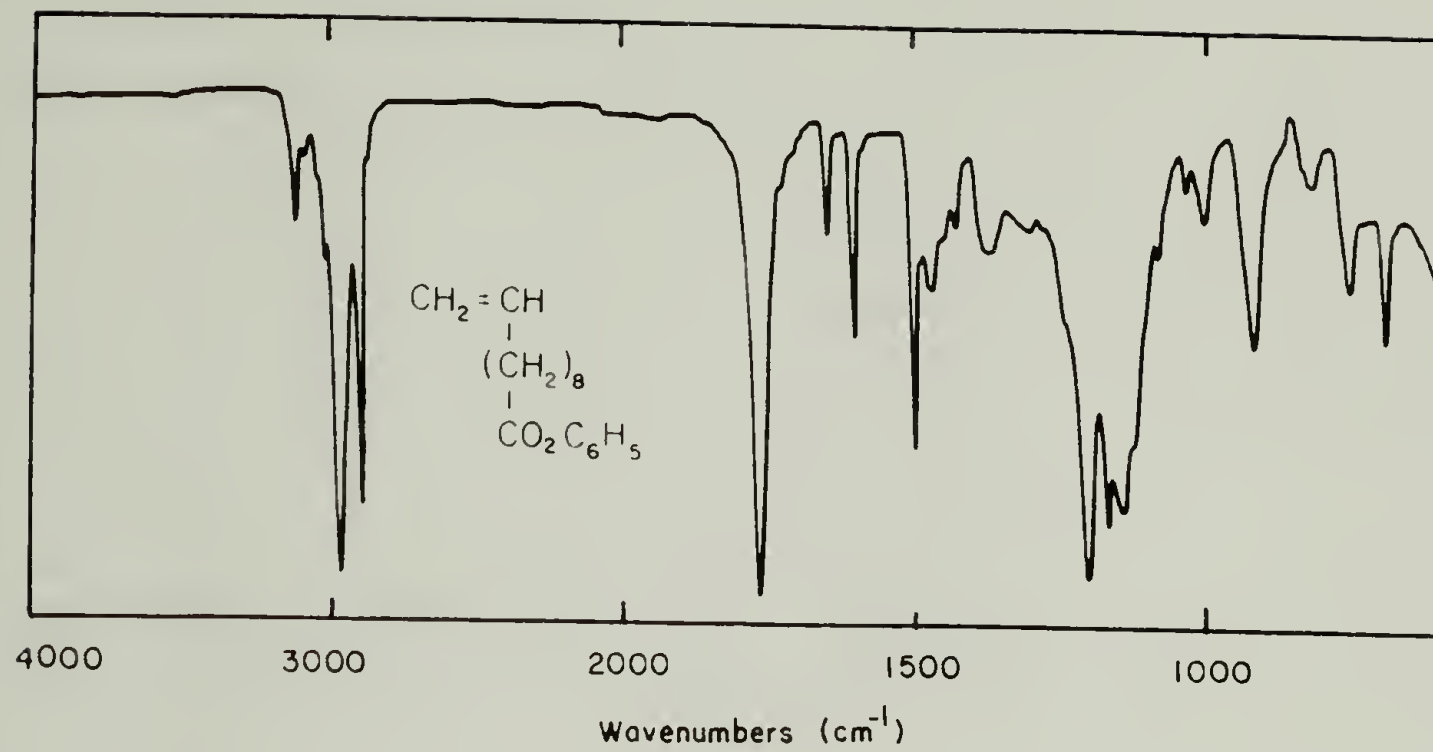
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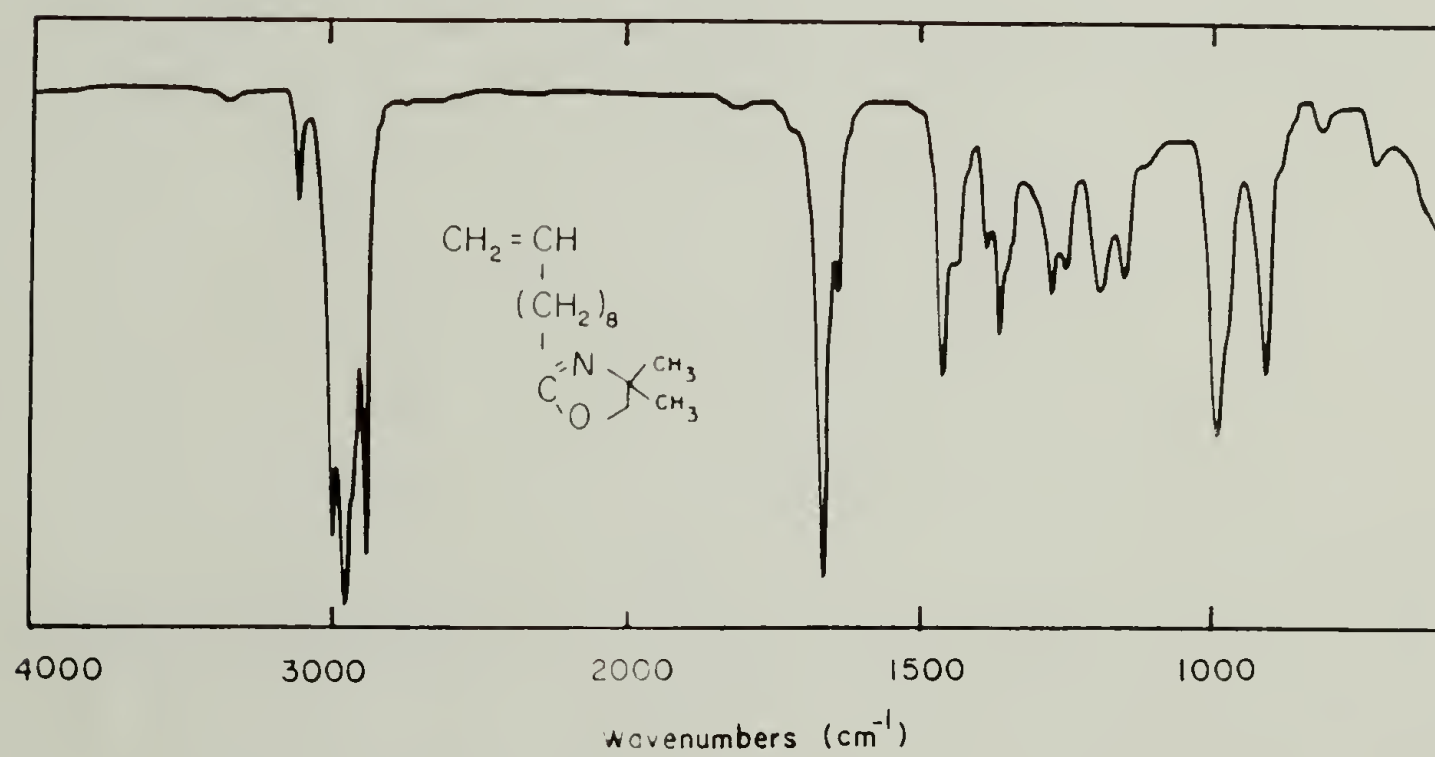
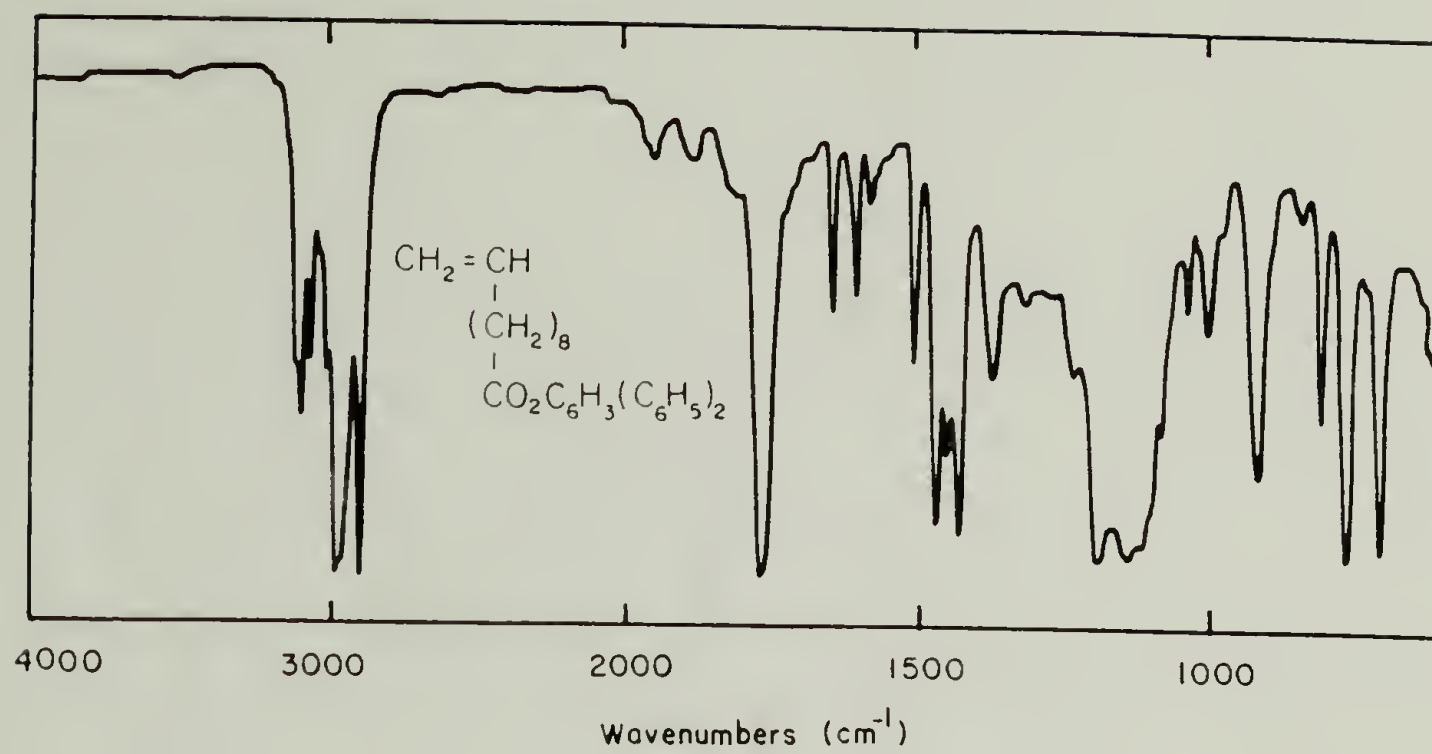
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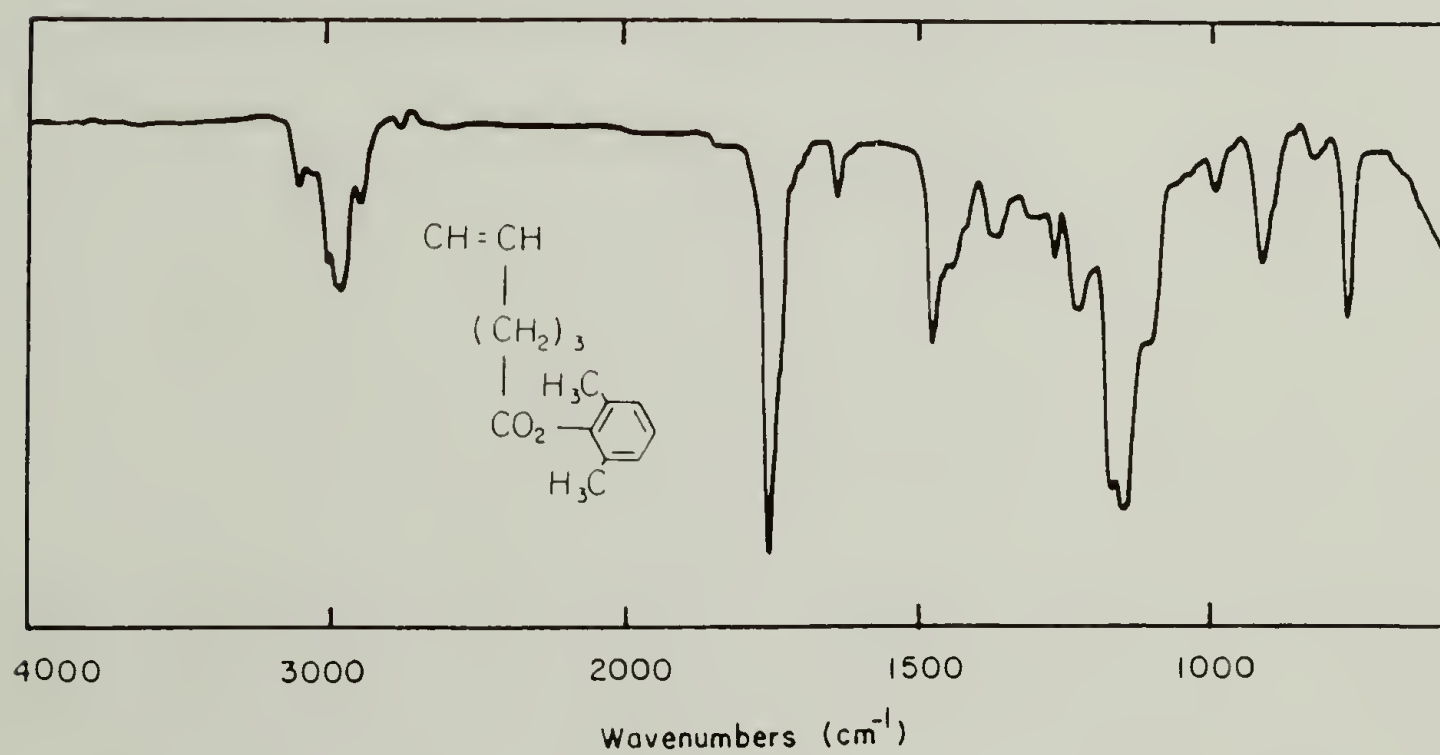
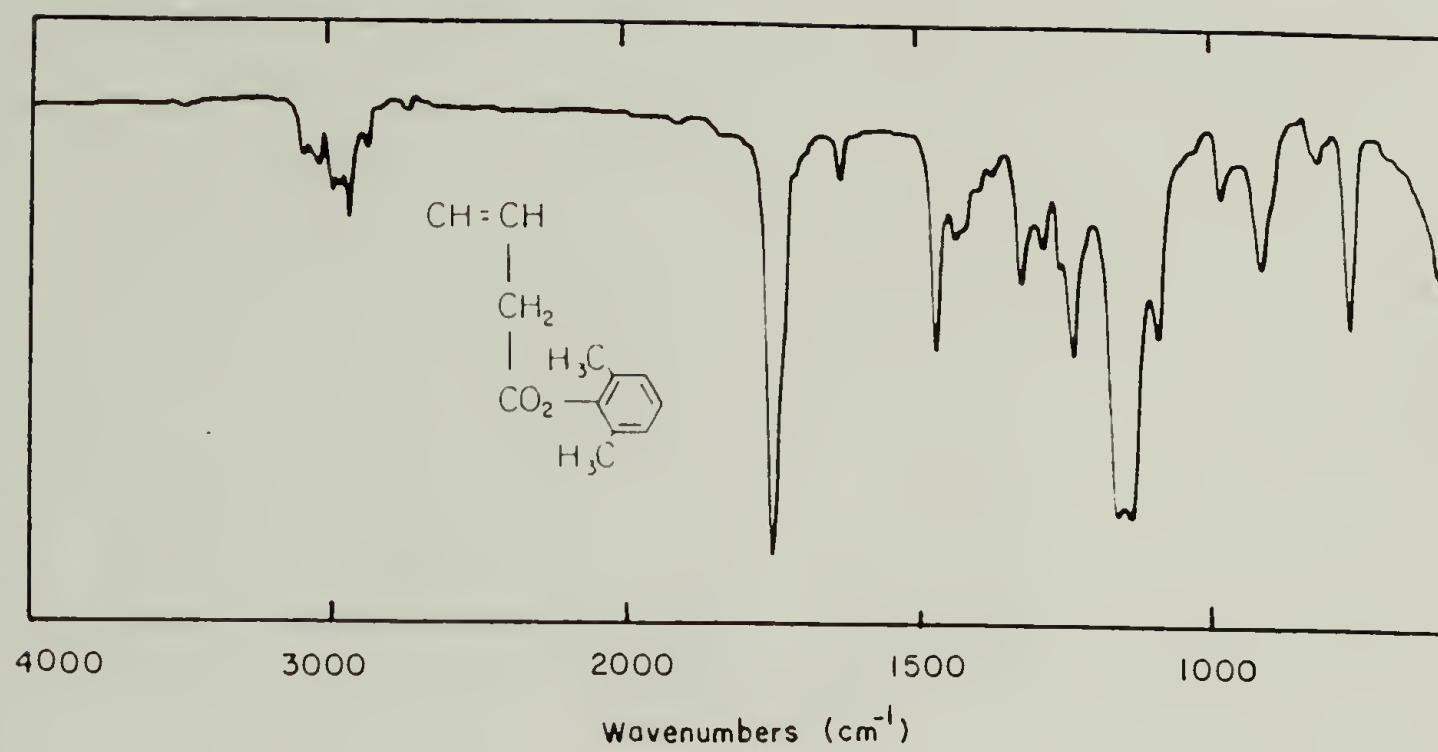


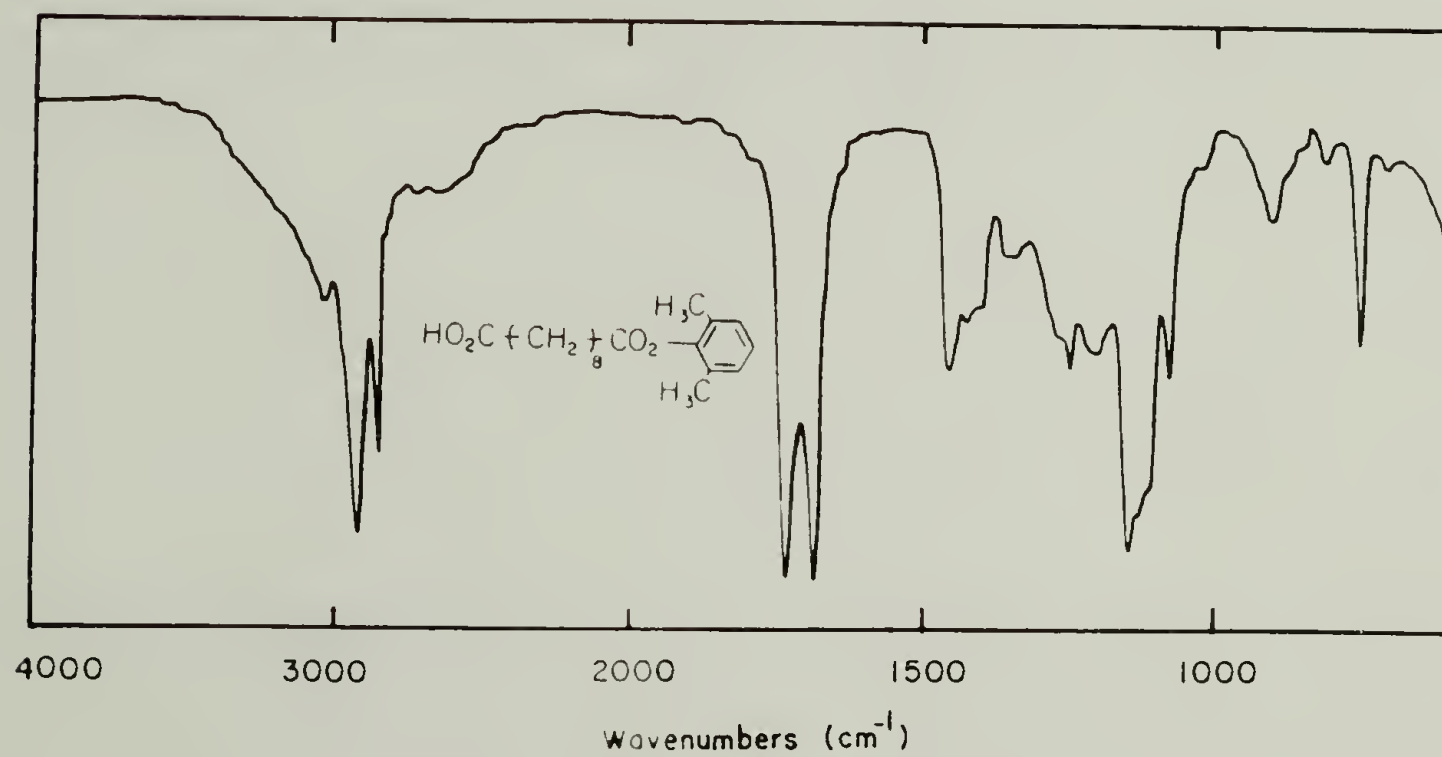
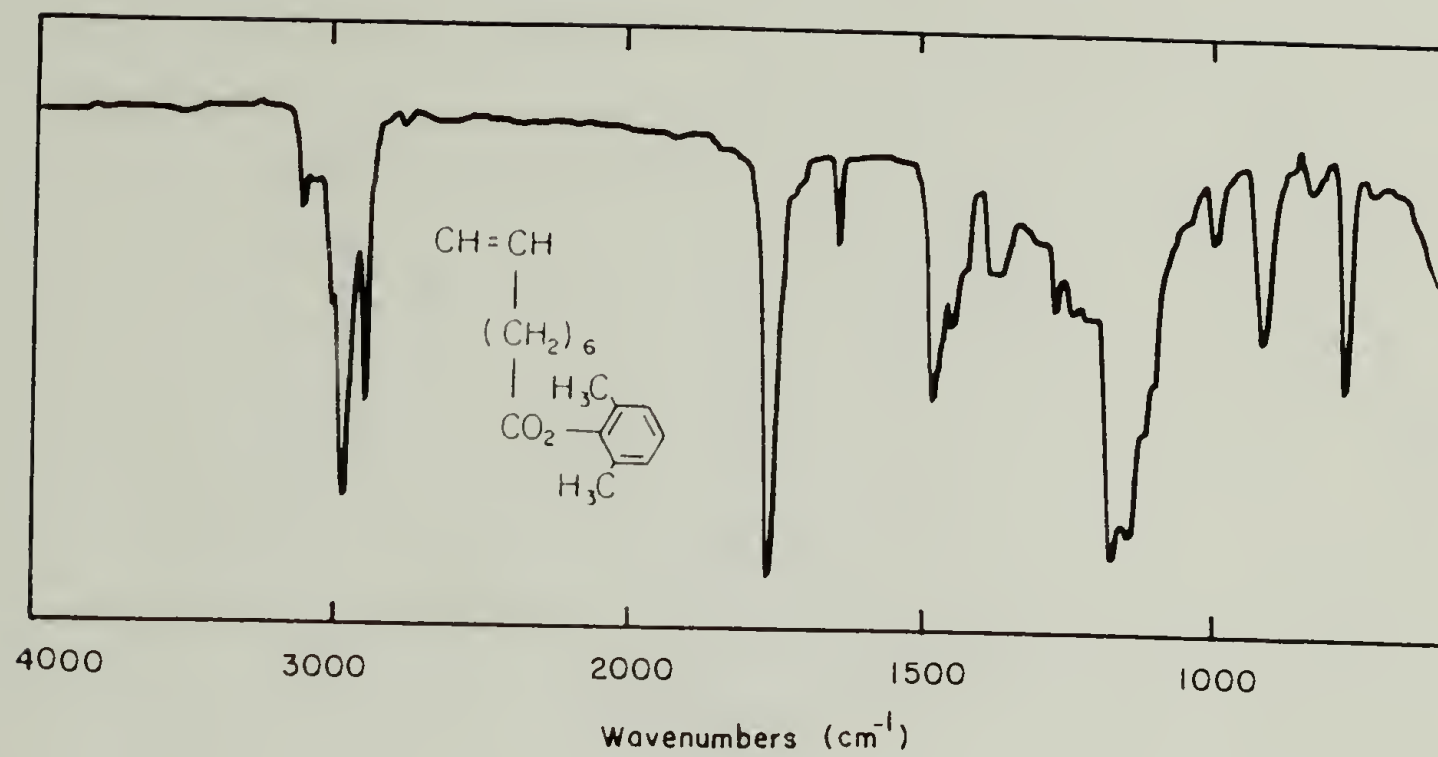


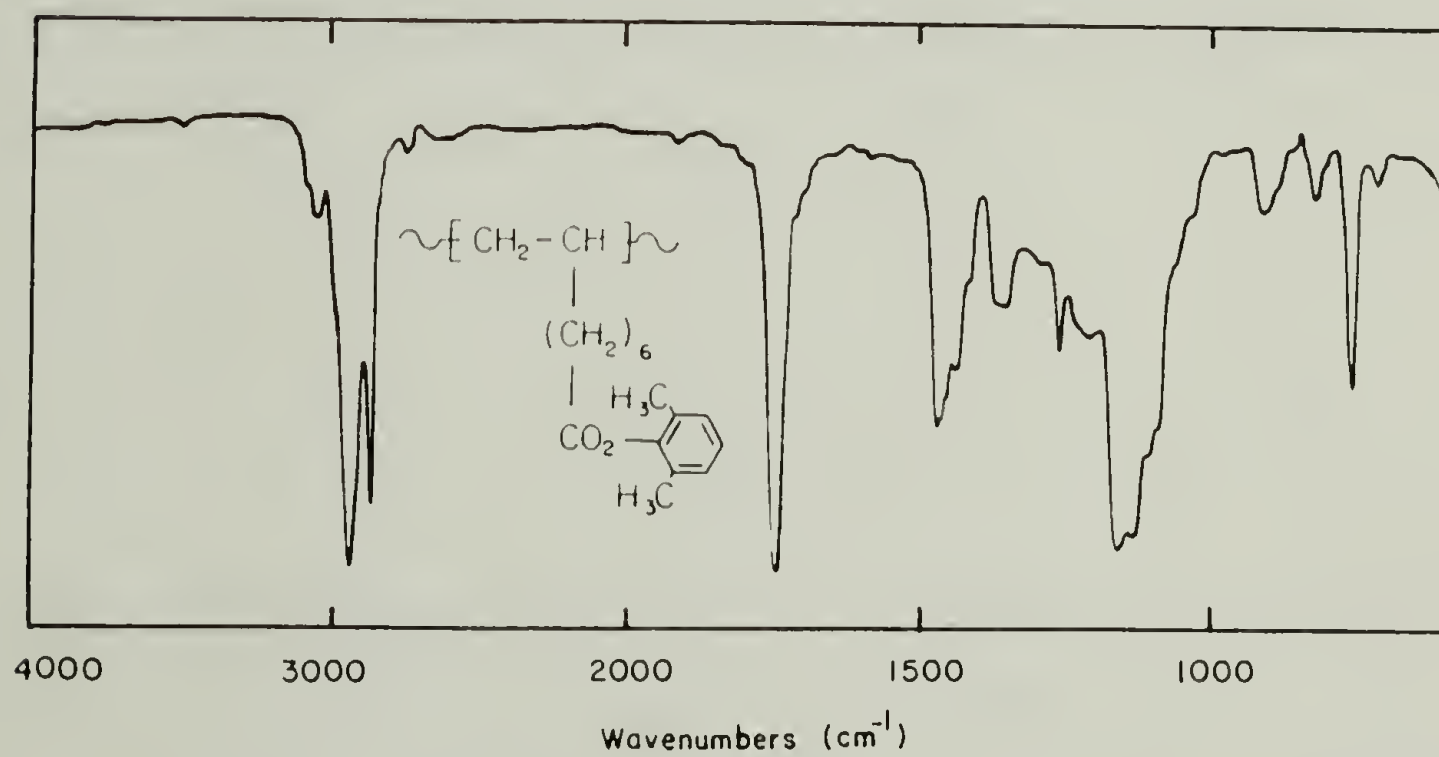
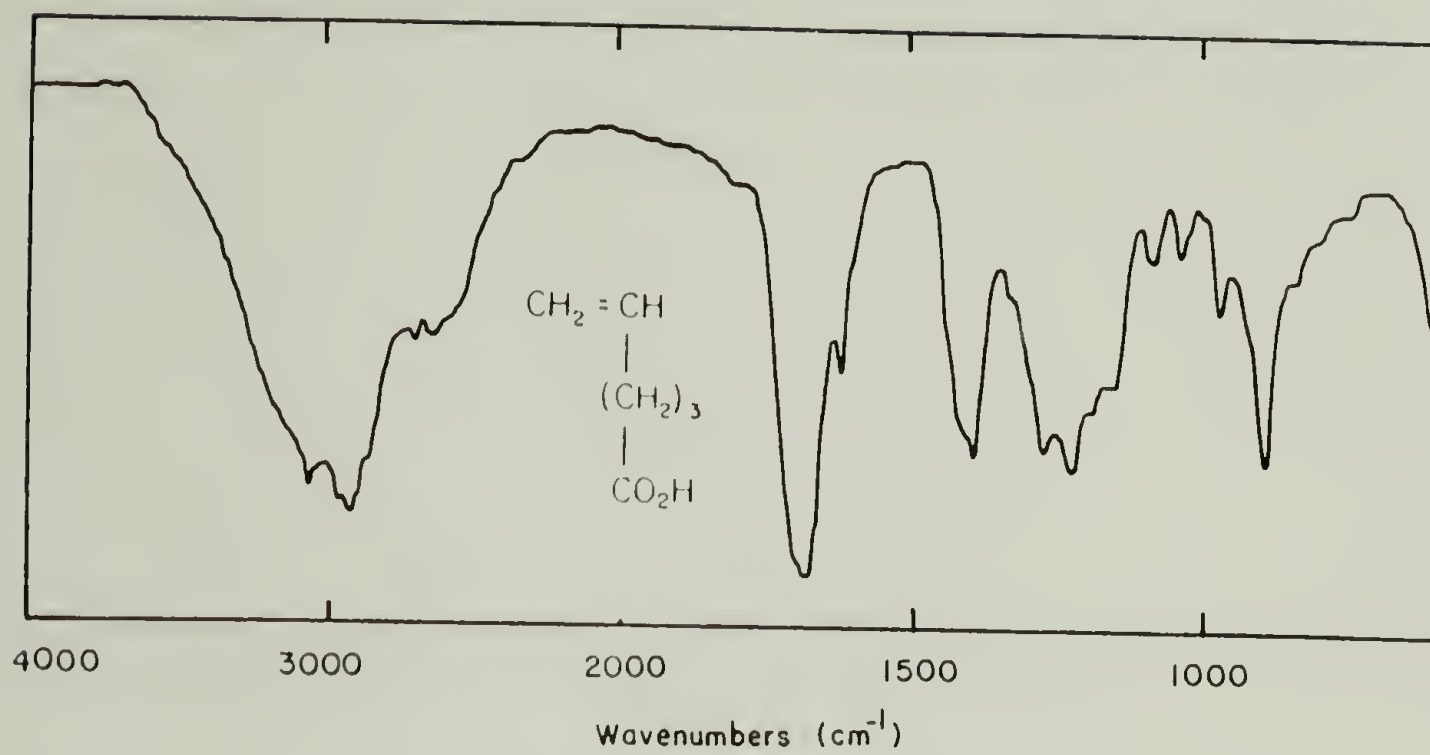




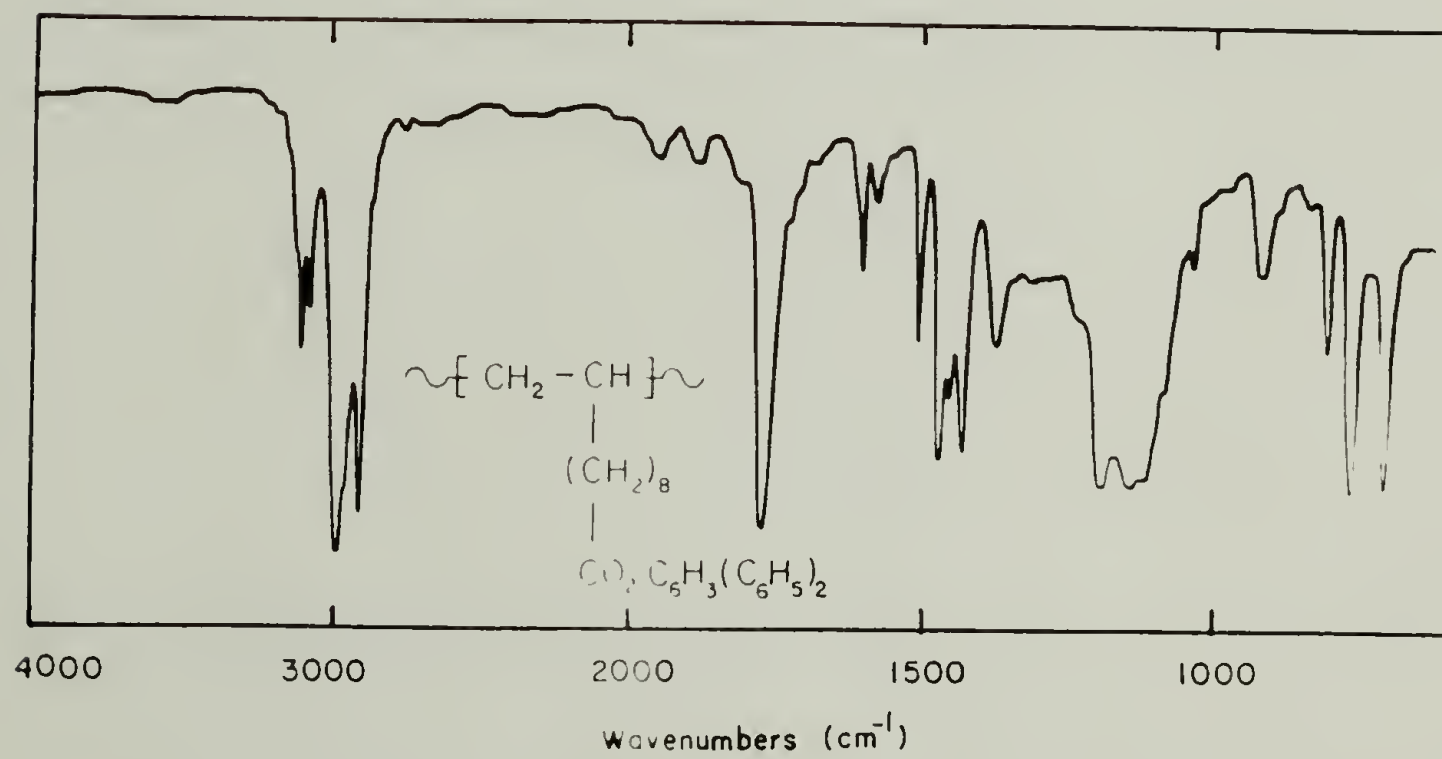
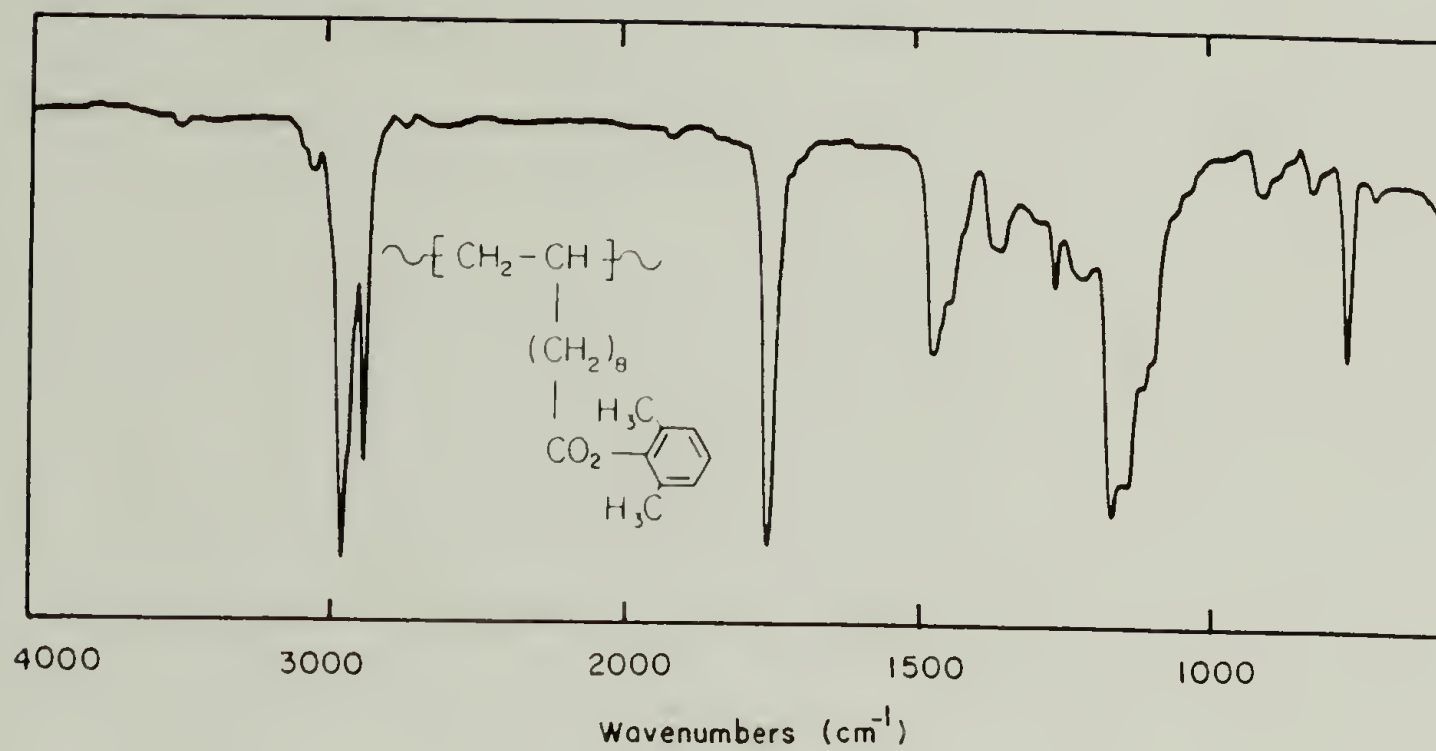


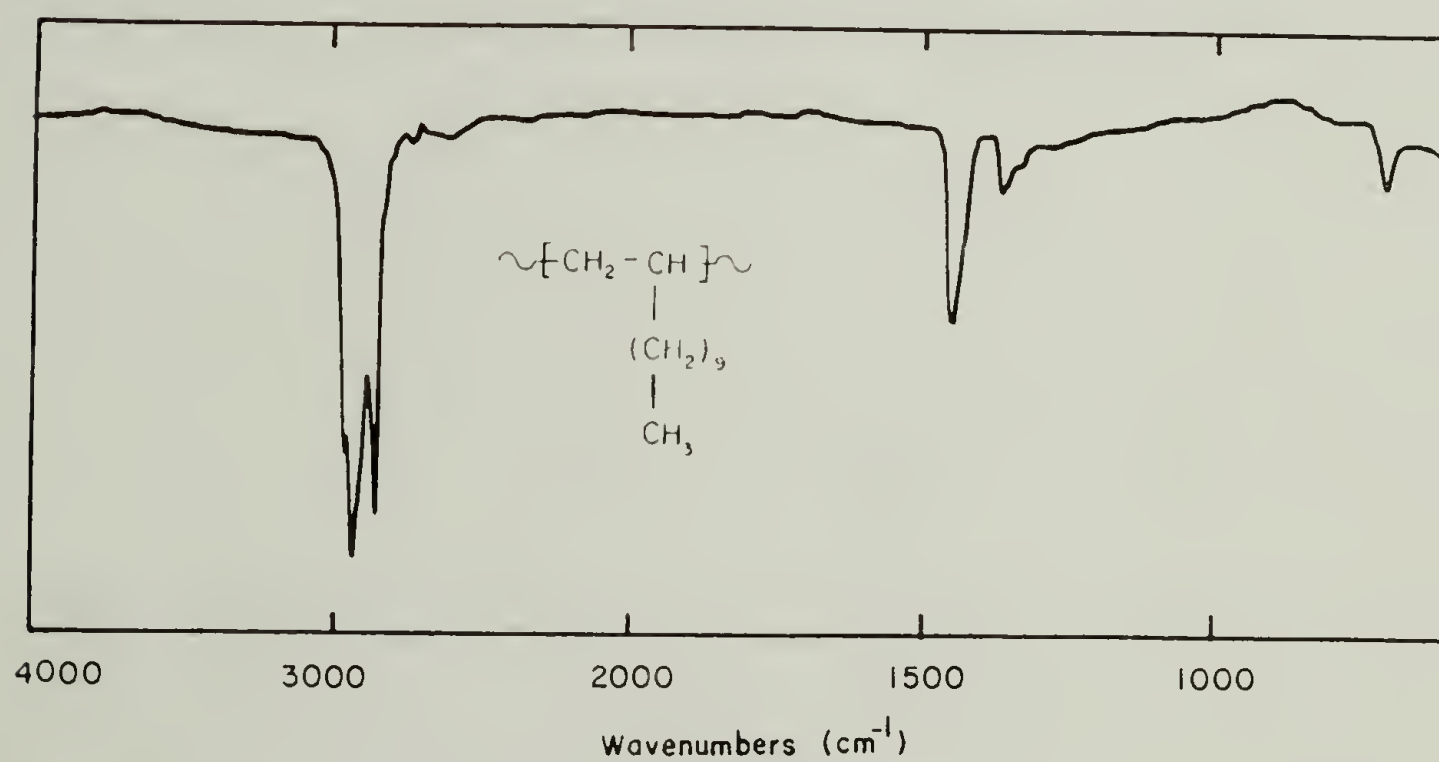
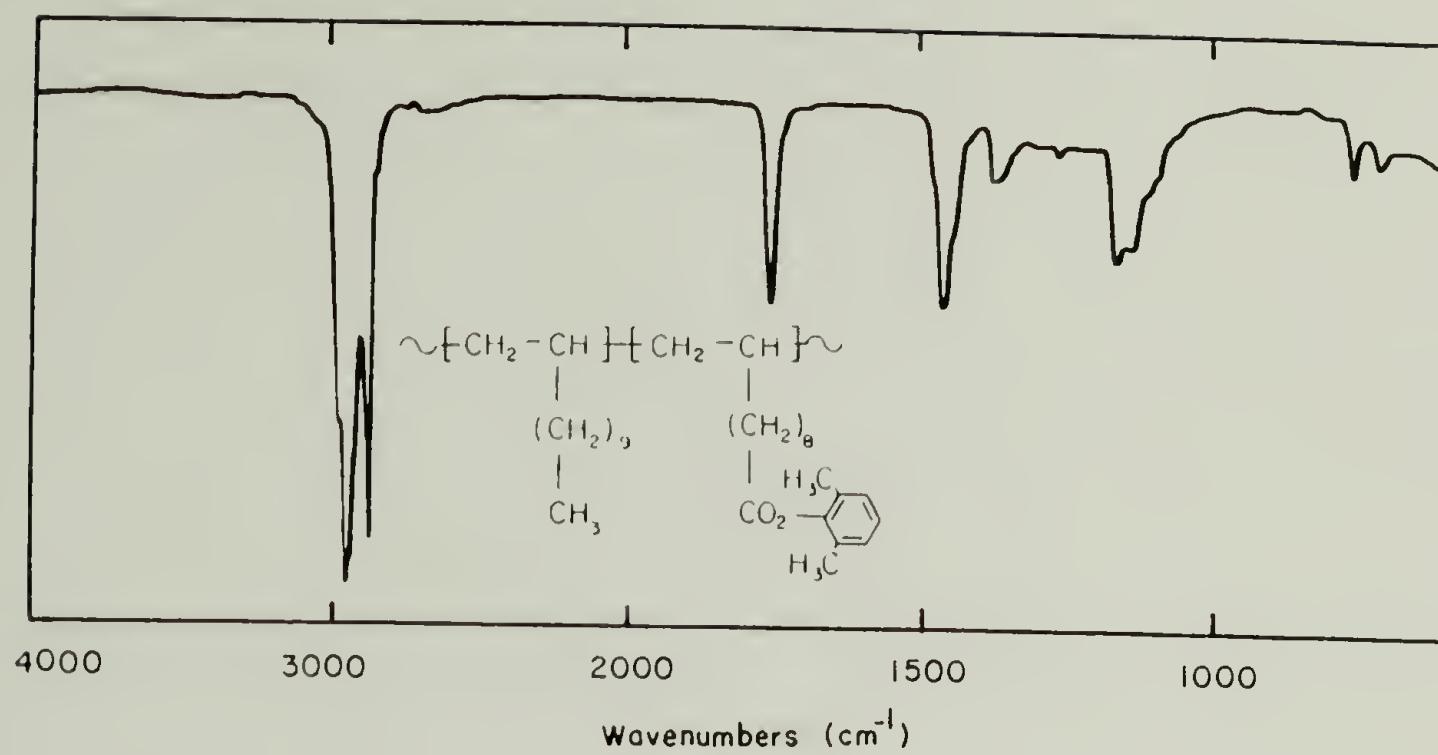


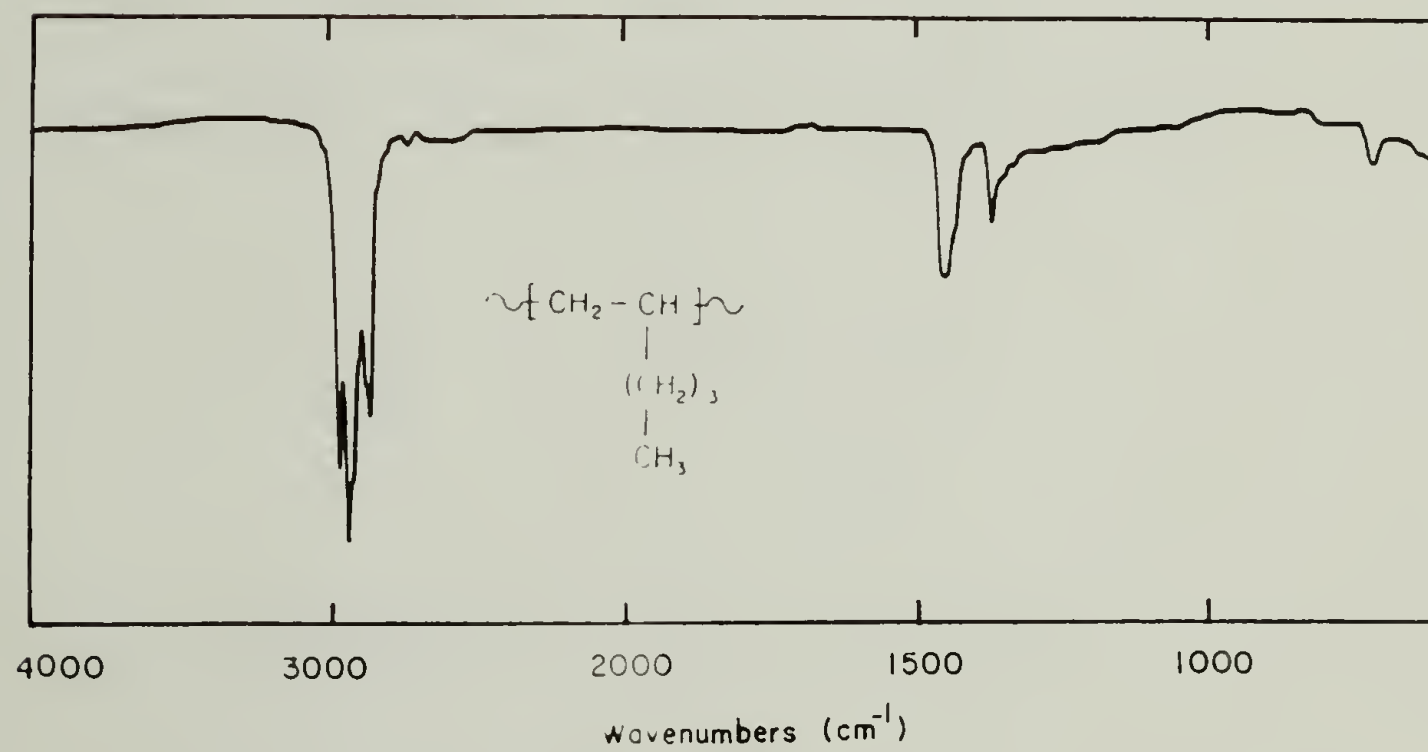
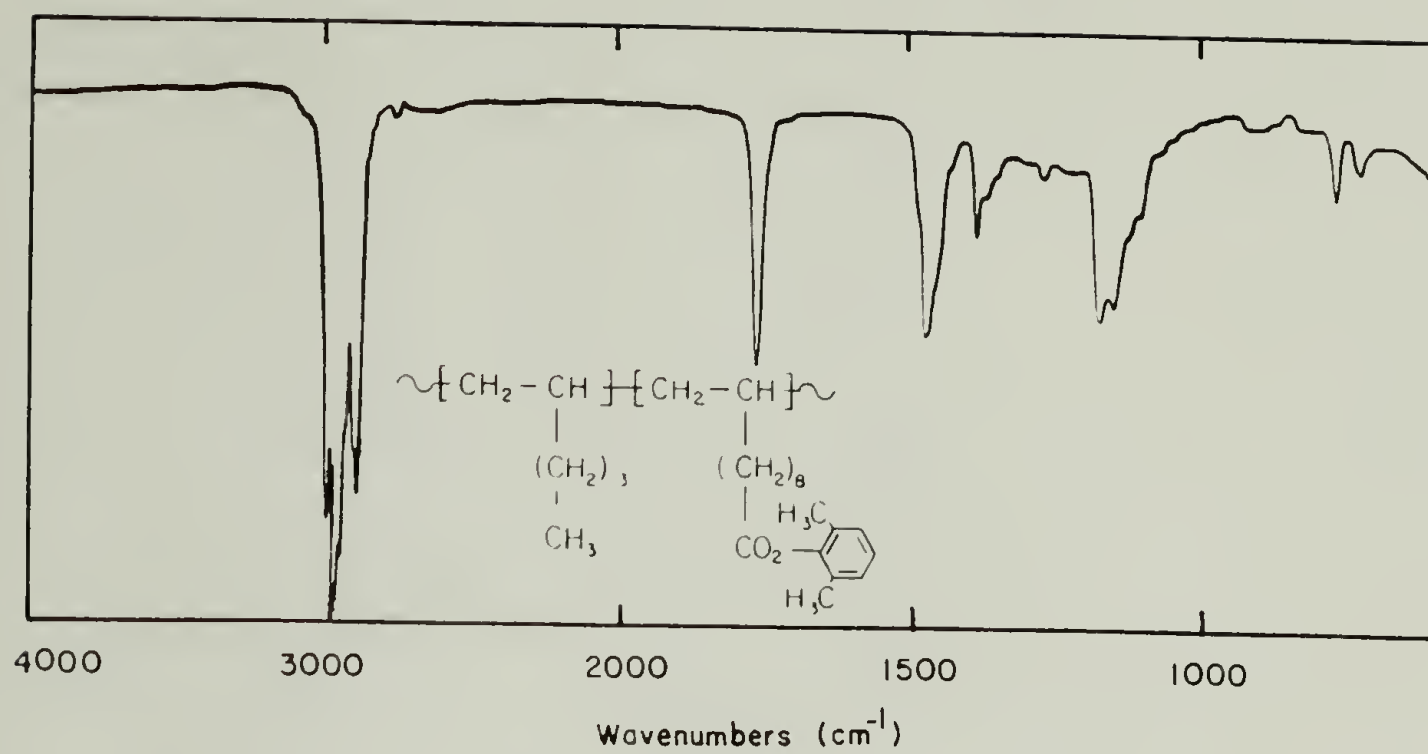


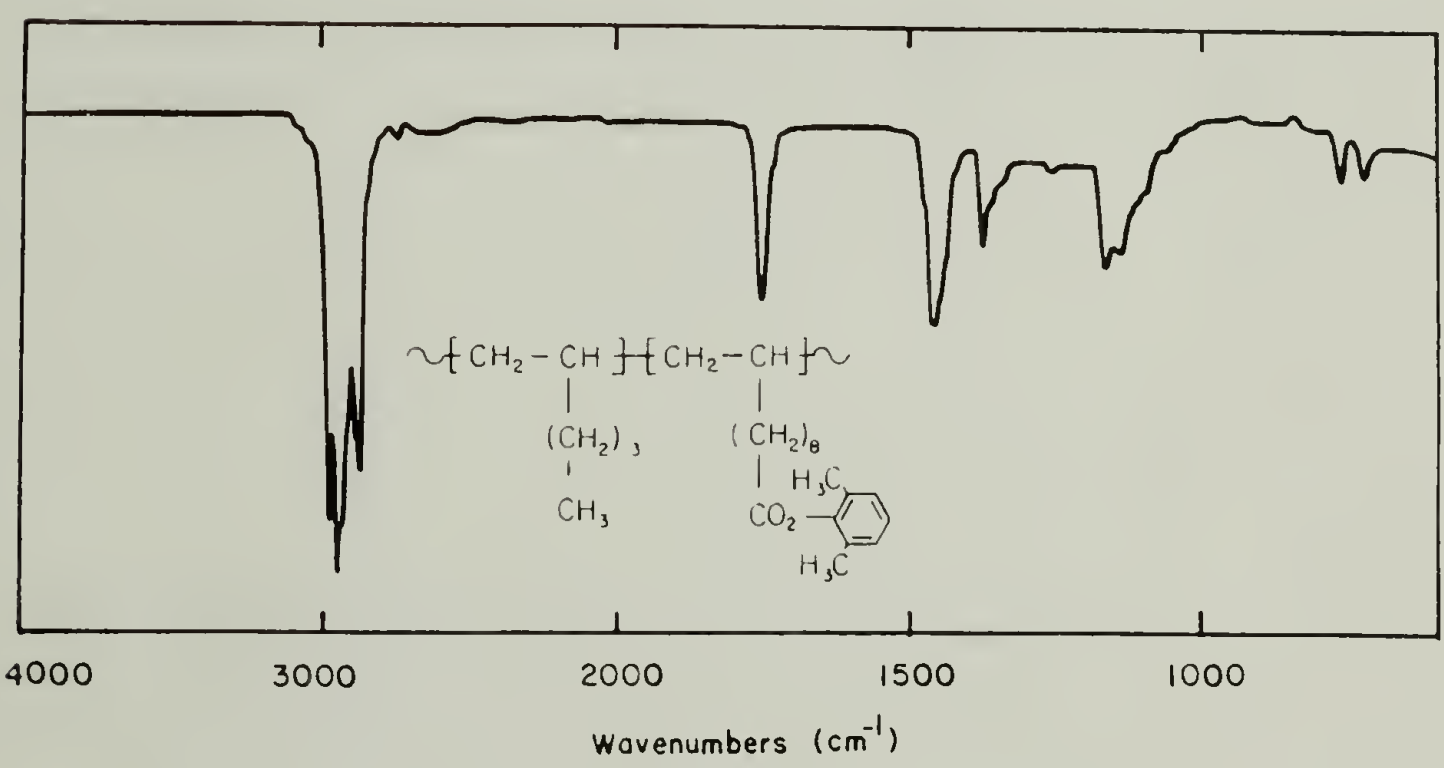
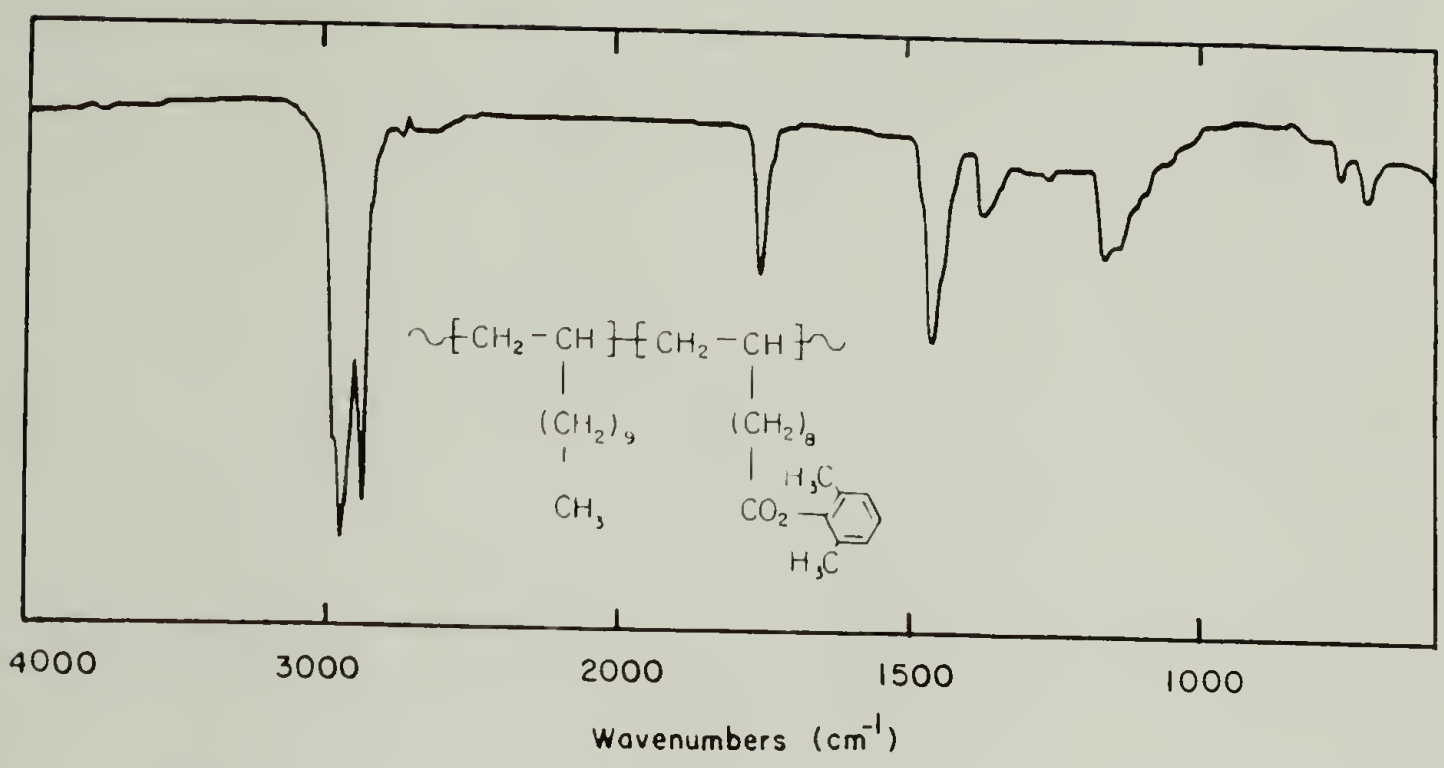


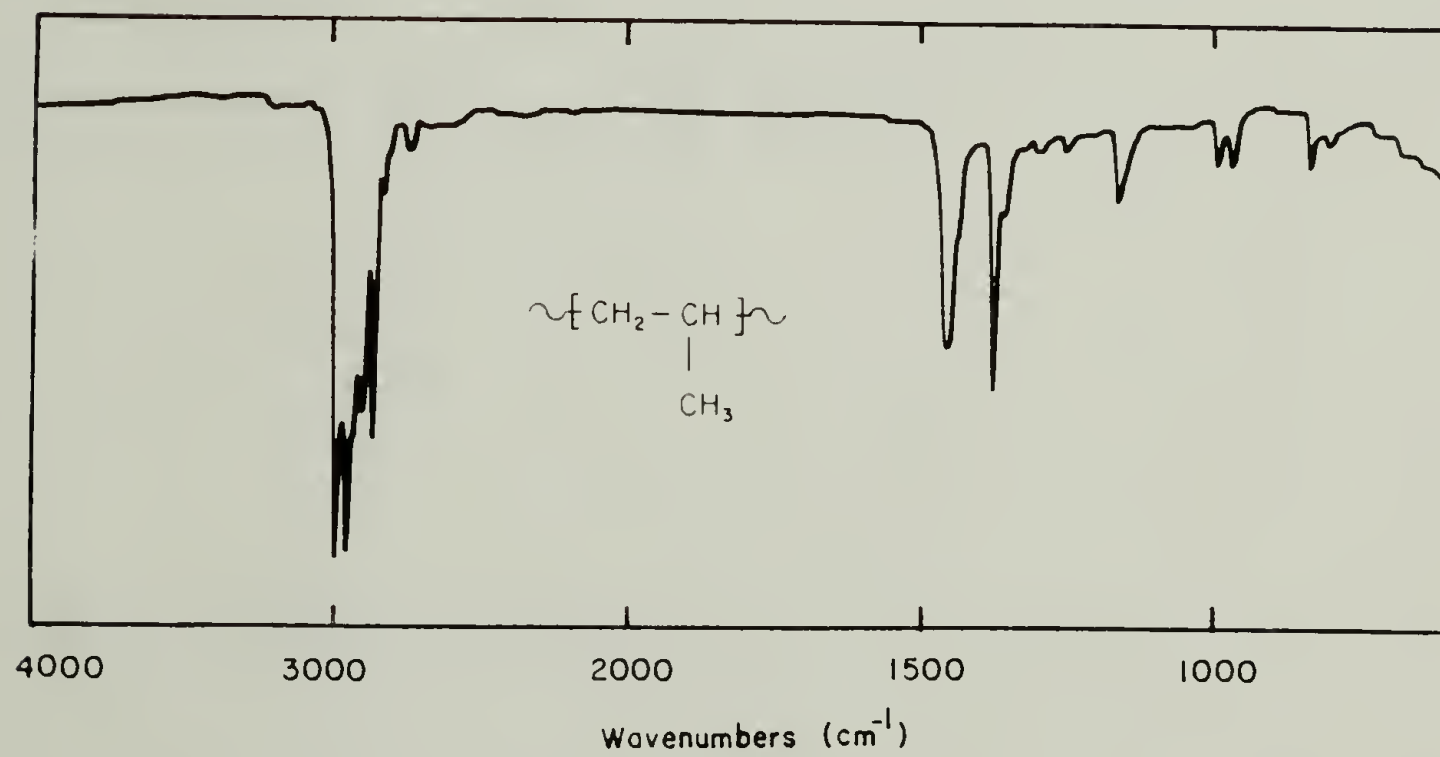
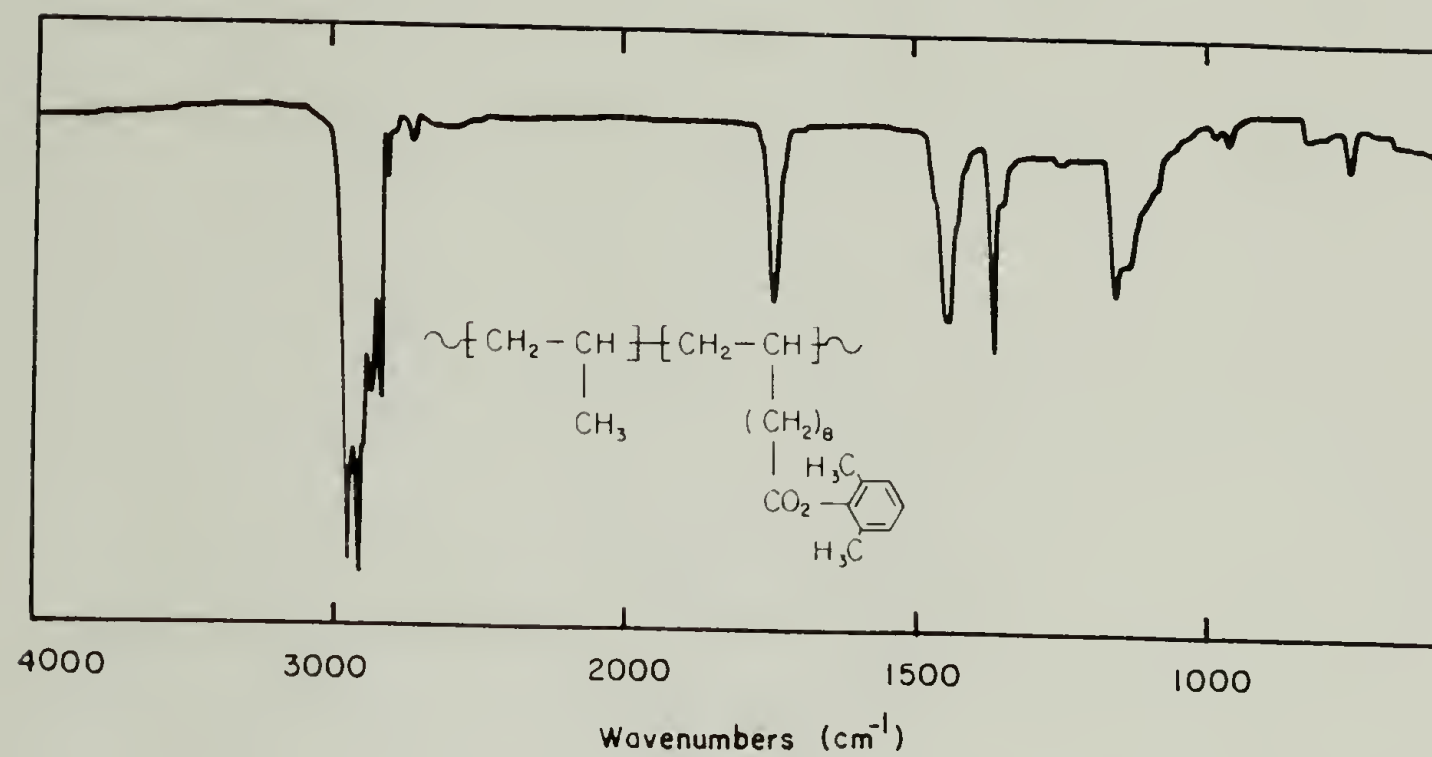




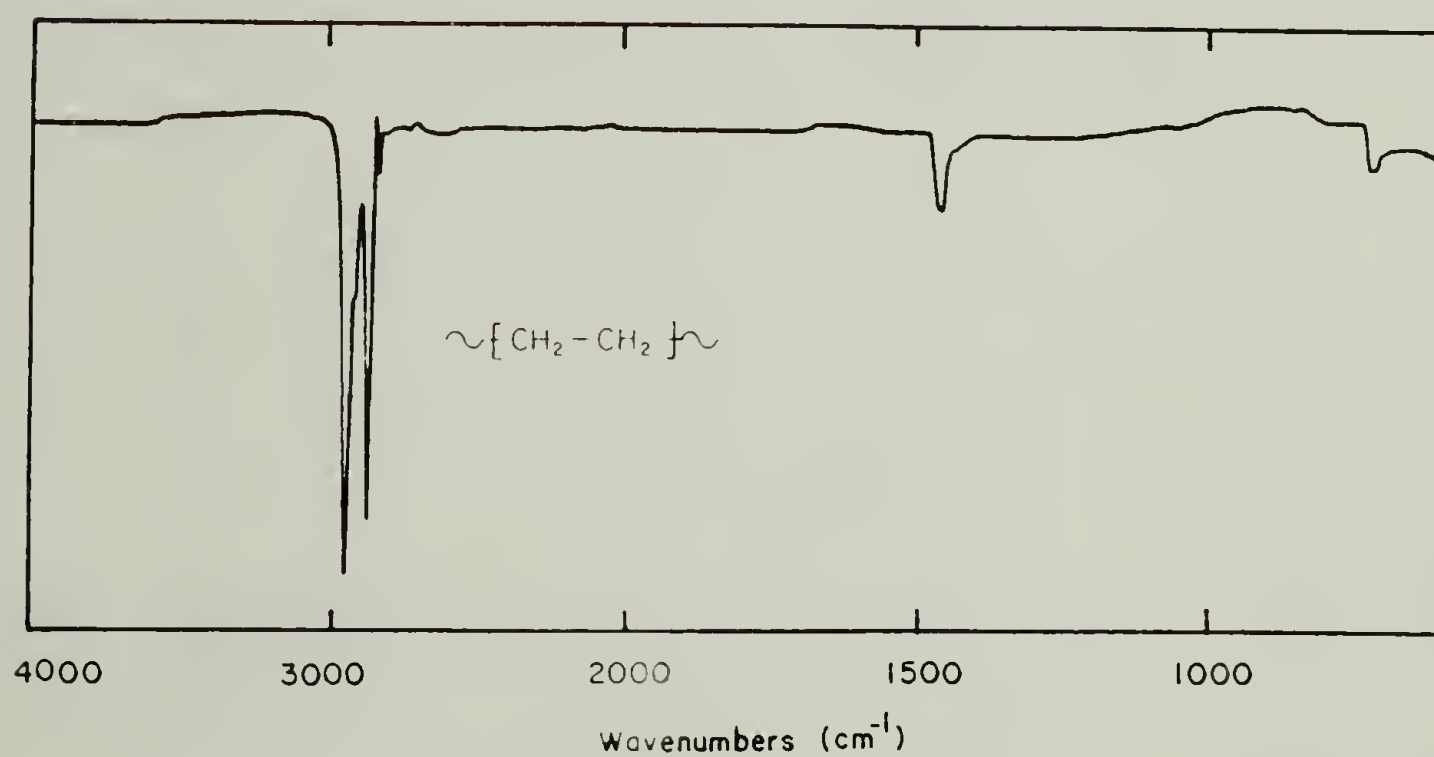
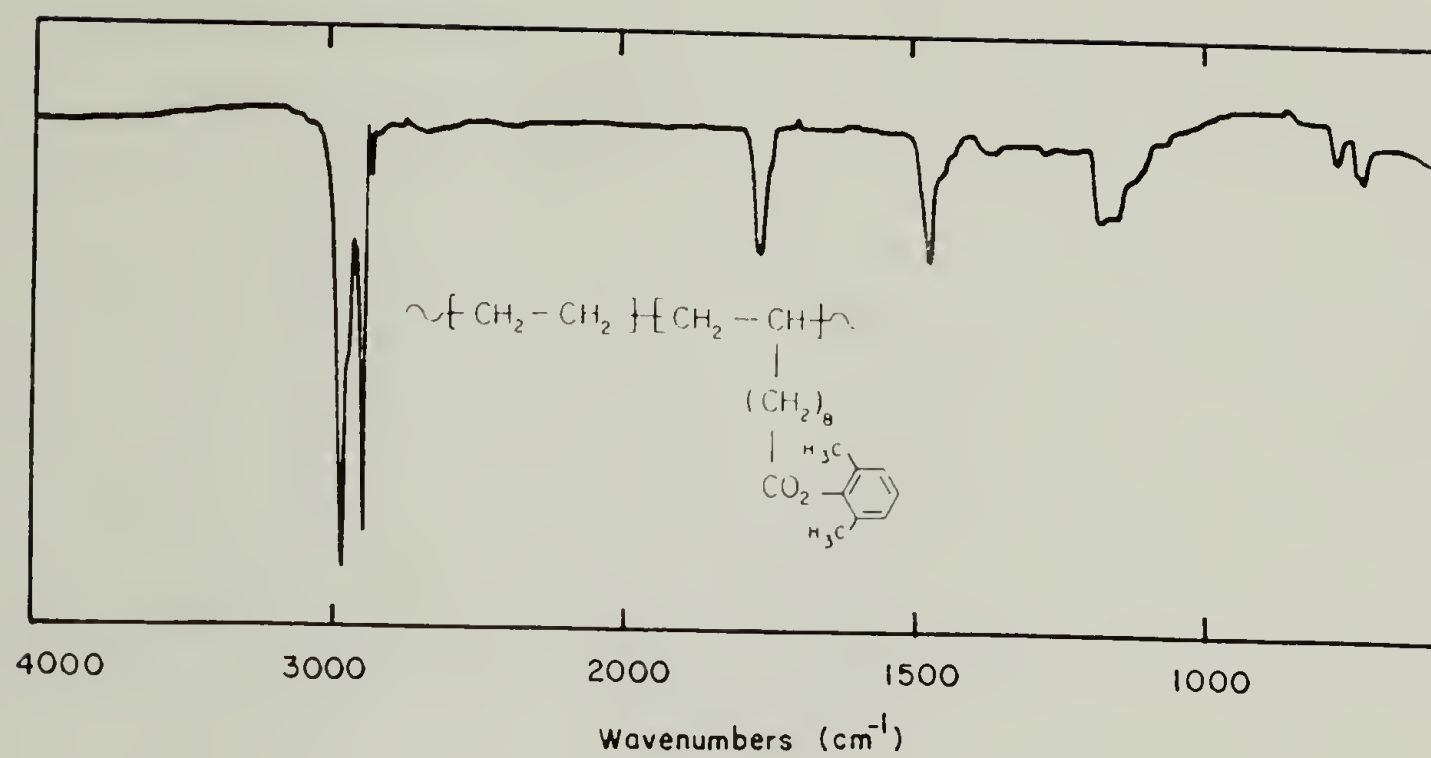


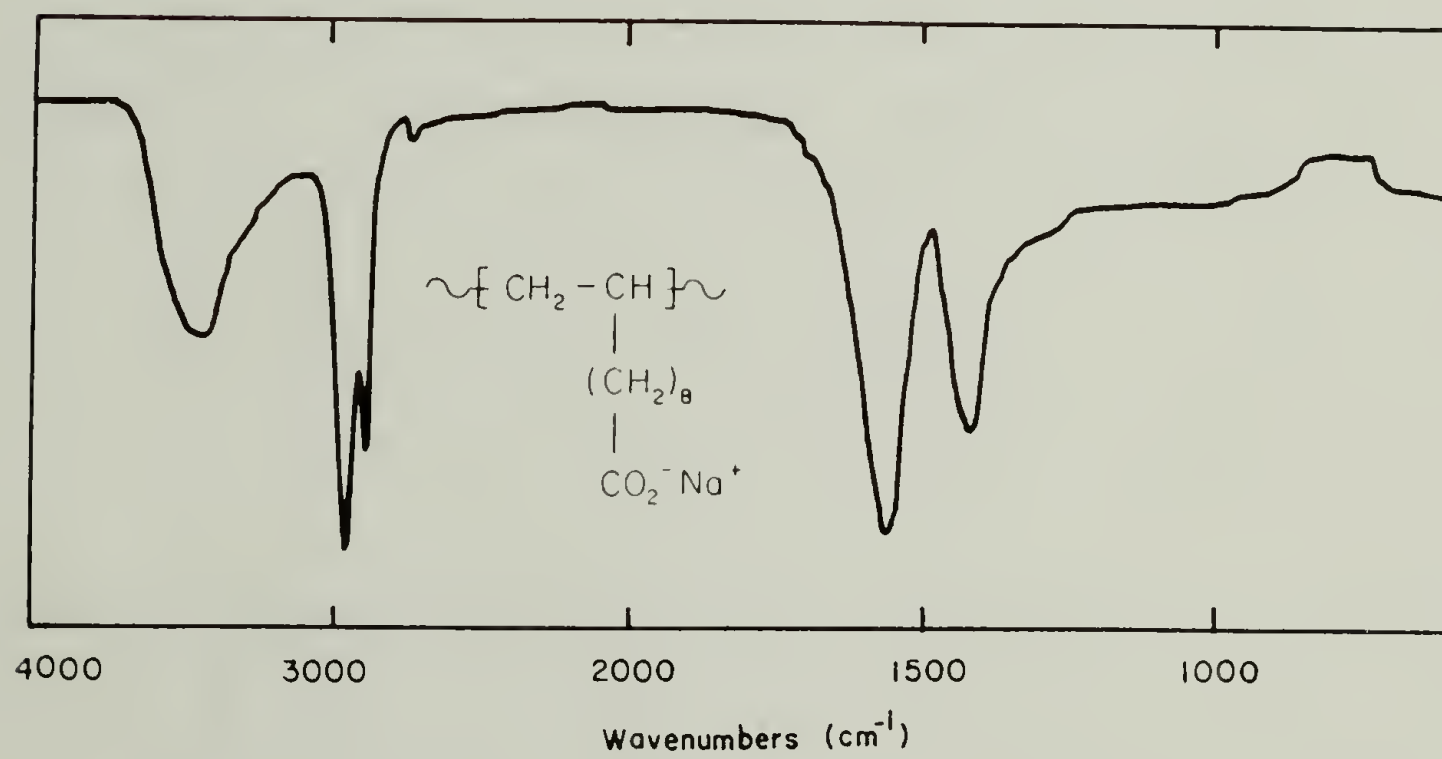
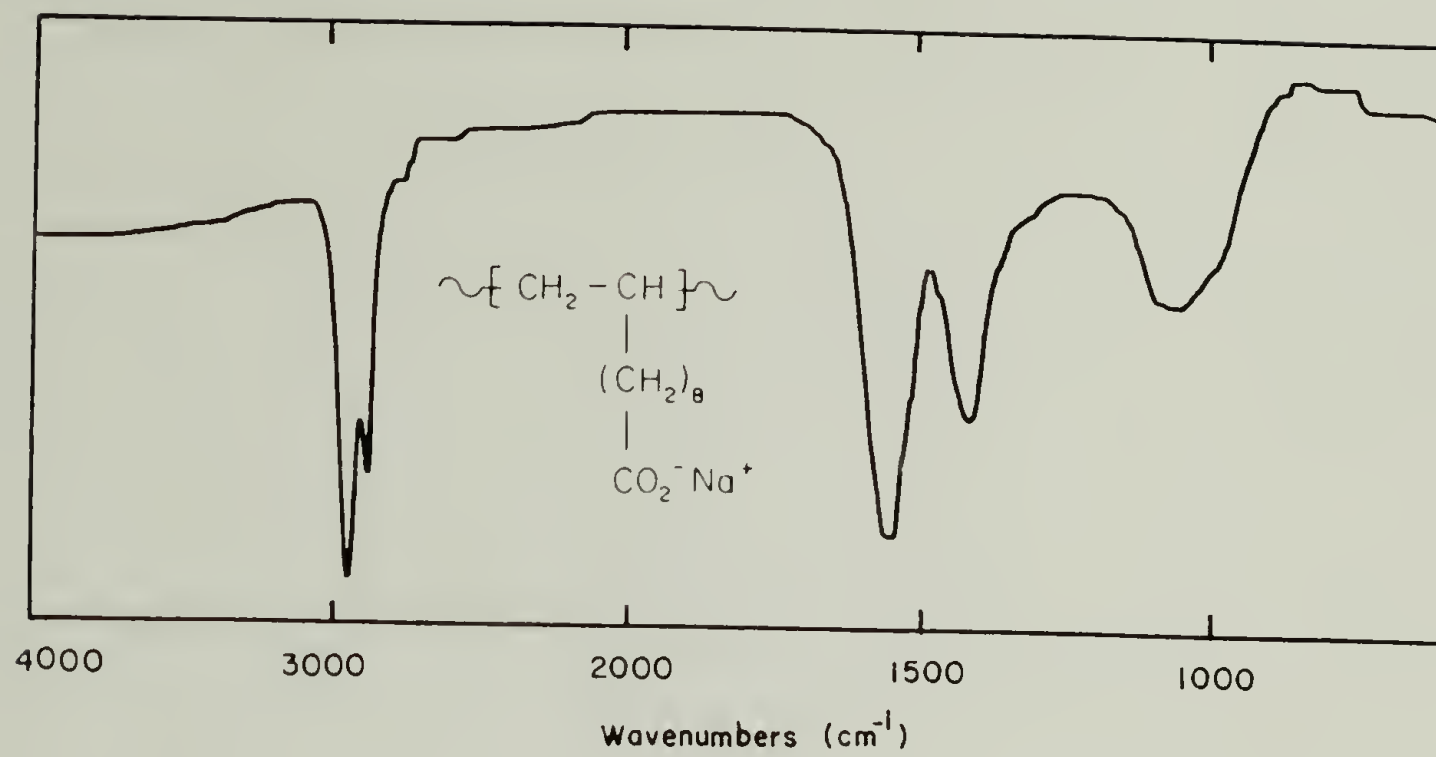


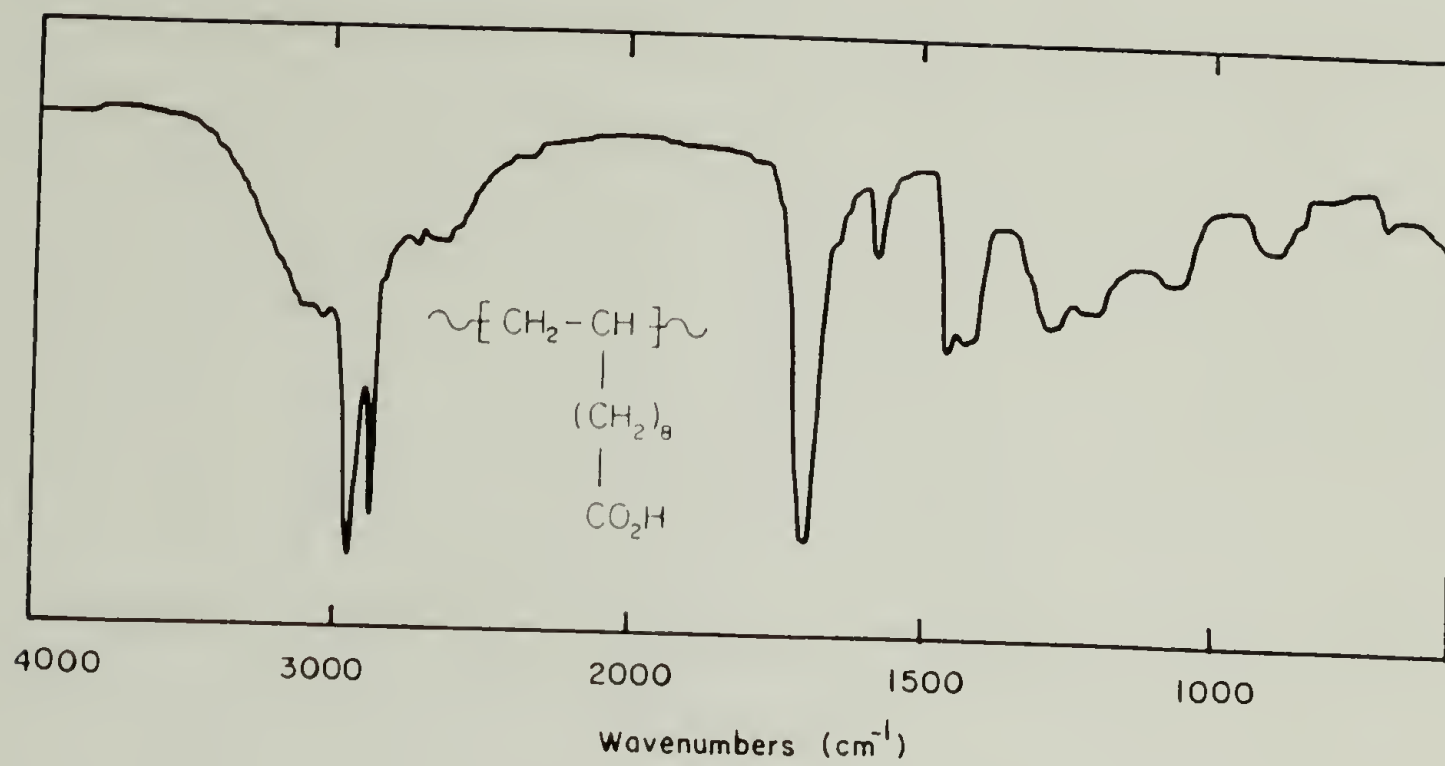


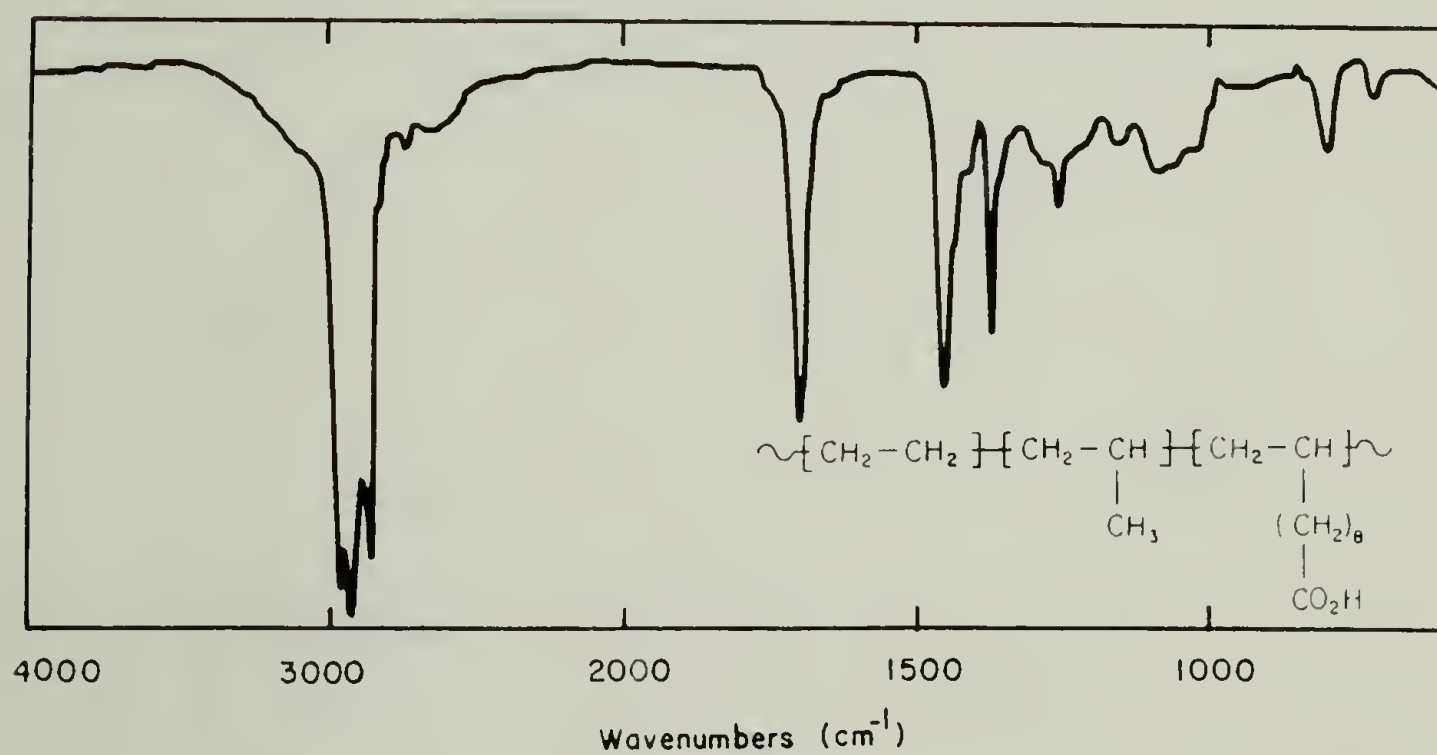
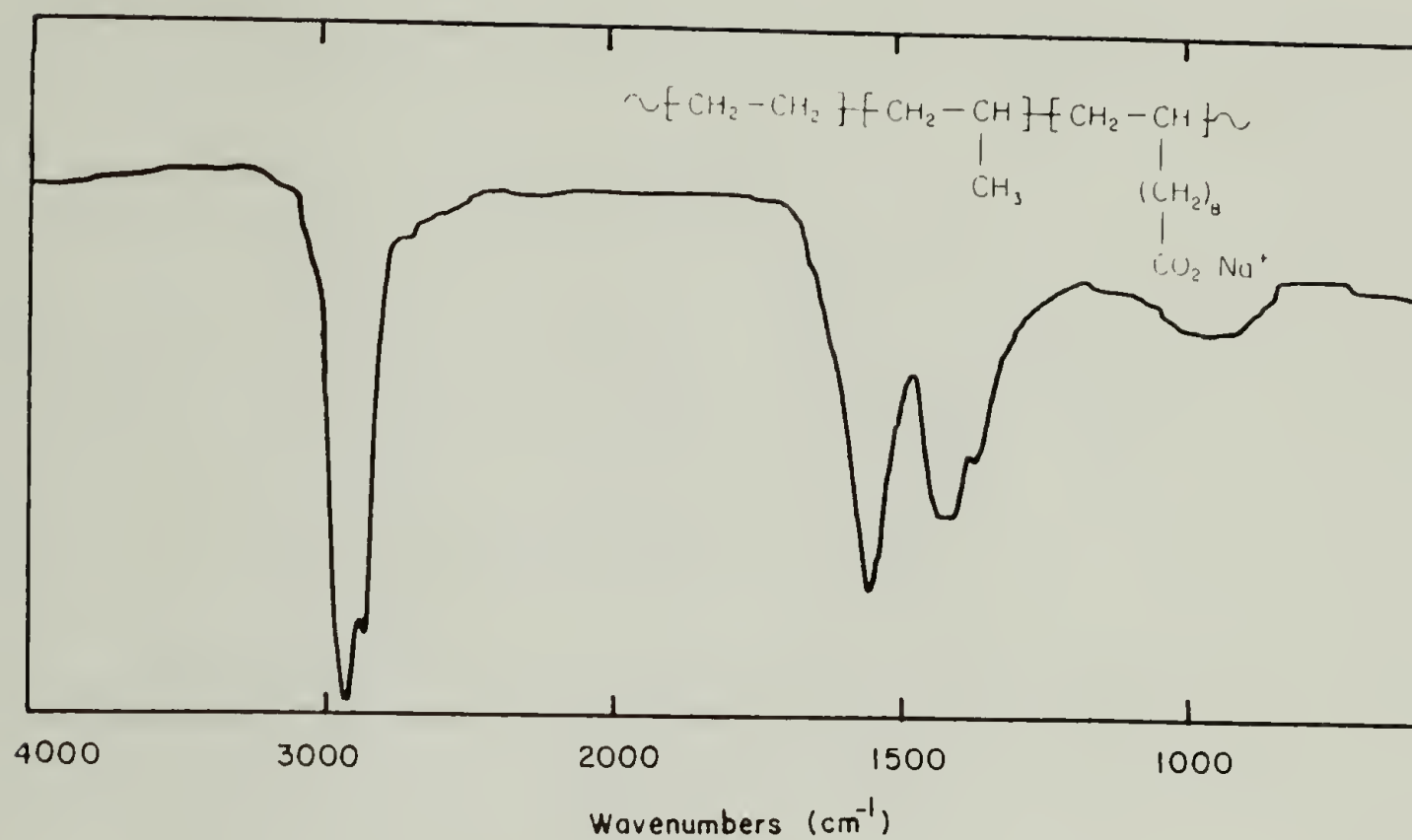


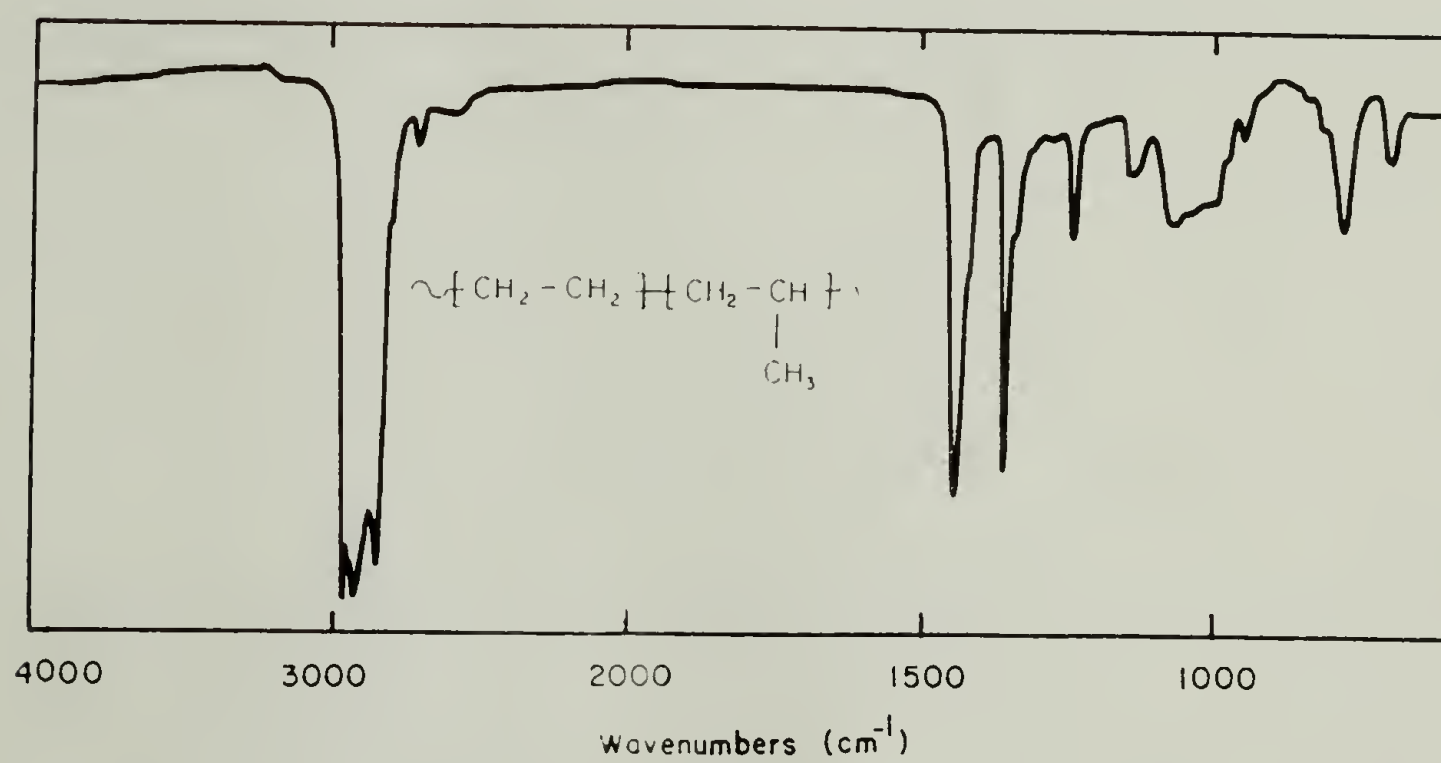
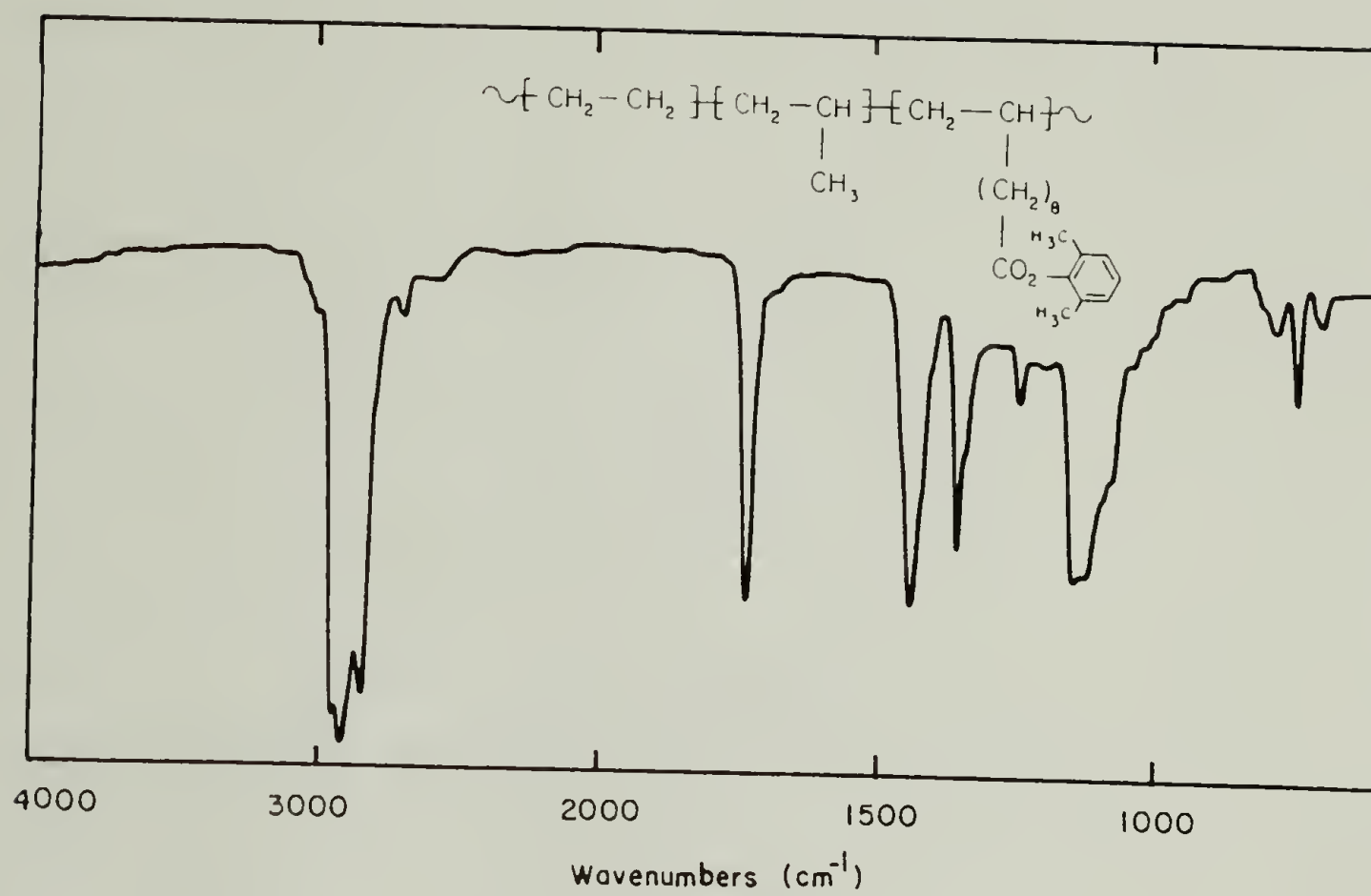








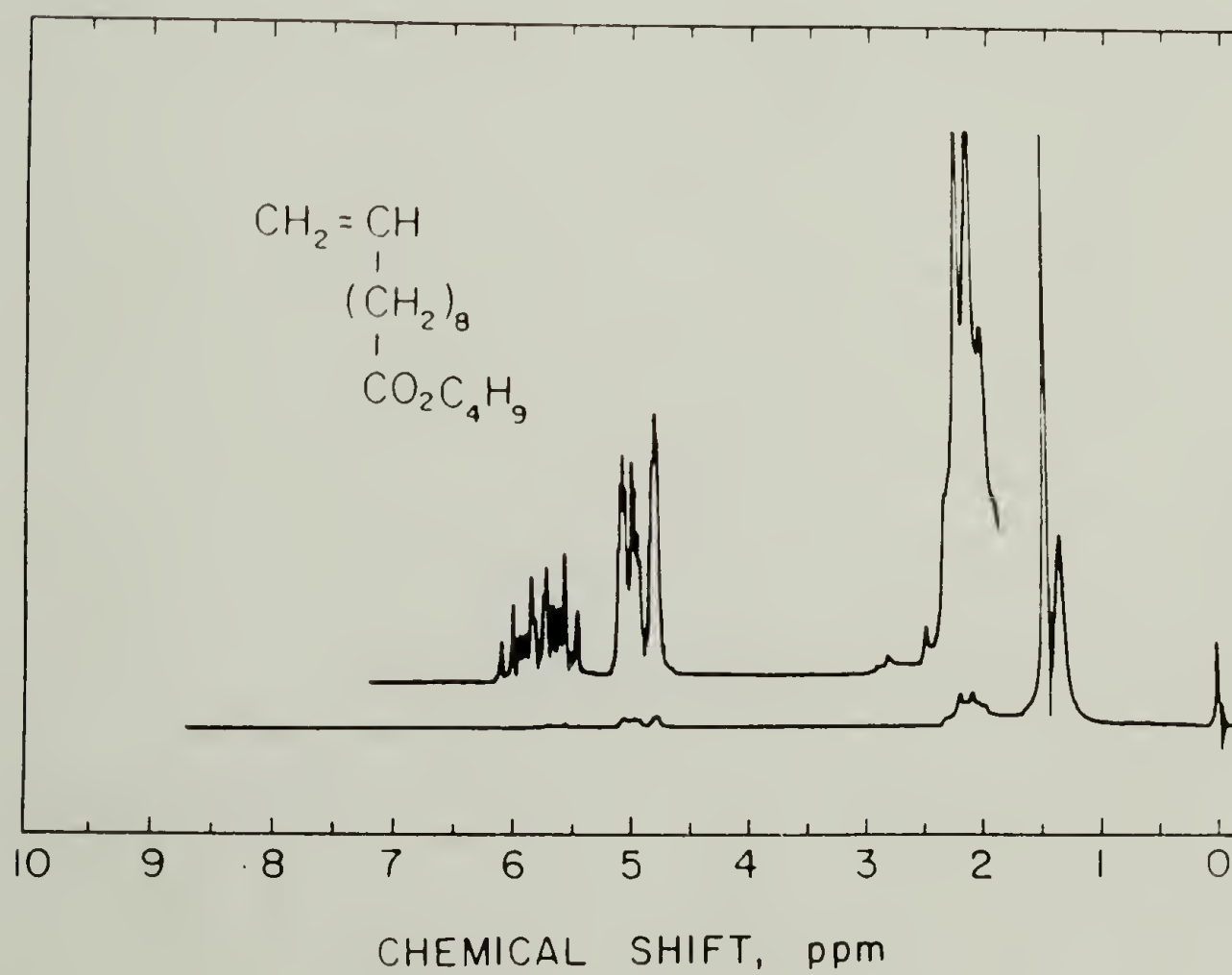
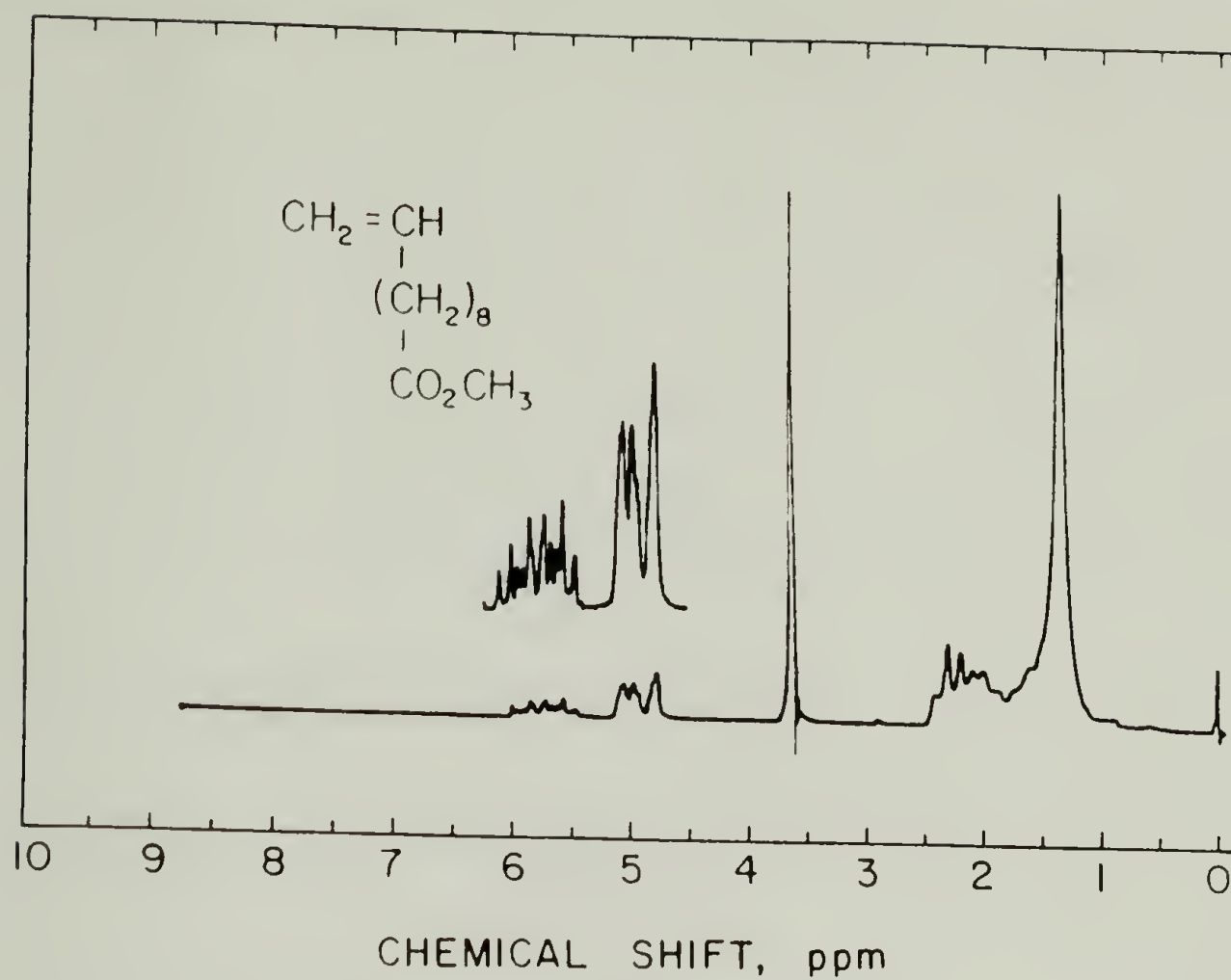


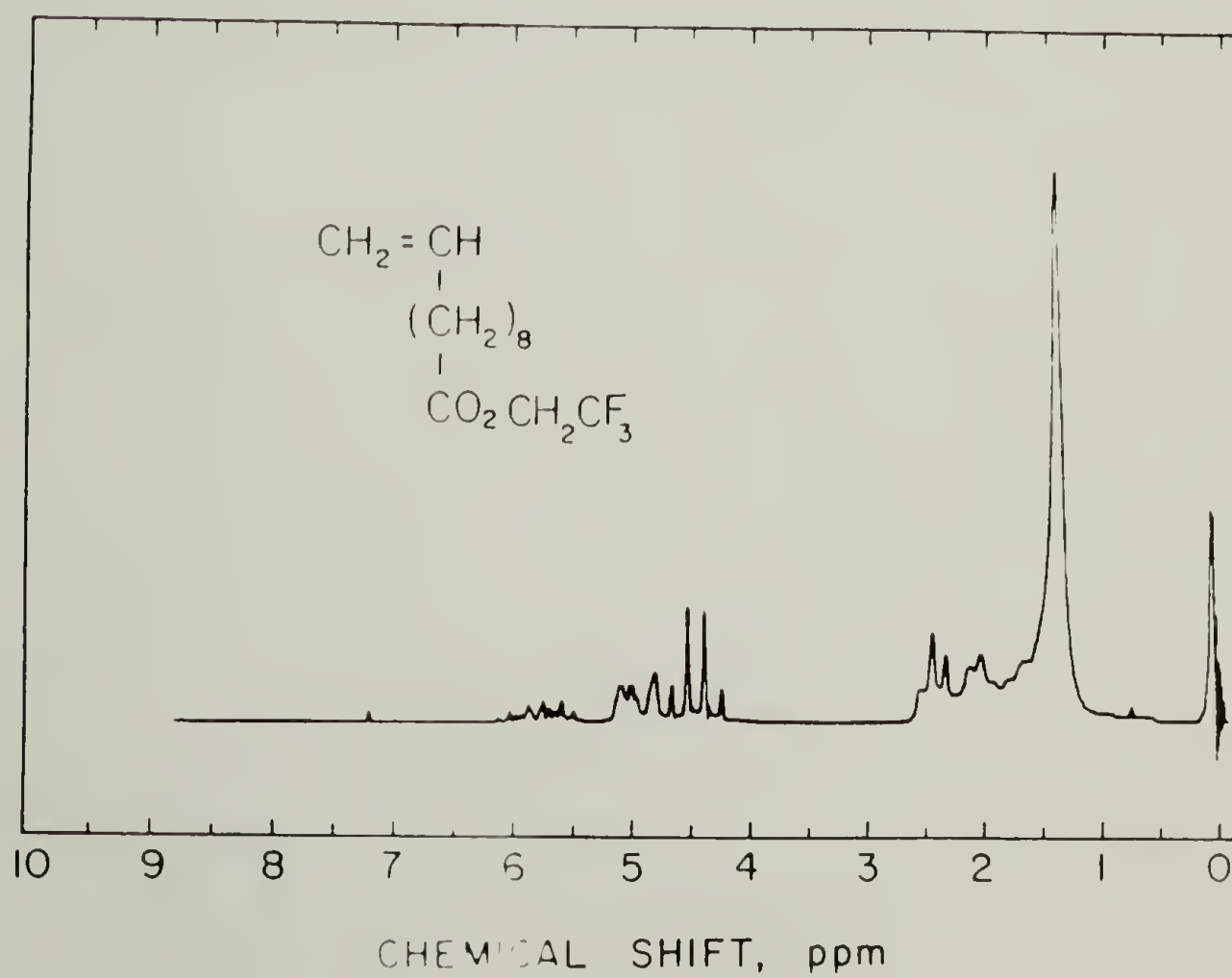
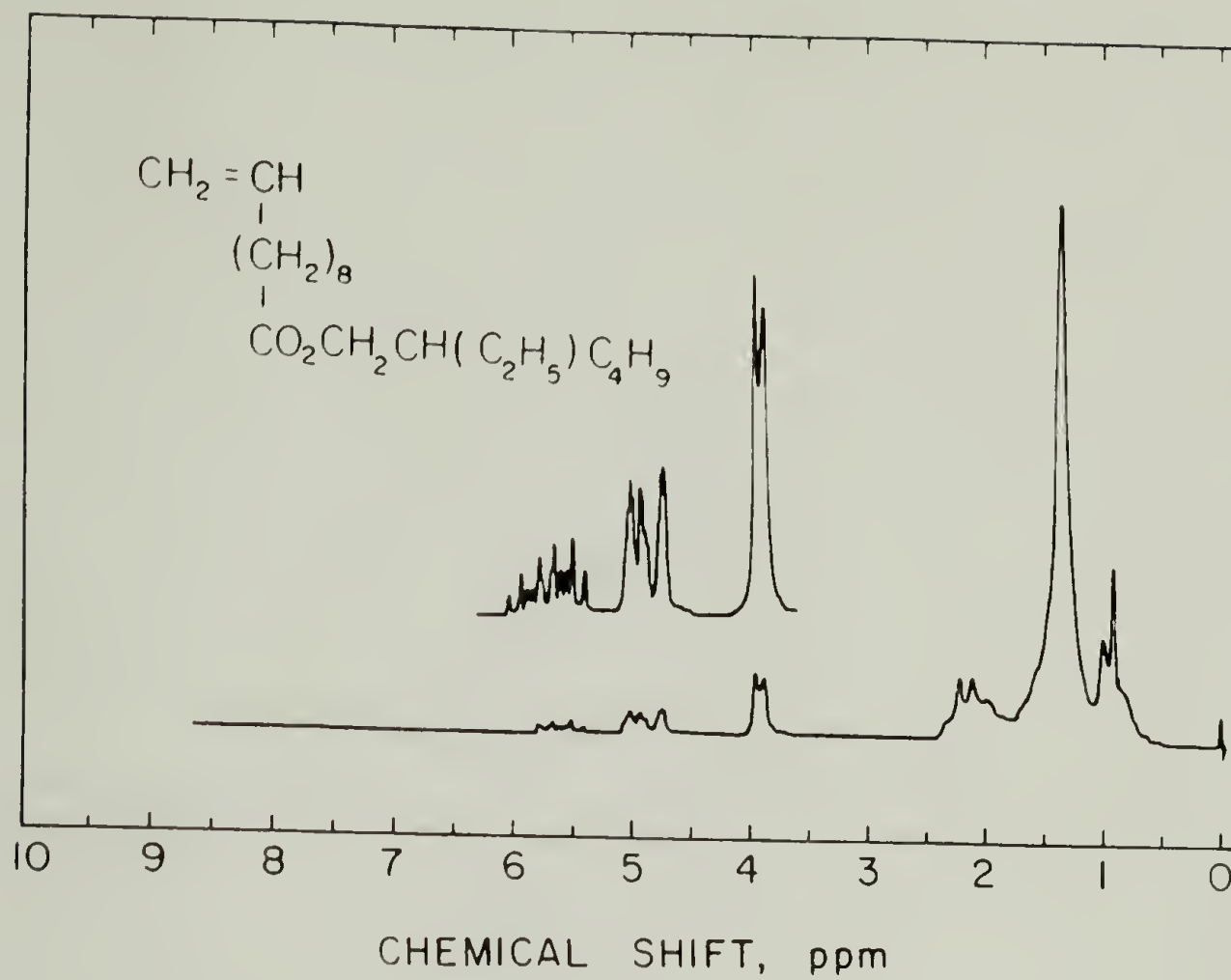


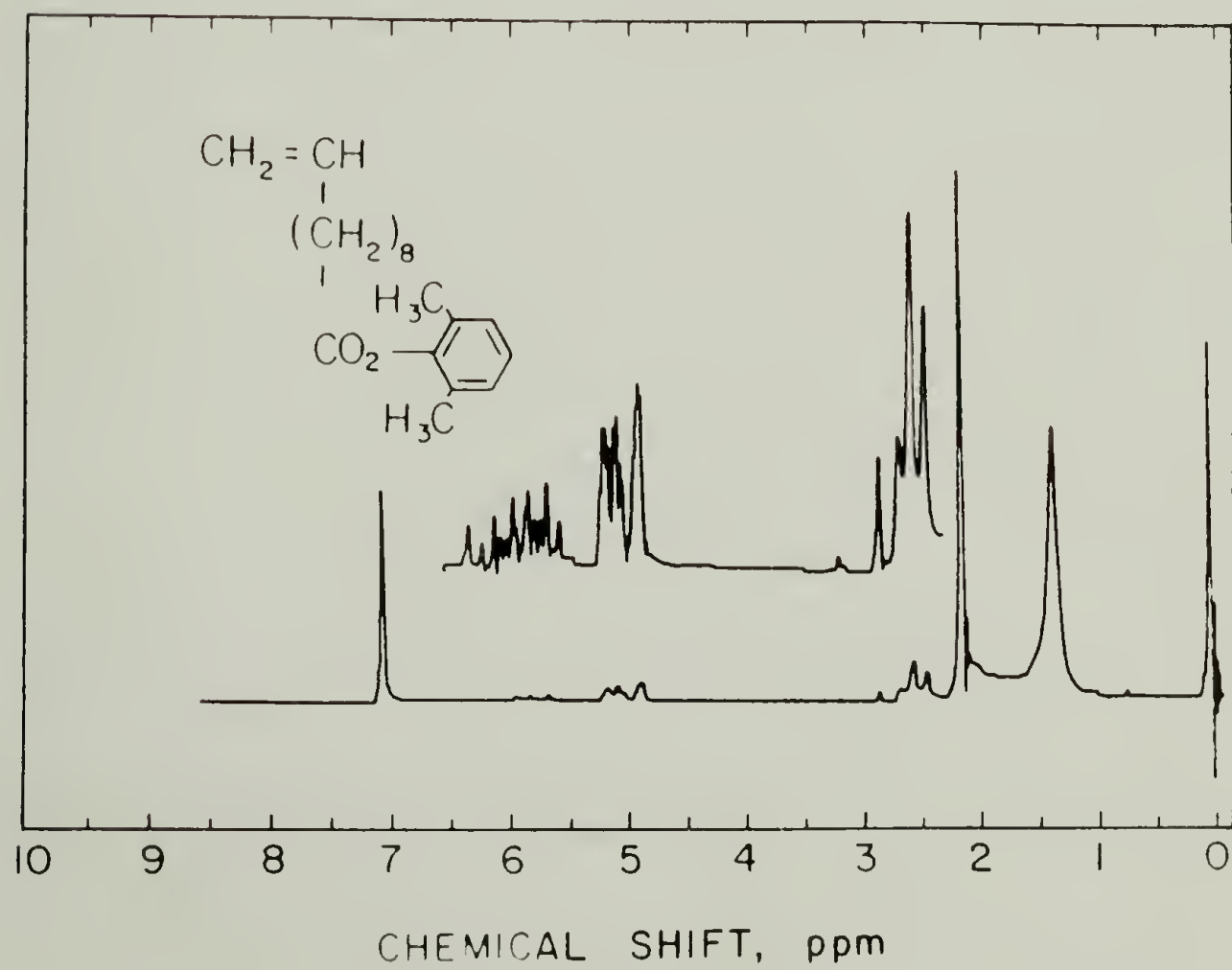
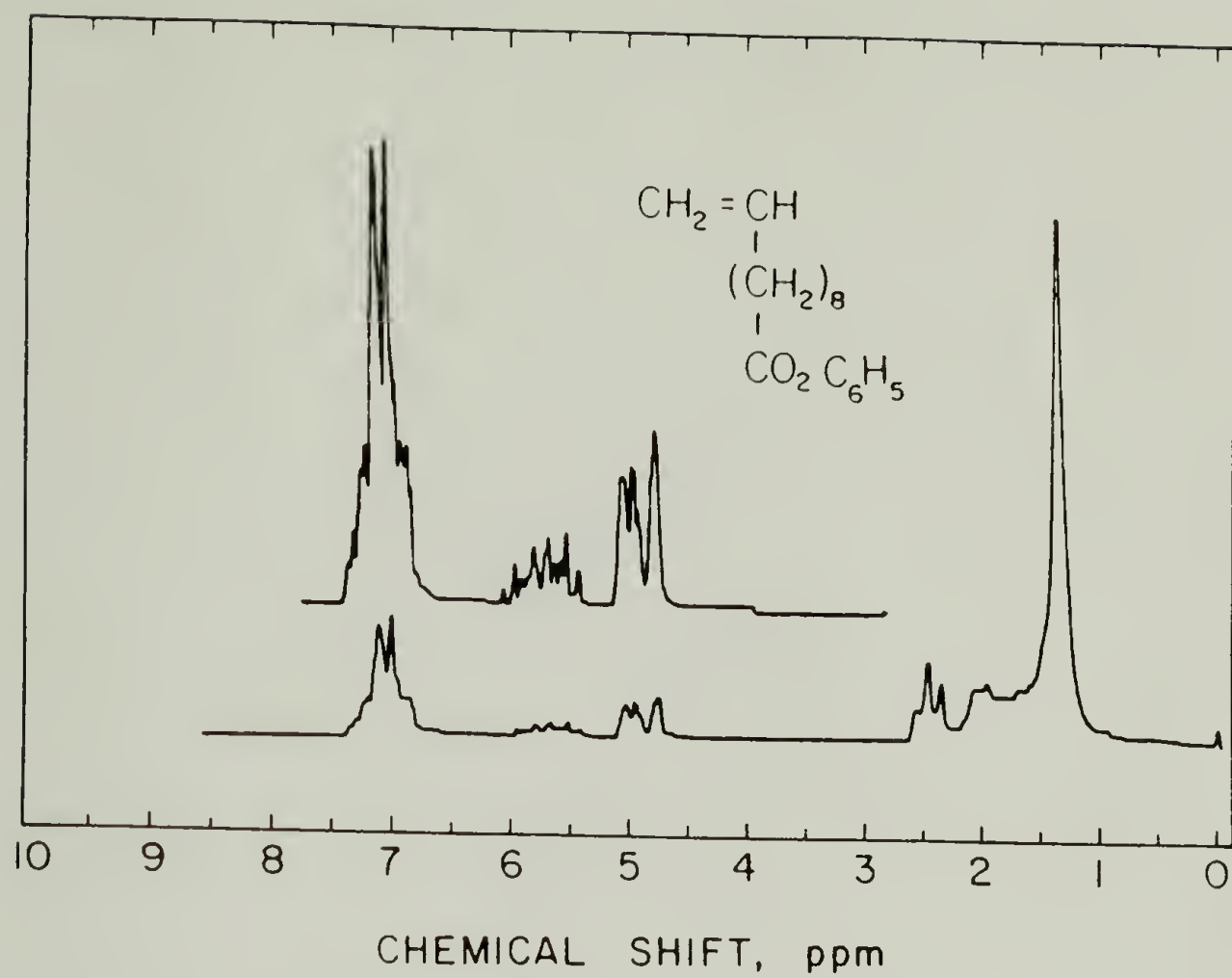




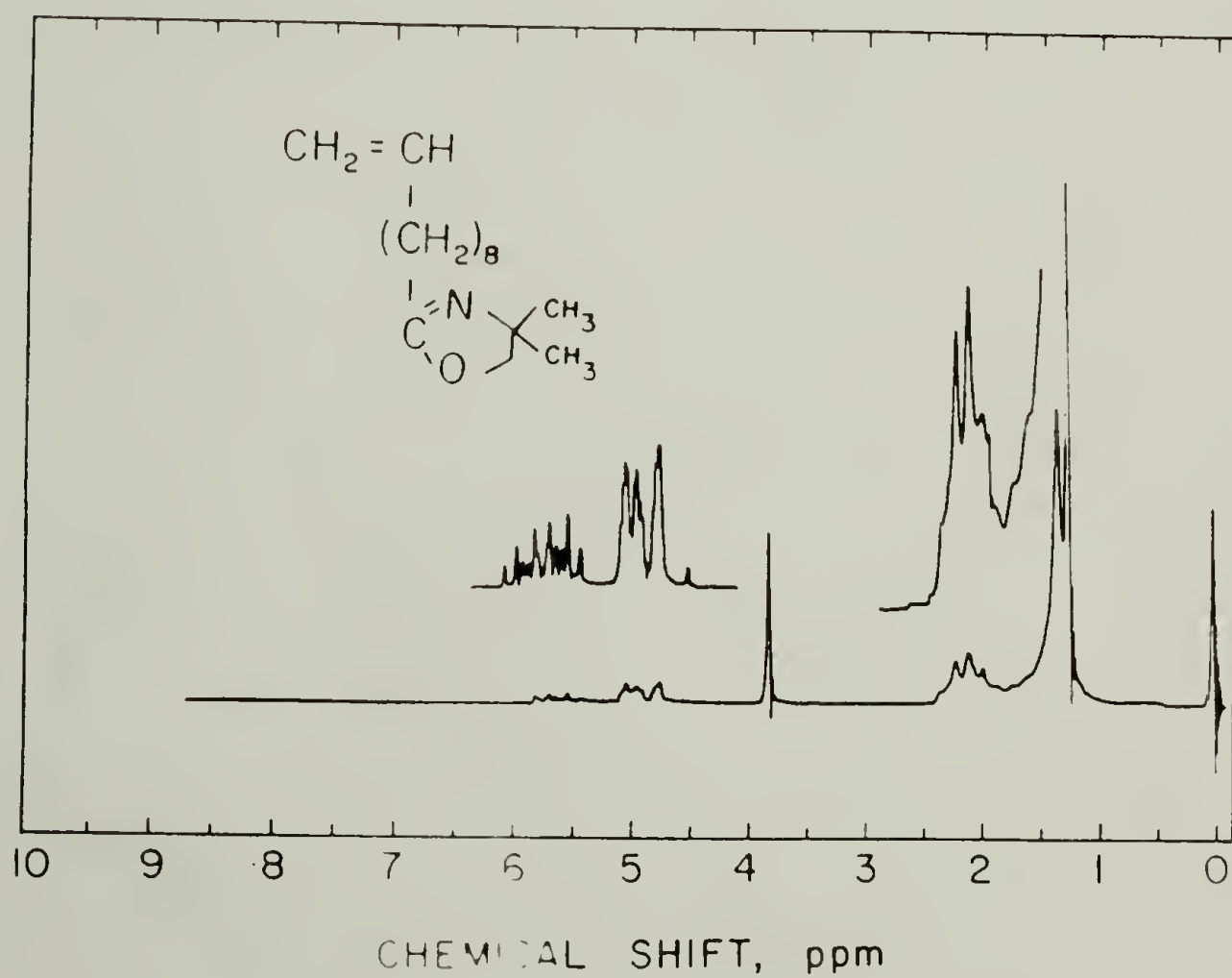
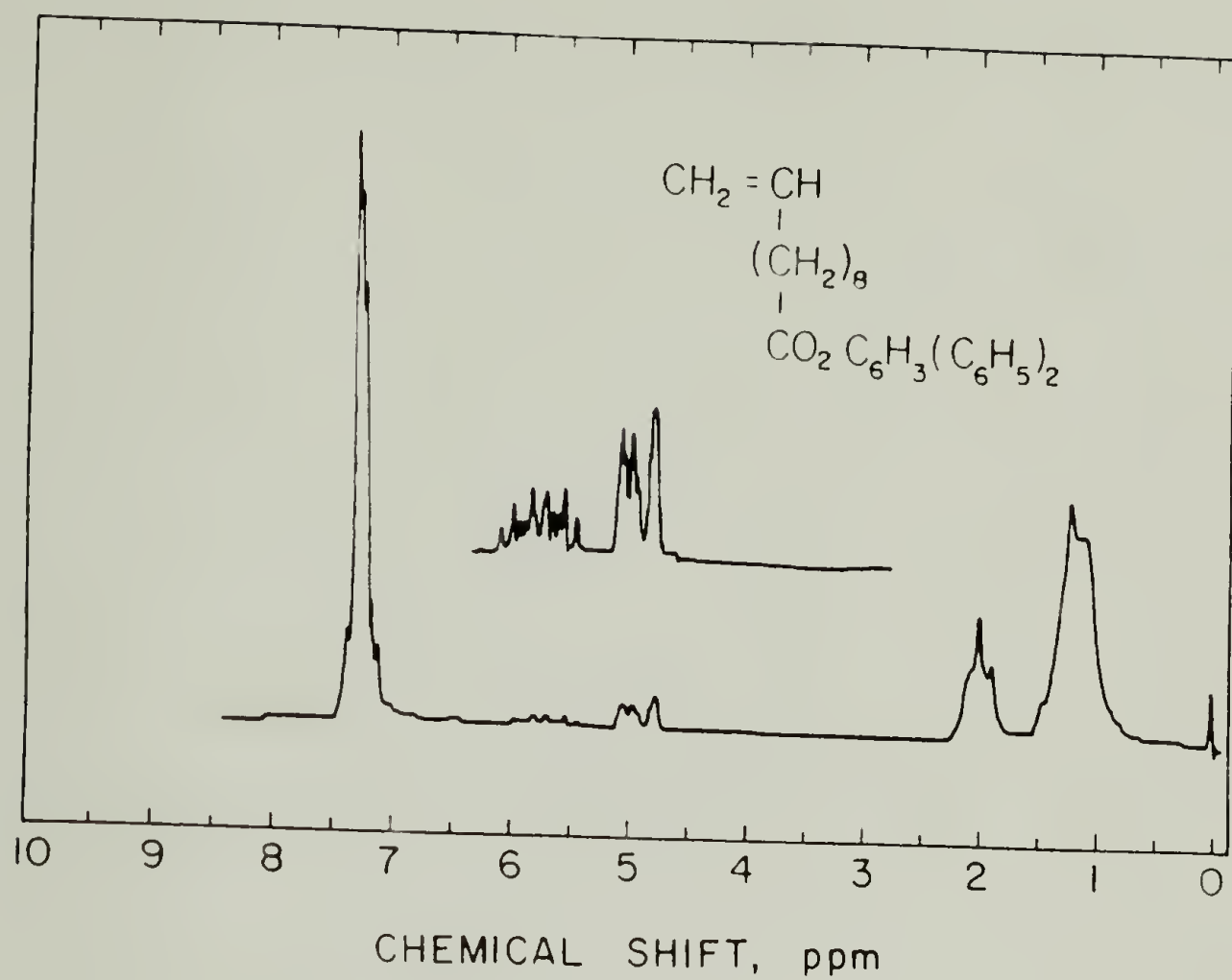
A P P E N D I X    B  
'H NUCLEAR MAGNETIC RESONANCE SPECTRA

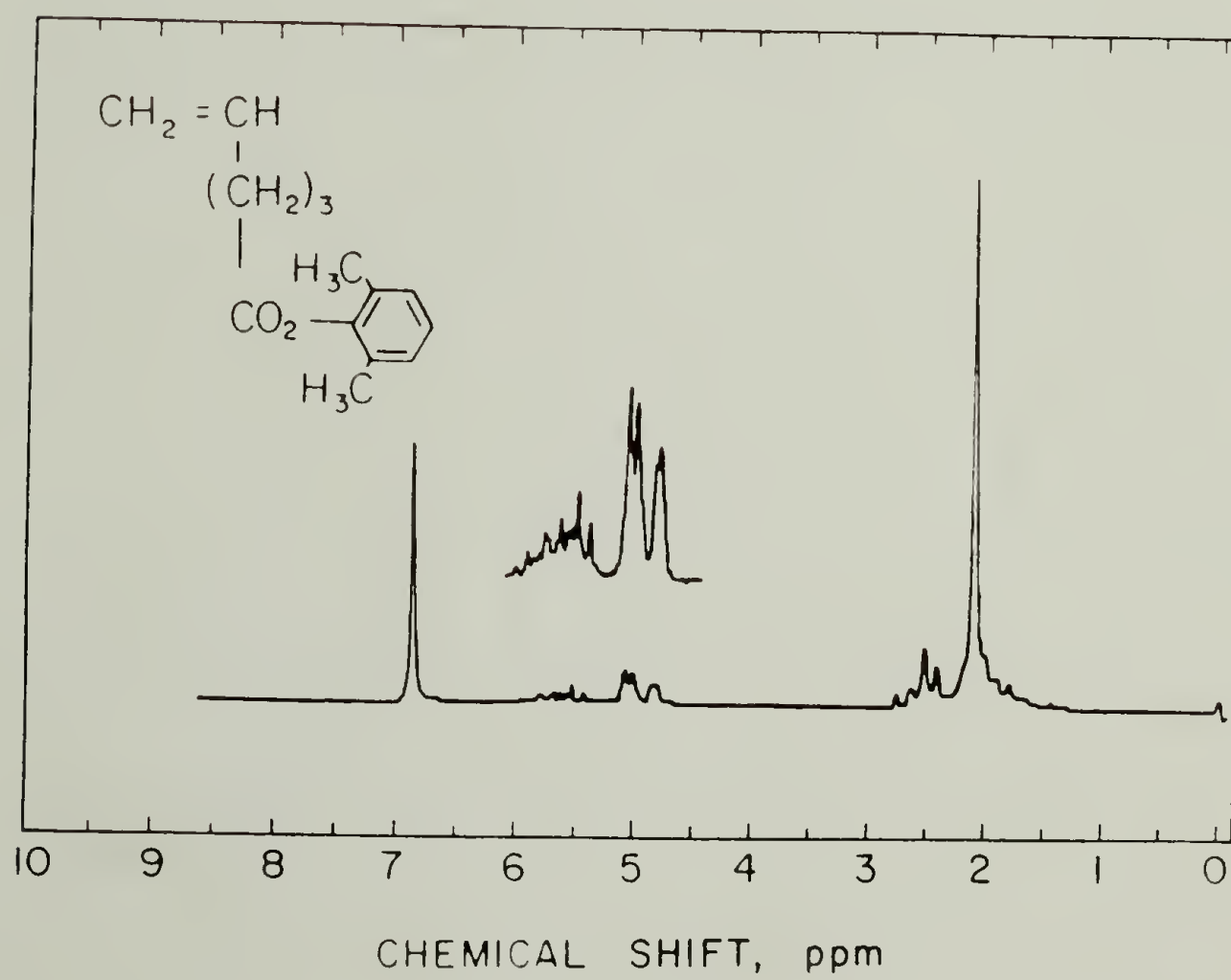
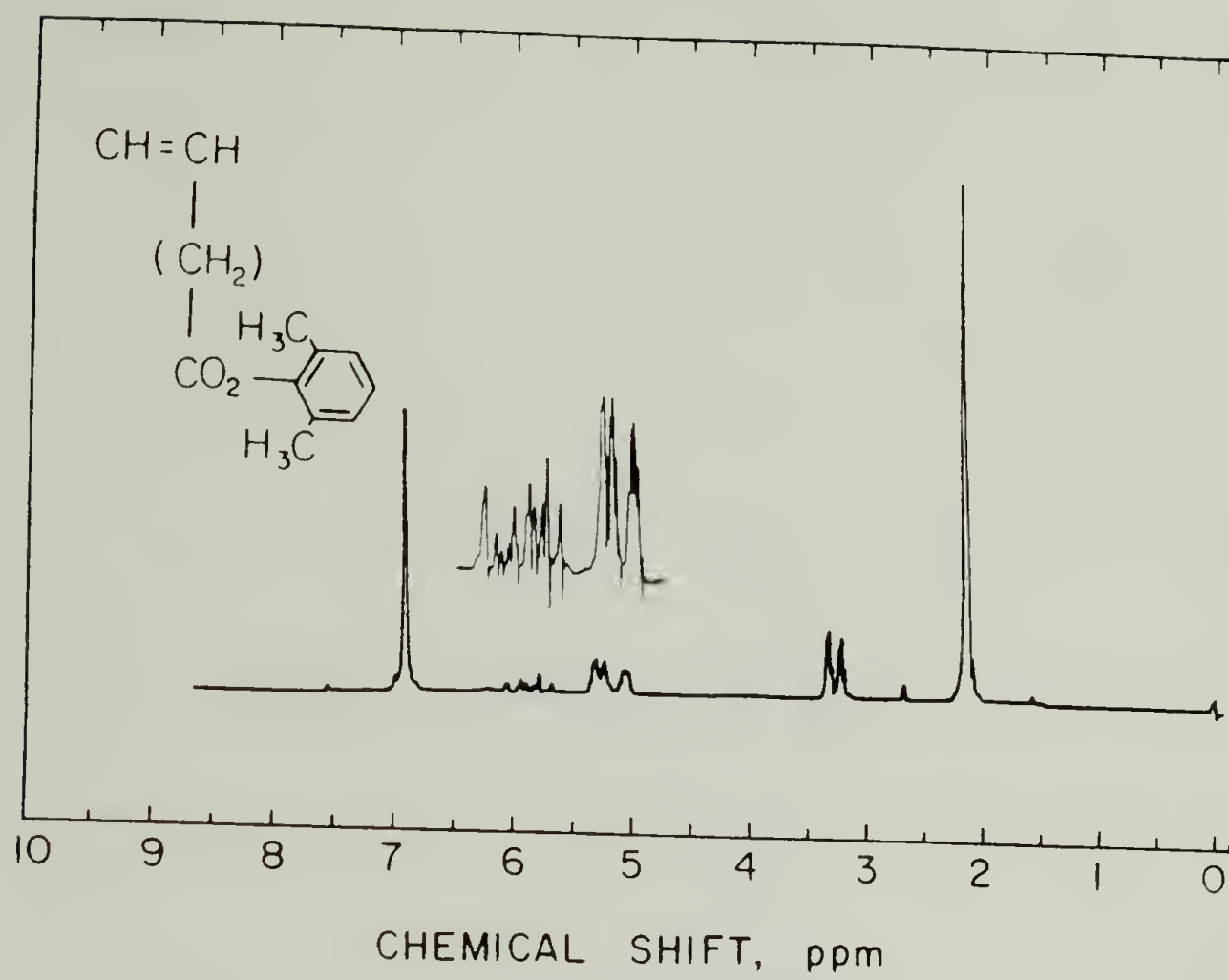


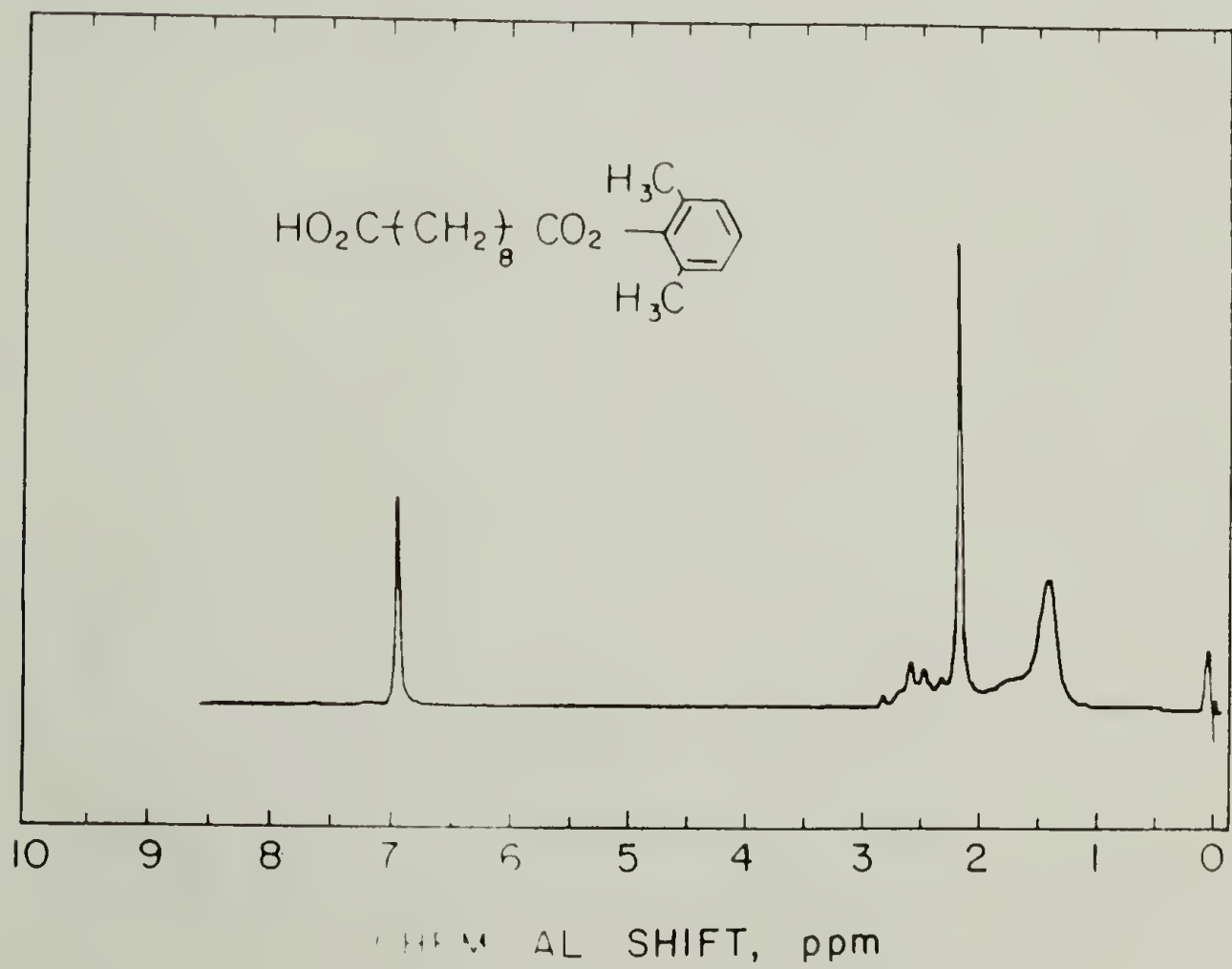
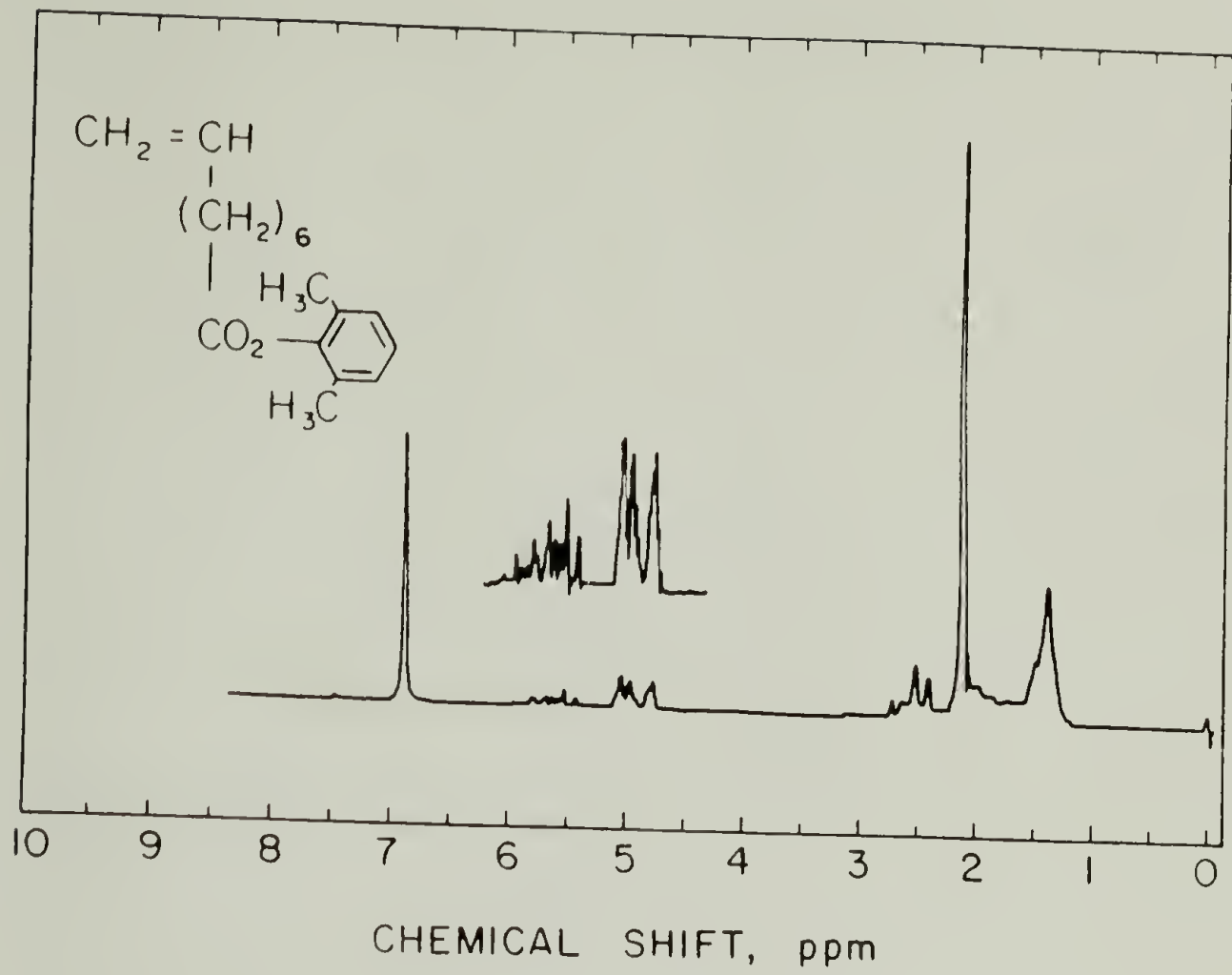


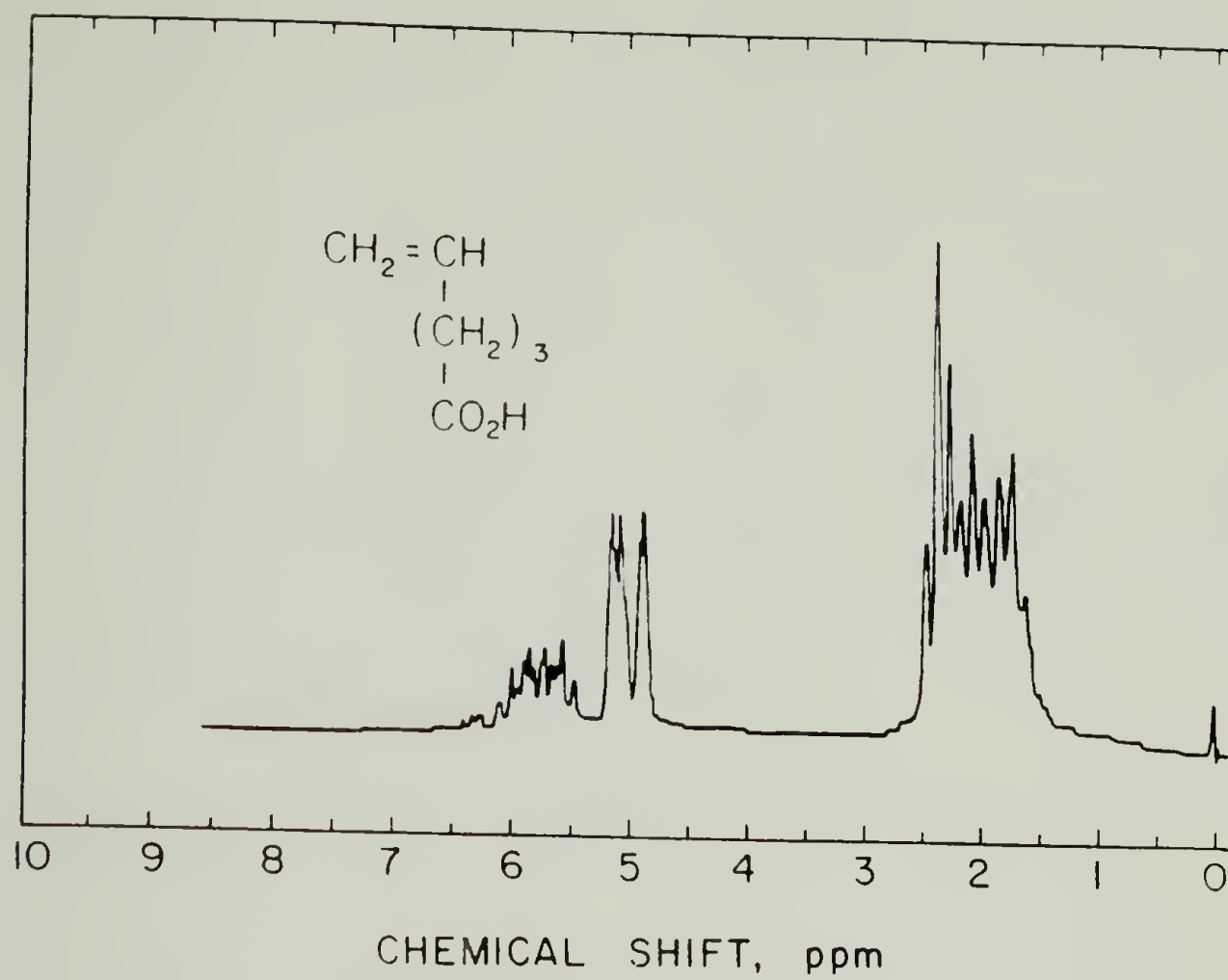


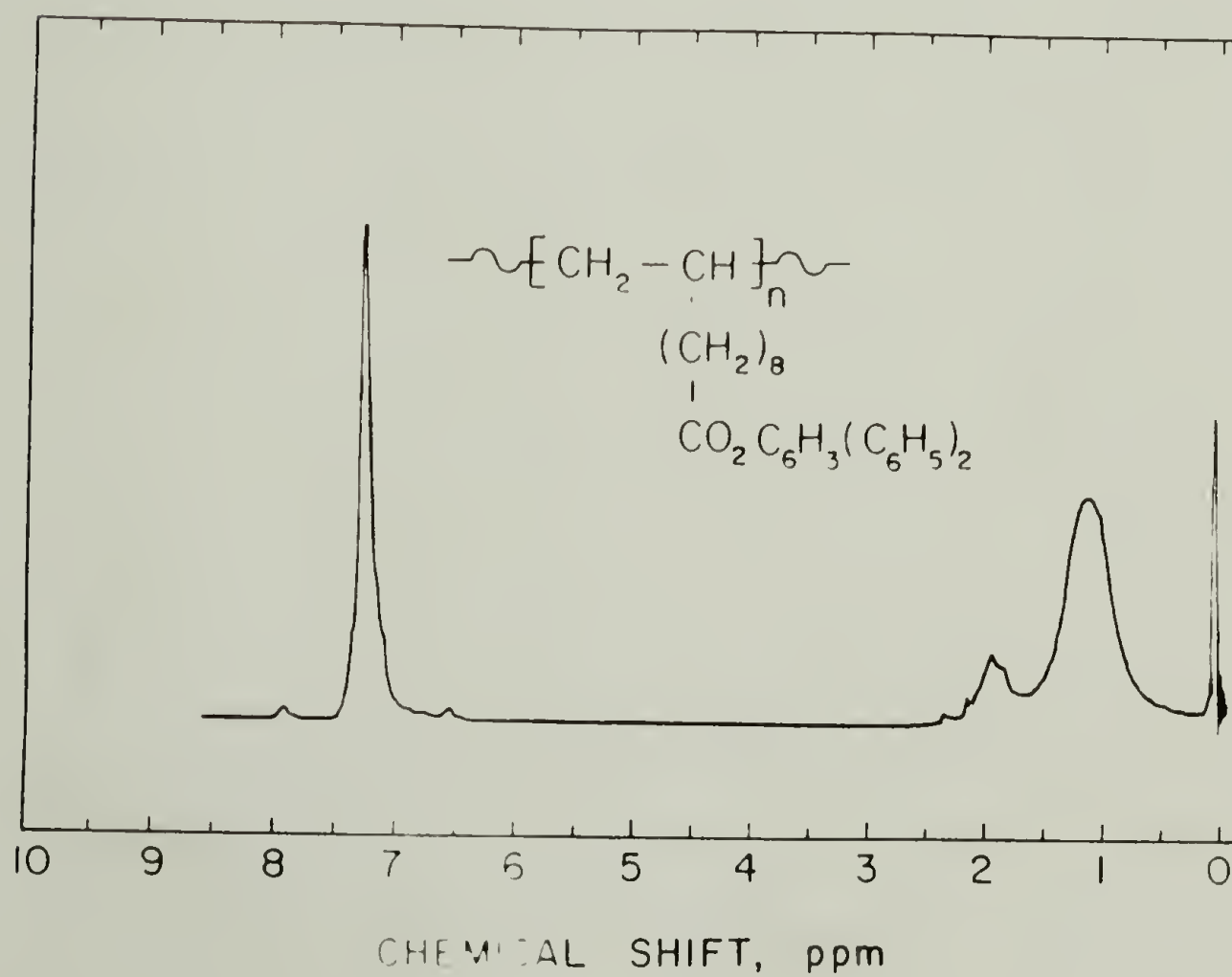
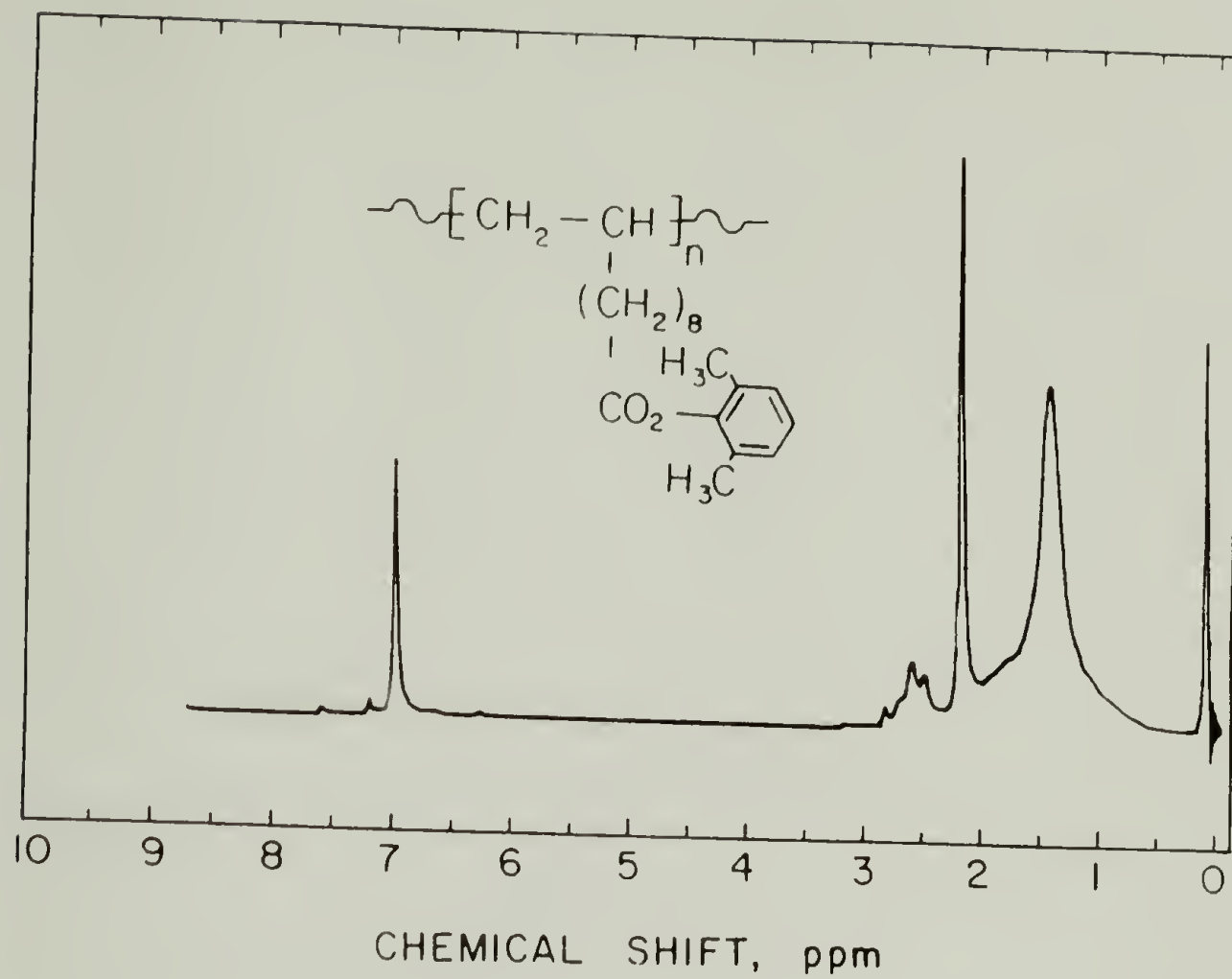




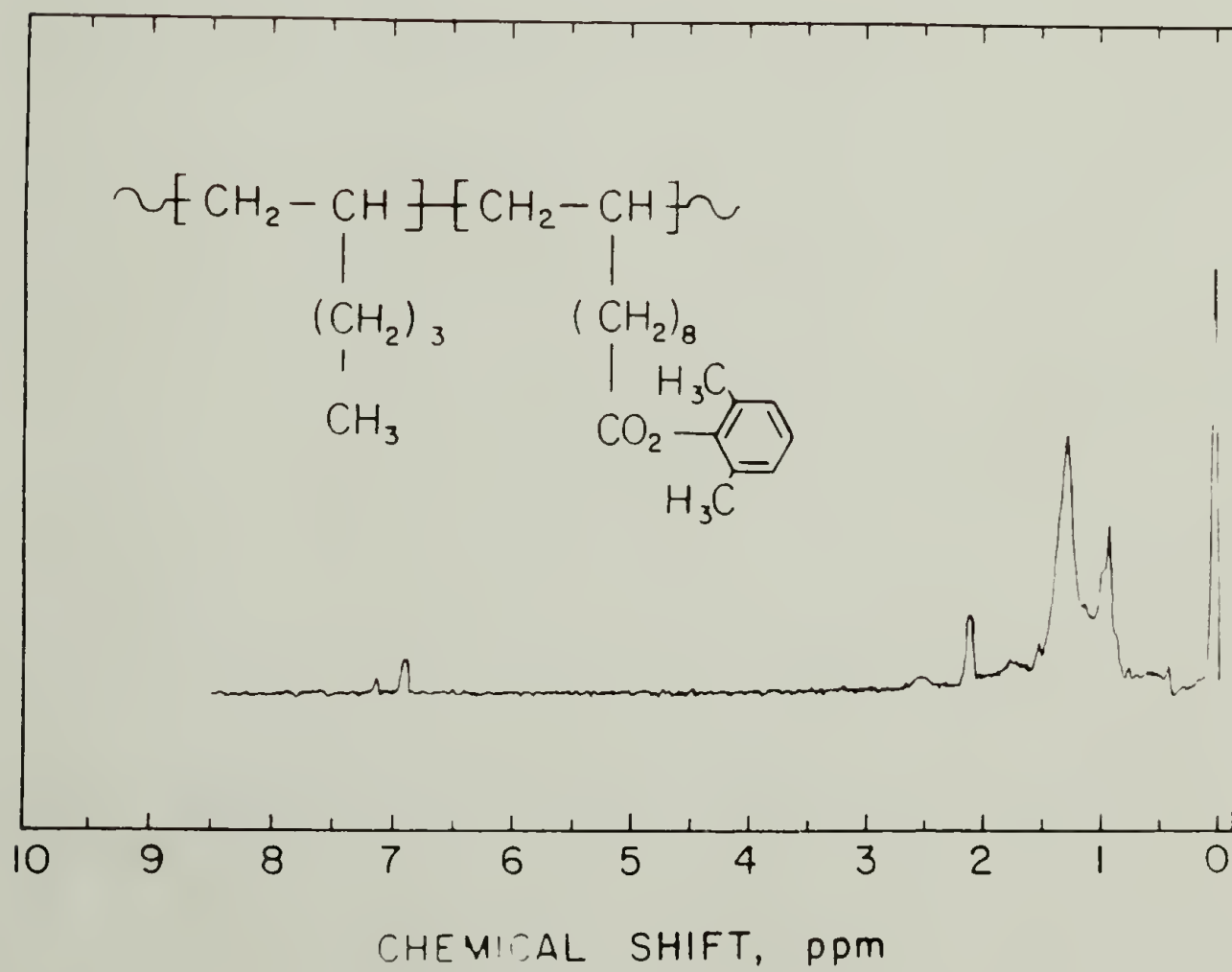
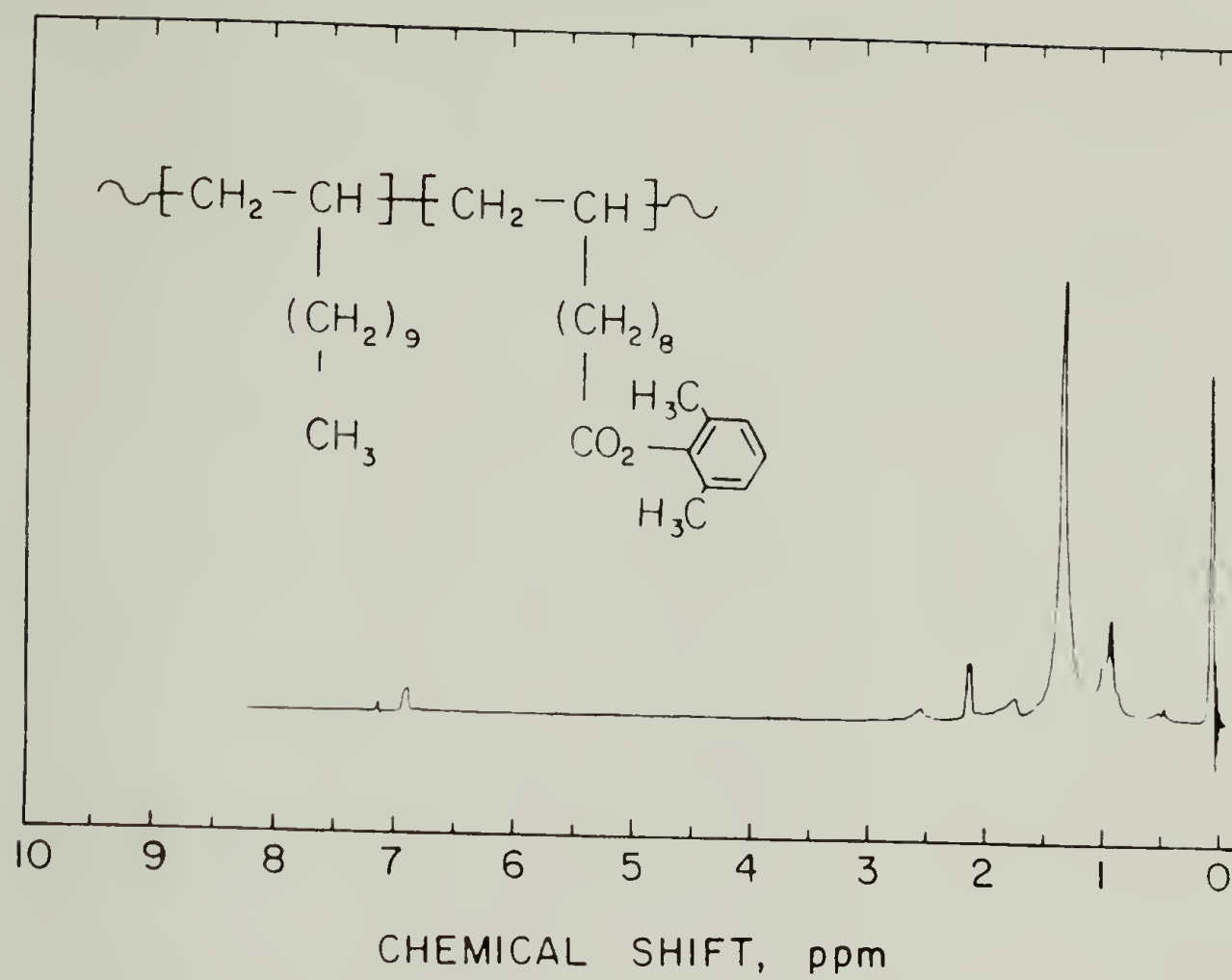






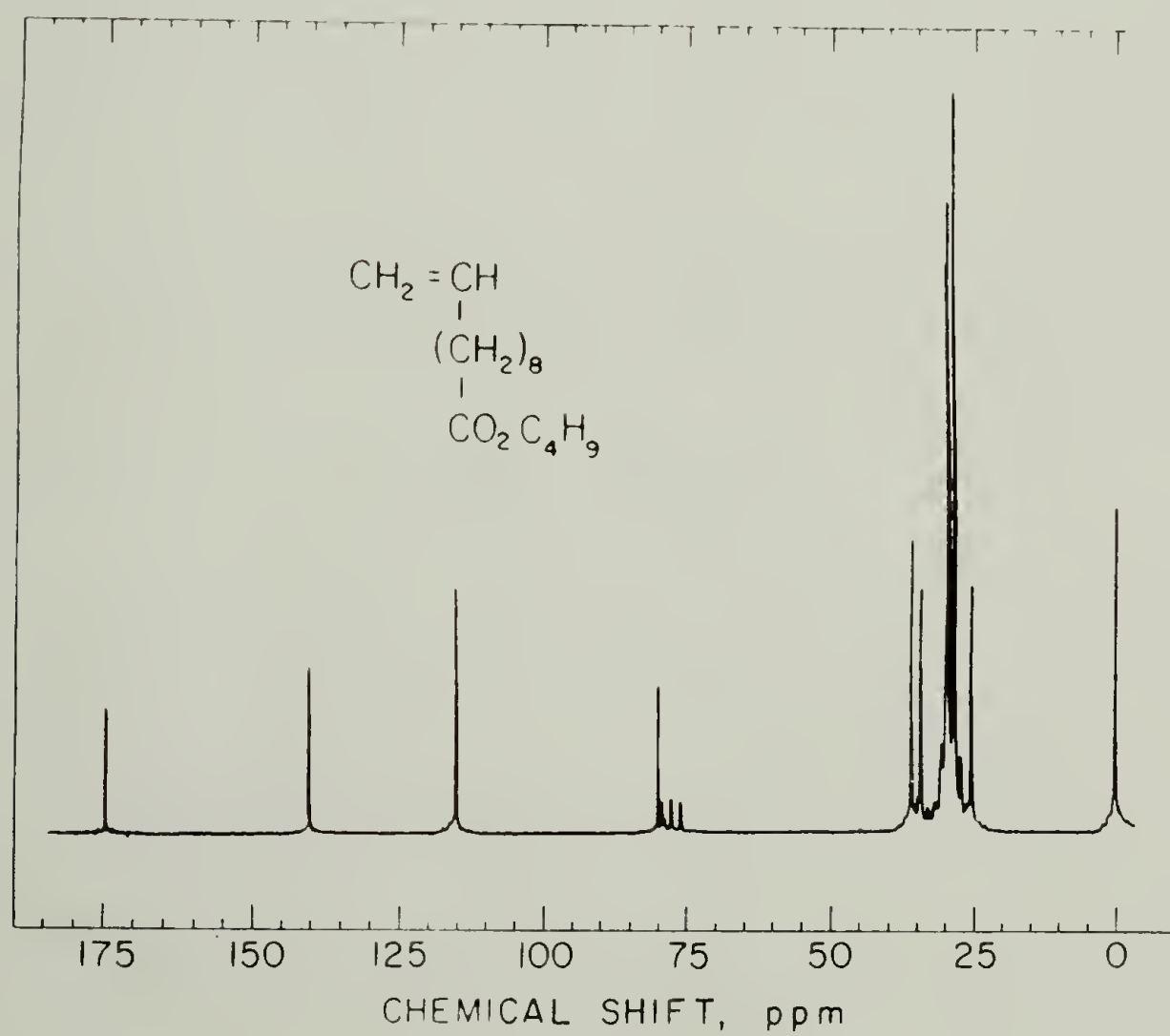
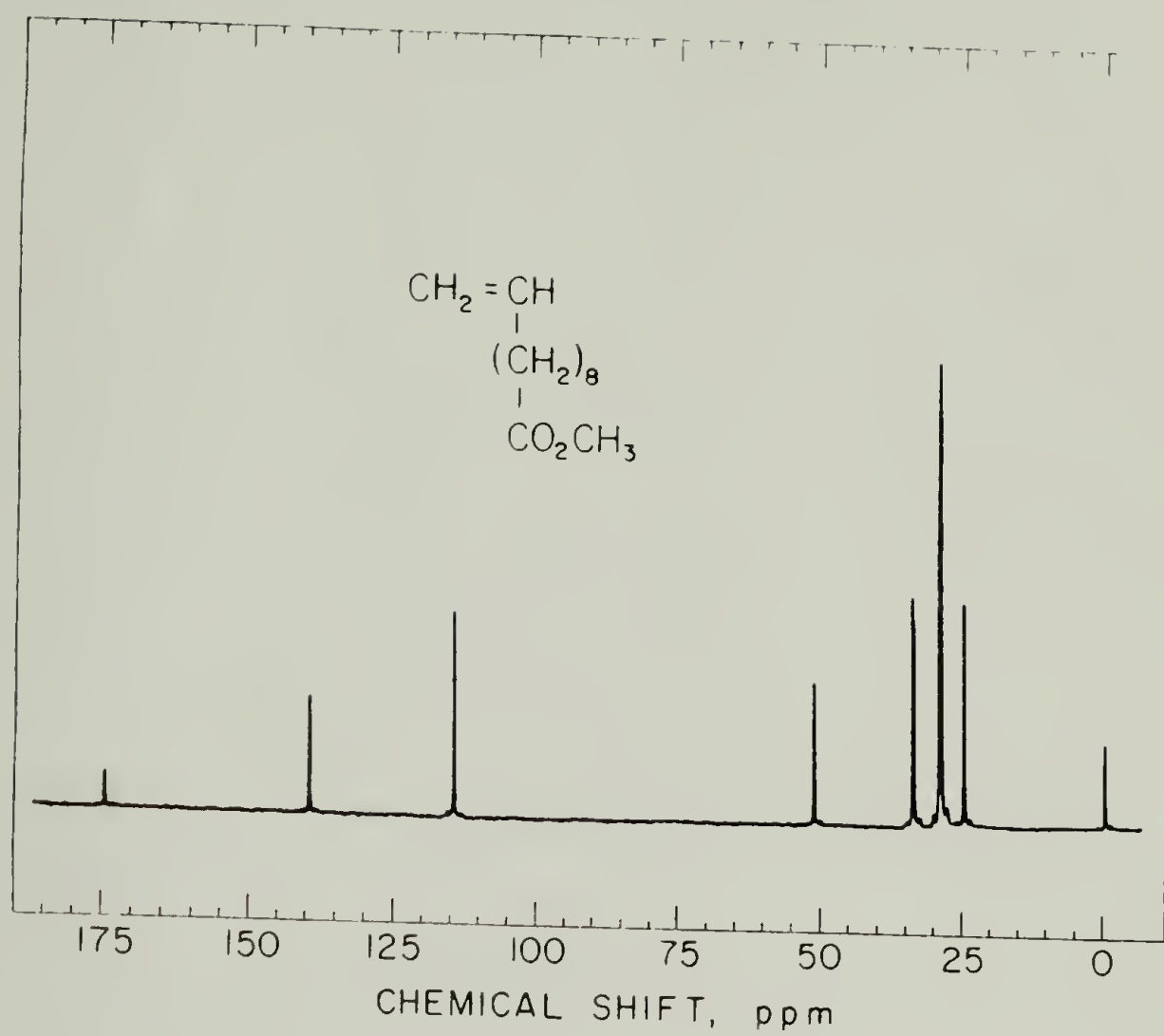


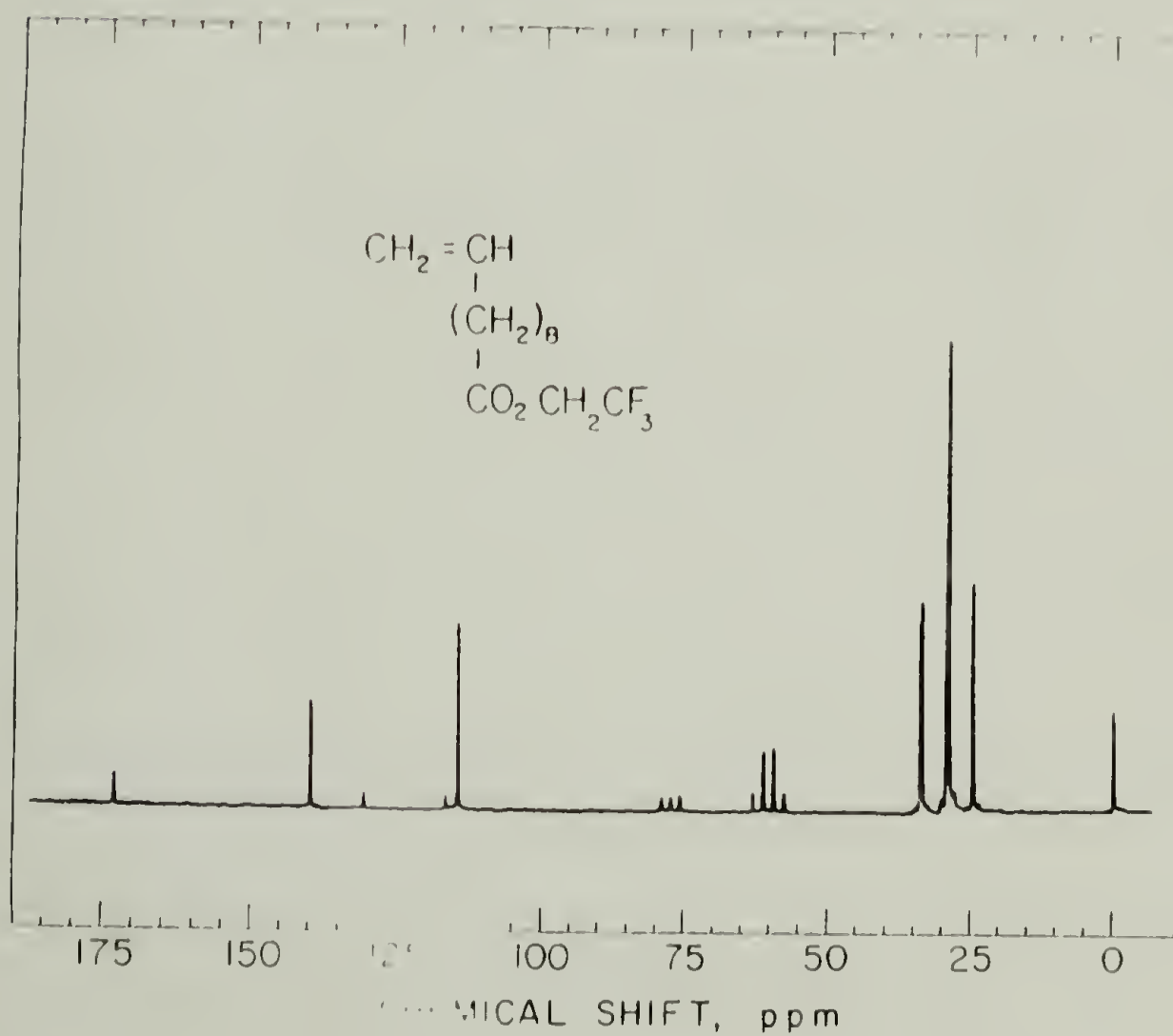
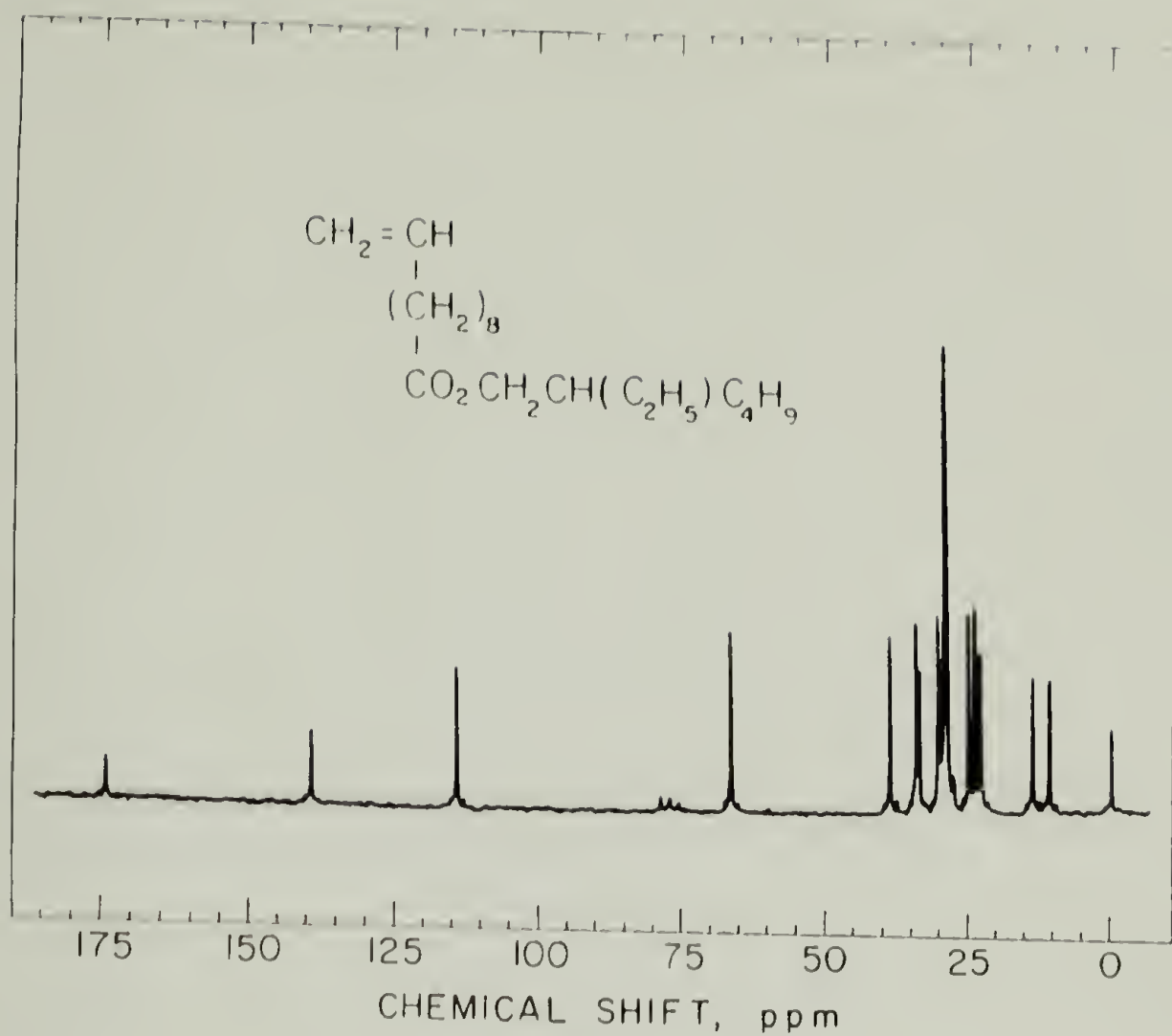


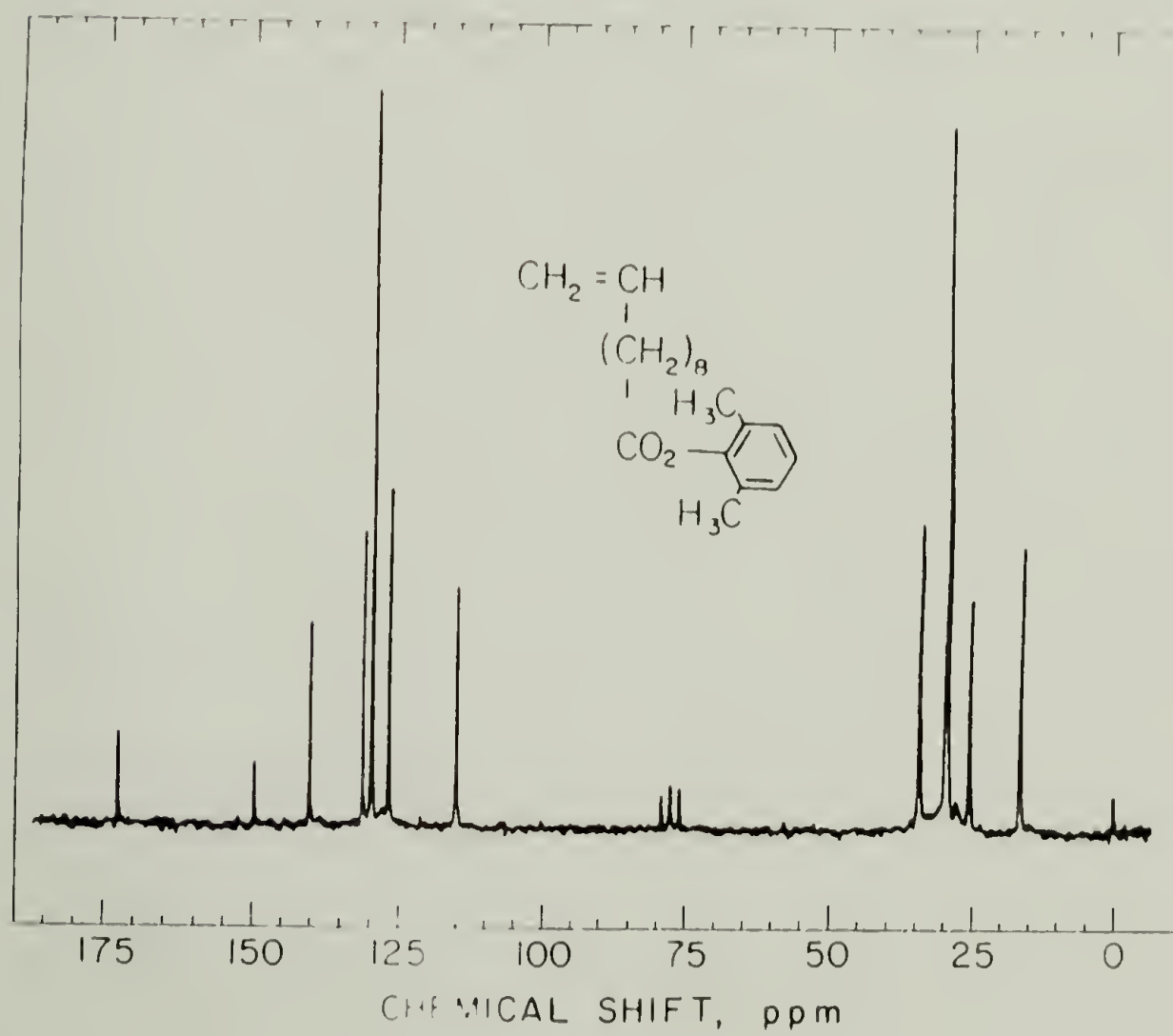
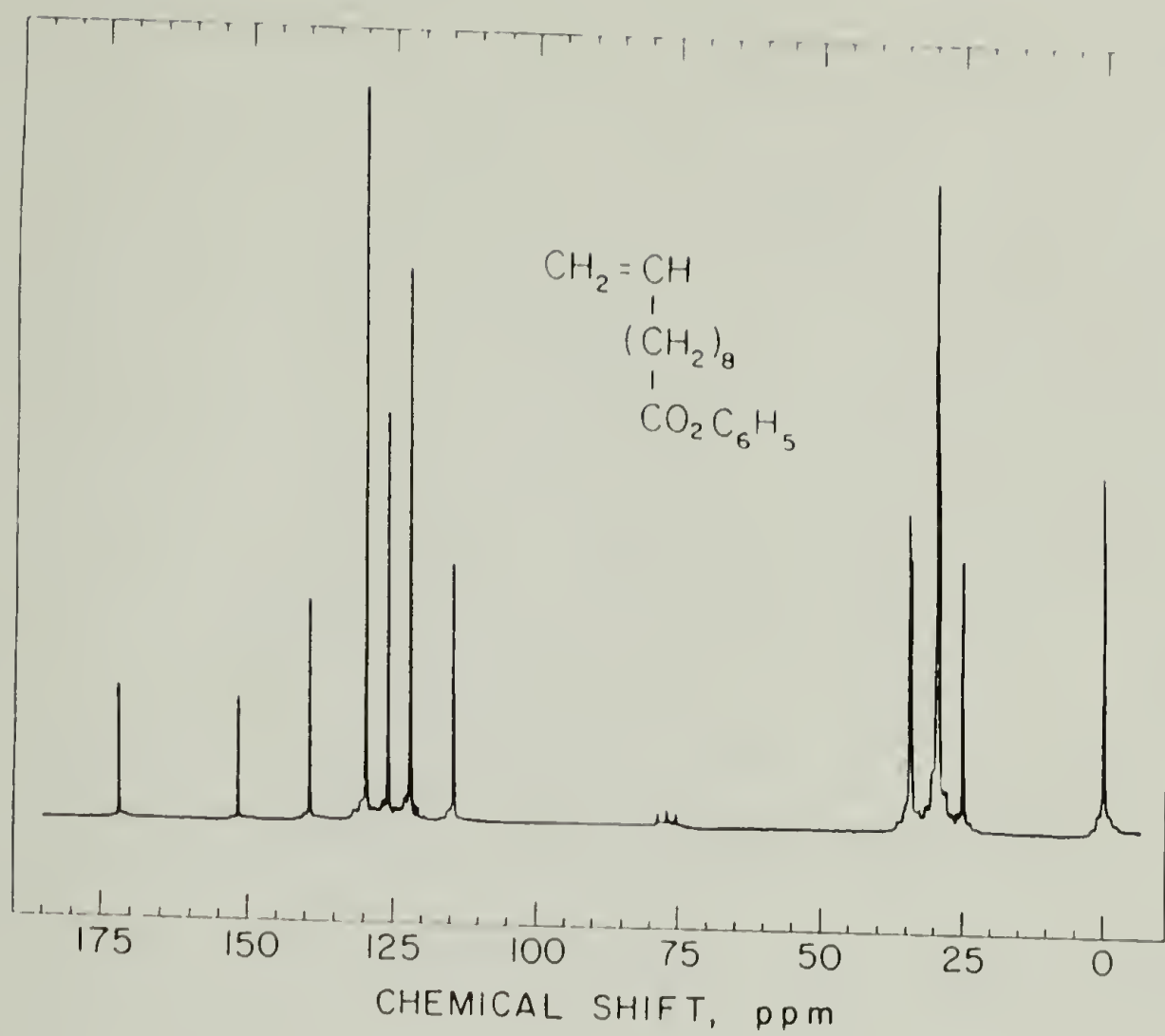


A P P E N D I X   C

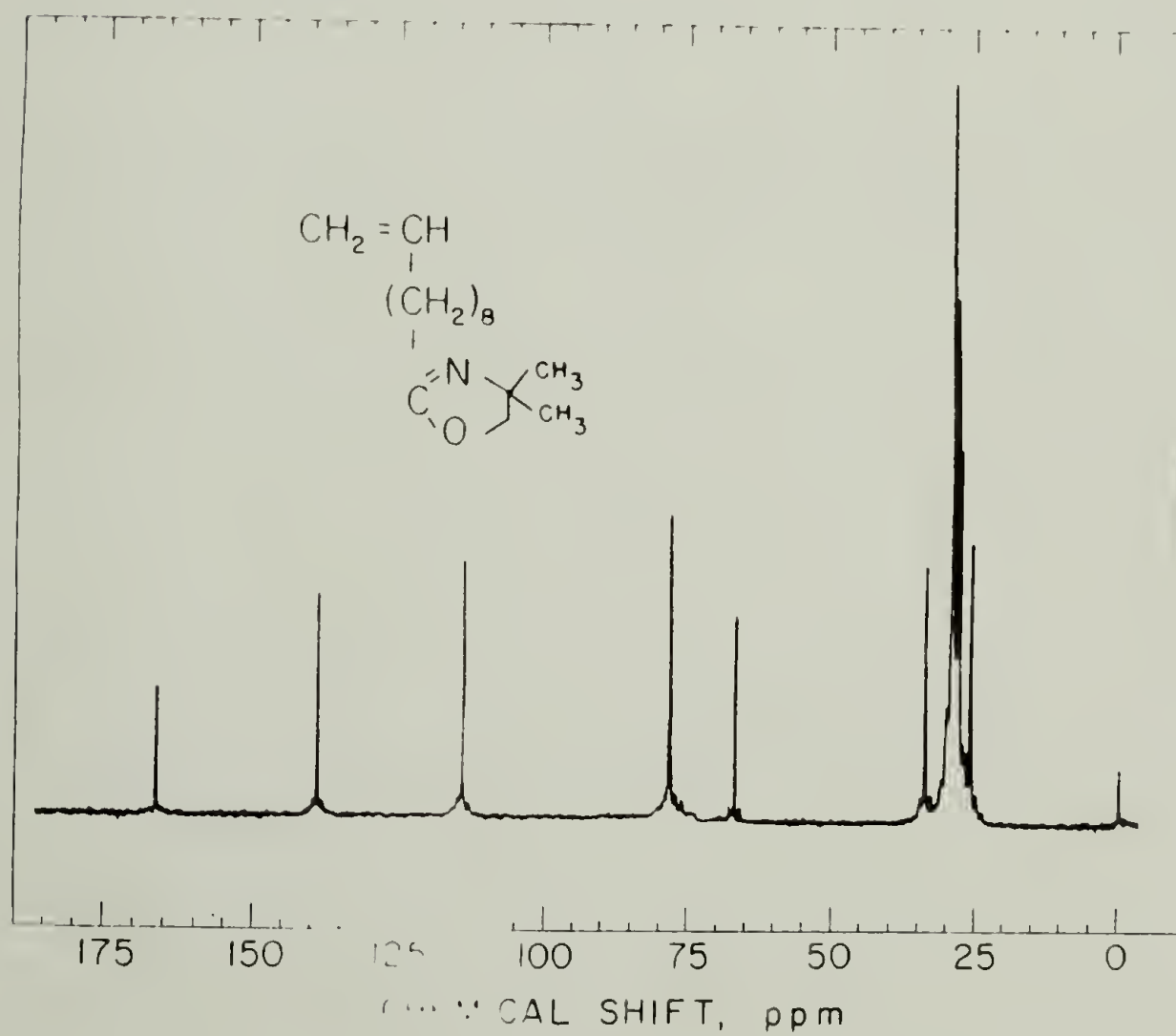
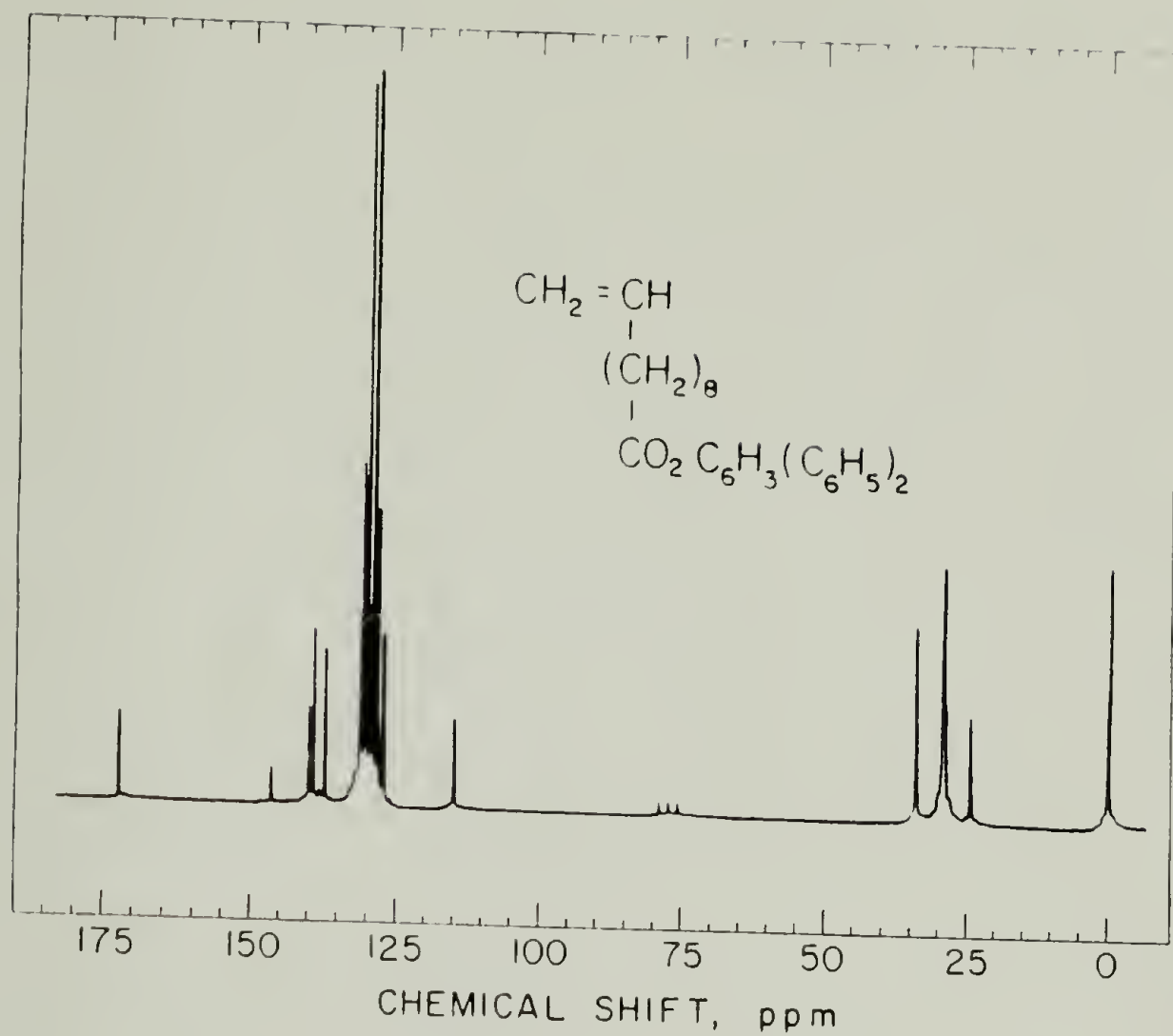
$^{13}\text{C}$  NUCLEAR MAGNETIC RESONANCE SPECTRA

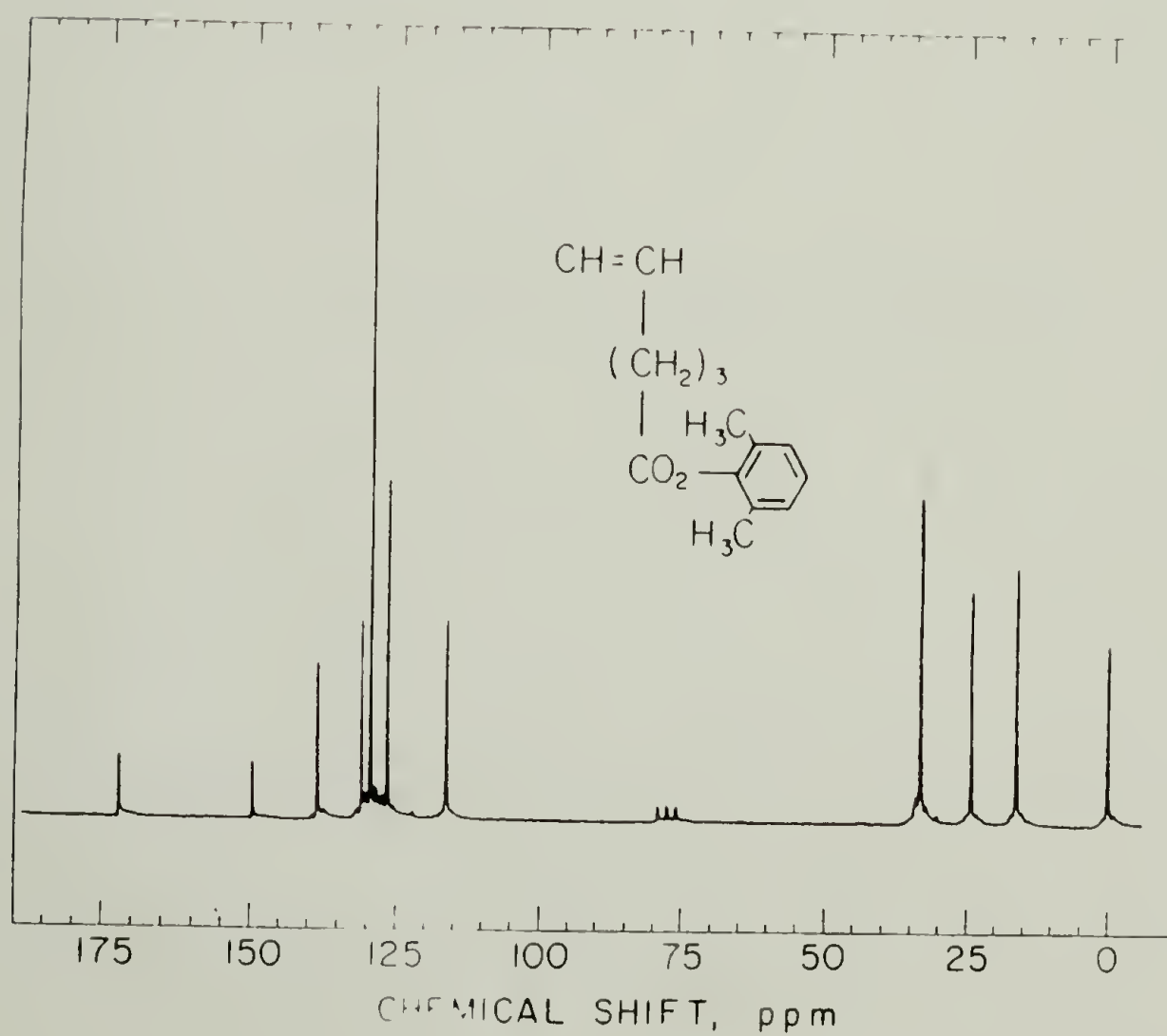
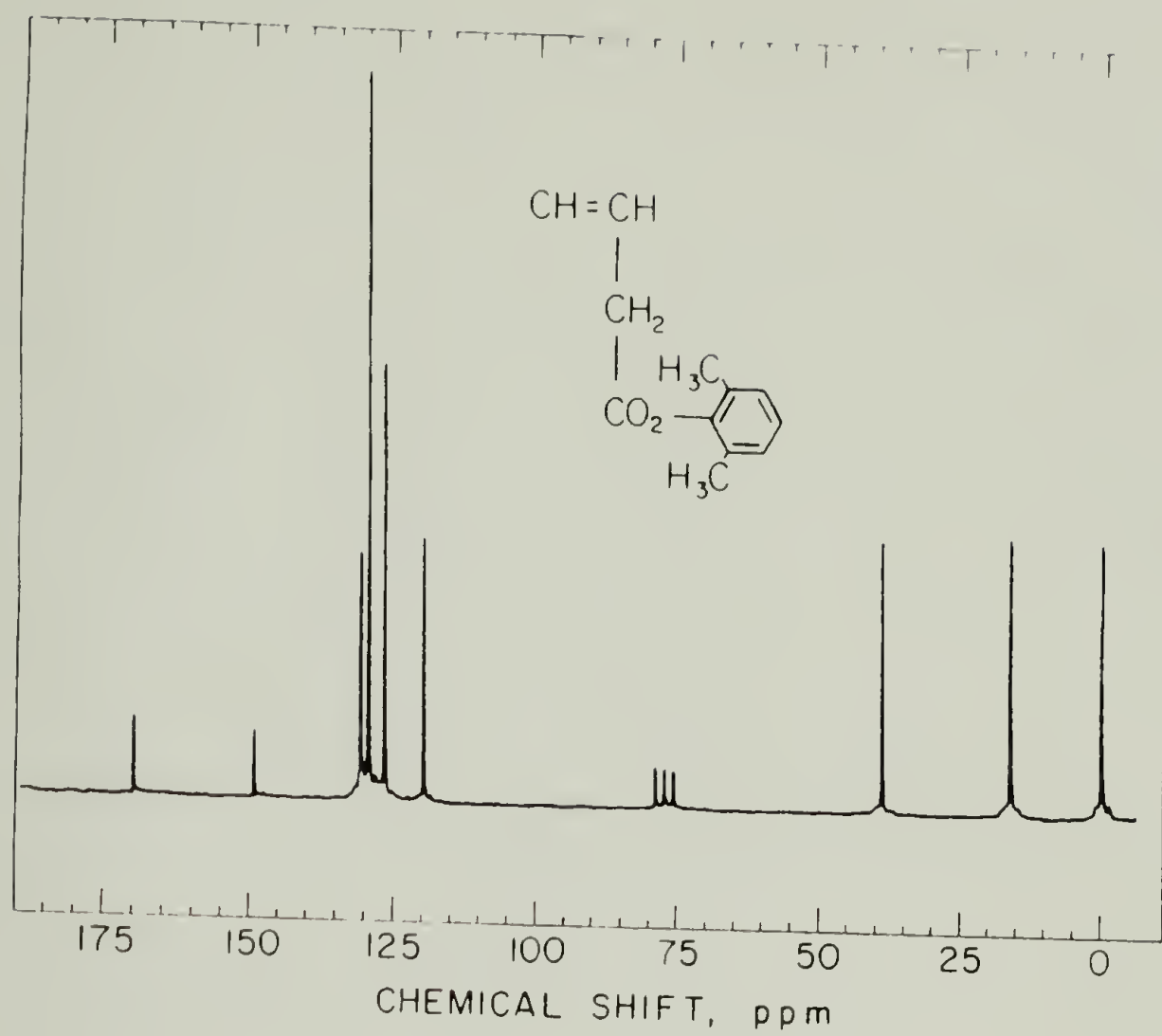


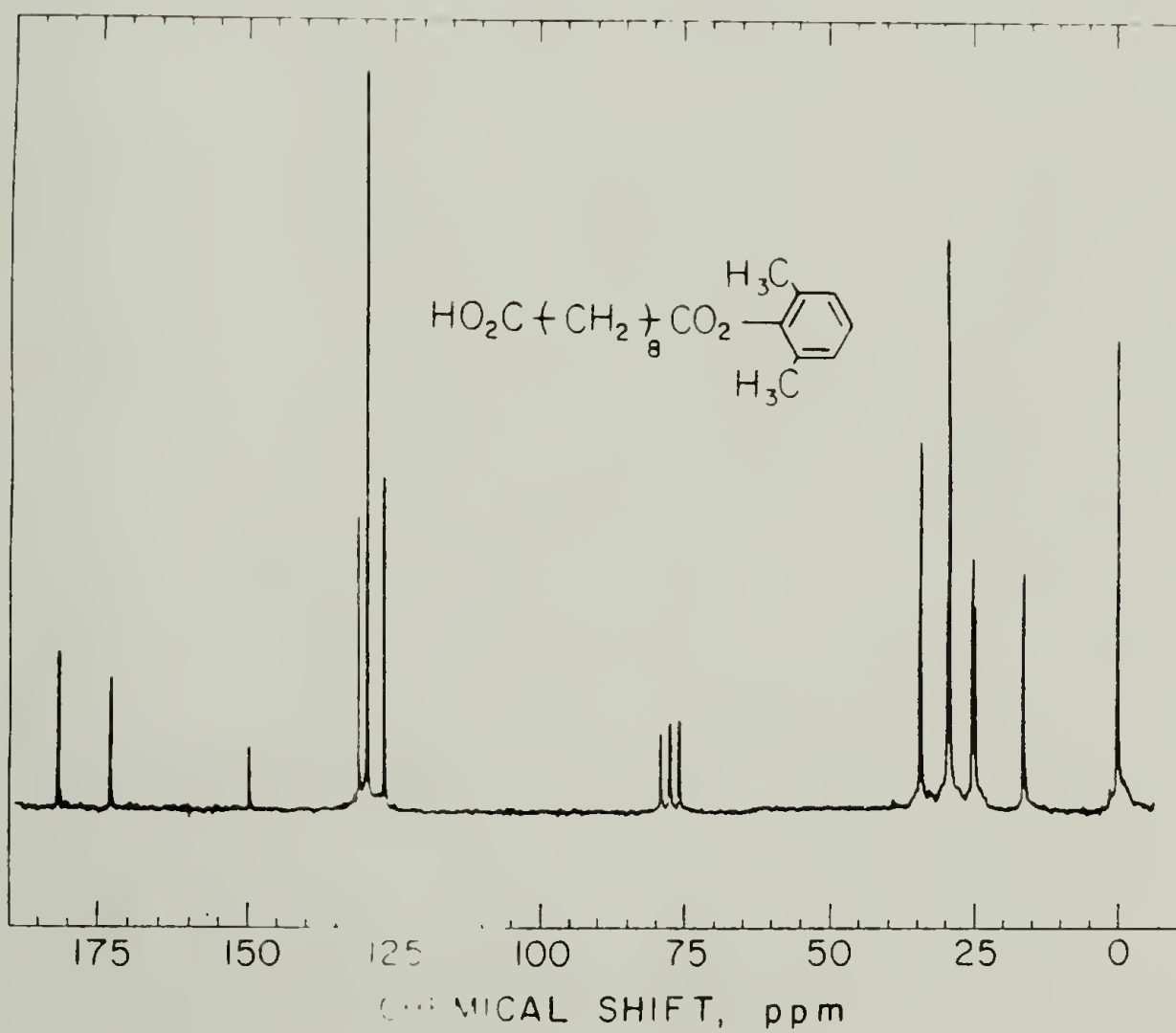
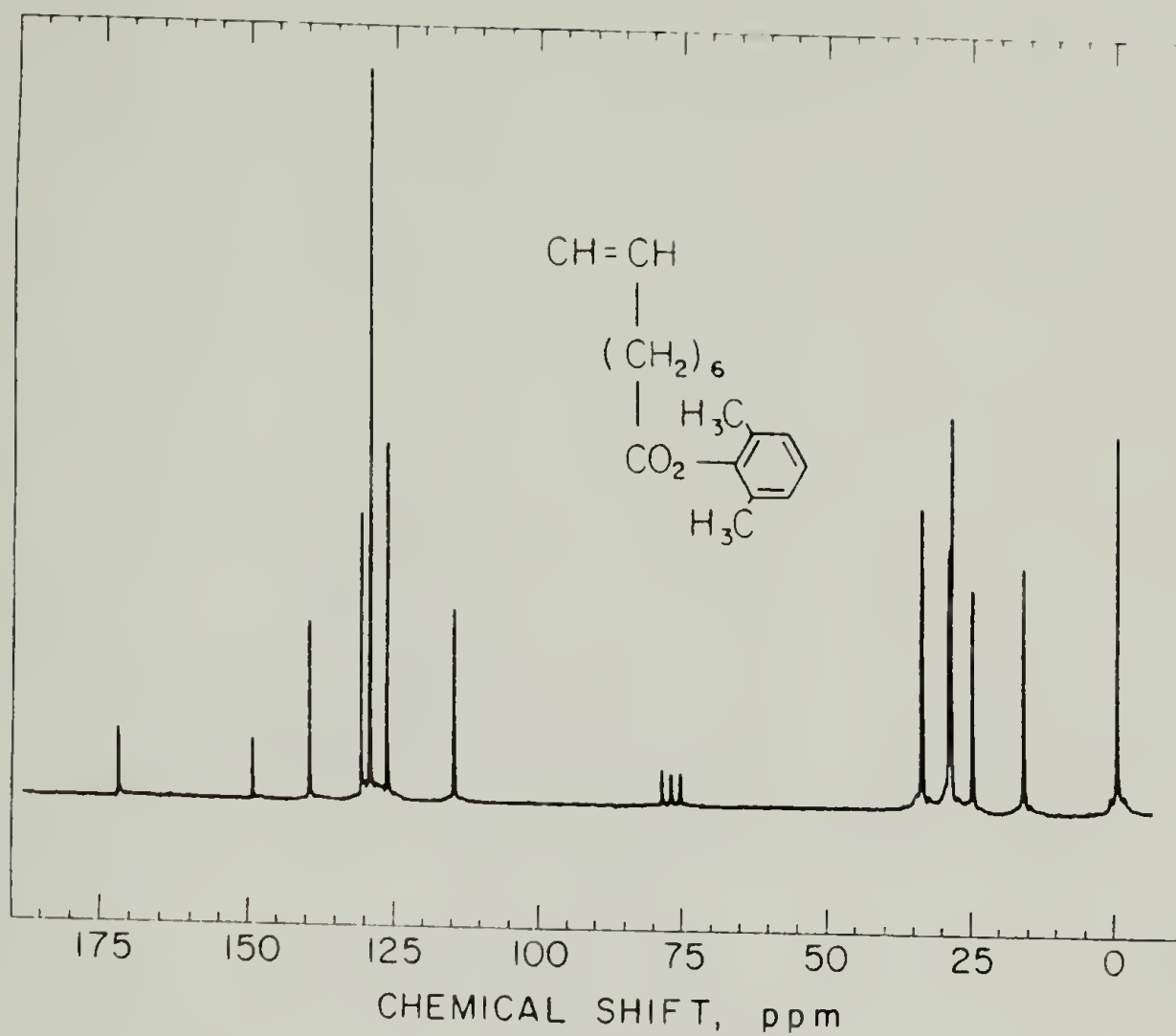


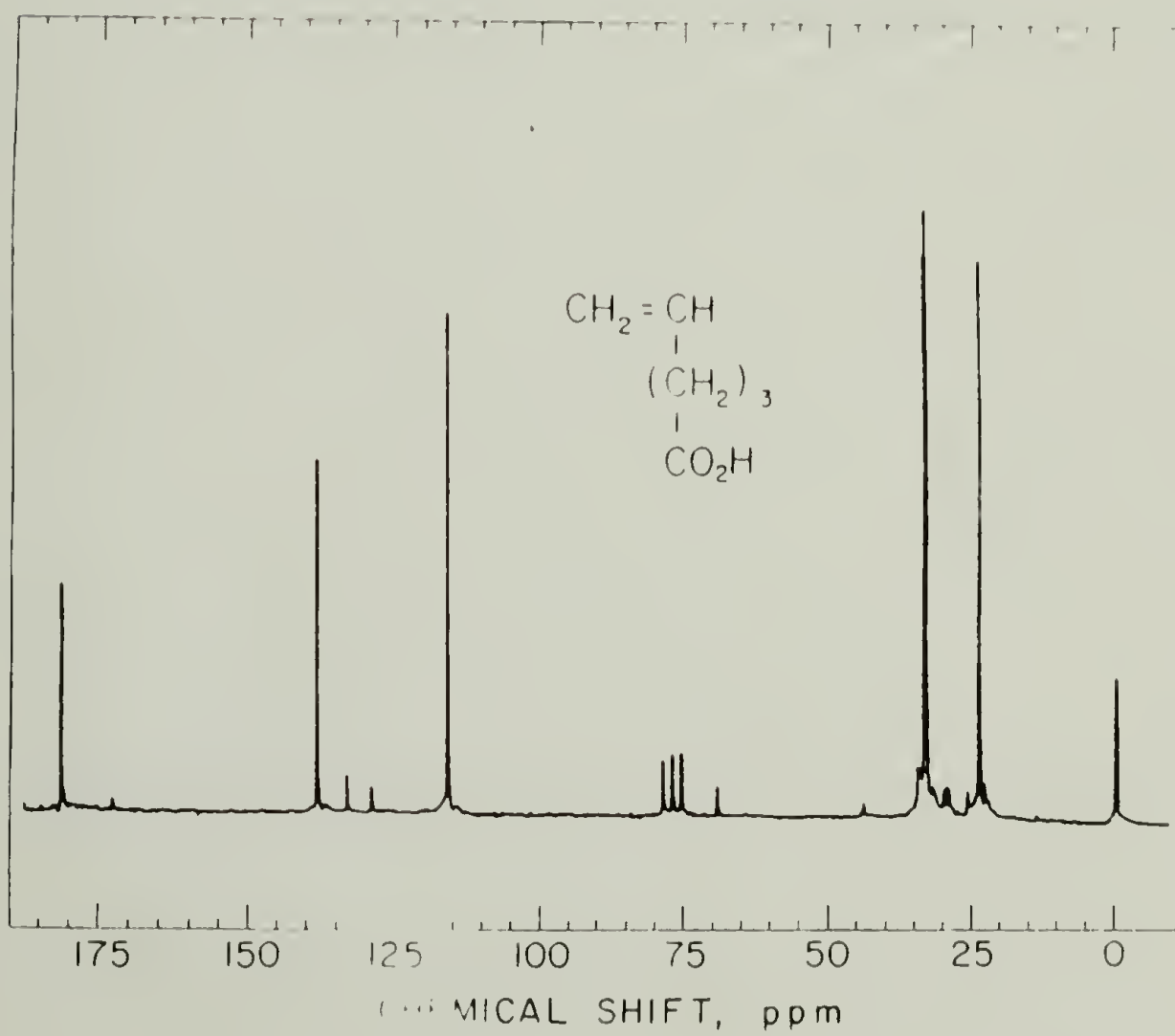
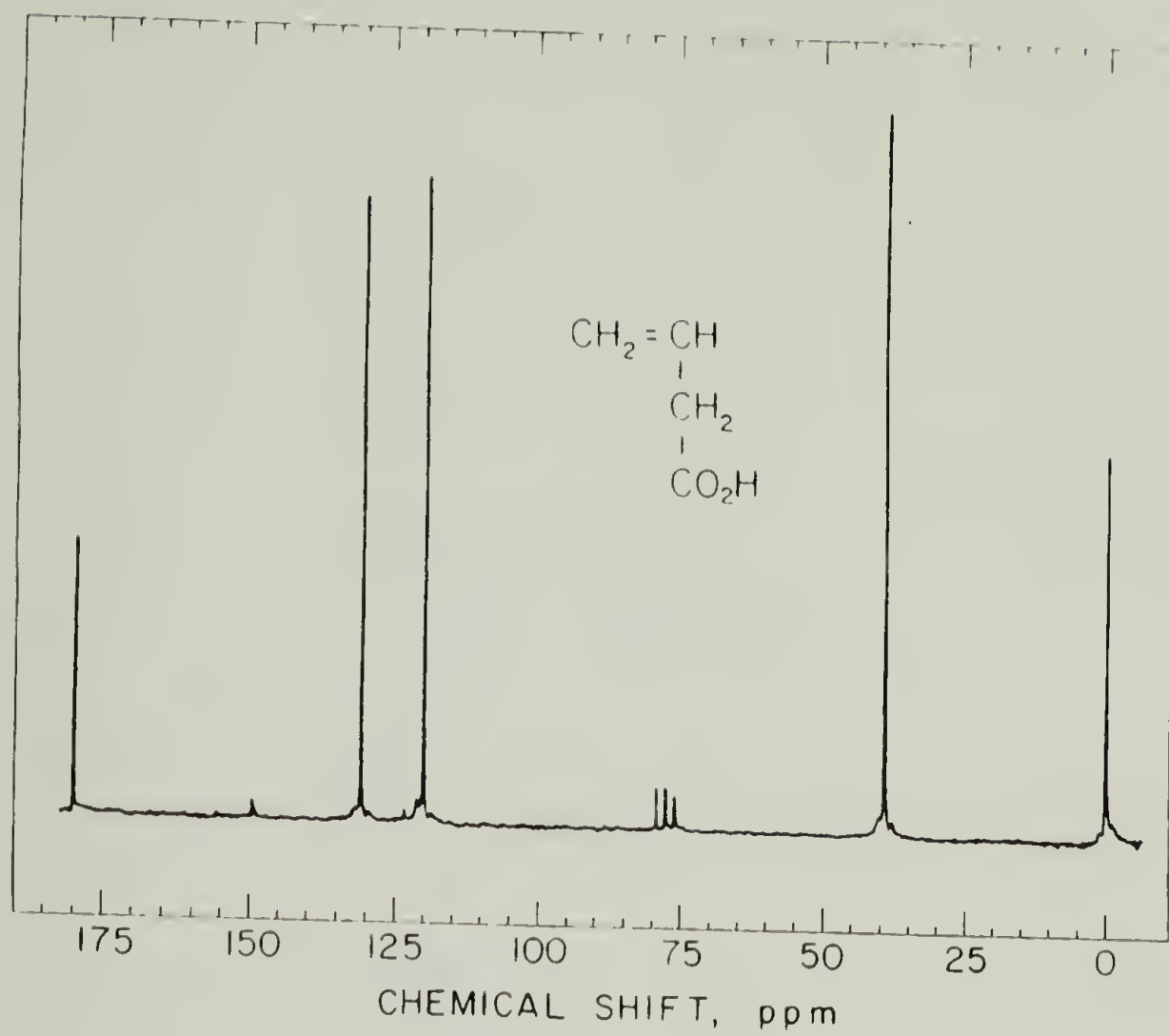


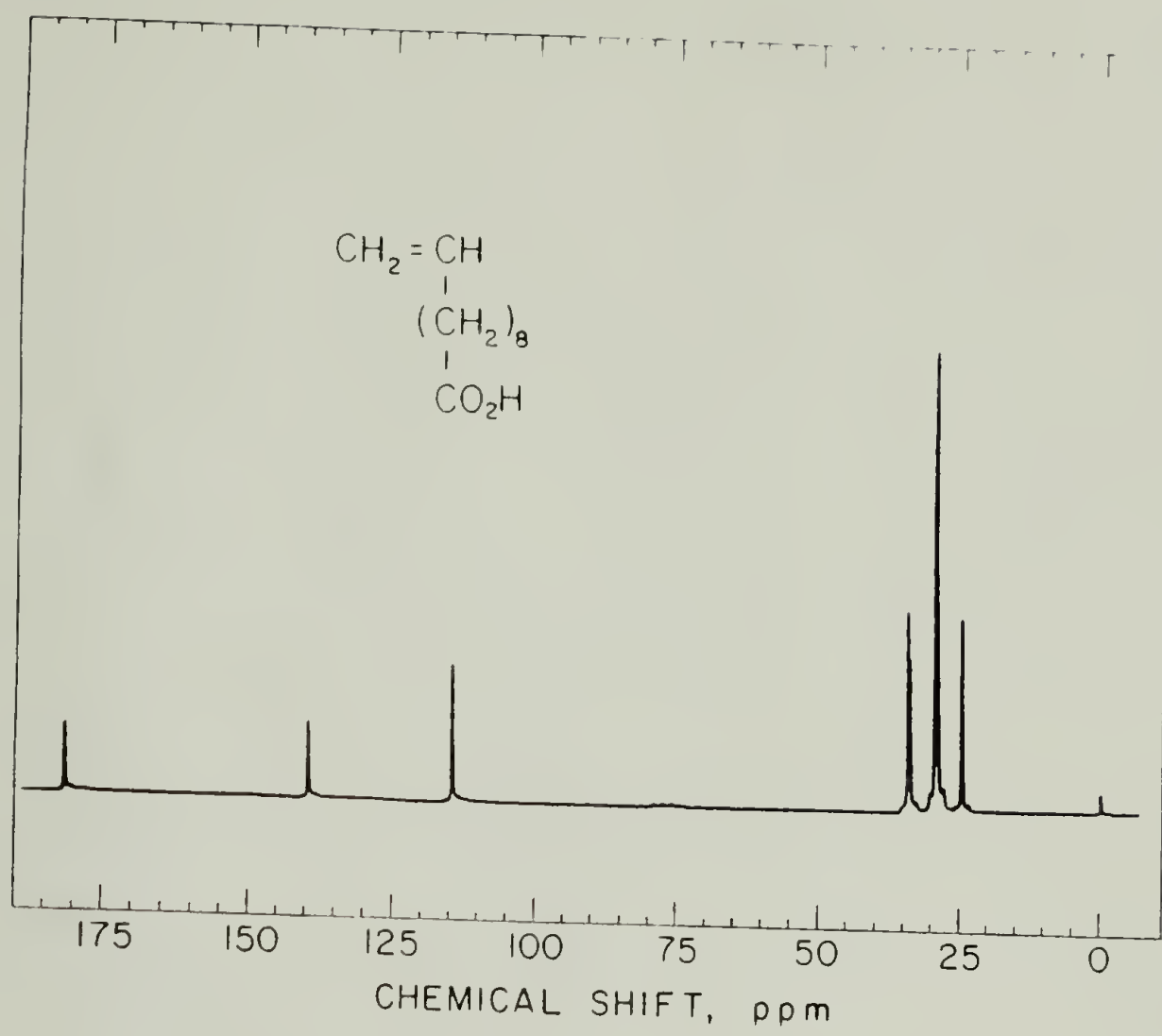






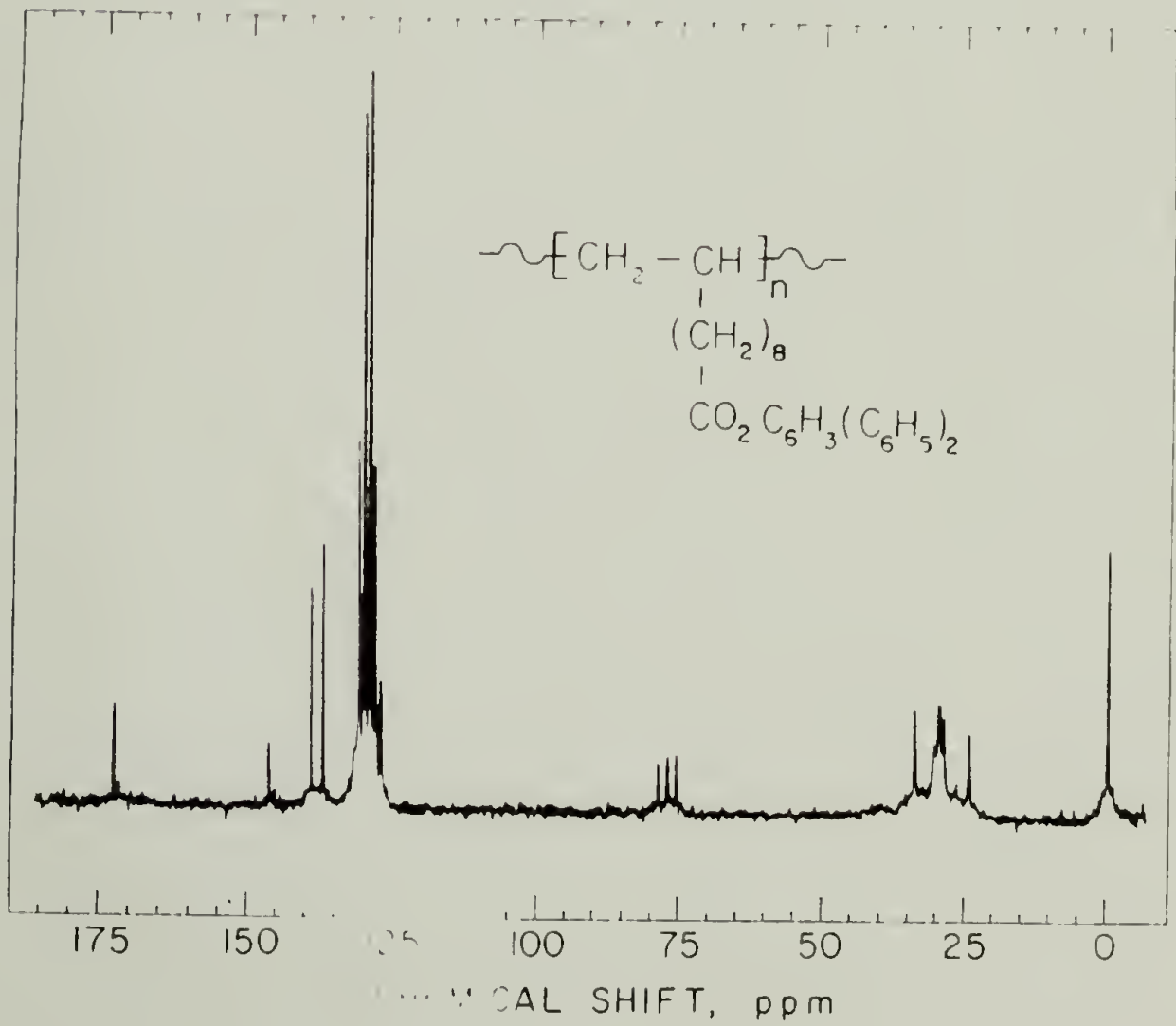
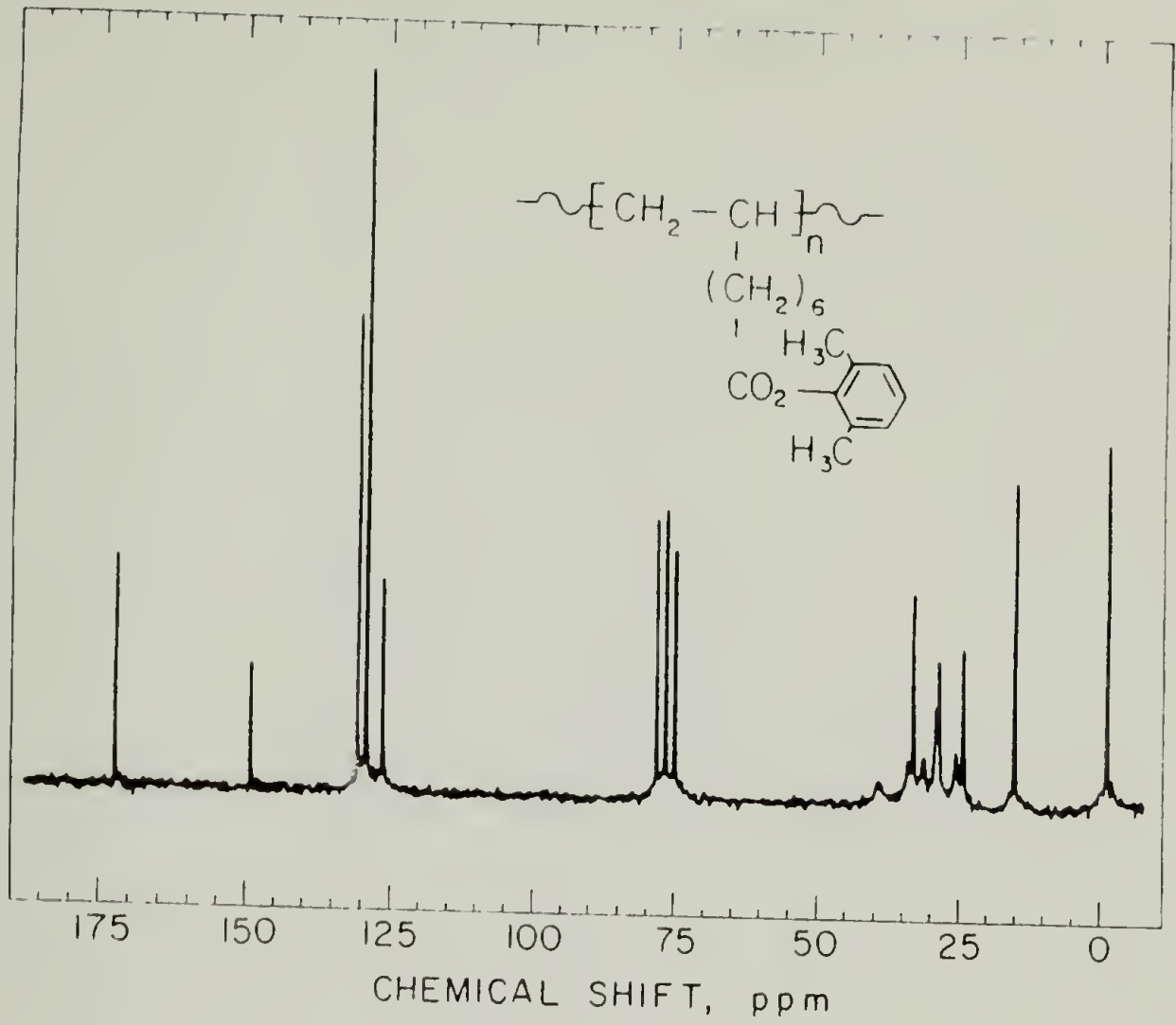


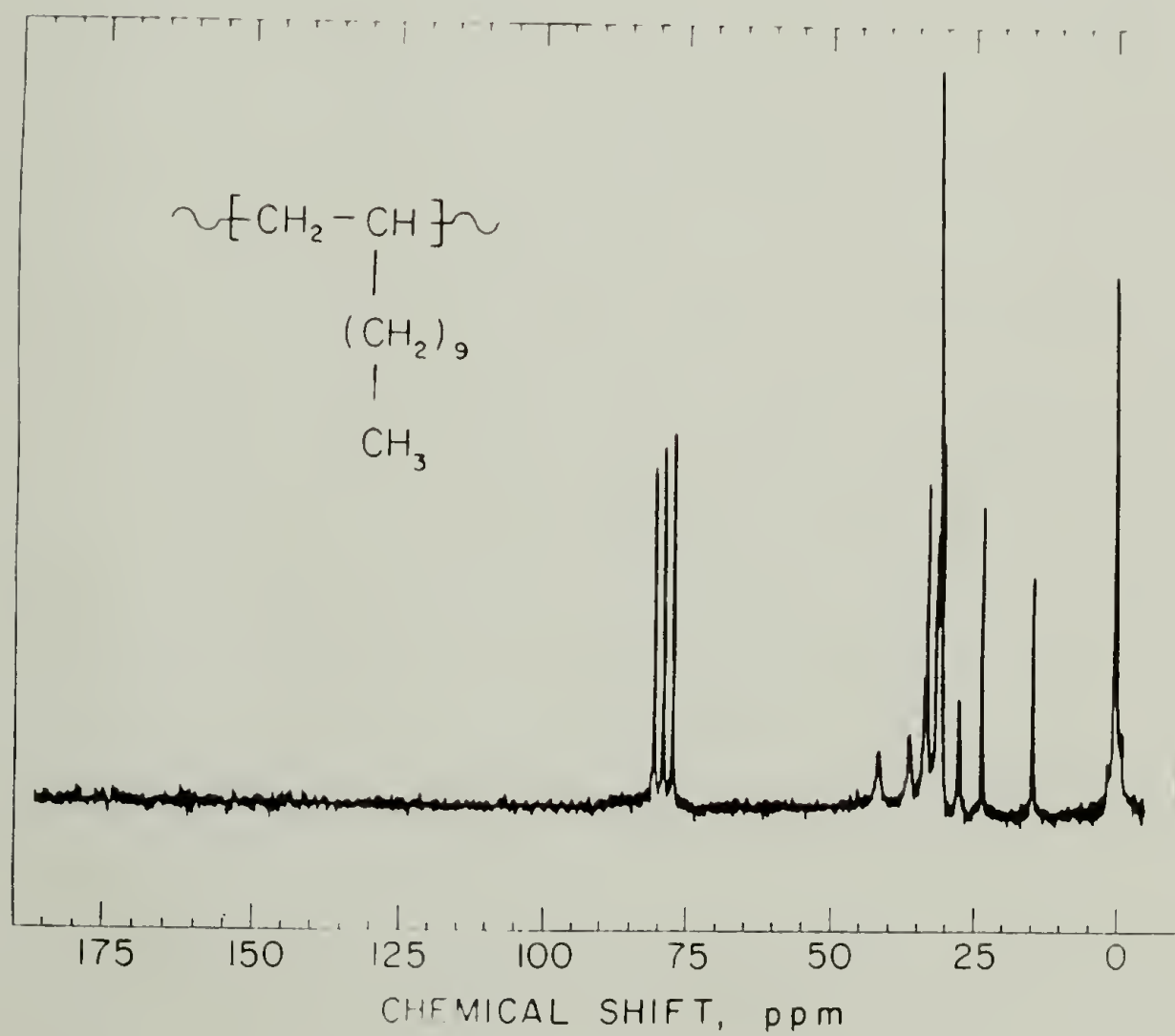
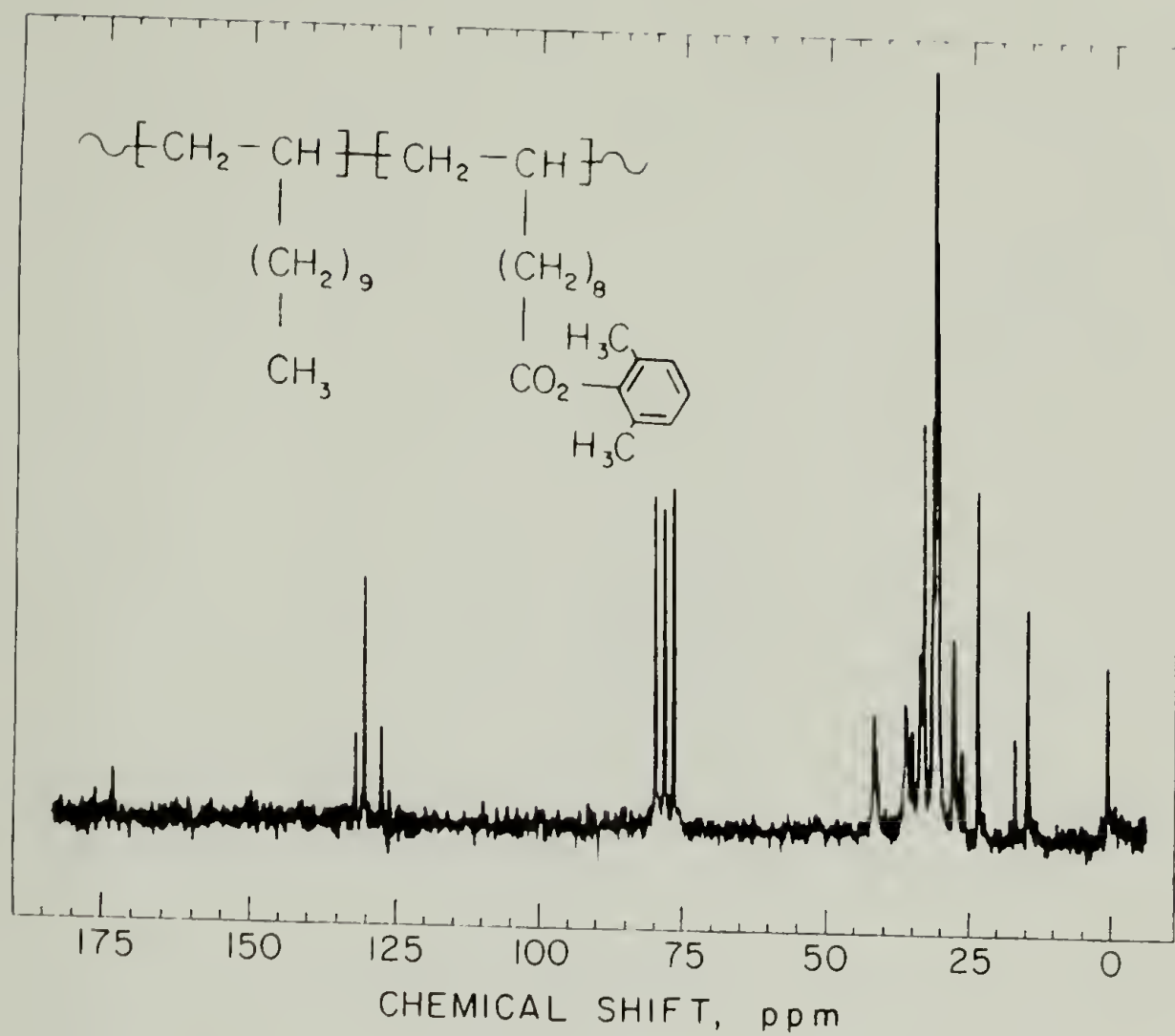


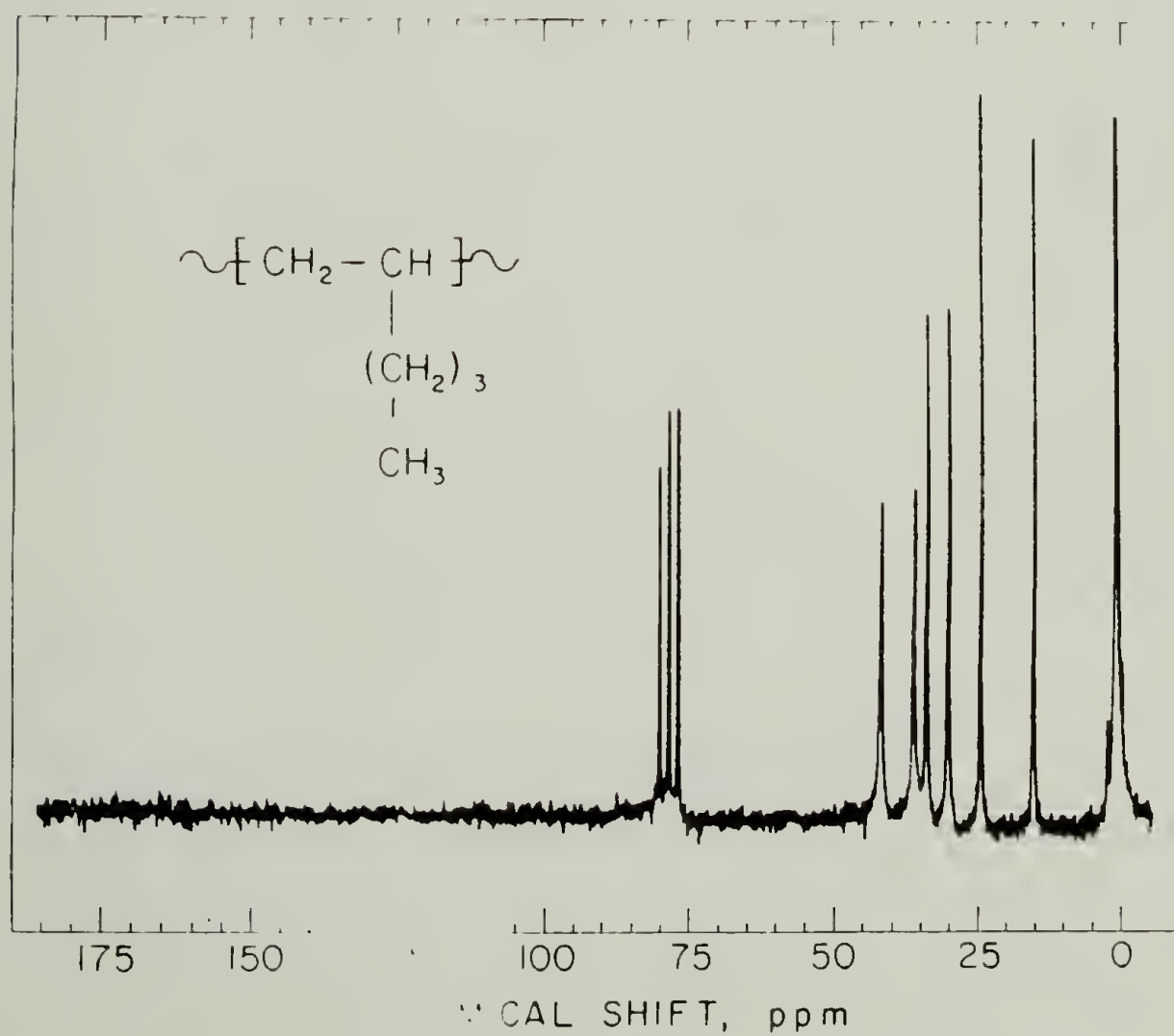
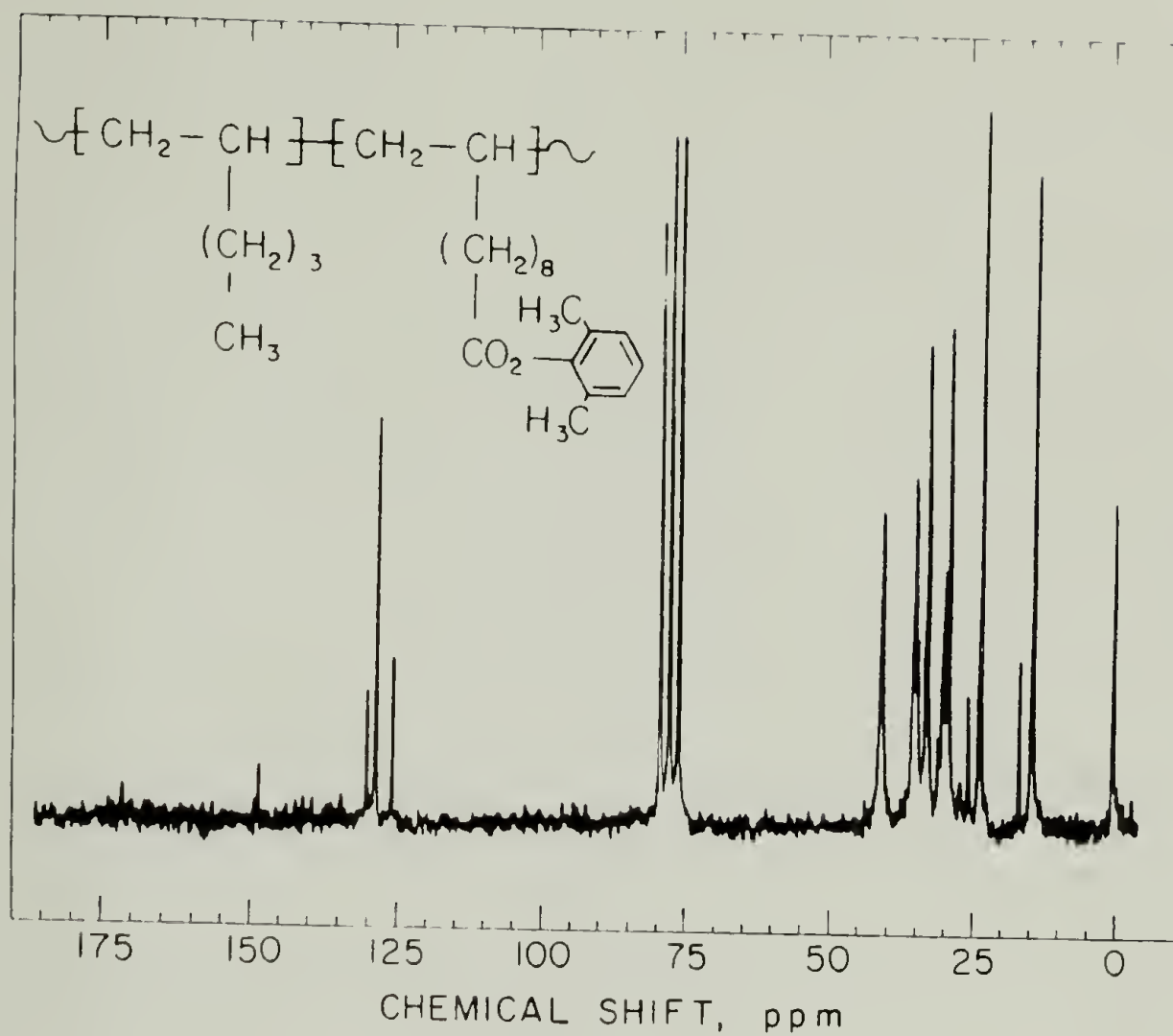


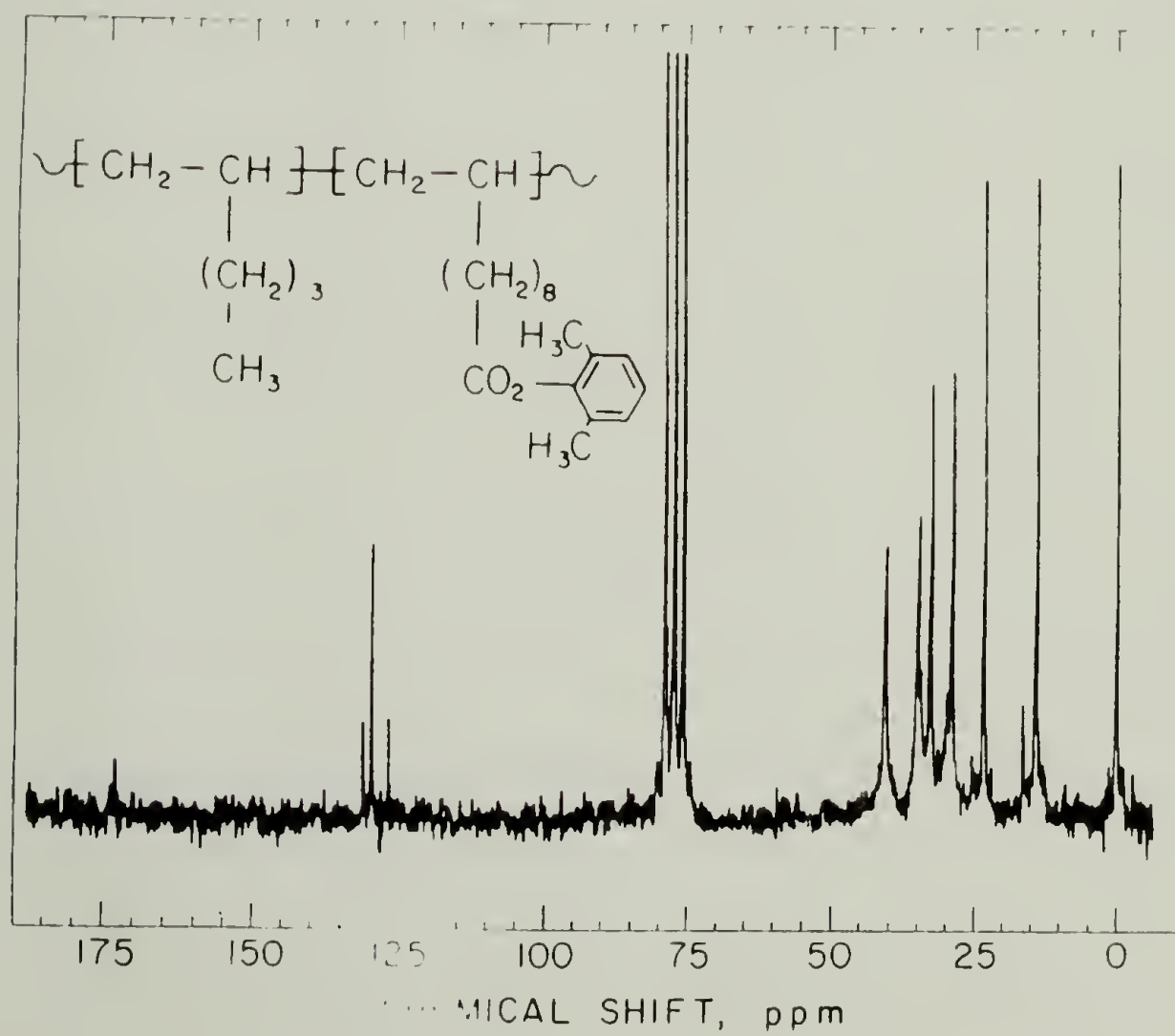
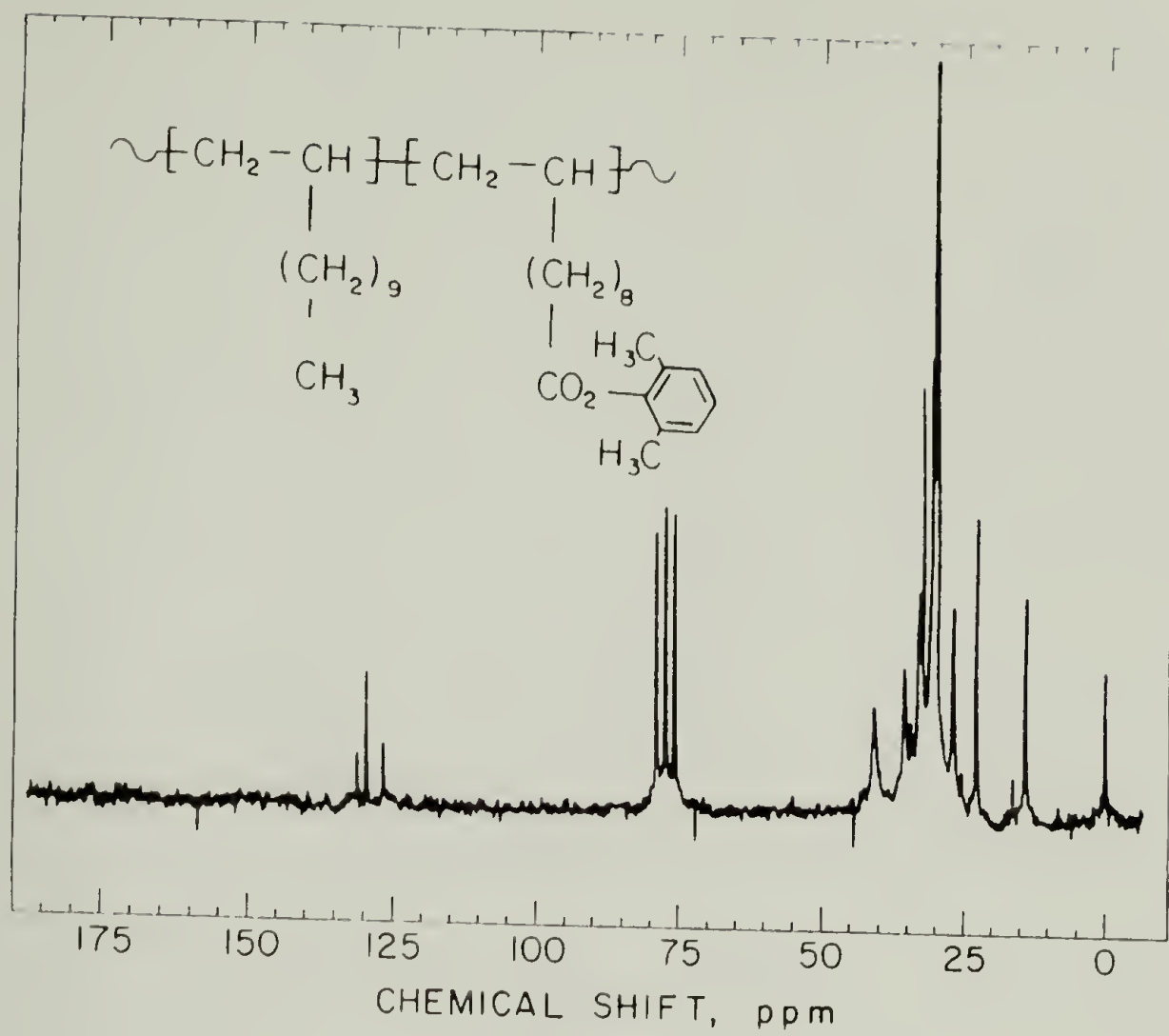




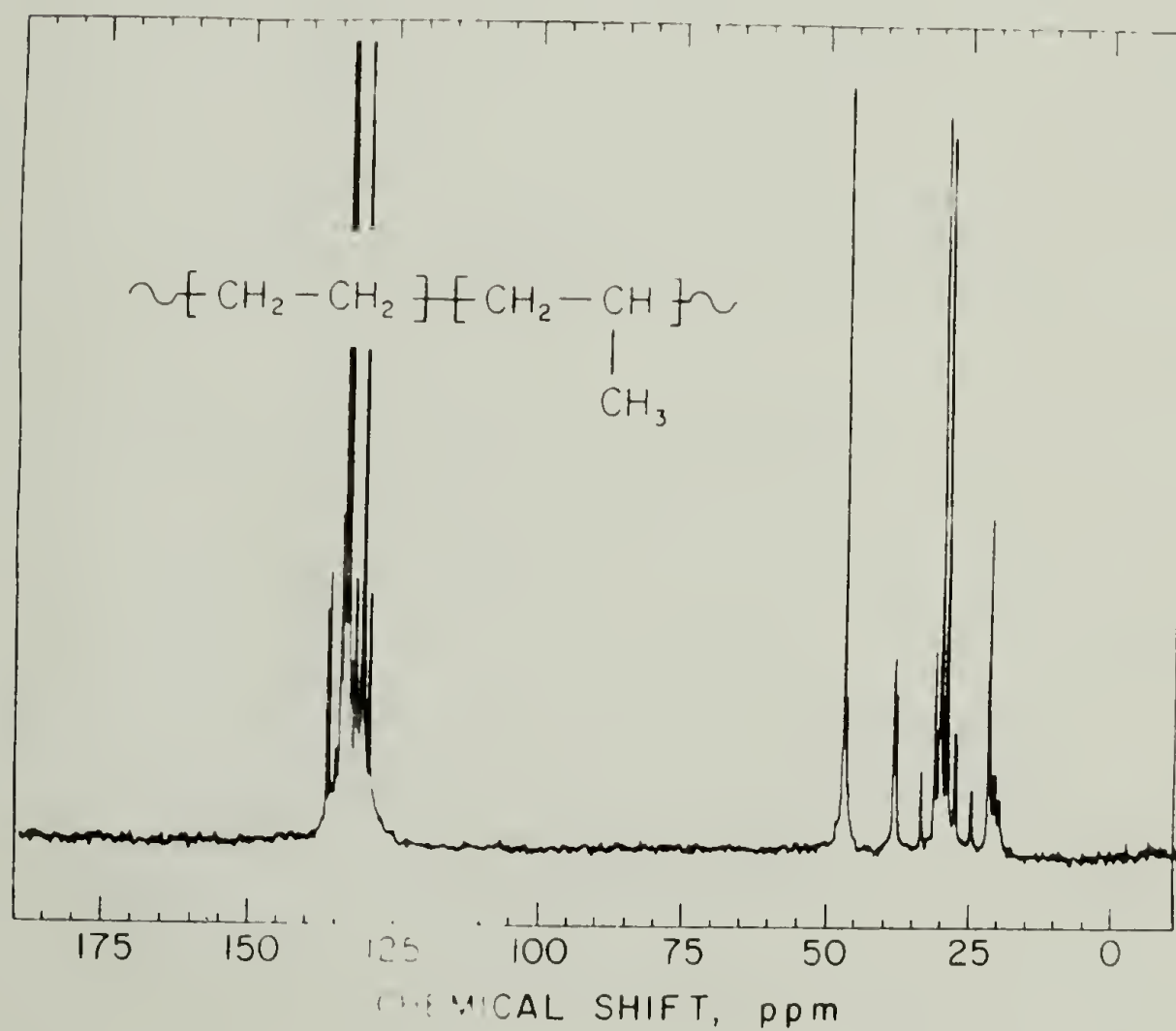
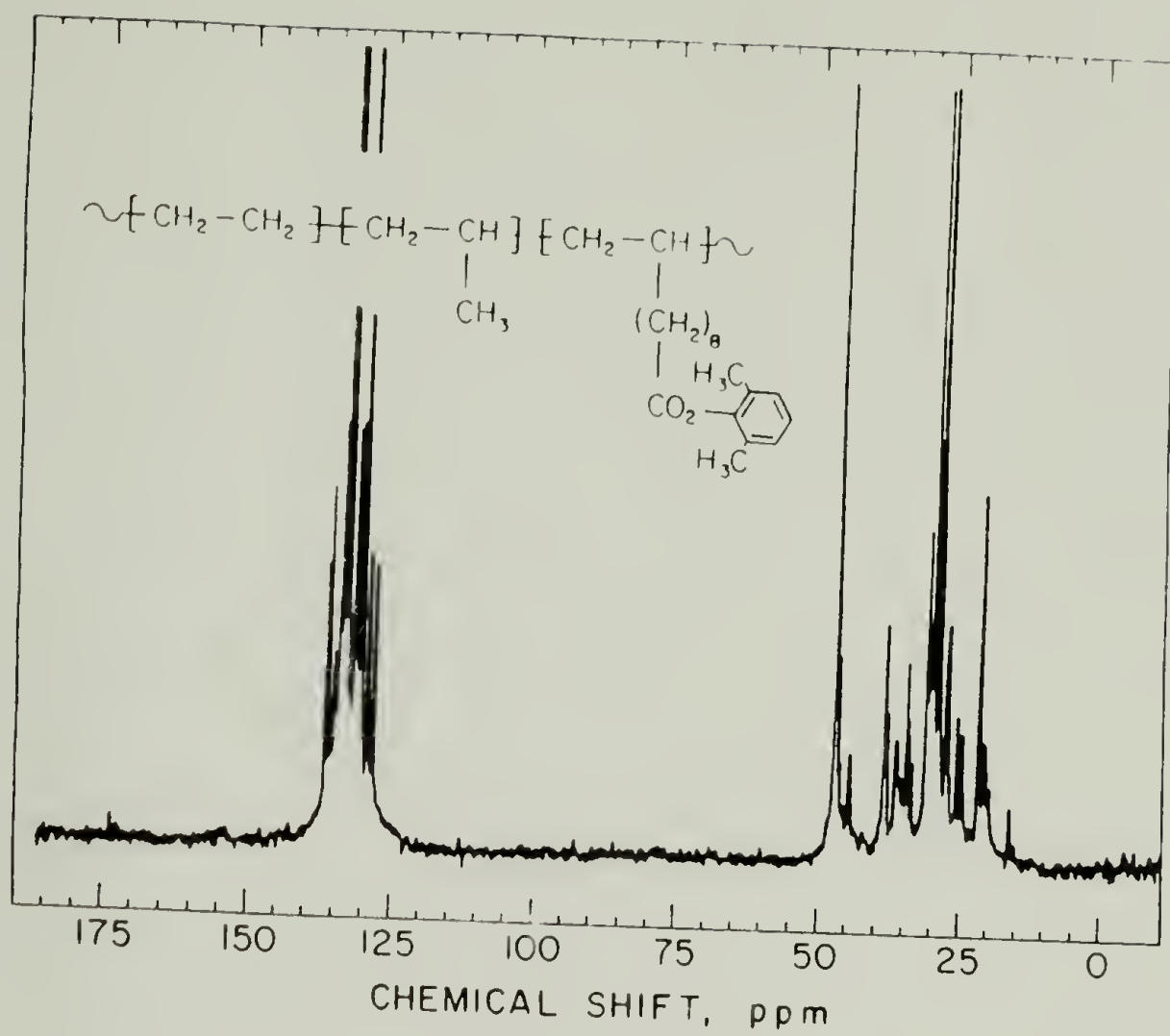


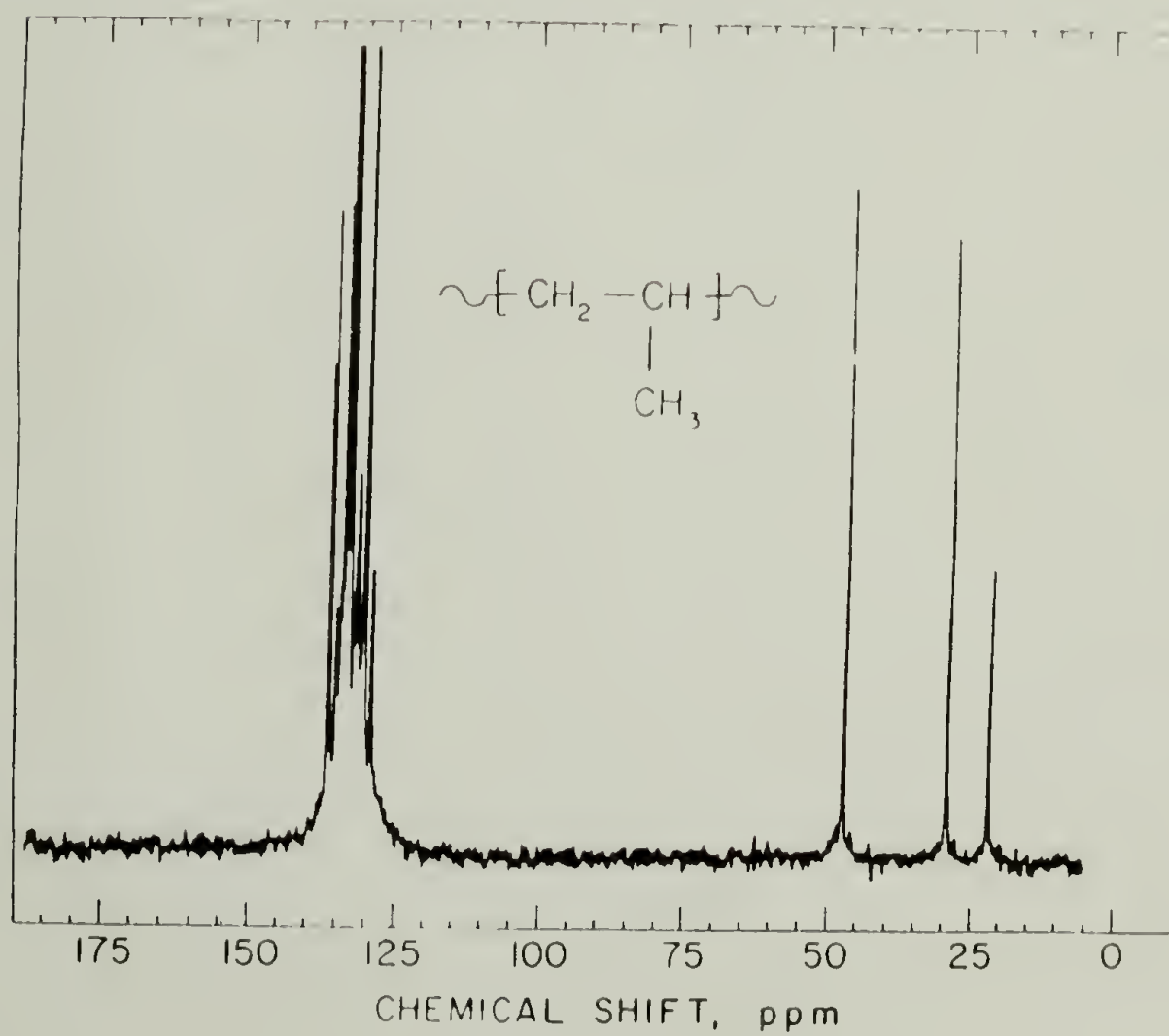
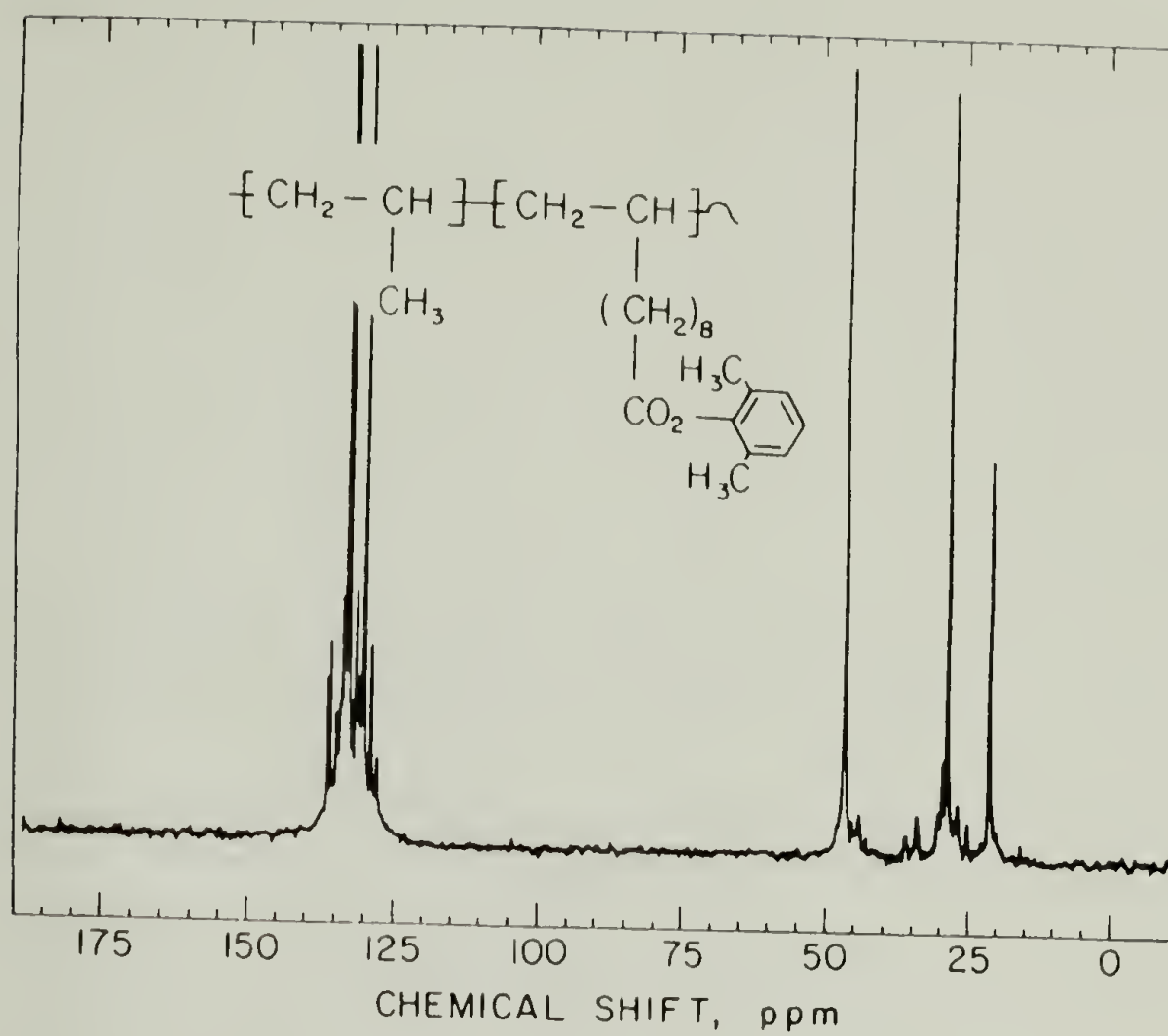


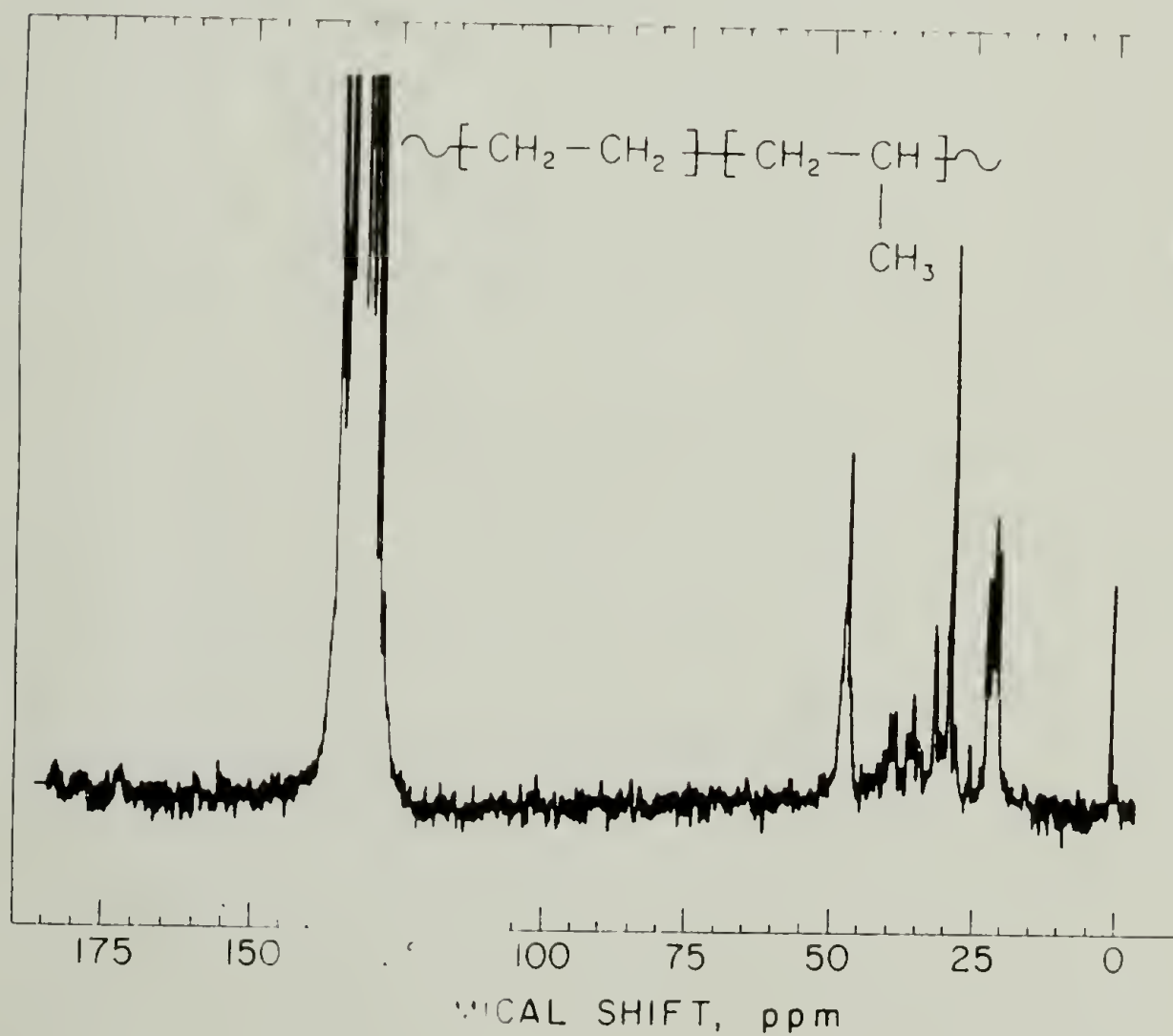
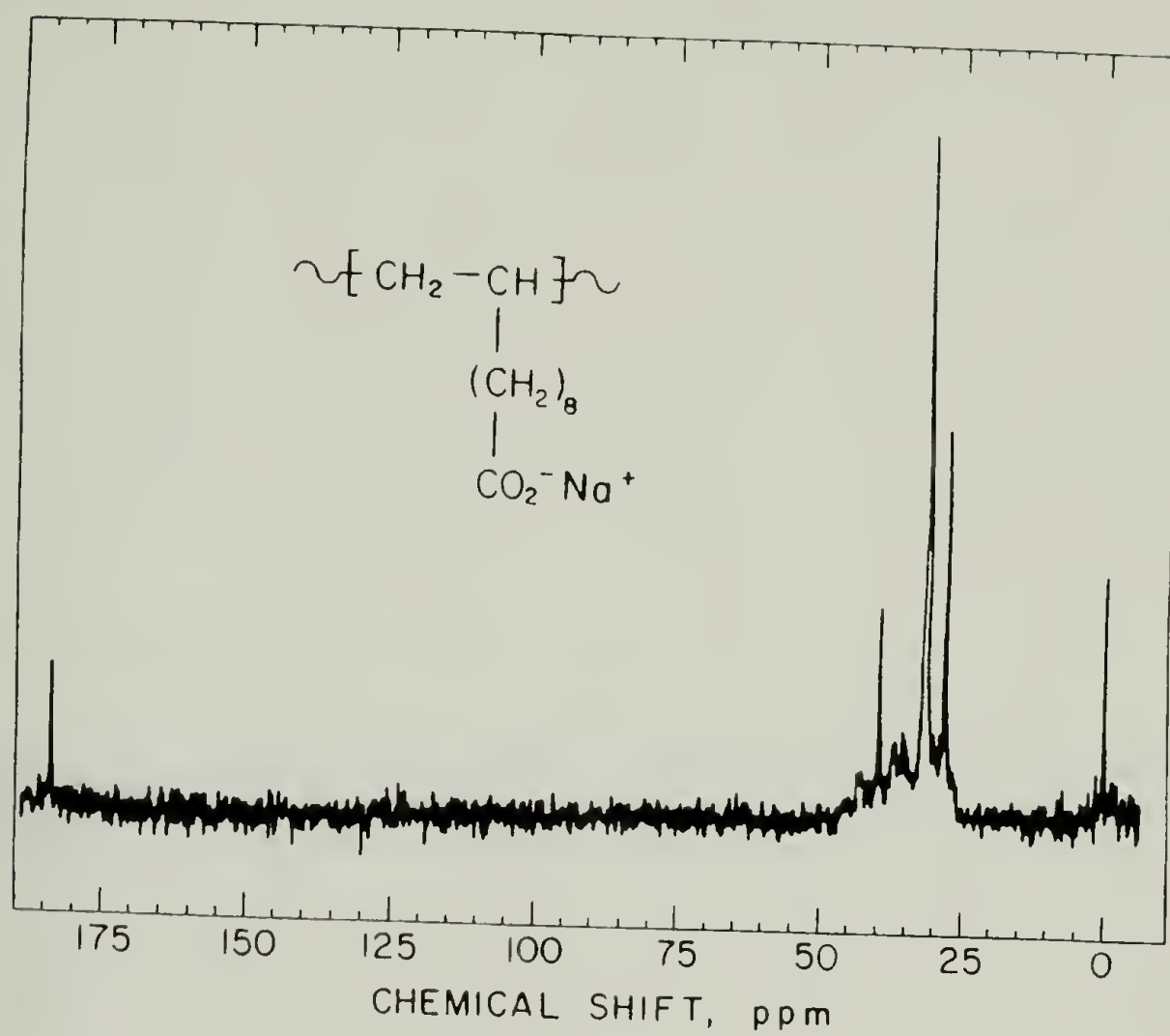




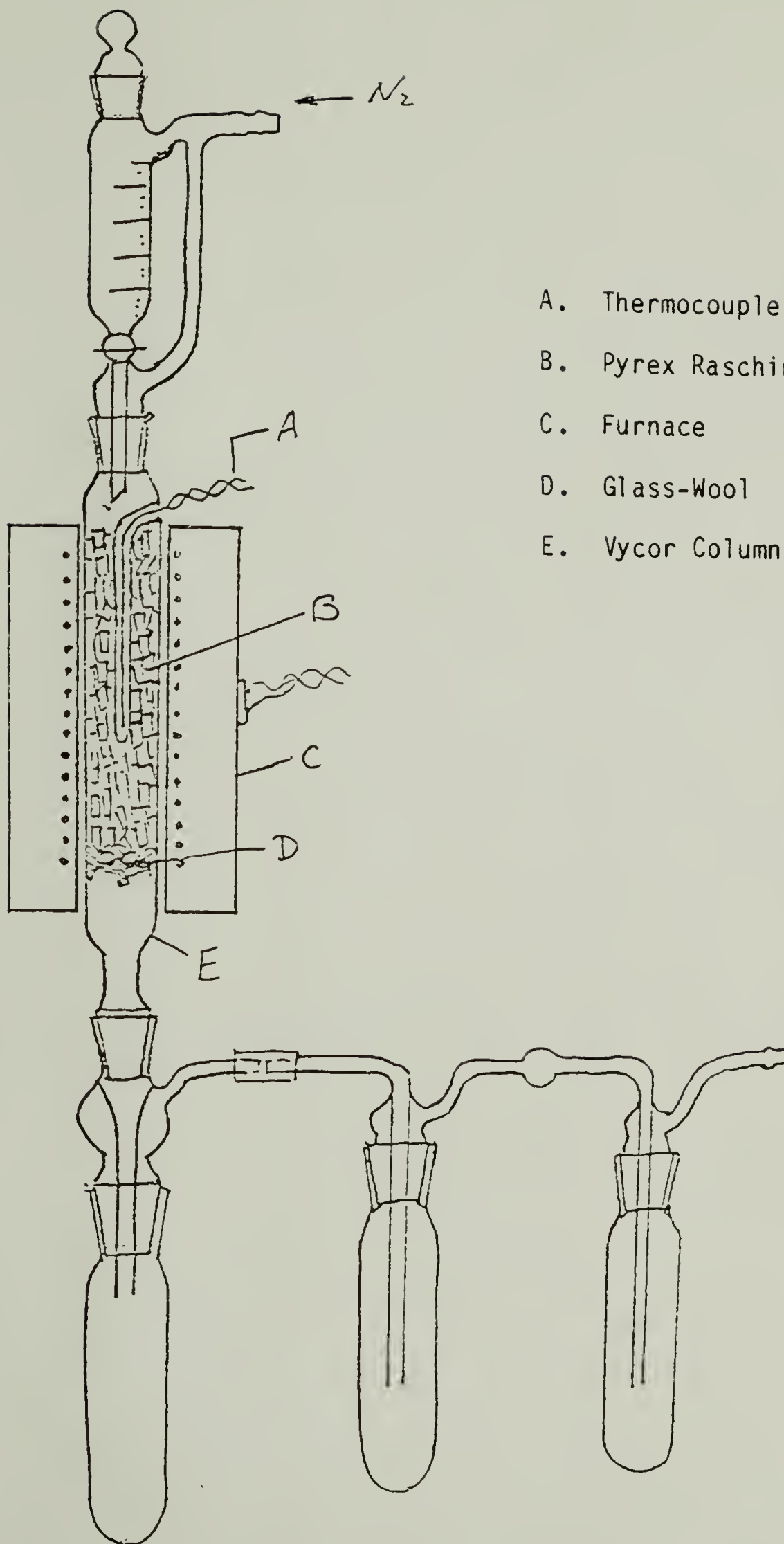








A P P E N D I X   D



- A. Thermocouple  $\frac{\text{chromel}}{\text{alumel}}$
- B. Pyrex Rasching Rings
- C. Furnace
- D. Glass-Wool
- E. Vycor Column





