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## Synthesis and characterization of homopolymers and copolymers of 2,6-Diarylphenols.

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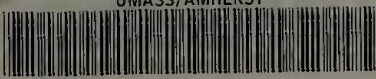
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SYNTHESIS AND CHARACTERIZATION OF  
HOMOPOLYMERS AND COPOLYMERS OF  
2,6-DIARYLPHENOLS

A Dissertation Presented

By

DAVID ERIC DANA

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

DOCTOR OF PHILOSOPHY

February 1981

Polymer Science and Engineering

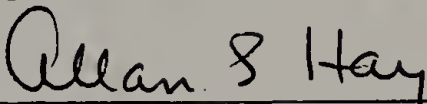
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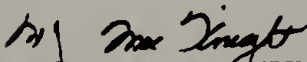
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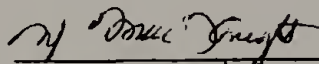
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Polymer Science and Engineering

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# ABSTRACT

## Synthesis and Characterization of Homopolymers and Copolymers of 2,6-Diarylphenols

(February 1981)

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M.S., University of Massachusetts

Ph.D., University of Massachusetts

Directed by: Dr. Allan S. Hay

A new synthetic route to symmetrical 2,6-diarylphenols (1) has been developed. This route has, as its key step, a phase transfer catalyzed double nucleophilic displacement reaction of 1,3-dibromopropane by a 1,3-diarylpropanone leading to a 2,6-diarylcyclohexanone. The latter compound is then converted to 1 by catalytic dehydrogenation. Phenols prepared in this way were 2,6-bis(p-tolyl)phenol (1a), 2,6-bis(p-methoxyphenyl)phenol (1b) and 2,6-bis(p-biphenylyl)phenol (1c). All intermediates and products were characterized by elemental analysis, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.

These phenols were then polymerized oxidatively to give the corresponding polyoxyphenylenes which were characterized by IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.

Molecular weights and molecular weight distributions were derived from gel permeation chromatography. Glass transition temperatures, crystallization temperatures and crystalline melting points were determined by differential scanning calorimetry. Thermal stability was monitored by thermal gravimetric analysis. The desired goal of a high molecular weight soluble polymer which crystallizes thermally but which has a lower crystalline melting point than poly(oxy-2,6-diphenyl-1,4-phenylene) (PDPP) (480°C) was achieved with poly[oxy-2,6-bis(p-tolyl)-1,4-phenylene] (PDTP), which melted at 321°C. The homopolymer from 1b (PDAP) could not be prepared with high molecular weight due to extensive crystallization and insolubilization during polymerization. Attempted polymerization of 1c produced only dimer.

The three monomers were each copolymerized randomly with 2,6-diphenylphenol. All copolymers were completely amorphous as determined by differential scanning calorimetry.

The blending behavior of PDTP and PDAP with PDPP was investigated by differential scanning calorimetry. Both blends produced clear films. In each case, however, the homopolymers crystallized and melted independently.



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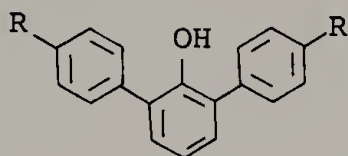
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# CHAPTER I

## INTRODUCTION AND HISTORICAL

One of the principal objectives of this thesis is the preparation of symmetrical 2,6-diarylphenols (1)



I

for use as monomers in the synthesis of polyphenylene oxides. The parent monomer, 2,6-diphenylphenol, has been synthesized by a variety of methods, most of which are not amenable to the synthesis of other symmetrical 2,6-diarylphenols. These syntheses fall into two general categories: Method A where the reactants which ultimately form the 2,6-diarylphenol are all aromatic or partially soluble precursors of aromatic rings and Method B which is characterized by a ring forming reaction to generate the central phenolic moiety.

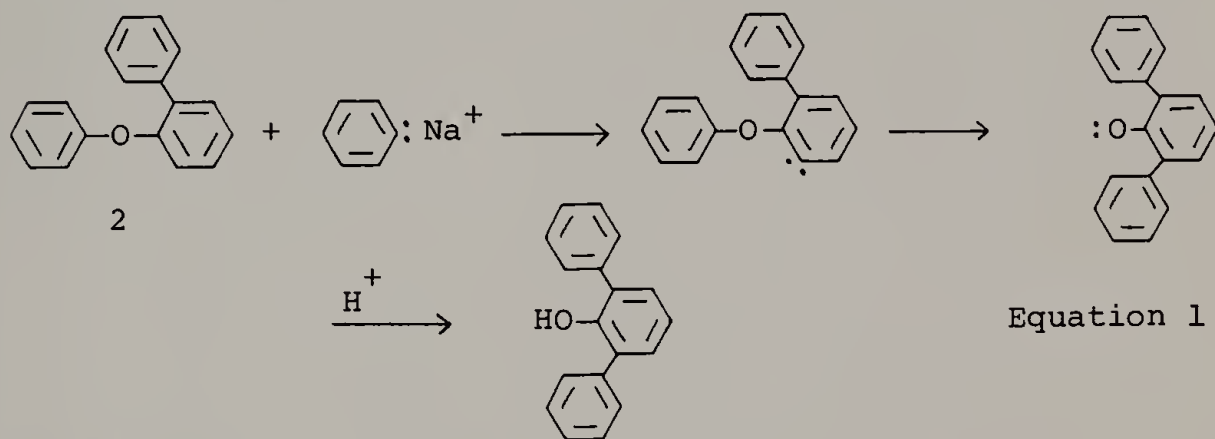
When applied to the synthesis of symmetrical diarylphenols, Method A would be expected to give a mixture of products involving substitution in any or all of positions 2, 4, 6 of the central ring. In addition the required precursors for this method are not generally available. In contrast Method B requires starting materials which are



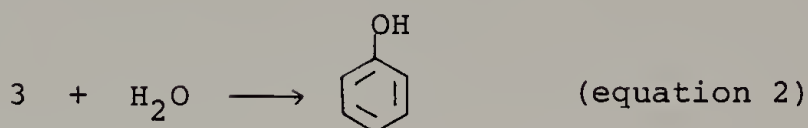
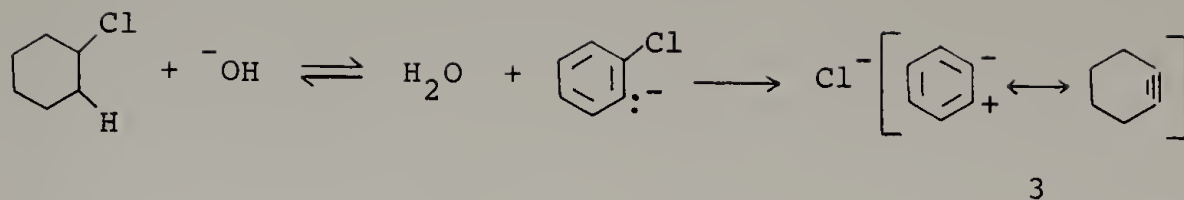
commercially available and which generate intermediates by a variety of straightforward routes. The disadvantage of the latter method is the competition of non ringforming reactions with the desired cyclization. The established kinetic and thermodynamic favorability of six membered ring formation diminishes the importance of this shortcoming and makes Method B the method of choice. This will become apparent through consideration of examples of both systems.

#### Method A

2,6-Diphenylphenol (DPP) is prepared by treatment of 2-phenoxybiphenyl(2) with phenyl sodium (equation 1).<sup>1</sup>

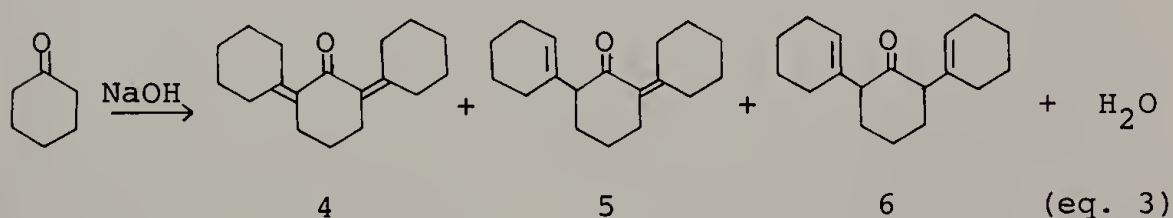


The synthesis of 2 involves reaction of phenyl sodium with diphenyl ether and in the process minor amounts of DPP are also generated.<sup>1</sup> Another closely related source of DPP is as a byproduct in a commercial synthesis of phenol from the treatment of chlorobenzene with aqueous alkali at elevated temperatures (equation 2).<sup>2</sup>



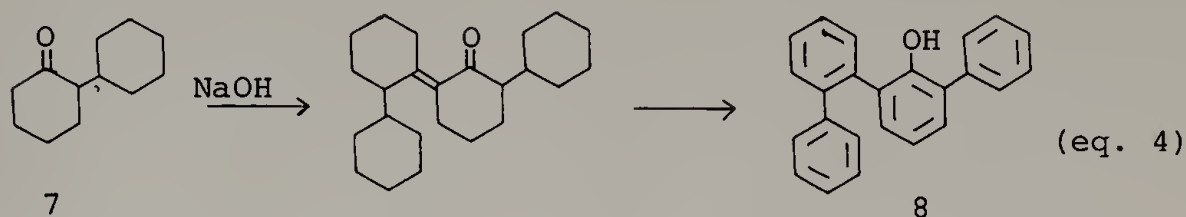
Once again, DPP is a minor product under these conditions. However, even if the efficiency of these reactions were vastly improved, they could not be used in the synthesis of 1 as para substitution in the central phenol could not be avoided.

Another method used for the preparation of 2,6-diphenylphenol was originally reported by Plesek<sup>3</sup> and is now its principal commercial source.<sup>4</sup> Cyclohexanone is self condensed in the presence of sodium hydroxide to produce trimers of structures 4, 5, and 6 (equation 3).

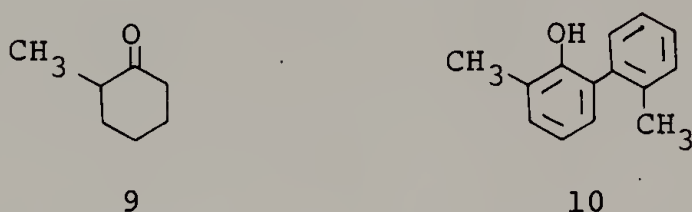


These are then dehydrogenated to the phenol. Self condensation of the dimer, 2-cyclohexylcyclohexane (7) under the same

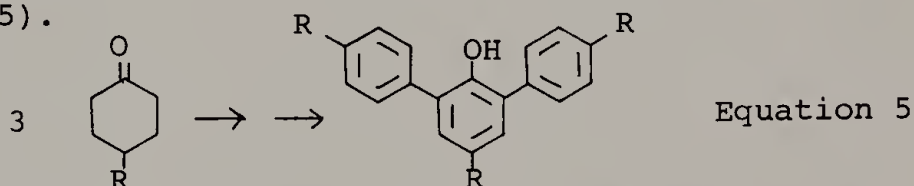
conditions gave a low yield of 2-(2-biphenylyl)-6-phenylphenol (8)<sup>5</sup> (equation 4).



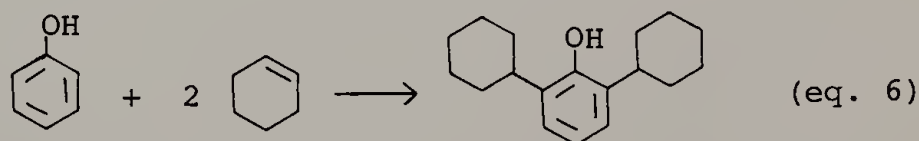
Also prepared in this way was 2-methyl-6-o-tolylphenol (10) from 2-methylcyclohexanone (9).



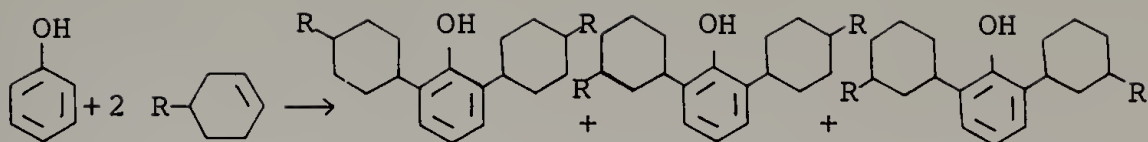
As in the previous instance, this reaction would not be applicable toward the generation of symmetrical 2,6-diarylphenols because it would produce a trisubstituted product (equation 5).



Alkylation of phenol with cyclohexenes to yield cyclohexylphenols has been reported<sup>6</sup> (equation 6).



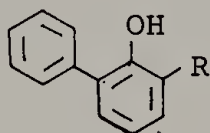
Utilizing substituted cyclohexenes (equation 7) a mixture of three isomers would be obtained.



(Equation 7)

Under acidic conditions, addition of cyclohexene to phenol produced primarily para substituted phenols. Utilizing  $\text{AlCl}_3$  in a Friedel-Craft alkylation, 56% of the ortho substituted product was formed with 20% para substituted and negligible diortho substitution.<sup>7</sup> 4-Methylcyclohexene would add only para to phenol when sulfuric acid was the catalyst at  $80^\circ\text{C}$ .<sup>8</sup>

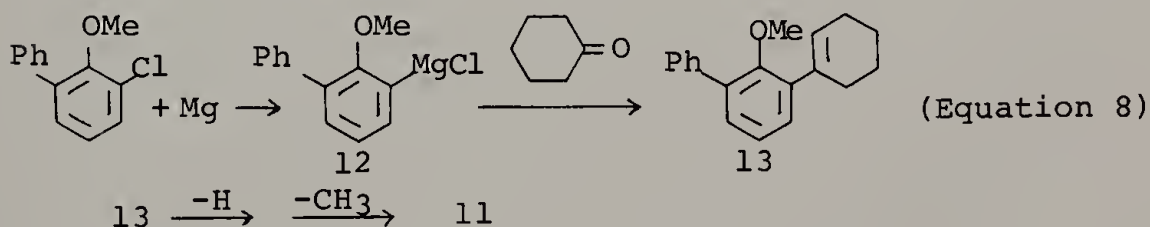
Hay and Clark<sup>5</sup> prepared unsymmetrical diaryl phenols of structure 11



11

R = m-tolyl,  
p-tolyl  
p-t-butylphenyl  
p-biphenyl  
3'-o-terphenyl  
x-naphthyl

by condensing the substituted cyclohexanone with the aryl-magnesium chloride (equation 8).



(Equation 8)

The anisole was used to avoid reaction with magnesium by the phenolic OH. This reaction could theoretically be extended to the synthesis of symmetrical 2,6-diaryl phenols by util-

izing 2,6-dichloroanisole as starting material in a "double barrelled" reaction. It does not appear to be an attractive route because of the low yields (9-25%) recorded for these syntheses.

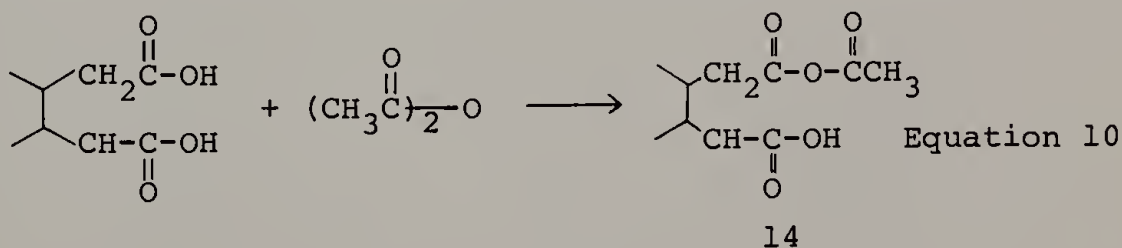
### Method B

A search of the literature has revealed several cyclization reactions which have the potential to generate precursors to 2,6-diarylphenols. All of these, with the exception of one, ultimately produce cyclic ketones which may be converted to phenols.

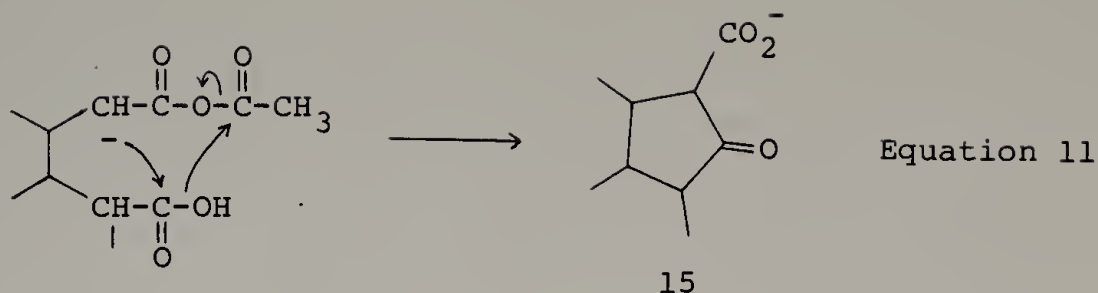
Various diacids when treated with anhydrides have been shown to form cyclic ketones as demonstrated by the example shown in equation 9.<sup>9</sup>



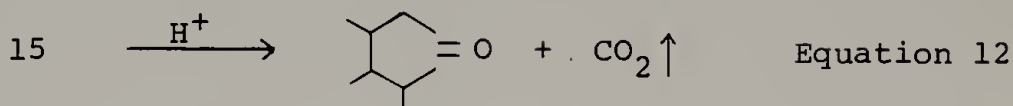
There is some question regarding the mechanism of this condensation, but most likely, there is initial formation of a mixed anhydride (14) by an acid anhydride exchange.<sup>10</sup>



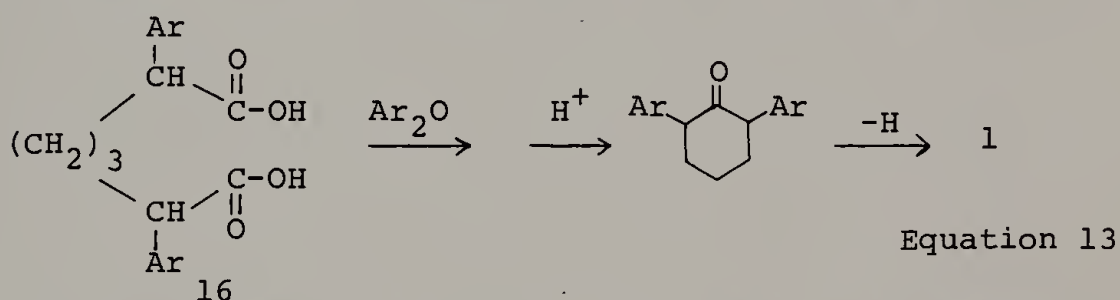
Loss of the  $\alpha$  proton may then occur triggering a ring forming attack by the anion on the acid carbonyl carbon as shown be-

low:<sup>11</sup>

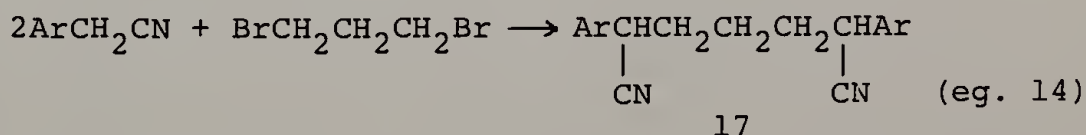
Decarboxylation then follows:



Although cyclopentanones have been synthesized in this manner, no reports of cyclohexanone syntheses by this route have been reported. The only clearly defined requirement for this reaction is the presence of at least one  $\alpha$ -hydrogen. Conceivably then, the desired cyclohexanone could be prepared from the corresponding 1,5-diarylpimelic acid (15).



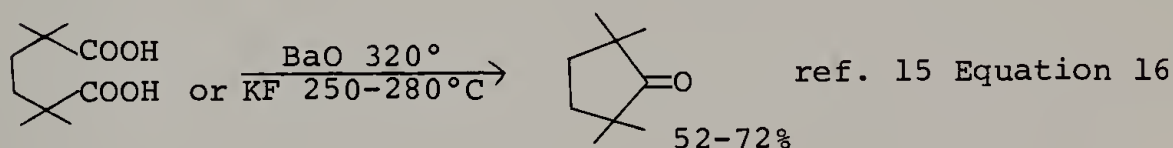
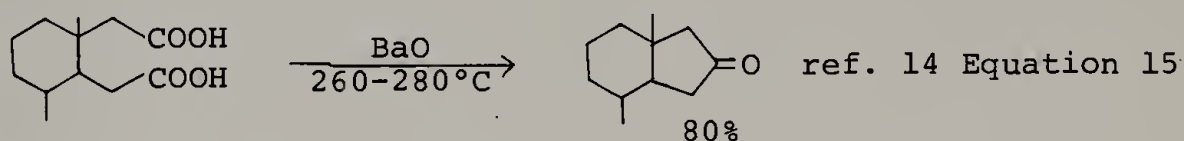
The precursor pimelic acids can be prepared most simply by the condensation of arylacetonitriles with 1,3-dibromopropane to form the pimelonitrile 17 (equation 14).



Masayuma et al<sup>12</sup> reported a yield of 96% for this reaction

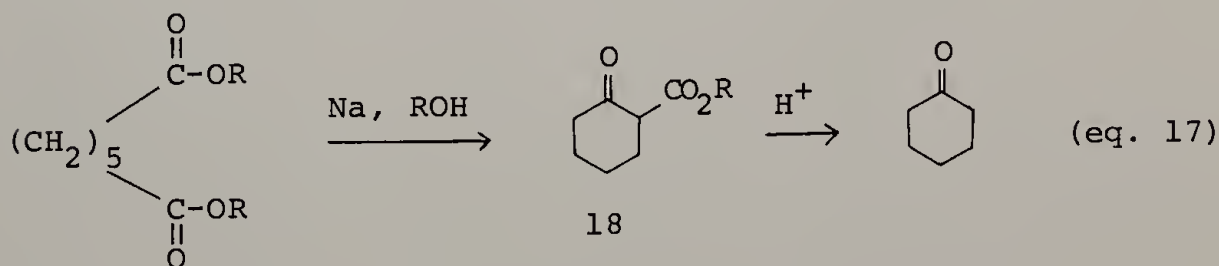
(Ar=C<sub>6</sub>H<sub>5</sub>) when performed under phase transfer conditions utilizing catalytic quantities of tetra-n-butylammonium iodide or triethylbenzylammonium chloride in benzene with 50% sodium hydroxide. This dinitrile can be easily hydrolyzed under acidic conditions to 16.<sup>13</sup>

Diacids have also been cyclized to ketones via pyrolysis reactions as indicated by the following examples:



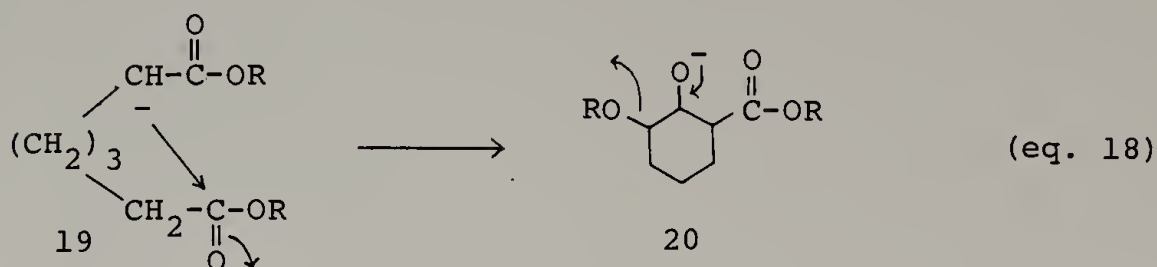
This reaction is also catalyzed by ThO<sub>2</sub>, when it is named the Ruzicka cyclization,<sup>16</sup> or by CdCO<sub>3</sub>.<sup>17</sup> A free radical mechanism has been suggested based upon analysis of side products.<sup>18</sup>

Perhaps the most thoroughly investigated route to cyclic ketones is the Dieckmann reaction. First reported in 1894 in a synthesis of cyclohexanone,<sup>19</sup> the reaction uses as its starting material, diesters, and is base catalyzed (equation 17)





The initial step of the reaction involves rapid and reversible formation of the enolate ion of the ester (19) which is then followed by the rate determining ring formation (equation 18).



Rapid decomposition of adduct 20 through loss of alkoxide leads to the  $\beta$ -keto ester 18. The reaction is catalyzed by a variety of bases. Alkoxides have been commonly used as bases but other bases such as sodium amide, sodium hydroxide or potassium hydroxide have been found to be preferable in many instances.<sup>20</sup> The reaction has found most of its use in the synthesis of five and six membered rings with larger rings requiring high dilution conditions. Many examples of this reaction have been reported in the literature and the reaction has been extensively reviewed.<sup>20</sup>

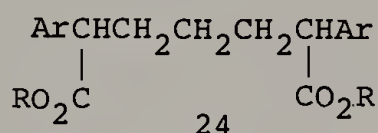
The decarboxylation reaction which necessarily follows the Dieckmann reaction to transform the  $\beta$ -keto ester to the ketone is most commonly effected by refluxing in the presence of sulfuric or hydrochloric acid. An alternative way recently reported by Krapcho et al<sup>21</sup> simply utilizes dimethylsulfoxide and water at reflux. An 87% yield of decarboxylation to cyclohexanone from 2-carbalkoxycyclohexanone



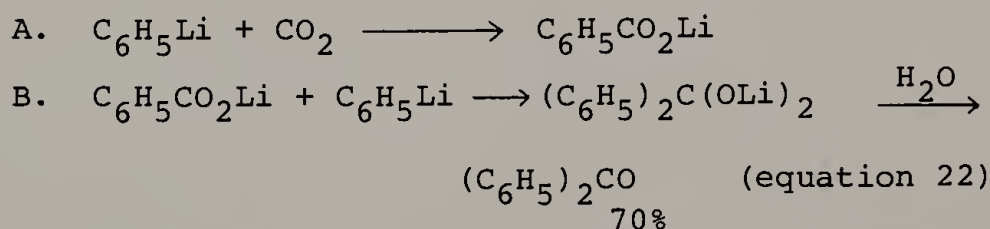


Generally better yields have been reported for the ring forming step.

No examples of 2,6-diarylcyclohexanones prepared via Dieckmann or Thorpe reactions have thus far been reported. However, it does appear to be an attractive route. For the Thorpe reaction, this would require 1,5-diarylpimelonitriles, the synthesis of which was described previously.<sup>12</sup> Acid catalyzed esterification of the dinitriles would produce the diester 24 which alternately could be used in the Dieckmann reaction.<sup>24</sup>

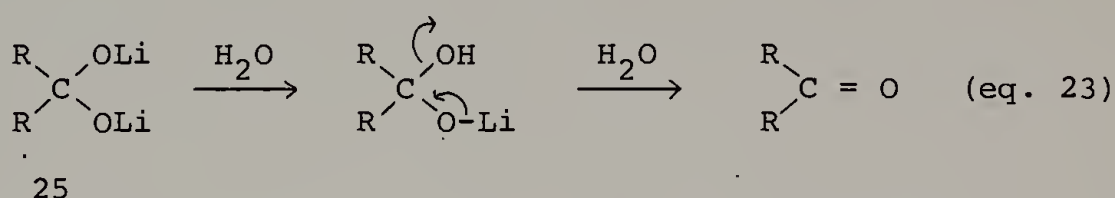


One established route to ketones, though rarely used for cyclic ketones, is worth mentioning as a potential source of phenol precursors. This is the reaction of organolithium compounds with carboxylic acids or carbon dioxide. The scope of this reaction has been reviewed by Jorgenson.<sup>25</sup> The reaction was first reported by Gilman and van Ess as a preparation of benzophenone<sup>26</sup> (equation 22).

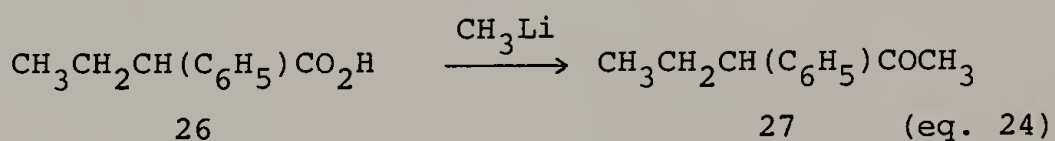


As illustrated above, the reaction takes place in two distinct steps. Step A is the insertion of CO<sub>2</sub> leading to the

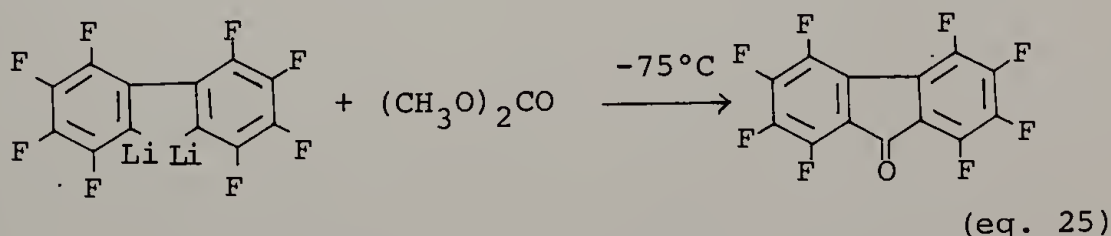
lithium salt of the carboxylic acid. Step B is the rate determining step, the nucleophilic attack by the organolithium reagent on the carbonyl carbon of the lithium carboxylate. This would translate to the ring forming step. The prominent feature that allows the formation of ketones from carboxylic acids is the stability of the intermediate dilithium compound 25 first detected by Bluhn et al.<sup>27</sup>



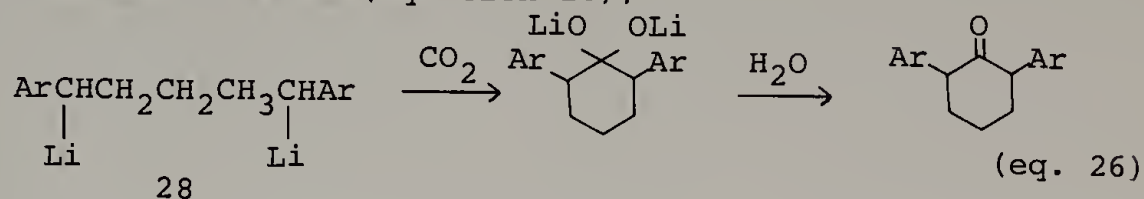
The hydrolysis then occurs rapidly as depicted in equation 23. Although benzophenone was the first reported compound prepared this way, the reaction has been used primarily to prepare aliphatic ketones. The reaction of 26 with methyllithium produced ketone 27 in 83% yield (equation 24).<sup>28</sup>



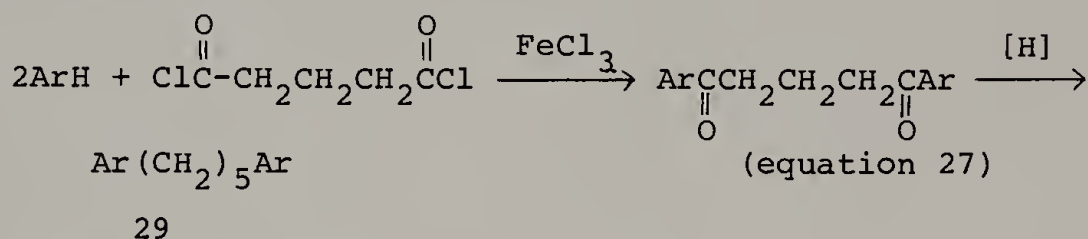
The use of dialkylcarbonates instead of  $\text{CO}_2$  provides one of the few examples of cyclic ketone formation (equation 25).<sup>29</sup>



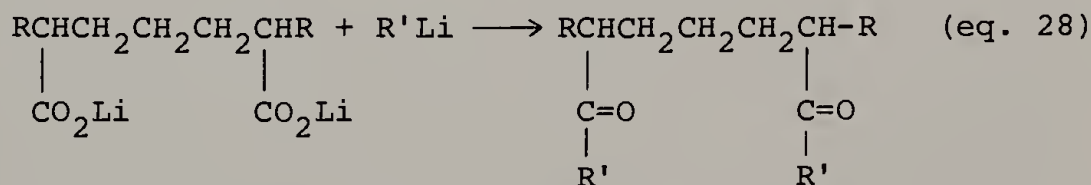
It would follow that the desired ketones might be prepared via reaction of the dilithium compound 28 with carbon dioxide as shown below (equation 26);



The synthesis of 28 could proceed via the diketone, prepared by first reacting glutaryl dichloride with the substituted aromatic in a Friedel-Crafts acylation,<sup>30</sup> followed by reduction (equation 27).



Lithiation of the hydrocarbon, 29 in the benzylic position using n-BuLi would give 28. A potential problem in this route is the avoidance of intermolecular condensation reaction indicated for example by equation 28.

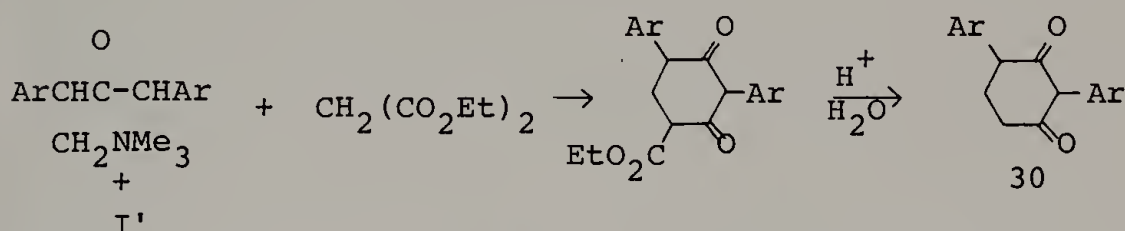


The cyclizations considered up to this point, have all been unimolecular reactions, that is, one end of the molecule joins with the other to form the ring. The routes that follow are bimolecular in nature, where two components

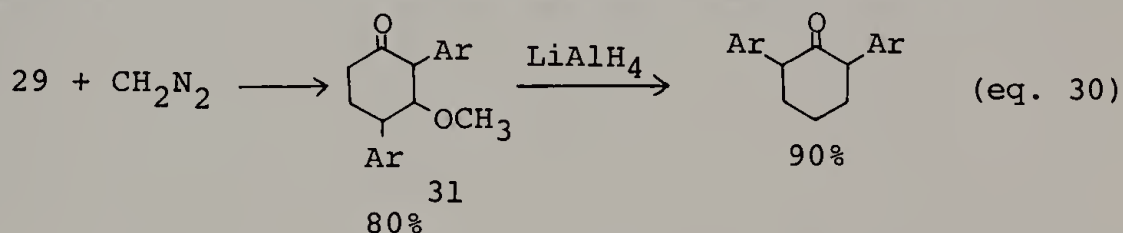
condense to form the phenol precursor.

Betts and Davey<sup>31</sup> reported the synthesis of 2,6-diarylcyclohexanone in a multistep procedure initiated by the reaction of 2,4-diphenyl-3-oxobutyltrimethylammonium iodide (Ar=Ph) with ethyl malonate to form 2,4-diphenylcyclohexane-1,3-dione 30 in a 15% yield.

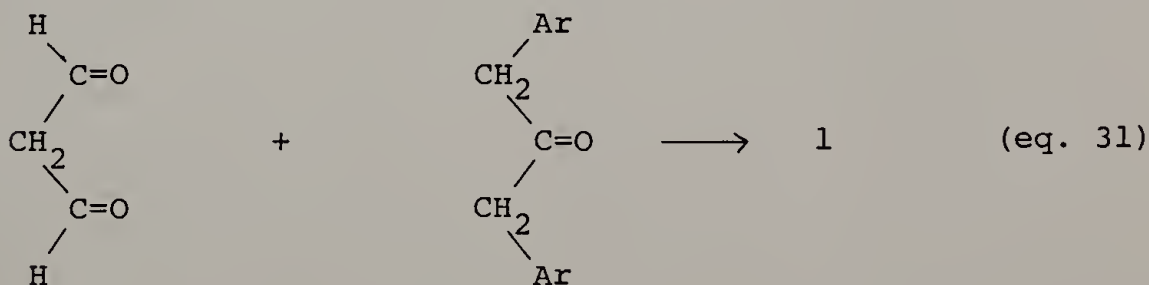
(eq. 29)



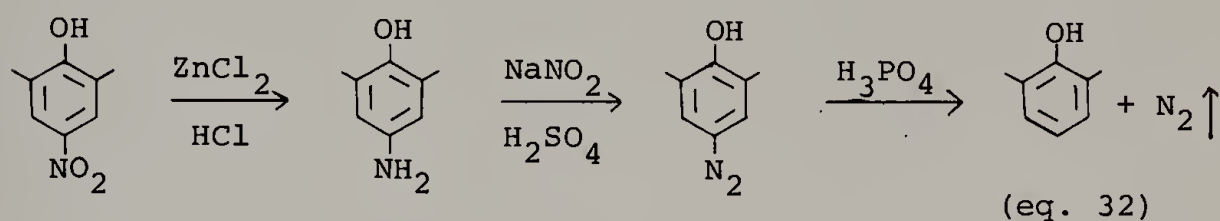
Reaction of 30 with diazomethane generates 3-methoxy-2,4-diphenylcyclohexen-1-one 31 which upon treatment with lithium aluminium hydride yields the desired compound (equation 30).



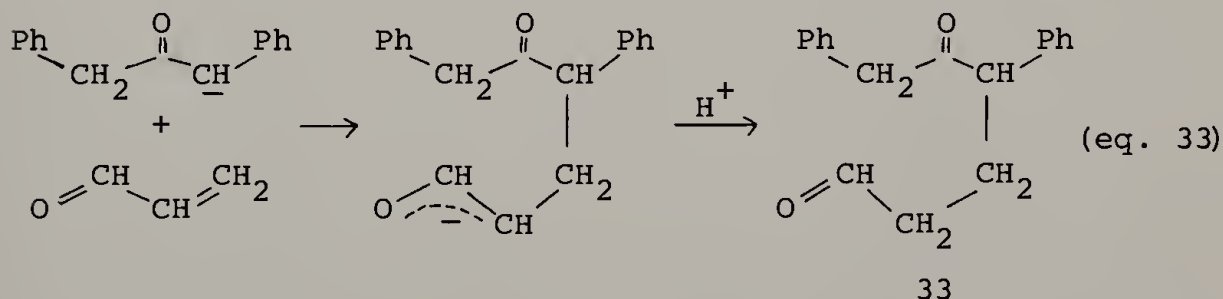
Perhaps the most straightforward bimolecular cyclization reaction would theoretically be the condensation of 1,3-diarylpropanones with malonaldehyde (equation 31) which



would generate the phenol directly. Unfortunately, malonaldehyde is extremely unstable and for this reason is of no potential use. The sodium salt of nitromalonaldehyde is stable and yields upon reaction with dibenzylketone, the 4-nitro-2,6-diphenylphenol with a 94.5% efficiency.<sup>32</sup> Conversion to 1 can then be accomplished by reduction to the 4-amino compound using  $\text{ZnCl}_2$  and  $\text{HCl}$  followed by conversion to the diazo derivative with sodium nitrite.<sup>1</sup> Nitrogen is then removed by treatment with phosphoric acid (equation 32).

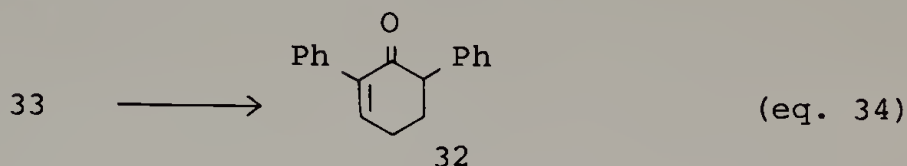


Hay and Clark<sup>5</sup> prepared 2,6-diphenyl-2-cyclohexenone 32 in a 48% yield from dibenzylketone and acrolein. This was inspired by the corresponding reactions of dibenzylketone with cinnamaldehyde<sup>33</sup> or benzalacetophenone<sup>34</sup> producing 2,3,6-triphenyl-2-cyclohexenone or 2,3,5,6-tetraphenyl-2-cyclohexenone respectively. Under basic conditions, the benzyanion adds in a Michael reaction to the acrolein as follows:

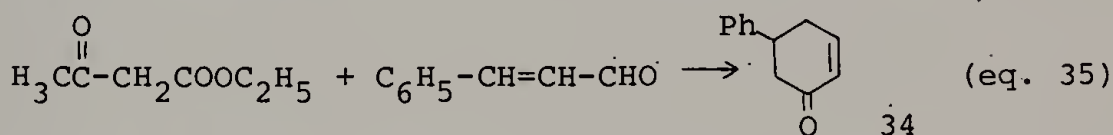




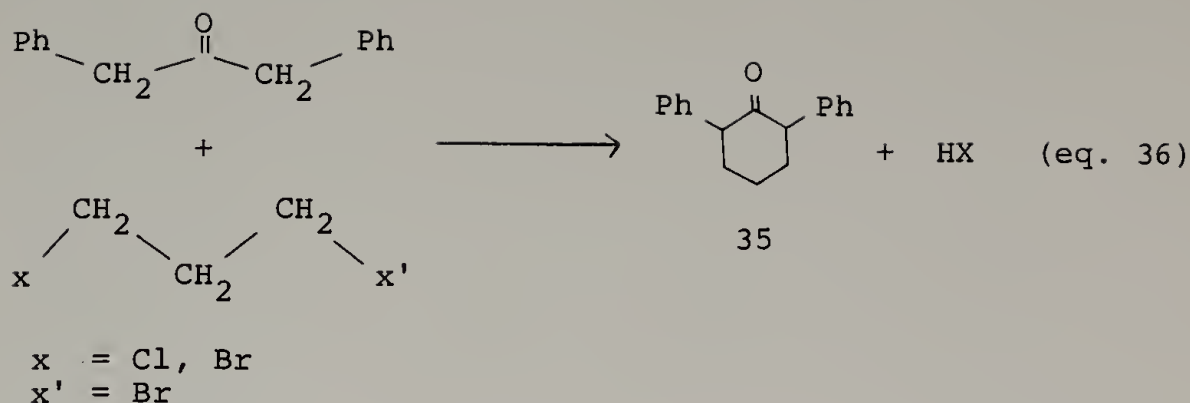
Ring closure is effected by a Knoevenagel type condensation at the other benzylic carbon (equation 34).



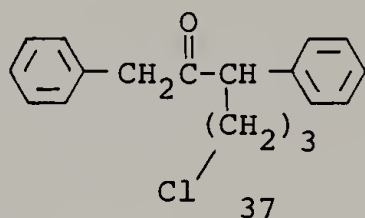
The success of this reaction sequence depends on the acidity of the benzyl group. The greater the acidity, the greater the ease of carbanion formation. Electron withdrawing groups on the aryl substituents would increase this acidity and thereby the reactivity. A variety of bases may be used for this reaction. Generally tertiary amines or alkoxides are adequate. Stronger bases may be used with less reactive benzyl compounds. Phase transfer catalysts were employed in the preparation of 5-phenyl-2-cyclohexenone 34 from cinnamaldehyde and ethylacetoacetate (equation 35).<sup>35</sup>



A 55% yield of this product was obtained utilizing triethylbenzylammonium chloride and sodium carbonate. Also utilizing dibenzyl ketone as a starting material is the base catalyzed double nucleophilic displacement reaction on 1,3-dihalopropane yielding the cyclohexanone 35 (equation 36).



Two examples of this reaction exist in the literature. The dibenzylketone carbanion was generated using NaOH powder and at room temperature, 1-bromo-3-chloropropane was added to produce the monoalkylated intermediate (37),



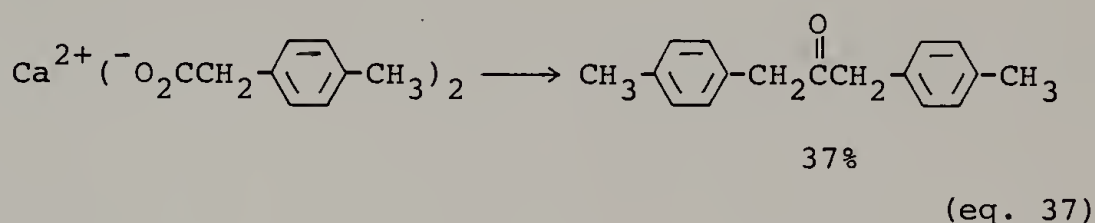
which is then cyclized in the presence of additional NaOH powder at elevated temperatures. A 26% yield of 2,6-diphenylcyclohexanone was obtained.<sup>36</sup> Australian workers produced the same compound in a 23% yield using 1,3-dibromopropane with potassium t-butoxide as the catalyst.<sup>37</sup>

The double nucleophilic displacement reaction, as well as the two previous routes involving nitromalonaldehyde and acrolein, all require 1,3-diaryl-2-propanones as co-reactants. It is also evident that in order to produce phenols with varied aryl groups in the 2,6 positions from the above reactions, the corresponding 1,3-diarylpropanones



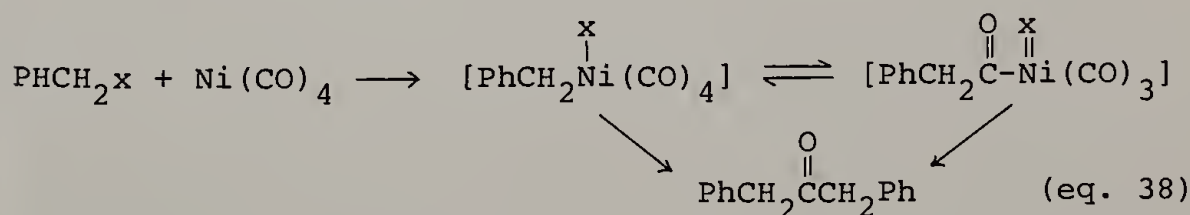
must be synthesized. It would therefore be desirable to provide a general route or routes to these compounds.

Perhaps the simplest route to these ketones is the pyrolysis of arylacetic acids or their salts. Pyrolysis of calcium or barium salts of arylacetic acids generally gives low yields of ketones.<sup>38</sup> The pyrolysis of calcium p-tolylacetate to 1,3-bis(p-tolyl)-2-propane is a specific example (equation 37).<sup>39</sup>



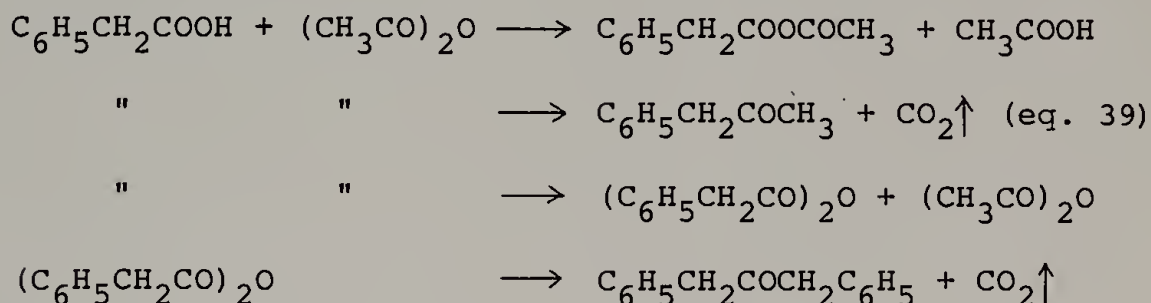
Thorium oxide at 410°-435°, produced dibenzylketone from phenylacetic acid in quantitative yield.<sup>40</sup> This is analogous to the Ruzicka reaction reported earlier. This has not been expanded to other acetic acids. The advantage of these pyrolysis reactions is their simplicity. The disadvantage is the high temperature necessary for reaction which tends to introduce side reactions.

Dibenzylketone was prepared in yields as high as 95% from benzylhalides and nickel carbonyl (equation 38).<sup>41</sup>

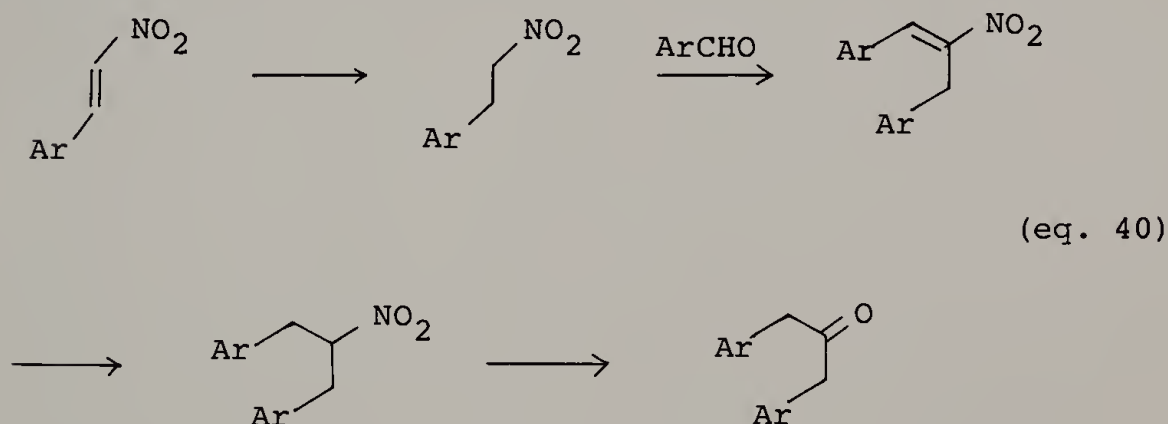


Iron carbonyl was also used in this reaction. The disadvantage here is the high toxicity associated with metal carbonyl complexes.

A 41% yield of dibenzylketone was achieved by reaction of phenylacetic acid with acetic anhydride and potassium acetate in the following manner:<sup>42</sup> (equation 39)



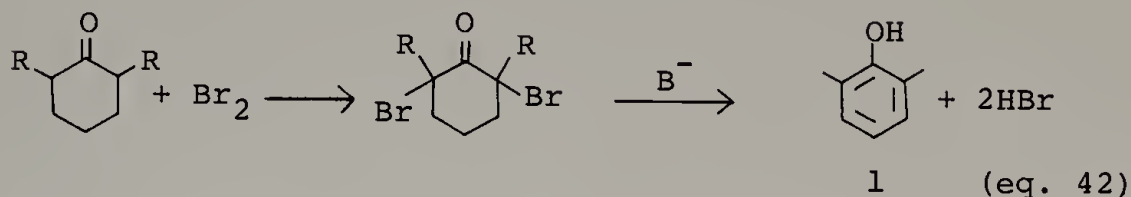
A diarylketone was prepared by a four step procedure in 67% overall yield as shown schematically below:<sup>43</sup> (equation 40)



In step 1, the  $\beta$ -nitrostyrene was reduced to the ethane by sodium borohydride in methanol. Condensation with benzylaldehyde

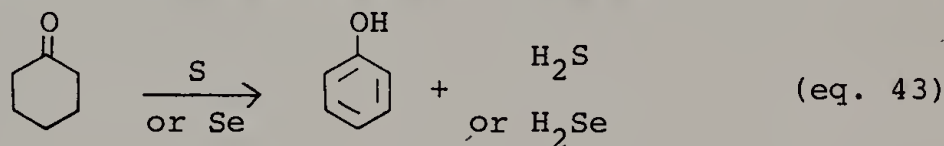


be transformed into the desired phenols (1) by various dehydrogenation reactions. The most involved procedure is indicated by equation 42.



Overall yields for this reaction (R=H) are approximately 18% using pyridine as the base.<sup>47</sup> Some improvement in yield might be expected using a stronger base as dehydrobrominating agent.

The uses and limitations of sulfur or selenium as dehydrogenating agents have been surveyed<sup>48</sup> (equation 43).



Optimum temperatures for sulfur and selenium dehydrogenation are 180-260°C and 250-350°C respectively. Product yields generally range from 20-30% in both cases. At higher temperatures side reactions become significant, particularly with sulfur.

The importance of sulfur or selenium as dehydrogenation catalysts has been superseded by palladium or platinum on charcoal in concentrations of 3-5%. At 200-300°C, substantially higher yields are generally obtained. Another advantage to this system is that it is heterogeneous. Spent

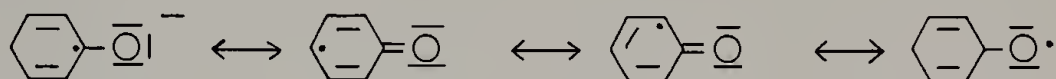
catalyst can be removed easily allowing easier purification of products.

## C H A P T E R   I I

### RESULTS AND DISCUSSION

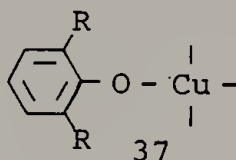
#### A. Introduction

Phenols capable of polymerizing oxidatively to linear high molecular weight polyphenylene oxides must meet certain requirements. The general chemistry and mechanistic aspects of the polymerization systems will be discussed extensively in Chapter IV. Principally, however, the first step in the oxidation of a phenol is considered to be formation of an aryloxy radical.<sup>49</sup> The unsubstituted phenoxy radical is a resonance hybrid of 4 structures shown below.<sup>50</sup>

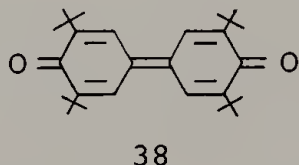


It is apparent that carbon-oxygen and carbon-carbon coupling can occur at both the ortho and para positions. As a result, oxidative polymerization of phenol yields a complex highly branched mixture.<sup>49</sup> It is therefore a general requirement for the production of linear high molecular weight material that there be substituents in both ortho positions. This then allows only the oxygen and para carbon for coupling.

These substituents in turn, must satisfy several requirements. First, they must not contain labile functionalities, easily removed under polymerization conditions or any post polymerization treatment. They should not contain any functionality which itself reacts with the polymerization catalysts. This immediately rules out substituents which are readily oxidized. As the polymerization catalysts are transition metals which initially must form complexes with the phenol (37),



functionalities which would preferentially chelate such catalysts must also be avoided. Stereochemistry is also a factor. Bulky groups have been shown with molecular models to hamper linkage with oxidation catalysts. The best example of this is the oxidative coupling of 2,6-di-*t*-butylphenol.<sup>51</sup> Only the carbon-carbon coupled diphenoquinone (38) was obtained with this bulky group in both ortho positions.



The last factor which must be taken into account with regard to the general requirements of the substituents is the effect of the substituent on the reactivity or



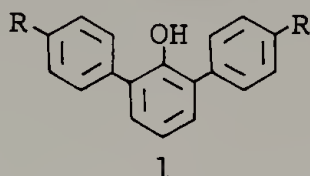
oxidation potential of the phenol. Strongly electronegative functionalities which increase the oxidation potential of the phenol, decrease its reactivity in the polymerization reaction. 2,6-Diphenylphenol has a higher oxidation potential than 2,6-dimethylphenol, and as a result, must be polymerized at a higher temperature.<sup>52</sup> Phenols with electronegative o-nitro substituents do not polymerize at all.<sup>51</sup> This implies that, although substituents which increase oxidation potential may not prevent polymerization to high molecular weight, they may significantly affect the conditions necessary to achieve it.

There are further requirements dictated by the ultimate objective of this thesis. That objective is the preparation of crystallizable polyphenylene oxides. The first requirement is that both ortho substituents of the phenol be aromatic. Polyphenylene oxides with aliphatic substituents, notably poly(oxy-2,6-dimethyl-1,4-phenylene), do not crystallize thermally.<sup>53</sup> The polymer from 2,6-diphenylphenol crystallizes quite readily upon annealing.<sup>52</sup> The second requirement is that these aromatic substituents be substituted only in the para positions. As in the case of 2,6-di-t-butylphenol, ortho substituents would interfere sterically with the polymerization reaction. This has been demonstrated, for example, in the attempted polymerization of 2-phenyl-6-o-biphenylylphenol, where a maximum intrinsic viscosity of 0.14 dl/g was obtained.<sup>5</sup> Symmetry is a general



and most important requirement. Polymers prepared from non symmetrical 2,6-diarylphenols were shown to be completely amorphous.<sup>5</sup> Greater symmetry would allow the chains to align more efficiently and thus promote crystallinity.

In summation, the new phenols reported on this thesis are defined by the general structure 1.



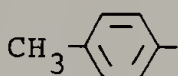
R may be any function of low to moderate electronegativity which does not oxidize readily under polymerization conditions, does not chelate with transition metal polymerization catalysts, or is not displaced under polymerization conditions or post polymerization treatment.

The synthetic pathways investigated were solely of the ring forming variety. There were no attempts at substitution onto phenol or its cyclic precursors. The routes attempted were the Michael addition followed by the Knoevenagel condensation of acrolein with 1,3-diaryl-2-propanones, and the double nucleophilic displacement reaction of 1,3-dibromopropane, also with diarylpropanones. These reactions yielded the phenol precursors, 2,6-diarylcyclohexenones and 2,6-diarylcyclohexanones, respectively.

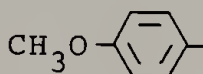
As both routes required 1,3-diaryl-2-propanones as starting materials, attempts were made to develop a general route to these compounds. This is of comparable importance

to the ring closing step, in that the symmetrical diaryl substituents are first incorporated as substituents on these dibenzylketones.

Considering also the commercial availability of starting materials, the aryl groups selected to be incorporated on the phenol precursors and subsequent monomers were the p-tolyl (a), p-methoxyphenyl (b) and p-biphenylyl (c) groups.



a



b

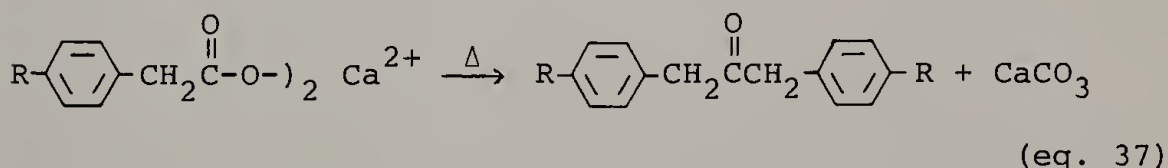


c

### B. Preparation of 1,3-diaryl-2-propanones

Three alternate methods were investigated for the preparation of 1,3-diaryl-2-propanones. All of these used arylacetic acids or their salts and esters as starting materials.

Pyrolysis of calcium salts of arylacetic acids (equation 37)

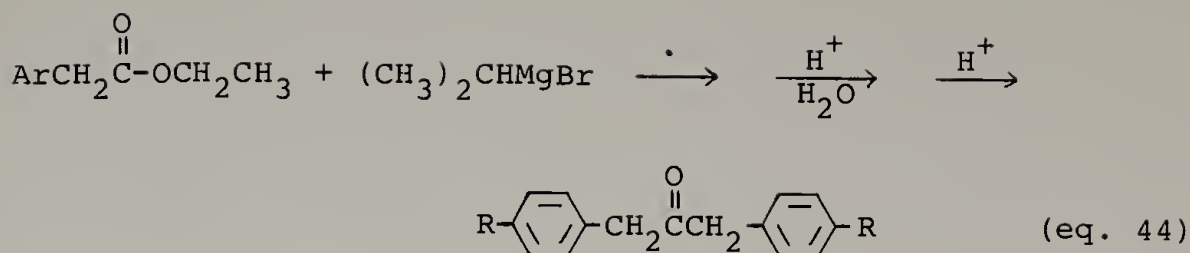


is a straightforward procedure, but did not prove to be a general route. The procedure involved heating the salt at temperatures in excess of two hundred degrees. The facility

of the reaction lies in the fact that, as the salt is pyrolyzed, the product formed immediately volatilizes and is collected as a distillate. 1,3-Bis(p-methoxyphenyl)-2-propanone was prepared by pyrolysis at 250°C, in a yield of 14.8%, considerably less than the 37% yield reported for 2,6-bis(p-tolyl)-2-propanone.<sup>39</sup> This decrease in efficiency is probably due to the higher boiling point of the former.

Also classified as pyrolysis reactions were so-called hot tube reactions, where the arylacetic acid itself was passed through a column at elevated temperature containing an inert support impregnated with catalyst. This route was inspired by the reported high yields of dibenzylketone achieved by passing phenylacetic acid over thorium oxide catalyst at 410-435°C.<sup>40</sup> A yield of 8.1% pure 1,3-bis(p-methoxyphenyl)-2-propanone was obtained by passing p-methoxyphenylacetic acid through a column of zinc oxide pellets impregnated with thorium carbonate at 410-430°C. A slight improvement up to 13.5% yield was achieved using calcium acetate impregnated pumice at 400°C. These yields were not adequate enough to warrant use as a source of the desired compounds.

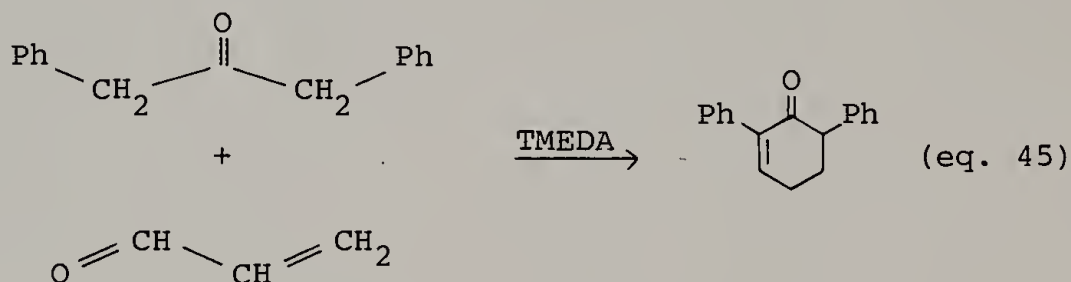
The system which proved to be a general route to symmetrical 1,3-diaryl-2-propanones was the self condensation of esters of arylacetic acids as initially reported by Conant and Blatt,<sup>44</sup> and expanded upon by Becker et al.<sup>45,46</sup> (equation 44).



The diaryl propanones prepared by this route are listed in Table 2.

### C. Preparation of 2,6-diaryl-2-cyclohexenones

As mentioned earlier, Hay and Clark<sup>5</sup> reported a 48.6% yield of 2,6-diphenyl-2-cyclohexenone by the addition of stoichiometric quantities of acrolein to dibenzylketone in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) as in equation 45.



A significant competing reaction to this addition/condensation is the TMEDA catalyzed anionic polymerization of acrolein. A polymer of general structure 39 is produced.<sup>54</sup>

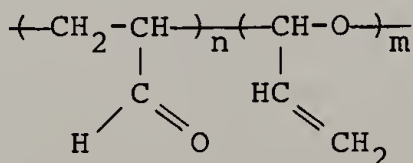
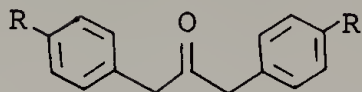


TABLE 2  
Synthesis of 1,3-Diarylpropanones



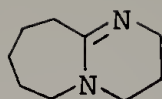
R =	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
yield (%)	42	74	40
melting pt. (°C)	52-53	86	162-164
Lit. m.p. (°C)	53.2-54.4	86-86.2	166
<u>Spectral Data</u>			
<u>IR (cm<sup>-1</sup>)</u>			
C=O stretch	1700	1701	1699
<u><sup>1</sup>H NMR (ppm)</u>			
Aromatic (m)	7.07	6.94	7.41
benzylic CH <sub>2</sub> (s)	3.65	3.62	3.79
R (s)	2.32	3.76	--

This also occurred under other reaction conditions. For example, under phase transfer catalysis, which utilized 50% NaOH solutions or dry  $\text{Na}_2\text{CO}_3$ , substantial resinification of the acrolein occurred.

Improving on the reported yield of this reaction was accomplished by using an excess of acrolein to compensate for what is lost to polymerization. With an acrolein to dibenzylketone ratio of 2:1, a 76% yield of 2,6-diphenyl-2-cyclohexenone was obtained as a distillation product at 190-210°C/0.2 mm Hg., though the melting point of 58-64°C was depressed from the literature value of 65-66.5°C.<sup>5</sup> IR spectroscopy shows the characteristic conjugated carbonyl stretch at  $1670\text{ cm}^{-1}$  and a peak at  $1601\text{ cm}^{-1}$ , indicative of an olefinic stretch conjugated with a carbonyl and/or aromatic ring. The proton NMR shows replacement of the benzylic singlet of dibenzylketone at 3.68 ppm, with a triplet as well as a multiplet at 2.22-2.45 ppm, characteristic of a ring methylene.

Using TMEDA as the base in the analogous reaction of acrolein and 1,3-bis(p-methoxyphenyl)-2-propanone, only polyacrolein was obtained as a product along with unreacted starting material. This result can be ascribed to the electron donating effect of the p-methoxy group, which reduces the acidity of the benzylic hydrogen. Use of the stronger base 1,5-diaza-bicyclo[5.4.0]undec-5-ene (DBU) (40),





40

proved somewhat more successful. Distillation of the reaction mixture in vacuo, at  $260^{\circ}\text{C}/0.05\text{ mm Hg}$  produced an orange viscous oil, which failed to crystallize. The presence of two fairly equal carbonyl stretches in the IR at  $1675\text{ cm}^{-1}$  and  $1712\text{ cm}^{-1}$  indicates that the distillation product was a mixture of starting propanone and the cyclohexenone. Further separation could not be effected, although evidence for the presence of the desired cyclohexenone was found in the IR which showed olefinic stretching at  $1610\text{ cm}^{-1}$  and  $1582\text{ cm}^{-1}$ , and also the presence of a multiplet at 1.7-2.7 ppm in the  $^1\text{H NMR}$ . The singlet at 3.61, characteristic of benzylic protons in the starting material, was still present.

It was apparent that the Michael addition, Knoevenagel condensation route could not be generalized to prepare cyclohexenones with larger substituents in the 2,6 positions. Although the reactions may very well occur, isolation and purification is extremely difficult, if not impossible. This is due primarily to the unavoidable presence of acrolein polymer. It is unavoidable because the conditions for cyclohexenone formation are comparable to those desired for this polymerization. The presence of large amounts of this polymer as impurity makes isolation



by crystallization difficult. And, as is evident from the attempted synthesis of the p-methoxy analog, distillation is not an effective means of isolation due both to the high temperatures necessary and the closeness of the boiling points between the starting material and product. Even in the simplest case, a small amount of dibenzylketone in the product distillate could not be avoided as indicated by a shoulder at  $1720\text{ cm}^{-1}$  of the IR.

#### D. Preparation of 2,6-diarylcyclohexanones

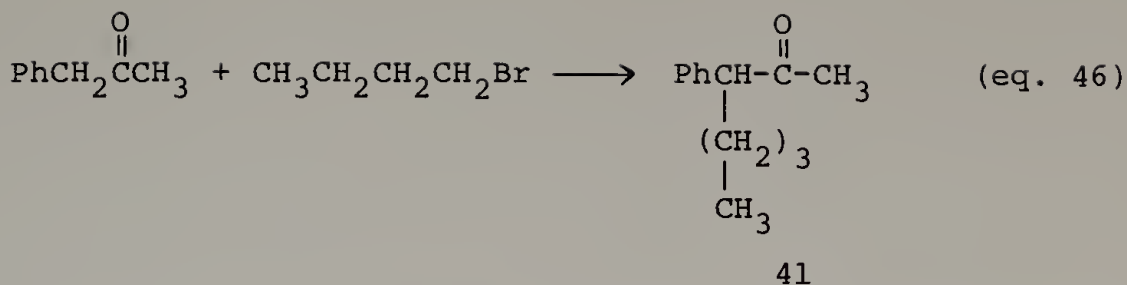
The double nucleophilic displacement reaction involving the diarylpropanones with 1,3-dibromopropane proved to be an acceptable general route to the phenol precursor cyclohexanones, when performed under phase transfer catalysis in lieu of anhydrous bases. Phase transfer catalysis, a term originated by Starks,<sup>55</sup> involves transfer of reactive species between two phases. A catalyst is present, a quaternary ammonium salt, for example, that can combine with anions present in one phase and transfer them to the phase where reaction takes place. Such multiphase systems offer numerous advantages over traditional anhydrous systems. Large amounts of hazardous solvents are eliminated. Most importantly, rigorous elimination of moisture is not necessary.

The wide utility of phase transfer catalysis has been demonstrated in several review articles.<sup>56</sup> Systems of

concentrated aqueous alkali and tetraalkylammonium salts have been used in the alkylation by alkyl halides of active methylene functions of  $\alpha$ -chloroethers,<sup>57</sup> chloronitriles<sup>58</sup> and ketoacetic acid<sup>59</sup> esters. Alkylation of phenylacetone-trile by this method is a standard procedure.<sup>60</sup> The pimelonitriles discussed earlier were synthesized by this method (eq. 14).<sup>12</sup> Also noted before was the phase transfer catalyzed Michael addition/Knoevenagel condensation synthesis of 5-phenyl-2-cyclohexenone (equation 25). In that case, the second phase was solid sodium carbonate.<sup>35</sup>

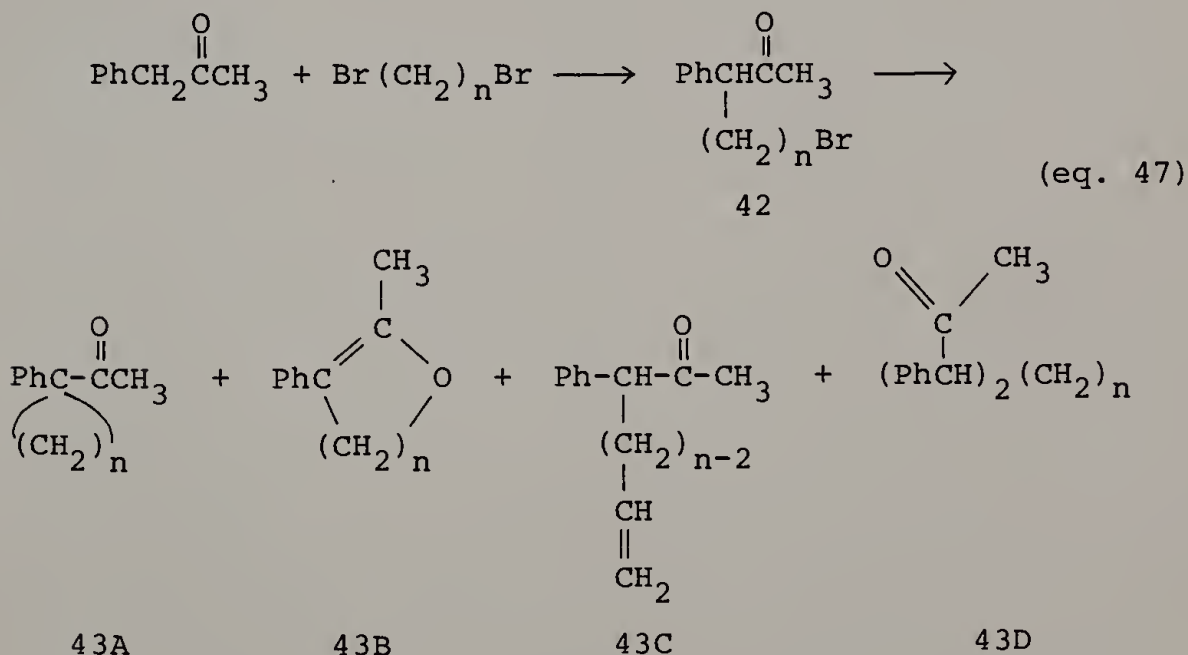
There have been no reported attempts at phase transfer catalyzed synthesis of cyclohexanones such as in the scheme depicted in equation 36. Directly related to this so-called double displacement reaction is the alkylation of phenylacetone, which differs only in that there is one benzylic functionality instead of the two in dibenzylketone. A study of the former in mono and dialkylation reactions under anhydrous conditions and using phase transfer catalysis, would give an indication as to how well the reaction of equation 36 would proceed.

In the presence of catalytic amounts of triethylbenzylammonium bromide (TEBAB), the monoalkylated product 41 was prepared in 90% yield from phenylacetone and *n*-butylbromide (equation 46).<sup>61</sup>



In contrast, attempted alkylation of phenylacetone with ethylbromide catalyzed by potassium *t*-butoxide, gave negligible amounts of alkylated product.<sup>62</sup> In the two phase system, dialkylation of the active methylene did not occur using these alkyl halides. Disubstitution only occurred with activated halides such as benzyl chloride or allyl chloride.<sup>61</sup>

The reaction of phenylacetone with dihaloalkanes is considerably more complicated. After initial monoalkylation (equation 47), 42 could potentially react further under phase transfer conditions to give four additional products:<sup>61</sup>



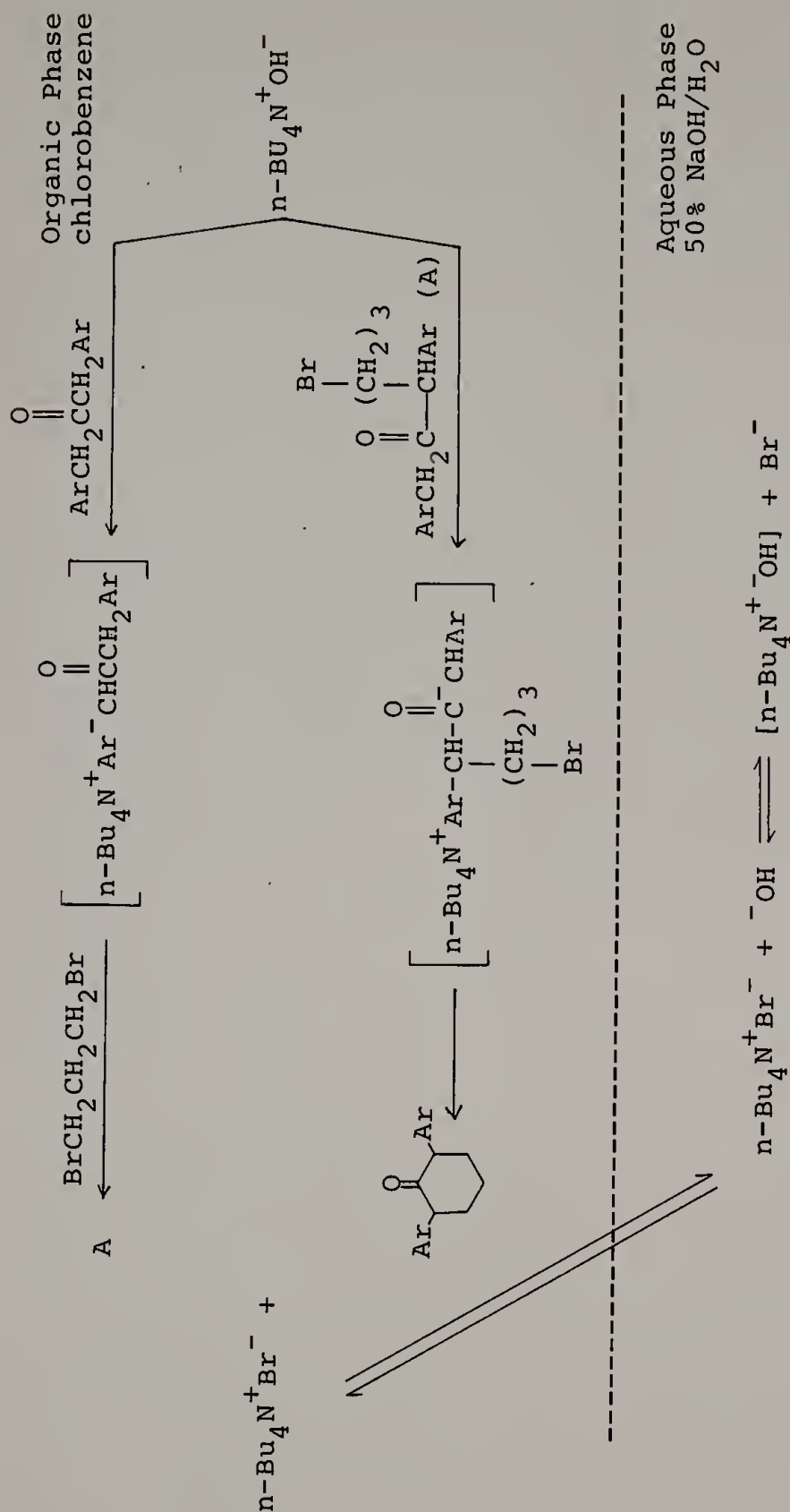
Using ethylene dibromide ( $n=2$ ), the predominant product was 43A (54%).<sup>61</sup> Surprisingly, however, when the dihalide was 1,3-dibromopropane ( $n=3$ ), no 43A was isolated. In this case, the product mixture was found to contain 8% 42, 37% 43B, 5% 43C, and 19.5% 43D. Conventional NaH catalysis of the same reaction gave 43C as the principal product.<sup>63</sup>

From the above results an assessment could be made regarding the potential of the dibenzylketone/1,3-dibromopropane cyclohexanone synthesis under phase transfer conditions. The occurrence of some side products similar to those mentioned above is certainly unavoidable, but there are two factors present in this system that would make some of these side reactions less favorable. The driving force for the formation of the cyclohexanone is first and foremost the presence of not one but two highly reactive benzylic methylene linkages, which both form carbanions readily under the conditions imposed by phase transfer systems. The second driving force is the established thermodynamic favorability of six membered ring formation, the cyclohexanone. The first factor could considerably reduce formation of 43B. This compound also contains a six membered ring, but the strong preference for C-alkylation over O-alkylation, as demonstrated by the high yield monohalide alkylation of phenylacetone<sup>60</sup> (equation 46), provides a strong argument for the ring closure to preferentially

proceed via C-C coupling, and yield the cyclohexanone. As in all cyclization reactions, major competition comes also from intermolecular reactions, which in this case would favor 43D as product. The ratio of the cyclized product with respect to the latter product would depend on the ease of ring formation under these conditions.

Potential differences between the anhydrous route and the phase transfer system for the cyclohexanone synthesis can be predicted from differences in the respective reactions of phenylacetone and 1,3-dibromopropane. As mentioned earlier, NaH catalysis produced 43C as the principal product in the latter system.<sup>63</sup> It would follow that an analogous allylic compound might be a major side product in the anhydrous cyclohexanone synthesis. In contrast, only 5% of 43C was isolated under phase transfer conditions. This observation coupled with the reported higher yields for monoalkylation of phenylacetone indicates good prospects for increasing the yield of 2,6-diarylcyclohexanones by using phase transfer catalysis in the reaction of 1,3-diarylpropane with 1,3-dibromopropane in place of anhydrous bases.

The system which was used in the syntheses performed herein consisted of tetrabutylammonium bromide in chlorobenzene with an aqueous phase of 50% sodium hydroxide. Mechanistically, this system can be visualized by the scheme in Figure 1. The quaternary ammonium salt has a limited



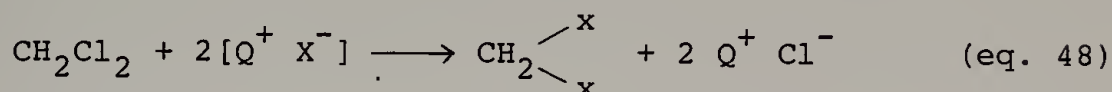


solubility in the aqueous phase. It is therefore in a position to undergo an exchange of anions,  $\text{Br}^-$  for the more electronegative  $\text{OH}^-$ . The new salt diffuses back to the organic phase where the hydroxide is capable of abstracting a proton from the benzylic carbon. The newly formed carbanion then rapidly displaces bromine from dibromopropane, regenerating the quaternary ammonium bromide and beginning the cycle anew. This regeneration allows one to use a small concentration of catalyst in relation to substrates.

There are various factors which may affect both rates and yields in these syntheses. The effectiveness of a phase transfer catalyst is measured by its ability to achieve partial solubility in both the organic and aqueous phases. This ability to extract the reactive anion into the organic phase is defined by the extraction or phase partition equilibrium constant. It is proportional to the ratio of the concentration of catalyst in water to the concentration in organic solvent. Generally, the higher this ratio, the greater the extraction rate. In the present system, the extraction constant for the distribution of 0.1 M tetrabutylammonium bromide between water and chlorobenzene is less than 0.1.<sup>64</sup> This is considerably lower than the values for organic phases of chloroform (47) and methylene (35).<sup>65</sup> One therefore might expect faster reactions in the latter two solvents when using TEBAB as catalyst. However,



in the presence of strong aqueous bases, chloroform is prone to dichlorocarbene formation.<sup>66</sup> And when strong nucleophiles are reacted with relatively unreactive alkylating agents, competing reactions with methylene chloride are also possible (equation 48)<sup>65</sup>



when  $\text{X}^-$  is the propanone carbanion. Similar side reactions, to varying degrees, would occur using other aliphatic halocarbons as solvents. With solvents other than aliphatic halocarbons, high extraction constants generally coincide with relatively high water solubility, which is also potentially harmful to reaction efficiency primarily due to anion solvation. Also affecting the efficiency of the anion are anion-cation interactions. The concentration of hydroxide in the organic phase is determined by the dissociation equilibrium:



The more polar the solvent, the greater the degree of dissociation and rate of reaction. Chlorobenzene, having higher polarity, was favored over benzene for this latter reason. A factor which influences the extent of reaction is the phase partitioning equilibrium of the anions. The subject syntheses can only proceed quantitatively if the

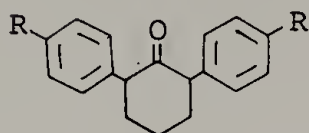
aqueous organic partitioning equilibrium permits preferential transfer of displaced  $\text{Br}^-$  into the aqueous phase. Once equilibrium concentrations are achieved, the reactions will cease. In this case, further reaction would necessitate replacing the aqueous phase with a fresh solution of 50% NaOH. It was hoped that, as is generally the case with weakly acidic materials, although the local concentration of ion pairs is low, the reactivity of the carbanion is so high that it always is rapidly removed from the partition equilibrium.

With regard to the choice of quaternary ammonium salt, little research has been done in determining the optimum phase transfer catalysts for various reactions. However, one study has determined that tetrabutylammonium salts were most effective in the alkylation of benzyl cyanide.<sup>67</sup>

Thus, the subject syntheses were conducted by combining an organic phase of 1,3-diaryl-2-propanone, tetrabutylammonium bromide and chlorobenzene with an aqueous phase of 50% sodium hydroxide. The mixture was stirred vigorously to insure efficient phase transfer and 1,3-dibromopropane was added dropwise. 2,6-Diarylcyclohexanones prepared in this way are listed in Table 3.

Detailed analyses of product mixtures to determine the nature and amounts of side products were not conducted here, as the primary goal was obtaining the phenol

TABLE 3  
SYNTHESIS OF 2,6-DIARYLCYCLOHEXANONES



P =	H	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
Yield (%)	36	42	51	30
Melting Pt. (°C)	119-121	139	169	191-193
Analysis: (%)				
Calculated for:				
C	86.40	86.33	77.42	89.55
H	7.20	7.91	7.10	6.47
Found:				
C	86.24	86.20	77.51	89.69
H	7.12	7.75	7.16	6.66

precursors. A gas chromatograph of a product mixture using dibenzylketone starting material showed two substantial side products in addition to residual ketone (a) and the desired product (b) (Figure 2).

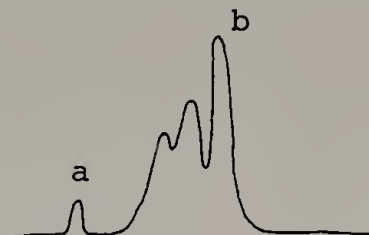
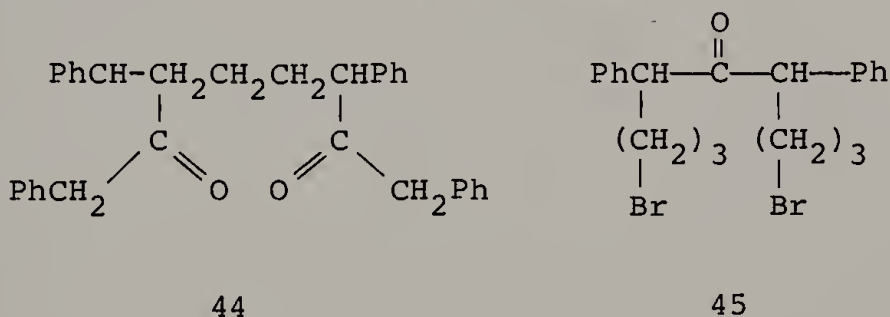
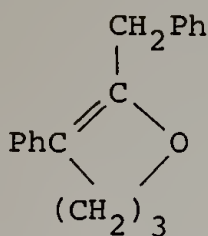


Figure 2.

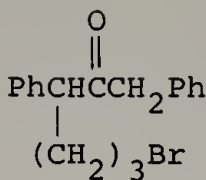
Judging by the results reported earlier (equation 46), for the reaction of phenylacetone with 1,3-dibromopropane, there are several possible candidates for these side products. As no 43A was isolated in the earlier case, there is little reason to assume the analogous compound exists in the present case. In spite of the fact that the doubly substituted material 43D was found in appreciable amounts, lower G.C. retention times for both side products would tend to rule out 44 as well as 45



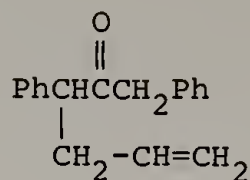
Although it was argued that C-C coupled ring closure is preferred over C-O coupling, the high percentage reported for 43 production does not eliminate 46 as a possible principal side product.



46



47



48

Structures 47 and 48 are also likely side products.

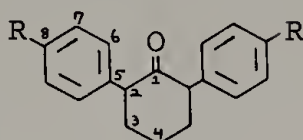
#### E. Spectrometric Characterization of 2,6-diarylcyclohexanones

Infrared analysis. Analysis of infrared spectra of the product cyclohexanones provided three characteristic bands for structural confirmation. These are listed in Table 4.

Carbonyl stretching vibrations were noted at 1701-1715  $\text{cm}^{-1}$ . Confirmation of ring structure was made through the presence of a symmetrical  $\text{CH}_2$  stretch at 2850-2870  $\text{cm}^{-1}$  and an asymmetrical  $\text{CH}_2$  stretch at 2910-2945  $\text{cm}^{-1}$ .

$^1\text{H}$ NMR analysis. The conversion of propane to cyclohexanone was marked by the disappearance of the characteristic benzylic singlet at 3.5-3.8 ppm. These were replaced by triplets at 3.71-3.9 ppm, caused by the splitting of the benzylic proton by the newly formed methylene linkages. Also indicative of the cyclohexanone structure is the multiplet at 2-2.3 ppm, attributable to the ring methylenes. Specific assignments are given in Table 4.

TABLE 4  
2,6-DIARYLCYCLOHEXANONE SPECTRAL DATA



R =	CH	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
<u>IR (cm<sup>-1</sup>, KBr)</u>				
C=O stretch	1705	1701	1710	1715
CH <sub>2</sub> -ring asym. stretch	2930	*	2910	2945
CH <sub>2</sub> -ring sym. stretch	2870	2860	2850	2870
<u><sup>1</sup>H NMR (ppm from TMS)</u>				
Aromatic	7.75 (m)	7.16 (m)	7.01 (m)	7.40 (m)
CH	3.75 (t)	3.71 (t)	3.79 (t)	3.90 (t)
(CH <sub>2</sub> ) <sub>3</sub>	2.15 (m)	2.06 (m)	2.06 (m)	2.23 (m)
(R)	--	2.31 (CH <sub>3</sub> , s)	3.77 (CH <sub>3</sub> -O, s)	--
<u><sup>13</sup>C NMR (ppm from TMS)</u>				
1	207.94	183.78	183.57	207.78
2	57.56	57.49	57.14	57.66
3	36.17	36.46	36.62	36.41
4	25.64	26.01	26.14	26.04
5	138.67	135.78	113.62	*
6	127.94	128.64	130.27	
7	128.72	128.79	129.69	
8	126.59	136.07	158.54	
(R)	--	21.02	55.19	

\* unresolvable

$^{13}\text{C}$  NMR analysis. The shift values relative to TMS are given in Table 4. Electron donating substituents located in the para position of the 2,6-aryl groups caused a shift upfield of approximately 25 ppm in values for the carbonyl carbon when compared to unsubstituted cyclohexanone (211.2 ppm).<sup>68</sup> Thus, the methyl group and the methoxy group which have comparable electron donating ability show approximately the same shift values for their carbonyl carbons. On the other hand, the p-phenyl substituent provides virtually no inductive effect, and has a similar carbonyl shift to the value for 2,6-diphenylcyclohexanone. The similarity of values for carbons 2, 3, 4 in all the cyclohexanones indicates little, if any, inductive effect of the p-substituents on these carbons. However, the aryl groups have the general effect of a downfield shift on the 2 carbon when compared to the values for unsubstituted cyclohexanones (40.4).<sup>68</sup>

Mass spectral data. The molecular weight of 2,6-bis(p-tolyl)cyclohexanone was 277.8 as indicated by a molecular ion peak at 85.68% of base peak intensity. The spectra demonstrated several major fragmentation peaks. Likely structures of the fragments are given in Figure 3.

The molecular weight of 2,6-bis(p-methoxyphenyl)-cyclohexanone was represented by a parent peak of mass 309.8, which was 61.3% of base peak intensity. Likely



Figure 3. Fragmentation of 2,6-bis (p-tolyl) cyclohexanone from mass spectrometry.

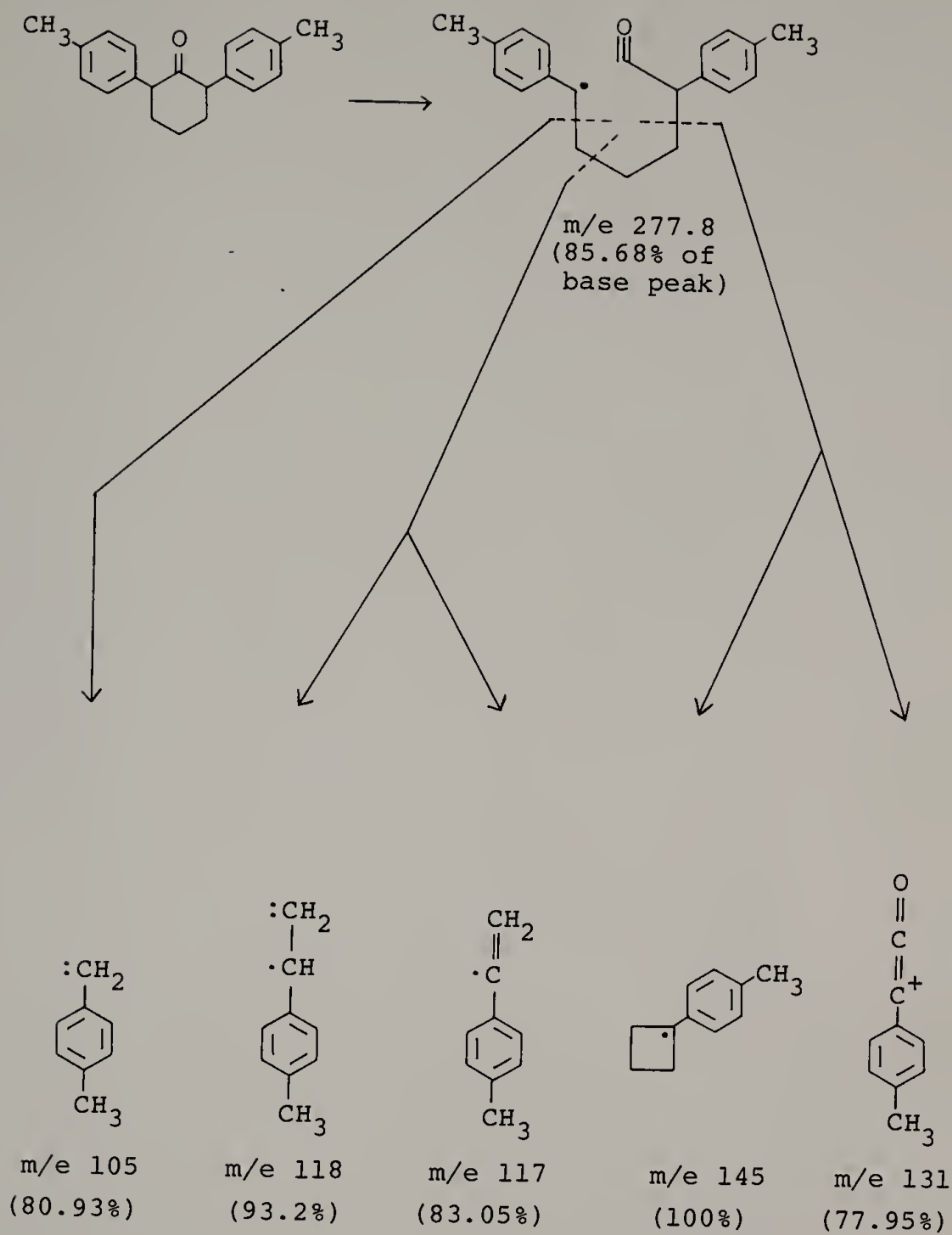
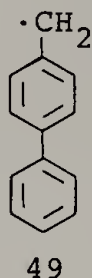


Figure 3.

principal fragments are depicted in Figure 4.

A parent peak of mass 400 and 50% intensity was found for 2,6-bis(p-biphenylyl)cyclohexanone. Unlike the previous cases, the spectrum did not demonstrate extensive fragmentation. The base peak occurred at  $m/e$  28, implying a facile cleavage of carbon monoxide. A peak of 32.5% intensity occurred at  $m/e$  167, which probably means a fragment of structure 49.



#### F. Preparation of Phenols from the Cyclohexanones

The subject phenols were prepared in high yield by dehydrogenation reactions of the corresponding cyclohexanones. Ia and Ib were prepared using 5% Pd on carbon. Ic was prepared using a stoichiometric amount of elemental sulfur. Dehydrogenations such as these are traditionally run in the melt at temperatures of 200-300°C. An improvement of yield was achieved by performing the reaction in refluxing diphenyl ether. The increased efficiency was probably due to more efficient stirring over the viscous melt, which is vital in heterogeneous systems like those used here. The refluxing liquid also allows for easy

Figure 4. Fragmentation of 2,6-bis (p-methoxyphenyl) cyclohexanone from mass spectrometry.

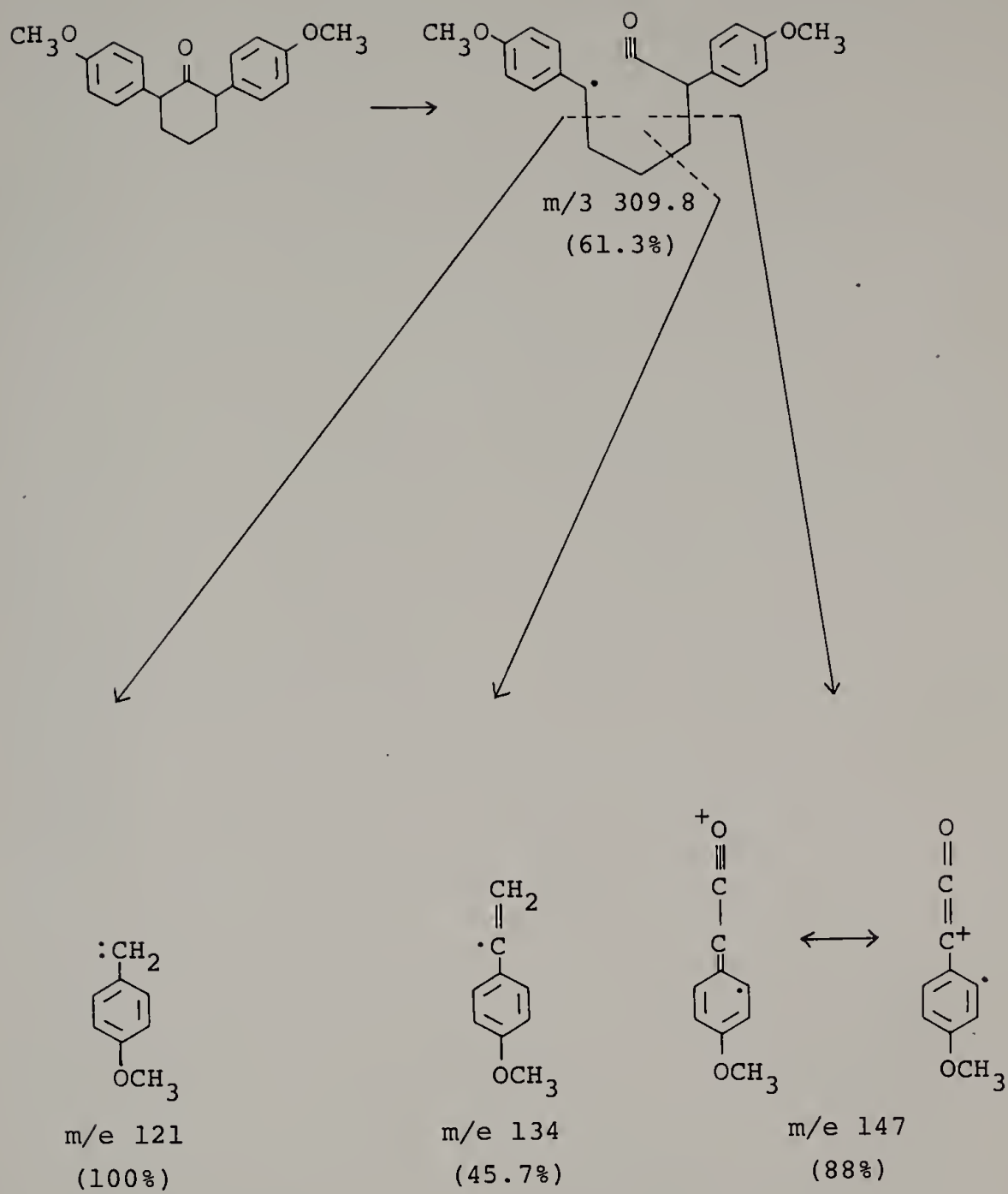


Figure 4.

removal of hydrogen or hydrogen sulfide gas from the reaction mixture, thus pushing the reaction equilibrium to the right. The results of these syntheses are listed in Table 5.

#### G. Spectrometric Characterization of Phenols (Table 6)

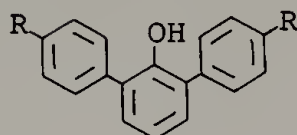
IR analysis. The phenols exhibited a hydroxide stretch at 3460-3550  $\text{cm}^{-1}$ . The sharpness of the bands indicated absence of hydrogen bonding in all cases. Also indicative of phenolic structure was the C-O stretch at 1215  $\text{cm}^{-1}$  - 1240  $\text{cm}^{-1}$ .

$^1\text{H}$ NMR analysis. All phenols exhibited a characteristic sharp singlet for hydroxide at 5.34-5.37 ppm in deuteriochloroform.

$^{13}\text{C}$ NMR analysis. Of note here is the chemical shift (relative to TMS = 0) of the carbon directly bonded to the hydroxide carbon. These values, ranging from 149.34-150.81 ppm, represent an upfield shift from the value of unsubstituted phenol (155.1 ppm),<sup>69</sup> caused by the 2,6-diaryl substituents. Electron donating groups on the aryl substituents appear to increase this shift, though slightly. As might be expected, the remaining aromatic carbons could not be assigned with any certainty.

Mass spectral analysis. As is generally the case, the

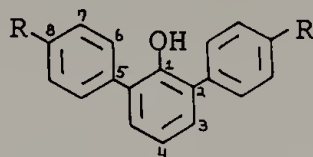
TABLE 5  
SYNTHESIS OF 2,6-DIARYLPHENOLS



R =	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
Yield (%)	55	80	75
Melting Pt. (°C)	95	109	243
Analysis: (%)			
Calculated for:			
C	87.59	78.13	90.45
H	6.57	5.88	5.52
Found:			
C	87.73	78.41	90.36
H	6.61	5.88	5.48
M.W.:			
Calculated	274.4	306.4	398.5
Found (m.s. molecular ion)	274.0	306.0	398.0



TABLE 6  
2,6-DIARYLPHENOL SPECTRAL DATA



R =	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
<u>IR (cm<sup>-1</sup> KBr)</u>			
OH stretch	3550	3460	3520
CH bend	1319	1330	1320
C-O stretch	1219	1240	1215
<u><sup>1</sup>H NMR (ppm from TMS)</u>			
OH	5.37 (s)	5.34 (s)	5.48 (s)
Aromatic	6.97-7.50 (s)	6.93-7.54 (s)	7.24-7.72 (m)
other (R)	2.39 (s)	3.85 (s)	--
<u><sup>13</sup>C NMR (ppm from TMS)</u>			
1	149.51	149.34	150.81
2	129.71	129.35	*
3	128.75	128.24	
4	120.59	120.41	
5	134.78	129.75	
6	129.24	150.32	
7	129.53	114.13	
8	137.29	159.9	
(R)	21.14	55.12	

\*-unresolvable

phenols proved considerably more stable to fragmentation than the analogous cyclohexanones. The molecular ion or parent peaks were also the base peaks, and these values for molecular weight are given in Table 5.

## C H A P T E R   I I I

### EXPERIMENTAL

#### A. Spectrometric Analysis

Infrared spectra were obtained neat or as KBr pellets on the Perkin-Elmer model 283 spectrophotometer.

$^1\text{H}$  NMR spectra were obtained neat or as solutions of  $\text{CDCl}_3$  with a standard of tetramethylsilane on the Perkin-Elmer model R-32, R-24, or Varian FT-20 spectrophotometers.

$^{13}\text{C}$  NMR spectra were obtained in  $\text{CDCl}_3$  solution with tetramethylsilane standard on the Varian CFT-20 spectrophotometer. All samples were run in the decoupled mode.

#### B. Synthetic Procedures

Ethyl p-methoxyphenylacetate. p-Methoxyphenylacetic acid (166.17 g, 1.0 mole) was dissolved in 95% ethanol (460 g, 583 ml, 10 mole). To this solution was added 1 ml  $\text{H}_2\text{SO}_4$  and the mixture heated at reflux for 24 hours. Excess ethanol was distilled in vacuo to reduce the solution to 20% of the original volume. The concentrated solution was added to 500 ml  $\text{H}_2\text{O}$ , forming two phases. The crude ester was taken up in ether and the ether phase washed with 10%

$\text{NaHCO}_3$  solution (200 ml), followed by  $\text{H}_2\text{O}$  until the wash water tested neutral (2 x 100 ml). The ether phase was dried over anhydrous  $\text{MgSO}_4$ . After filtration and evaporation of ether, the crude ester was distilled in vacuo. The pure ester was obtained at  $108-110^\circ/1$  mm Hg, weighing 178.5 g (92%) [Lit. b.p.  $108-110^\circ/1$  mm].<sup>45</sup>

Ethyl p-methylphenylacetate. Sodium cyanide (55.12 g, 1.13 mole) was combined with 50 ml  $\text{H}_2\text{O}$  and the mixture heated with stirring to  $100^\circ$  to partially induce dissolution. To the warm solution was added dropwise, a solution of p-tolylchloromethane (140.5 g, 1.0 mole), in 95% ethanol (110 ml). The mixture was then heated to reflux for 4 hours. Following cooling to room temperature, precipitated NaCl was removed via filtration. The filtrate was evaporated in vacuo to remove excess ethanol, and the residue was poured into 250 ml  $\text{H}_2\text{O}$ . The organic phase was dissolved in ether and the ether phase washed with  $\text{H}_2\text{O}$  (2 x 100 ml).

After drying over  $\text{MgSO}_4$  and evaporation of ether, the crude brown nitrile was dissolved in 95% ethanol (360 ml) and to this solution was added concentrated  $\text{H}_2\text{SO}_4$  (131 ml). The solution was heated at reflux overnight (16 hours), during which time two phases developed. Upon cooling, the mixture was flooded with  $\text{H}_2\text{O}$  (450 ml). The aqueous layer was discarded and the brown oil dissolved

in ether. The ether solution was washed with 10% sodium bicarbonate solution and then  $H_2O$  until the aqueous phase tested neutral to pH. The ether phase was dried over  $MgSO_4$ . Ether was evaporated, and the brown oil distilled in vacuo, collecting the principal fraction at  $45-52^\circ/0.01$  mm Hg. [Lit. b.p.  $124^\circ/20$  mm].<sup>70</sup> The yield of ester was 129 g (72%).

Ethyl p-biphenylacetate. Ethyl p-biphenylacetate was prepared by heating at reflux a mixture of biphenyl-acetonitrile (193.25 g, 1.0 mole), in 95% ethanol (414.6 ml), and sulfuric acid (164.2 ml) for eight hours. After cooling the brown mixture was added to 500 ml  $H_2O$  and the organic layer extracted into methylene chloride. The methylene chloride phase was washed with 10% sodium bicarbonate followed by water until neutral pH. The methylene chloride solution was dried over  $MgSO_4$  and the solvent evaporated. Distillation at  $134-136^\circ/0.2$  mm Hg produced a 76% yield (183 g) of product ester [Lit. b.p.  $134-136^\circ/0.2$  mm].<sup>71</sup>

1,3-Bis(p-methoxyphenyl)-2-propanone. 1,3-bis(p-methoxyphenyl)-2-propanone was prepared according to the method of Conant and Blatt.<sup>44</sup>

Isopropylmagnesium bromide was prepared by dropwise addition of isopropyl bromide (215.1 g, 1.75 mole), purified by heating at reflux over phosphorous pentoxide

under nitrogen, followed by distillation at 59°, to magnesium turnings (42.55 g, 1.75 mole), in anhydrous ether (1:1). The isopropyl bromide was added at such a rate as to allow moderate refluxing of ether. When addition was complete, the mixture was stirred at room temperature until all magnesium was dissolved.

To the gray solution was added dropwise with stirring, ethyl-p-methoxyphenylacetate (194 g, 1.0 mole), at such a rate as to allow moderate refluxing of ether. When addition was complete, the mixture was allowed to stand overnight (12 hours). The reaction mixture was cooled to 0°C in an ice bath and a 10% solution of ammonium chloride (535 ml) was added dropwise. This was followed by a dropwise addition of a 10% solution of hydrochloric acid until the pH of the aqueous phase tested acidic. The phases were separated, and the aqueous phase washed with ether. The ether phases were combined and the ether evaporated. The remaining orange oil was dissolved in one liter glacial acetic acid combined with 200 ml 18% HCl. The red solution was refluxed overnight (12 hours), or until CO<sub>2</sub> evolution ceased. The volume of acid solution was reduced via distillation in vacuo to 20% of the original volume. The residue was dissolved in ether and the ether solution was dried over MgSO<sub>4</sub>. The ether was evaporated, yielding 124.2 g (92%) of crude, orange-yellow, granular ketone. Recrystallization from hexane gave 99.4 g



(74%) yellow needles (m.p.  $86^{\circ}$ ), (lit.  $86-86.2^{\circ}\text{C}$ )<sup>45</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 6.94 ppm (m-aromatic, 8H), 3.76 ppm (s,  $\text{CH}_3\text{-O}$ , 6H), 3.62 ppm (s,  $\text{CH}_2$ , 4H).

1,3-Bis(p-tolyl)-2-propanone. 1,3-Bis(p-tolyl)-2-propanone was prepared from ethyl p-tolylacetate (178 g, 1.0 mole), in the same manner as in the preparation of 1,3-bis(p-methoxyphenyl)-2-propanone. After evaporation of ether in final workup, 87.4 g (73%) of crude, amorphous solid was obtained. Recrystallization in absolute ethanol produced colorless crystals (26.9 g, 23%), with a melting point of  $52-53^{\circ}\text{C}$  (lit.  $53.2-54.4^{\circ}\text{C}$ ).<sup>45</sup> Evaporation of ethanol from filtrate and distillation of the orange oil at  $110-120$  and  $5 \times 10^{-3}$  mm pressure produced a colorless oily distillate, which solidified into a colorless solid (22.6 g, 19%), with a melting point of  $52-53^{\circ}\text{C}$ , which also proved to be the desired product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 7.07 ppm (m, aromatic, 8H), 3.65 ppm (s,  $\text{-CH}_2\text{-}$ , 4H), 2.32 ppm (s,  $\text{-CH}_3$ , 6H).

1,3-Bis(p-biphenyl)-2-propanone. 1,3-Bis(p-biphenyl)-2-propanone was prepared by the self condensation of ethyl p-biphenyl-acetate (240 g, 1.0 mole), according to the procedure described above. After the acid catalyzed decarboxylation, product was extracted into chloroform instead of ether, due to better solubility. Isolation as above produced 108.2 g (60%) crude yellow solid.



Recrystallization from absolute ethanol produced 72.1 g (40%) pale yellow ketone (m.p. 164-166°C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 7.41 ppm (m-aromatic 18H), 3.79 ppm (s,  $-\text{CH}_2-$ , 4H).

2,6-Diphenyl-2-cyclohexenone. Dibenzylketone (25 g, 0.12 mole) was combined with N,N,N',N'-tetramethylene diamine (5.78 g, 0.05 mole), and the mixture cooled to 15-20° with vigorous stirring. Dropwise over a period of 2-1/2 hours, acrolein (13.4 g, 0.24 mole) was added overnight. Distillation directly from the reaction flask at 0.1-0.2 mm pressure produced a viscous yellow oil at 190-210°C. Upon standing, the oil solidified into a pale yellow, solid product, m.p. 58-64°C (lit. 65-66°C).<sup>5</sup> The yield was 22.9 g (76%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 7.20 ppm (m-aromatic, 10H), 3.68 ppm (t,  $\text{CH}$ , 1H), 2.32 ppm (m,  $\text{CH}-\text{CH}_2-\text{CH}_2$ , 5H).

2,6-Bis(p-methoxyphenyl)-2-cyclohexenone. 1,3-Bis(p-methoxyphenyl)-2-propanone (9.6 g, 0.035 mole) was combined with 1,5-diazabicyclo[5.4.0]undec-5-ene (3.05 g, 0.02 mole) and 25 ml benzene. The mixture was cooled to 0°C and acrolein (3.96 g, 0.07 mole) was added dropwise. The mixture was stirred at room temperature overnight. The benzene was evaporated and the dark orange, viscous liquid distilled in vacuo. The product was obtained at 260°C and at 0.05 mm. The yield was 3.0 g (28%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 6.8-7.55 ppm (m-aromatic, 8H), 3.8 ppm (d- $\text{OCH}_3$ , 6H), 3.61 ppm (s-,  $\text{CH}$ -, 1H), 1.7-2.7 ppm (m- $\text{CHCH}_2\text{CH}_2$ -, 5H).

2,6-Diphenylcyclohexanone (anhydrous method). To 100 ml t-butanol was added under nitrogen and with stirring, 3.91 g (0.1 mole) potassium metal. The mixture was then stirred under nitrogen for one hour or until all potassium was dissolved. 10.5 g (0.05 mole) dibenzylketone was then added quickly. After dissolution, 1,3-dibromopropane (10.1 g, 0.05 mole) was added dropwise over a one hour period. The cloudy orange mixture was then stirred for one hour and then refluxed for two hours. After cooling, 20 ml water was added, followed by 1 ml acetic acid to neutralize. The yellow mixture was poured into 50 ml water. The insoluble yellow oil was decanted and dissolved in ether. The ether phase was then washed with water, dried over anhydrous magnesium sulfate and the ether evaporated. The yellow oil, on standing developed needle shaped crystals which were filtered and washed with petroleum ether. After drying, the colorless white needles weighed 2.7 g (20%) and melted at 122°C sharp. The residual oil deposited more crystals (0.7 g, 5%), which melted at 115-119°C. Recrystallization from hexane produced colorless needles of melting point 122°C (lit. m.p. 124°C).<sup>37</sup>

2,6-Bis(p-methoxyphenyl)cyclohexanone. 2,6-Bis(p-methoxyphenyl)cyclohexanone was prepared as above. The reaction of 5.4 g (0.02 mole) 1,3-bis(p-methoxyphenyl)-2-propanone

with 4.04 g (0.02 mole) 1,3-dibromopropane produced 1.4 g (23%) of product as pale yellow needles of melting point 151-152°C. Chloroform was used as the extracting solvent in place of ether as the product precipitated from ether.

2,6-Diphenylcyclohexanone (phase transfer catalyzed).

Dibenzylketone (21.03 g, 0.01 mole) was dissolved in chlorobenzene (100 ml) in a 500 ml round bottom flask. To this was added tetrabutylammonium bromide (1.61 g, 0.005 mole). The solution was mixed vigorously under nitrogen atmosphere with 100 ml of a 50% solution of sodium hydroxide. 1,3-Dibromopropane (20.2 g, 0.1 mole) was added dropwise over one hour and the mixture stirred vigorously overnight. 200 ml water was then added and the layers separated. The organic phase was washed with 5% hydrochloric acid, then water until neutral. After drying over anhydrous magnesium sulfate, the solvent was evaporated to 20% volume and crystallization occurred upon standing. The white needles, after filtration and drying, weighed 9.0 g, a yield of 36%. The melting point of the isolated sample was 115-119°C. Recrystallization from hexane gave white needles of melting point 119-121°C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 7.75 ppm (m, aromatic, 10H), 3.75 ppm (t,  $-\text{CH}_2$ , 2H), 2.15 ppm (m,  $-\text{CH}_2\text{CH}_2\text{CH}_2$ , 5H). Analysis: Calculated for  $\text{C}_{18}\text{H}_{18}\text{O}$ ; C, 86.40%; H, 7.20%. Found: C, 86.24%; H, 7.12%.

2,6-Bis(p-methoxyphenyl)cyclohexanone. In a 250 ml 3 neck round bottom flask equipped with nitrogen inlet, mechanical stirrer and addition funnel were combined 1,3-bis(p-methoxyphenyl)-2-propanone (13.5 g, 0.05 mole), tetrabutylammonium bromide (6.45 g, 0.02 mole), 50% sodium hydroxide (25 ml), and 15 ml chlorobenzene. The mixture was stirred vigorously under nitrogen and to this was added, dropwise, 1,3-dibromopropane (10.1 g, 0.05 mole) at such a rate that the temperature did not exceed 40°C. Following addition, the reaction was allowed to stir for 16 hours. The mixture was then poured into 200 ml water and the organic phase dissolved in  $\text{CHCl}_3$  (50 ml). The chloroform solution was washed with water until neutral. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the crude yellow solid was washed with ether. Filtration produced a white powder which weighed 7.9 g after drying, a yield of 51%. The melting point of this material as isolated was 165-166°C. Recrystallization from hexane failed to improve it.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.01 ppm (m, aromatic, 8H), 3.79 ppm (t,  $-\text{CH}_2$ , 2H), 3.77 ppm (s,  $\text{CH}_3\text{O}-$ , 6H), 2.06 ppm (m,  $-\text{CH}_2\text{CH}_2\text{CH}_2$ , 6H). Analysis: calculated for  $\text{C}_{20}\text{H}_{22}\text{O}_3$ ; C, 77.42%; H, 7.10%. Found: C, 77.51%; H, 7.05%.

2,6-Bis(p-tolyl)cyclohexanone. 2,6-Bis(p-tolyl)cyclohexanone was prepared according to the preceding procedure.

11.9 g (0.05 mole) 1,3-bis(p-tolyl)-2-propanone produced 5.6 g (42%) crude off-white powder isolated by washing the product residue with hexane. The melting point was 129-133°C. Recrystallization from 95% ethanol gave white needles which melted sharply at 139°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.16 ppm (m-aromatic, 8H), 3.71 ppm (t,  $-\text{CH}_2-$ , 2H), 2.31 ppm (s,  $-\text{CH}_3$ , 6H). Analysis: calculated for  $\text{C}_{20}\text{H}_{22}\text{O}$ ; C, 86.33%; H, 7.91%. Found: C, 86.20%; H, 7.75%.

2,6-Bis(p-biphenyl)cyclohexanone. 2,6-Bis(p-biphenyl)-cyclohexanone was prepared as above. 9.05 g (0.025 mole) 1,3-bis(p-biphenyl)propanone yielded 3.1 g (30%) of a white powder obtained by washing the crude product with ether. The melting point of this material was 191-193°C. Recrystallization of this material from chloroform failed to increase the melting point.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.40 ppm (m-aromatic, 18H), 3.90 ppm (t,  $-\text{CH}_2-$ , 2H), 2.23 ppm (m,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , 6H). Analysis: calculated for  $\text{C}_{30}\text{H}_{26}\text{O}$ ; C, 89.55%; H, 6.47%. Found: C, 89.69%; H, 6.66%.

2,6-Bis(p-methoxyphenyl)phenol. 3.1 g (0.01 mole) 2,6-bis(p-methoxyphenyl)cyclohexanone was combined with 0.63 g of 5% palladium on carbon and 10 ml phenyl ether. The mixture was refluxed with vigorous stirring for twenty four hours. The spent catalyst was removed by filtration and phenyl ether was removed by vacuum distillation. The orange residue was dissolved in hot absolute ethanol. Upon



cooling, pale brown crystals formed. Filtration and drying produced 2.5 g (80%) off-white phenol of melting point 105-107°C. Two recrystallizations from heptane produced colorless needles of melting point 109°C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 6.93-7.94 ppm (m, aromatic, 11H), 5.34 ppm (s, OH, 1H), 3.85 ppm (s,  $-\text{CH}_3$ , 6H). Analysis: calculated for  $\text{C}_{20}\text{H}_{18}\text{O}_3$ ; C, 78.43%; H, 5.88%. Found: C, 78.42%; H, 5.88%.

2,6-Bis(p-tolyl)phenol. 2,6-Bis(p-tolyl)phenol was prepared by a nearly identical procedure. 2,6-bis(p-tolyl)-cyclohexanone (1.88 g, 0.0068 mole) and 0.7 g, 5% palladium on carbon catalyst were refluxed three hours in 7.5 ml phenyl ether. Workup as above produced 1.5 g (82%) crude brown phenol of melting point 91-92°C. Recrystallization from absolute ethanol produced 1.0 g (55%) off-white crystals of melting point 94-95°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 6.97-7.50 ppm (m, aromatic, 11H), 5.37 (s, -OH, 1H), 2.39 ppm (s,  $-\text{CH}_3$ , 6H). Analysis: calculated for  $\text{C}_{20}\text{H}_{18}\text{O}$ ; C, 87.59%; H, 6.57%. Found: C, 87.73%; H, 6.61%.

2,6-Bis(p-biphenylyl)phenol. 4.02 g (0.01 mole) 2,6-bis(p-biphenylyl)cyclohexanone was combined with 0.64 g (0.02 mole) sulfur in 150 ml phenyl ether and the mixture heated to reflux for three hours. The phenyl ether was removed in vacuo and the brown residue recrystallized in a heptane chloroform mixture producing 3.3 g (84%) pale

brown plates of melting point 221-230°C. Recrystallization from chloroform twice gave 3.0 g (75%) of off-white plates, melting point 242-243°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.24-7.72 ppm (m, aromatic, 21H), 5.48 ppm (s, -OH, 1H).

Analysis: calculated for  $\text{C}_{30}\text{H}_{22}\text{O}$ ; C, 90.45%; H, 5.52%.

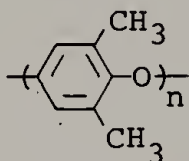
Found: C, 90.36%; H, 5.48%.



C H A P T E R   I V  
PREPARATION OF HOMOPOLYMERS AND COPOLYMERS  
OF SYMMETRICAL 2,6-DIARYLPHENOLS

Historical and Introduction

The polymerization technique employed was first reported by Hay in 1959.<sup>72</sup> 2,6-Dimethylphenol (DMP) was polymerized to poly(oxy-2,6-dimethyl-1,4-phenylene) (PDMP) 50,

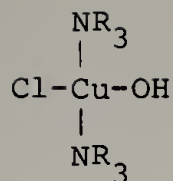


50

with number average molecular weight 28,000. The procedure involved bubbling oxygen through a solution of the phenol in an organic solvent at room temperature, with an amine and copper (I) salt as catalysts. Under these conditions, copper (I) is transformed to copper (II) as shown in equation 49:

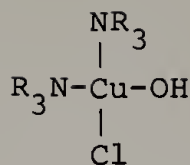


The sole purpose of  $\text{O}_2$  is to maintain the copper complex in the higher oxidation state. It is proposed that the basic amine ligands complex with copper (II) ion to form one of two possible isomers (51 and 52).<sup>73</sup>



trans

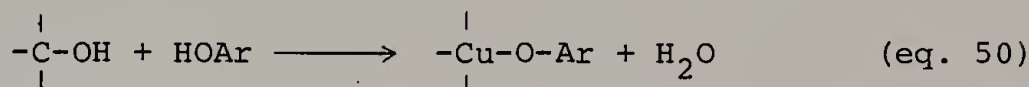
51



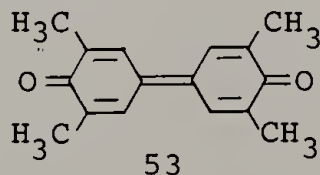
cis

52

The trans form occurs more frequently with monodentate amines such as pyridine, and the cis form with bidentate ligands such as N,N,N',N'-tetramethylethylenediamine (TMEDA). The first step in the polymerization is then theorized to be:<sup>74</sup>

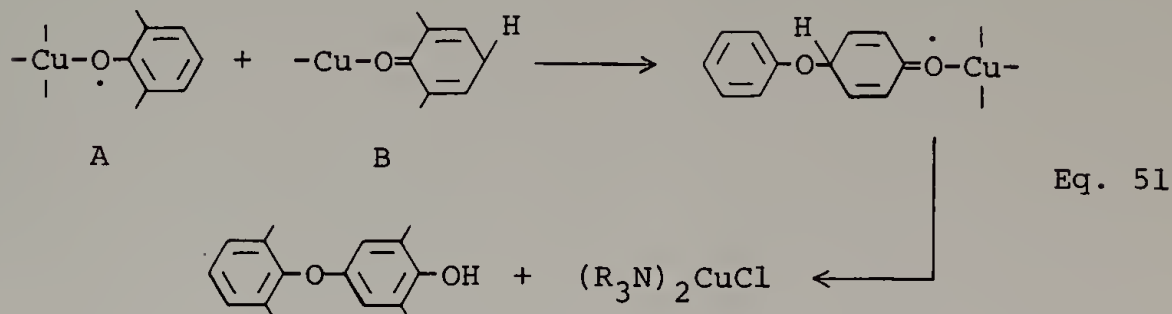


In this copper amine complex, electron transfer from oxygen to copper gives a phenoxy radical. If this were a free phenoxy radical one would expect a preference for carbon-carbon coupling upon cleavage from Cu, producing the diphenoquinone 53.



However, when 2,6-dimethylphenol is the monomer, carbon-oxygen bonds are formed almost exclusively when the amine ligands are small. This implies that the phenoxy radical must remain bound to the copper-amine complex during the coupling reaction and the initial coupling

reaction could be explained by the existence of two forms of bound radical defined by A and B in equation 51.



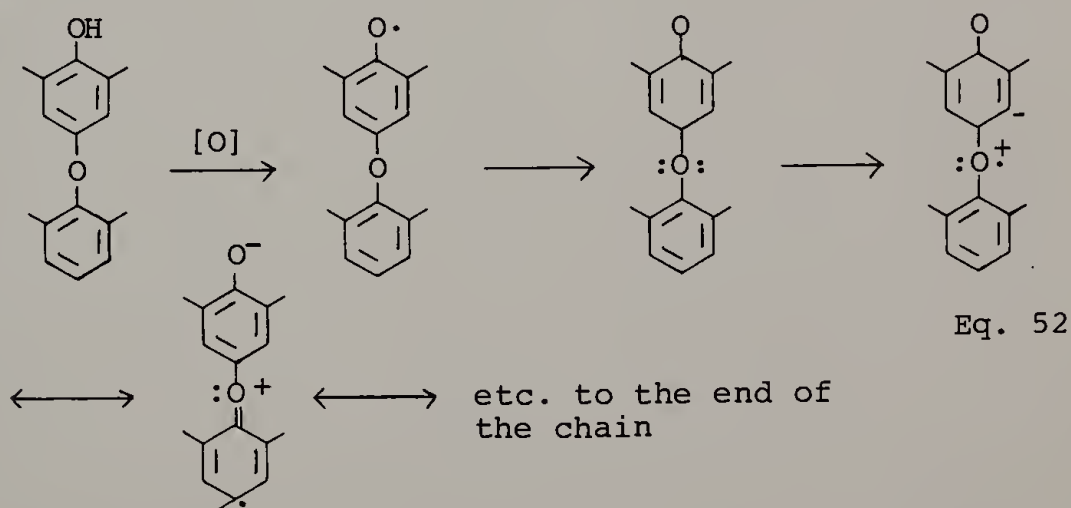
54

The spent Cu (I) complex 54 can then be reoxidized to Cu (II) by  $\text{O}_2$  and the process continued. In the polymerization of DMP, the proportion of C-O-C bonds to C-C bonds (diphenoquinone) is directly dependent upon the amount of amine present.<sup>75</sup> The C-O-C proportion increases with increasing pyridine to copper ratio until at values of 10:1, only minor amounts of diphenoquinone are formed. In the case where the strongly basic bidentate TMEDA is used, a ligand to copper ratio of 1:1 causes almost exclusive carbon-oxygen coupling.

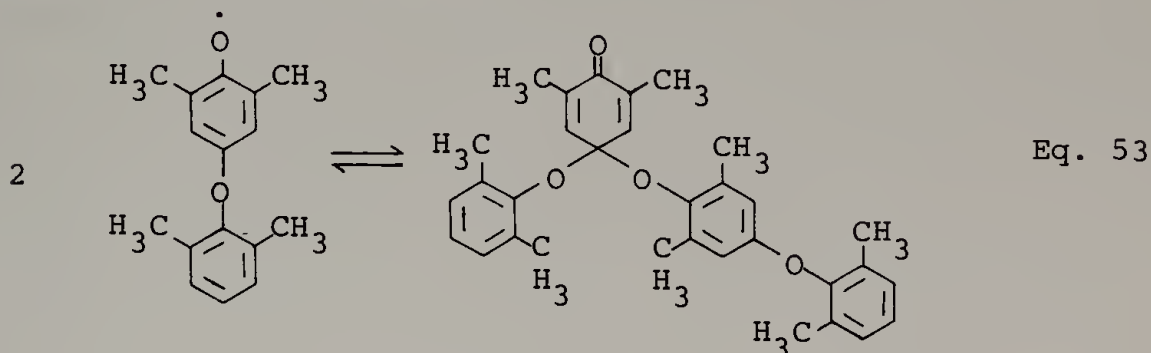
Transition metal ions other than copper may be used to catalyze these polymerizations. DMP has been polymerized to low molecular weight polymer using activated manganese dioxide,<sup>76</sup> lead dioxide<sup>77</sup> or silver oxide.<sup>78</sup> In these cases, no amine ligands were necessary. One study has shown that the most active catalysts in reactions of this type are transition metals which form complexes of

limited hydrolytic stability.<sup>79</sup> For successful reactions, the complexes must form aquo and hydroxo complexes upon hydrolysis.

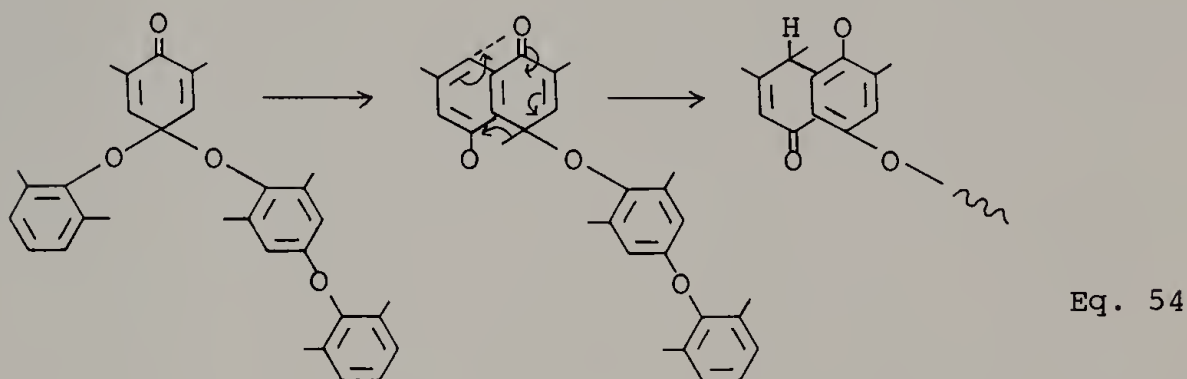
Although the initiation and propagation mechanisms are free radical in nature, the polymerization proceeds as in a condensation process. Oligomers were isolated from the polymerization reaction at early stages and a rapid increase in molecular weight was observed at high conversions. It was also found that protection of the hydroxyl group by methyl groups in monomeric or oligomeric species rendered them completely unreactive to further polymerization. There have been three mechanisms proposed to explain these observations. The first, referred to as the uncoupled electron mechanism,<sup>80</sup> assumed that oligomeric phenoxy radicals combined by a head to tail coupling reaction. The implication here is that the odd electron is capable of migrating to the chain end, as in the sequence below:



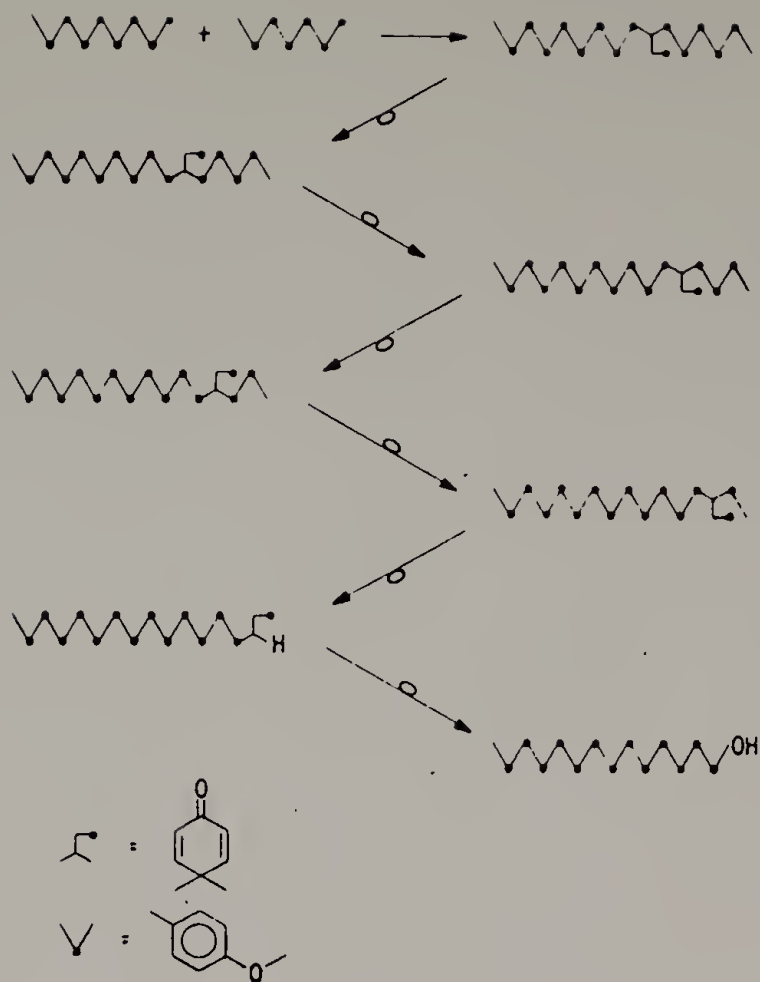
The second mechanism<sup>81</sup> involves initial formation of quinol ether intermediates from the coupling of oligomeric radicals (equation 53)



The next step is referred to as the quinol ether rearrangement:

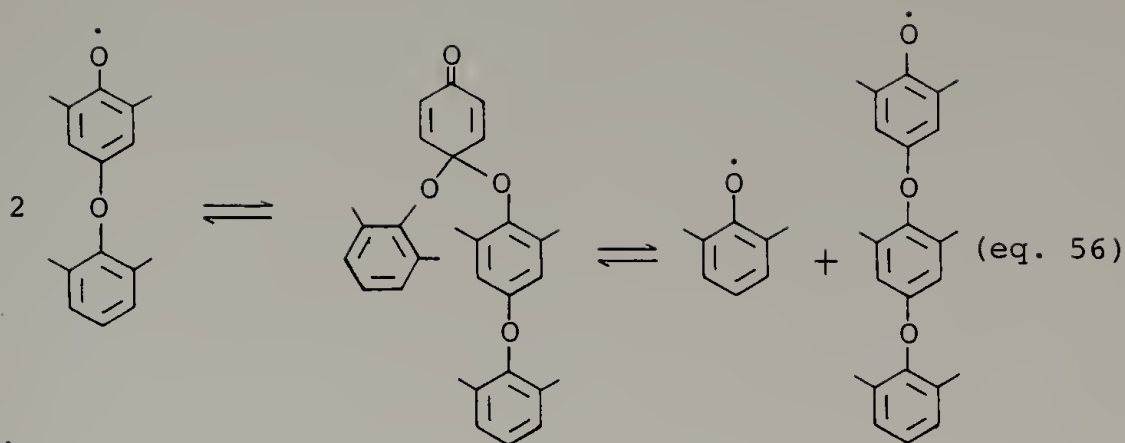


In this mechanism the formation of a new carbon-oxygen bond is accompanied by the breaking of one of the ether linkages leading to a new quinol ether. This reaction sequence is presumably perpetuated along the chain as shown schematically in Equation 55:



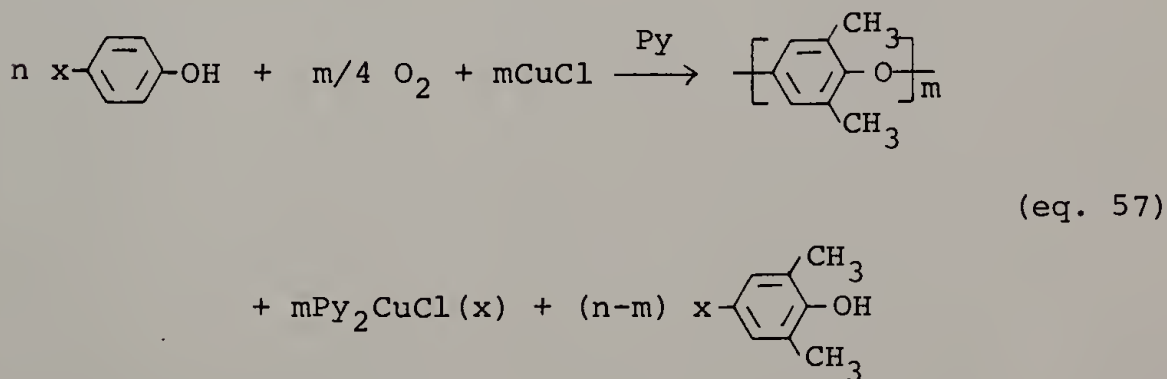
Equation 55

The third mechanism also begins with a quinol ether intermediate and has been named the quinol-ether redistribution.<sup>82</sup> In this case, the quinol-ether decomposes either to the original aryloxy radicals or to two different aryloxy radicals (equation 56):



The latter mechanism is the one most generally accepted, as large amounts of monomers and trimers are present in the reaction mixture after oxidation of dimers. The quinol-ether rearrangement mechanism provides only for even numbered oligomers as products of the oxidation of dimeric species.

Linear high molecular weight polyphenylene oxides have also been prepared from 4-halo-2,6-disubstituted phenols by oxidation with copper-amine catalysts and oxygen (equation 57).<sup>83</sup>





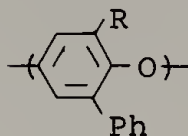
Stoichiometric amounts of copper salt or other halogen acceptors are necessary, because the amine complex of the Cu (II) halide 55 is not capable of oxidizing the phenol. Intrinsic viscosities as high as 1.2 dl/g have been achieved from the polymerization of 4-Cl-2,6-dimethylphenol in this manner. The advantage of this last system is the avoidance of any diphenoquinone production, due to the blocking of the C-4 position by a halogen.

In contrast to the polymerization of DMP, there have been few investigations into the oxidative coupling of 2,6-diarylphenols. The parent monomer, 2,6-diphenylphenol (DPP) has been polymerized to number and weight average molecular weights of 150,000 and 296,000 respectively, using a TMEDA complex of CuCl at 60°C as catalyst.<sup>52</sup> As mentioned in Chapter II, the higher temperature is necessary due to the higher oxidation potential of the monomer, because of the ortho phenyl substituents. Comparable molecular weights were obtained at room temperature using silver oxide or lead dioxide as oxidizing agents. Other examples of 2,6-diarylphenol polymerizations are listed in Table 7.<sup>5</sup>

As is evident from the intrinsic viscosity data, high molecular weight polymers could not be obtained using phenols with ortho substituted aryl substituents. As mentioned in Chapter II, this is due to steric hindrance.

The polymer from the oxidative coupling of DPP,

TABLE 7  
POLYMERIZATION OF UNSYMMETRICAL DIARYLPHENOLS



R	Polym. Cat.	$[\eta]$ (CHCl <sub>3</sub> @ 25°, dl/g)
m-tolyl	PbO <sub>2</sub>	0.17
p-tolyl	PbO <sub>2</sub>	0.58
p-t-butylphenyl	PbO <sub>2</sub>	0.59
o-biphenyl	Ag <sub>2</sub> O	0.14
3'-o-terphenyl	PbO <sub>2</sub>	0.28
α-naphthyl	AgO <sub>2</sub>	0.20

poly(oxy-2,6-diphenyl-1,4-phenylene) (PDPP) exhibits a strong tendency to crystallize above its  $T_g$  ( $230^{\circ}\text{C}$ ) as indicated by an endotherm (DSC) at approximately  $290\text{--}300^{\circ}\text{C}$ . The polymer has a crystalline melting point of  $480^{\circ}\text{C}$ . Crystallinity percentages determined by x-ray diffraction as high as 52% have been achieved for a sample annealed for 30 minutes at  $452^{\circ}\text{C}$ .<sup>84</sup> This behavior has proven to be a serious handicap with regard to the melt processibility of this polymer. Thermogravimetric analysis (TGA) shows commencement of weight loss in air at  $430^{\circ}\text{C}$ . Even under an inert atmosphere (helium), rapid decomposition commences at  $515^{\circ}\text{C}$ , reaching maximum rate of weight loss of 6.2%/min at  $550^{\circ}\text{C}$ . Films and fibers can be made by casting and spinning from solution, and the onset of crystallization above  $T_g$  then renders them insoluble.

The thermal behavior of PDPP is in marked contrast to the commercial polymer, poly(oxy-2,6-dimethyl-1,4-phenylene) (PDMP). This polymer does not crystallize thermally, even at long annealing times.<sup>85</sup> Crystallization has only been induced from solution, such as a 3:1 mixture of methanol-toluene, or in the form of a complex with methylene chloride.<sup>86</sup> Melting of crystalline PDMP commences at approximately  $235^{\circ}\text{C}$  with a maximum at  $257^{\circ}\text{C}$ .<sup>85</sup> Considering that the glass transition temperature of this polymer is  $225^{\circ}\text{C}$ , a very narrow range of annealing

temperatures are available where crystallization could occur at a reasonable rate. In fact, the observed ratio of  $T_g/T_m$ , 0.92, indicative of the narrowness of this range, is the highest value that has been recorded for a polymer. From this it is apparent that there is limited potential for thermal crystallization in PDMP.

There have been two means thus far pursued to develop a compromise between the highly crystalline, high melting PDPP and the low melting, non-thermally crystallizable PDMP. The goal is a material which crystallizes thermally above  $T_g$ , which melts at a temperature between PDMP and PDPP, and below the onset of thermal oxidative degradation.

One approach to this end was via the synthesis of substituted 2,6-diphenylphenols with a substituent on one of the ortho phenyl rings.<sup>5</sup> The polymers prepared from these various unsymmetrical diarylphenols are listed in Table 7. It was hoped that the additional substitution would affect packing efficiency only enough to lower the melting point without eliminating thermal crystallizability. However, analysis by differential scanning calorimetry (DSC) indicated that all of these polymers were completely amorphous.

A second approach which could potentially produce polymers with the desired properties is through the preparation of random and block copolymers of DPP with DMP or

2-methyl-6-phenylphenol (MPP). The structure and composition of copolymer products from oxidative coupling reactions is determined by rates of polymerization relative to rates of rearrangement and redistribution (equations 54 and 56). These rates are governed by the reactivity of each phenol which in turn is defined by oxidation potentials. As mentioned earlier, the oxidation potential of DPP is considerably higher than DMP, hence the latter is more reactive. When a mixture of the two monomers was copolymerized at 25° using CuCl and TMEDA as catalysts, a random copolymer was formed.<sup>87</sup> This also happened when DPP was added to a polymerization mixture containing DMP homopolymer. In the latter case, the random structure resulted because the rate of oxidation of DPP is much less than the rate of redistribution. Conversely, when the more reactive DMP was added to a homopolymer of DPP, a block copolymer was observed. This was also the case when a mixture of homopolymers was oxidized. Similar results were reported for the copolymerization of DPP with MPP.<sup>88</sup> Although less reactive than DMP, MPP is still considerably more reactive than DPP when polymerized at 25°C, with a CuCl/pyridine catalyst. Mixtures of monomers produced random copolymers, whereas mixtures of homopolymers produced block copolymers at 25°C. Addition of DPP to growing MPP at 60°C produced a so-called mixed block copolymer containing DPP blocks and blocks of randomly arranged MPP and DPP units.



The polymers formed from these reactions were found to exhibit varied morphologies. All random copolymers with approximately equimolar amounts of comonomers were found to be completely amorphous. The DPP portions in DMP-DPP block copolymers crystallized on heating at approximately 290°C, when of sufficient length ( $DP \geq 15$ ).<sup>88</sup> Melting still occurred at 480°C, however. More encouraging results were obtained from the polymerization of a DPP-MPP mixture containing 5-10% MPP. The large percentage of DPP produced blocks of sufficient length to crystallize even though the structure was a random one. In a copolymer containing 5 mole percent MPP, a melting endotherm maximum was observed at 474°. A maximum degree of crystallinity of 20% was obtained when this sample was annealed at 290°. At 10 mole percent MPP, the values were 455° for  $T_m$  and 18% crystallinity. Further significant reductions in  $T_m$  by increasing MPP content are not likely, since at >18 mole percent MPP, the polymer becomes completely amorphous. The reduction in  $T_m$  thus far obtained, 455°C, though encouraging, still exceeds the temperature for onset of thermal oxidative degradation. Other alternatives must therefore be pursued.

The next logical step in the search for a melt processible crystallizable polyphenylene oxide would be an extension of the first approach mentioned above. Instead of monosubstituted unsymmetrical diarylphenols, both ortho

phenyl groups are identically substituted. In this case, the greater symmetry might improve the packing efficiency over that in the unsymmetrical compounds, allowing them to crystallize while the  $T_m$  might be effectively lowered. This is the subject of the present study.



## CHAPTER V

### RESULTS AND DISCUSSION

#### A. Synthesis of Homopolymers

The symmetrical 2,6-diarylphenols, 2,6-bis(p-tolyl)-phenol (DTP), 2,6-bis(p-methoxyphenyl)phenol (DAP), and 2,6-bis(p-biphenyl)phenol (DBP) were oxidatively polymerized and the resulting products evaluated. The results of these polymerizations are summarized in Table 8.

DTP was polymerized with silver oxide as oxidizing agent, with benzene as solvent at room temperature. A fibrous material was obtained upon precipitation into methanol. The polymer had an inherent viscosity of 0.74 dl/g ( $\text{CHCl}_3$ , 25°C), which corresponds to an average degree of polymerization of 445. The value for molecular weight dispersion ( $M_w/M_n$ ) as determined by gel permeation chromatography was 1.49, which was comparable to values reported for the polymerization of 2,6-diphenylphenol using a system of cuprous chloride/TMEDA catalysis at 60°C.<sup>89</sup> Under such conditions, a dispersion of 1.67 was reported for a comparable degree of polymerization.

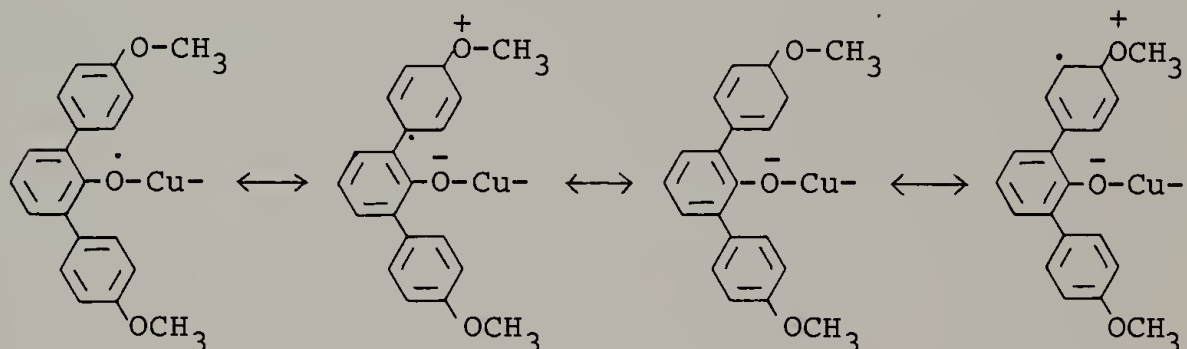
In contrast, DAP could not be polymerized to high

TABLE 8  
HOMOPOLYMERS OF 2,6-DIARYLPHENOLS

	PDTP	PDAP	PDBP
Polymerization System	Ag <sub>2</sub> O/25°	CuCl/TMEDA <sup>a</sup> /60°C	CuCl/TMEDA/60°C
Yield (%)	60	26	71
Analysis: (%)			
Calculated for:			
C	88.24	78.95	90.15
H	5.88	5.30	5.05
Found:			
C	88.21	78.10	88.93
H	5.88	5.16	4.86
$\eta_{inh}$ (dl/g)	0.74	0.38	0.084
Mn	$1.21 \times 10^5$	$1.72 \times 10^4$	$9.70 \times 10^2$
Mw	$1.81 \times 10^5$	$3.06 \times 10^4$	$2.05 \times 10^3$
Mz	$2.56 \times 10^5$	$4.55 \times 10^4$	$3.24 \times 10^3$
MWD	1.49	1.78	2.11
% diphenoquinone	14.29	11.51	--

<sup>a</sup>N,N,N',N'-tetramethylethylenediamine

molecular weight under these conditions. After sixteen hours at room temperature, material of inherent viscosity 0.05 dl/g was obtained. This may be due to monomer impurity and/or lack of sufficient reactivity under these polymerization conditions. The former was highly unlikely since the monomer purity was established by microanalysis, melting point and thin layer chromatography. The possibility of low monomer reactivity, however, could not be ruled out. The presence of the methoxy group may promote delocalization of the radical of the complexed intermediate as shown below.<sup>90</sup>

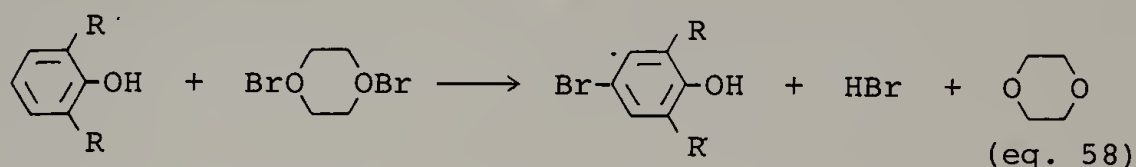


The existence of these additional resonance hybrid structures could stabilize the radical and thereby reduce its reactivity toward 1,4 coupling.

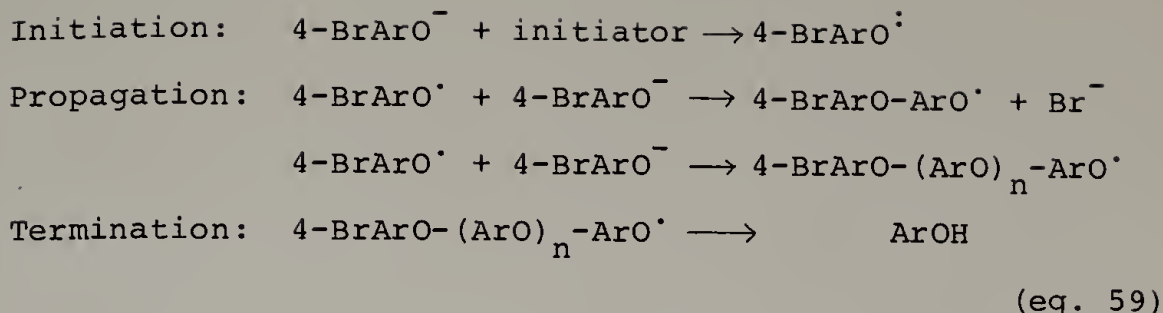
To compensate for this presumed decrease in reactivity, attempts were made to polymerize the para bromo substituted analog of the phenol. As mentioned in Chapter IV (re: equation 57), diphenoquinone production is prevented in this system. This, coupled with the fact that

bromine is displaced more easily than hydrogen, could provide the driving force for the polymerization reaction.

The monomer 4-bromo-2,6-bis(p-methoxyphenyl)phenol (BrDAP) was prepared in high yield by treatment of an ether solution of DAP at room temperature with an equivalent amount of dioxane dibromide (equation 58).



Two systems were used for the oxidative polymerization of BrDAP. As shown in equation 57, the cupric halide (55) generated as side product is incapable of oxidizing the phenol. Thus, in the first method used, the BrDAP was combined with a stoichiometric amount of CuCl in pyridine solvent. An equivalent amount of TMEDA was added to preferentially chelate with CuCl. A steady stream of oxygen was applied and the temperature maintained at 60°C. The resulting polymer was a gray brittle material of inherent viscosity 0.19 dl/g and obtained in a yield of 85%. Although a significant improvement, the molecular weight was still considerably below that obtained for DPP or DTP polymerization. The second attempt at BrDAP oxidative coupling polymerization was by a system referred to as initiated polymerization. In the presence of a catalytic amount of oxidizing agent and an inorganic base, the likely mechanism is as follows:



An inherent viscosity of 1.25 dl/g was reported when 4-bromo-2,6-dimethylphenol was polymerized in a two phase system.<sup>91</sup> The aqueous phase consisted of potassium hydroxide, copper sulfate, and ammonium persulfate as initiator. The monomer was dissolved in benzene and the mixture agitated under a steady stream of oxygen. Polymerization then proceeded at the interface. When BrDAP was polymerized under similar conditions, a low yield (20%) of low molecular weight material of inherent viscosity 0.06 dl/g was obtained. The low molecular weight in this case was most likely attributable to limited solubility of oligomeric intermediate. Clouding of the benzene layer was observed, indicating precipitation of low molecular weight material, which would cause further polymerization to cease.

Limited solubility of the growing polymer may be responsible for the low molecular weight products obtained in all the procedures thus far attempted.

Another indication that solubility may have been a factor in leading to molecular weight polymers was the observation that the highest molecular weight thus far

obtained was in the system using pyridine rather than the less polar benzene as solvent. An attempt was therefore made to polymerize DAP with silver oxide at room temperature using the more polar o-dichlorobenzene in place of benzene. In this case, a 25% yield of polymer with inherent viscosity 0.16 dl/g was obtained. Higher molecular weight polymer was obtained in a system consisting of CuCl, TMEDA, o-dichlorobenzene and molecular oxygen. As in the polymerization of DPP, an elevated temperature of 60°C was maintained during the polymerization. It was hoped that the increased temperature coupled with the utilization of the polar o-dichlorobenzene as the solvent would markedly improve the solubility of the growing polymer. Utilizing a catalyst with a Cu:N ratio of 1:1, an inherent viscosity of 0.32 dl/g was obtained. The maximum inherent viscosity of 0.38 dl/g corresponding to a  $M_n$  of  $1.72 \times 10^4$  or an average  $D_p$  of 56, was achieved with a Cu:N ratio of 1:2. In these latter two cases, the ability to form brittle films when cast from solution was evident for the first time. In neither case, however, was any tendency for fiber formation noted. Neither polymer was totally soluble in chloroform, and the reported viscosity values were obtained by an indirect method described in Chapter VI. This involved solubilizing the polymer by a process of perbromination, recording the viscosity and extrapolating to 0% bromine. The molecular weight could not be improved



further by increasing the temperature. This is probably due to the fact that, although solubility would improve, the amount of C-C coupling and other side reactions tend to increase with temperature. Results of the various attempts at PDAP preparation are summarized in Table 9.

We were not able to obtain high molecular weight polymers from 2,6-bis(p-biphenyl)phenol. In this case, the solubility problem was considerably more acute. From a polymerization system consisting of  $O_2$ , CuCl, TMEDA, and o-dichlorobenzene, an insoluble granular solid precipitated soon after commencement of the reaction. The material was insoluble in all organic solvents and did not melt up to  $500^\circ C$ . Perbromination as above produced a material with 53.5% bromine content. The soluble brominated material had an inherent viscosity of 0.04 dl/g, which extrapolates to 0.08 dl/g for nonbrominated material. The number average molecular weight of the brominated material was  $2.08 \times 10^3$ , which translates to 970 for the unbrominated material, indicating that dimer was the principal product.

#### B. Determination of Weight Percent Diphenoquinone as Side Product

As is evident from the mechanism of oxidative coupling polymerization discussed in Chapter IV, there is concomitant C-C coupling or diphenoquinone production in



TABLE 9  
ATTEMPTED POLYMERIZATIONS OF 2,6-BIS(p-  
METHOXYPHENYL) PHENOL

Method	Solvent <sup>a</sup>	Yield (%) <sup>b</sup>	$\eta_{inh}$ (dl/g, CHCl <sub>3</sub> , 25°C)
CuCl/TMEDA/60° (Cu:N = 1:1)	o-DCB	68	0.38
CuCl/TMEDA/60° (Cu:N = 1:2)	o-DCB	60	0.32
Ag <sub>2</sub> O/25°	B	10	0.05
Ag <sub>2</sub> O/25°	o-DCB	25	0.16
BrDAP/CuCl/ TMEDA/60°	Py	85	0.19
BrDAP/KOH/CuSO <sub>4</sub> / NH <sub>4</sub> S <sub>2</sub> O <sub>8</sub>	B	20	0.06

<sup>a</sup>o-DCB = o-dichlorobenzene

B = benzene

Py = pyridine

<sup>b</sup>crude yield

the polymerizations. In order to determine the percentage of this side product, the respective diphenoquinones had to be prepared in their pure form. This was accomplished by simply oxidizing the phenols as in the polymerizations except the chelating amine was omitted. Diphenoquinones prepared in this manner are listed in Table 10. The absorption maxima and molar absorptivities for these compounds were determined in  $\text{CHCl}_3$  and their values tabulated in Table 10.

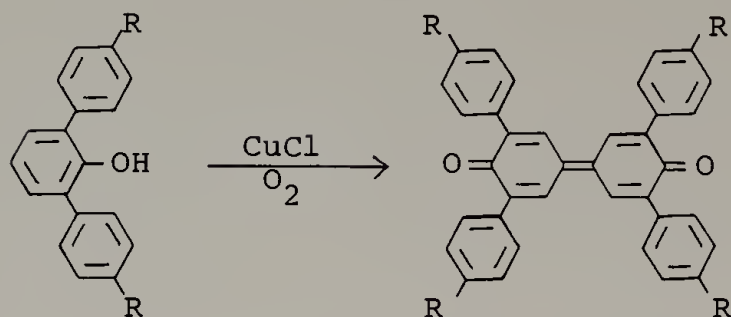
Of note is the fact that the methoxy or phenyl substituents induce a bathochromic shift in the absorption spectra of the diphenoquinone, whereas the methyl groups have no such effect.

The weight percent diphenoquinone formed in polymerization reactions were then determined by utilizing the Lambert-Beer Law,<sup>92</sup> as described in Chapter VI. Calculated values for DTP and DAP polymerizations are listed in Table 8. The insolubility of the product of DBP polymerization prevented the accurate determination of values in this case.

### C. Spectrometric Evaluation of Homopolymers (Table 11)

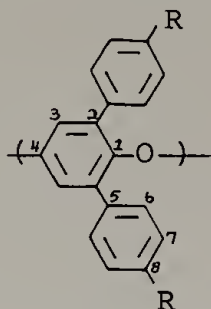
Infrared analysis. The infrared spectra of the polymers revealed several common bands indicative of their structure. Each spectrum showed a strong band at  $1180 \pm 8 \text{ cm}^{-1}$ ,

TABLE 10

PREPARATION OF 3,3',5,5'-TETRAARYLDIPHENO-  
QUINONES

	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
Yield (%)	52.8	69	45
Melting Point (°C)	284-286	290-292	>500
Analysis:			
Calculated for:			
C	88.24	78.95	90.91
H	5.88	5.26	5.05
Found:			
C	88.39	79.13	90.98
H	5.78	5.30	5.16
U.V. (in CHCl <sub>3</sub> )			
Wavelength at abs. maxima (nm)	490	544	530
ε (molar absorptivity)	60.057	36.784	18.810

TABLE 11  
HOMOPOLYMER SPECTRAL DATA



	PDPP	PDTP	PDAP	PDBP
<u>IR (cm<sup>-1</sup>)</u>				
out of plane CH	870 <sup>a</sup>	870 <sup>a</sup>	865 <sup>a</sup>	870 <sup>b</sup>
C-O stretch	1180	1180	1172	1183
<u><sup>1</sup>H NMR (ppm) (CHCl<sub>3</sub>)</u>				
C-3 proton	6.22	6.27	6.32	c
other aromatics	6.88- 7.19	6.85- 7.23	7.09- 7.25	
<u><sup>13</sup>C NMR (ppm from TMS) (CDCl<sub>3</sub>)</u>				
C-1	142.9 <sup>d</sup>	143.6	143.2 <sup>e</sup>	
C-2	135.4	135.3	135.7	
C-3	116.9	117.8	117.2	
C-4	155.9	155.4	155.1	
C-5	136.9	136.2	130.2	
C-6	126.9	129.1	129.6	
C-7	128.1	128.6	113.5	
C-8	125.9	136.8	158.8	
Other (R)	--	21.0 (CH <sub>3</sub> ) (55.1 (CH <sub>3</sub> O))		
<sup>a</sup> film	<sup>b</sup> KBr		<sup>c</sup> insoluble	
<sup>d</sup> Ref. 97	<sup>e</sup> in 1,1,2,2-tetrachloroethane			

indicative of C-O stretching. Strong absorption at  $863 \pm 3 \text{ cm}^{-1}$  represented tetrasubstitution in main chain aromatics. Characteristic C=C stretching at  $1603 \pm 7 \text{ cm}^{-1}$  was indicative of aromaticity.

$^1\text{H}$  NMR analysis. Of note here is the presence of a sharp singlet in the aromatic region considerably upfield from other aromatic peaks. This singlet, at 6.29 ppm for PDTP and at 6.32 ppm for PDAP, represents hydrogen attached to the meta carbon of the main chain. PDTP also exhibited a singlet due to methyl protons at 2.15 ppm, and PDAP showed a singlet at 3.61 ppm due to the methoxy protons. As the product from the polymerization of DBP was insoluble in common organic solvents, no NMR data is available.

$^{13}\text{C}$  NMR analysis. Likely shift assignments with respect to tetramethyl silane (TMS) are given in Table 11. A consistent feature of these polyphenylene ethers is the shift of the C-4 carbon in the main chain which is always approximately 155 ppm from TMS. Also fairly constant is the value for C-1, which was found to occur in each polymer in the vicinity of 143 ppm. The main chain meta carbons appeared considerably further upfield than all other aromatic carbons at values of 117.16 and 117.79 for PDAP and PDTP respectively. This is in reasonably close agreement with the value of 116.9 reported for the same carbon in PDPP.<sup>93</sup> Less certain were the assignments for other

aromatic carbons. In PDAP, the peak furthest downfield is assigned to the carbon adjacent to the methoxy substituent as the shift of 158.04 ppm is in close agreement to that of the analogous carbon in anisole. A value of 159.8 has been reported in the latter case.<sup>94</sup> Similarly, the assignments for the carbons meta and ortho to the methoxy groups in PDAP were made by comparison with those reported for the meta (129.5 ppm) and ortho (113.5) carbons of anisole. The closeness of C-2 and C-5 made accurate assignments of these carbons difficult in both polymers.

#### D. Thermal Analysis of Homopolymers

The polymers PDTP and PDAP were subjected to thermal analysis utilizing the Perkin-Elmer model DSC-2 differential scanning calorimeter. Sample preparations and thermal histories were as described in the experimental section (Chapter VI).

A pelletized sample of PDTP was heated at a rate of 40°/min from 400°K to 650°K. This initial scan (Figure 5A) showed a discontinuity in  $C_p$ , indicative of a glass transition, at 494°K or 221°C. The scan showed no crystallization exotherm or melting endotherm. The sample was cooled to 520°K and then maintained at that temperature, under nitrogen, for 16 hours. After cooling rapidly to 400°K, the annealed polymer was reheated at 40°/min (Figure 5B). The glass transition deflection was no longer

Figure 5. DSC scans of poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene]; (A) Initial scan (B) after annealing 16 hours at 520°K.



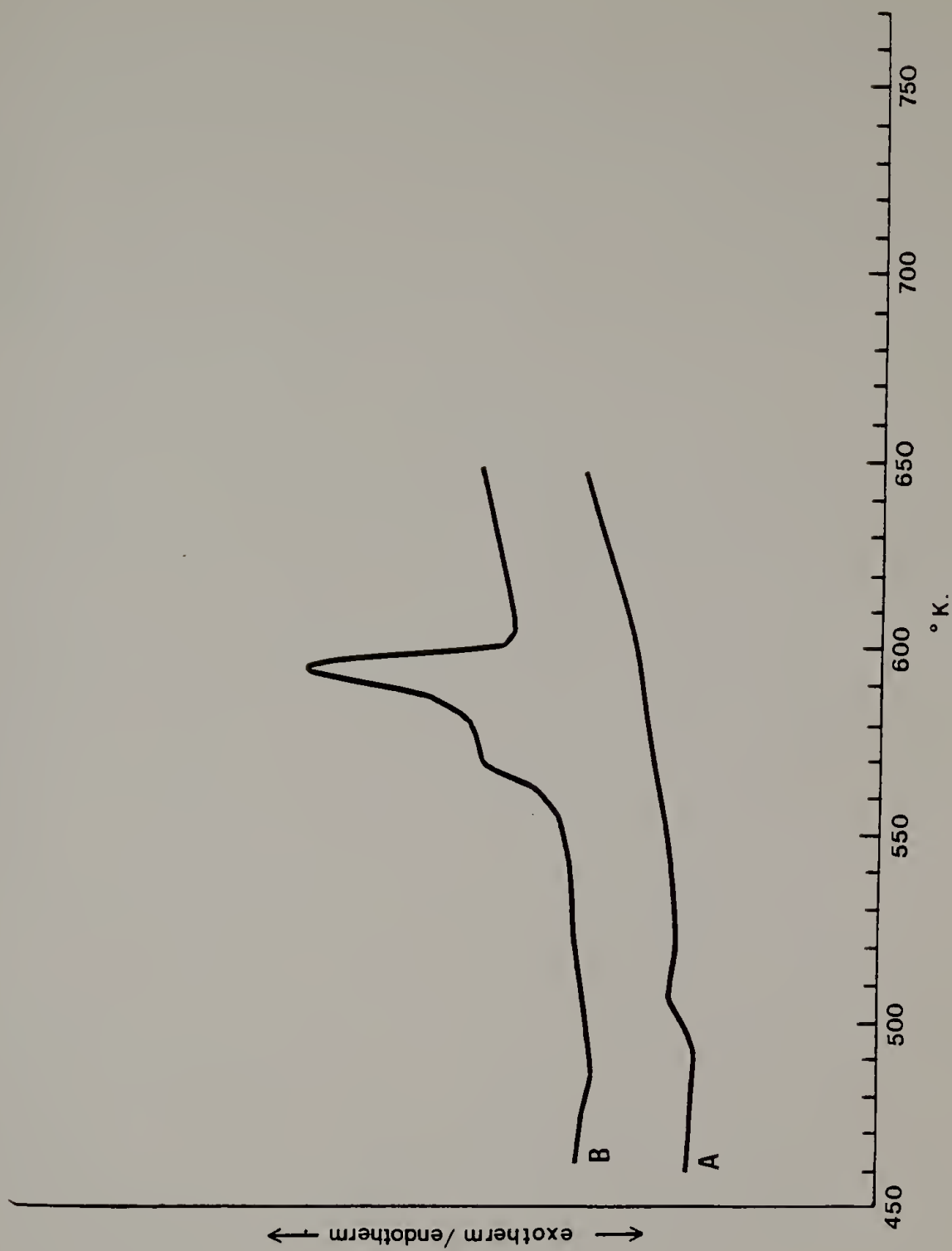


Figure 5

evident and, as before, there was no visible crystallization exotherm. This scan, however, revealed an endotherm indicative of crystalline melting. The endotherm began as a broad peak with a maximum at 570°K (297°C). This peak shouldered a much sharper and more pronounced endotherm with a maximum at 594°K (321°C).

The appearance of the two endotherms is probably explained by the initial melting of some smaller or less perfect crystals. This then allows favorable interaction of remaining nuclei and the amorphous phase inducing more and better crystallization, the ultimate melting of which is indicated by the second endotherm. A similar effect was observed in the melting behavior of PDMP (Figure 6),<sup>85</sup> although in the latter case, the premelt peak was not nearly so pronounced. In contrast, there is no evidence of premelt phenomena in the thermal treatment of PDPP. In this case, a single, somewhat symmetrical endotherm was observed (Figure 7). These observations seem to imply that the aliphatic substituent is in some way responsible for the premelt behavior.

The crystallinity of the annealed sample of PDTP was also clearly discernable from the wide angle x-ray scattering (WAXS) photo (Figure 8), as evidenced by the pattern of sharp concentric rings. The percent crystallinity of this material was estimated by a procedure described in Chapter 6 to be approximately 19%.

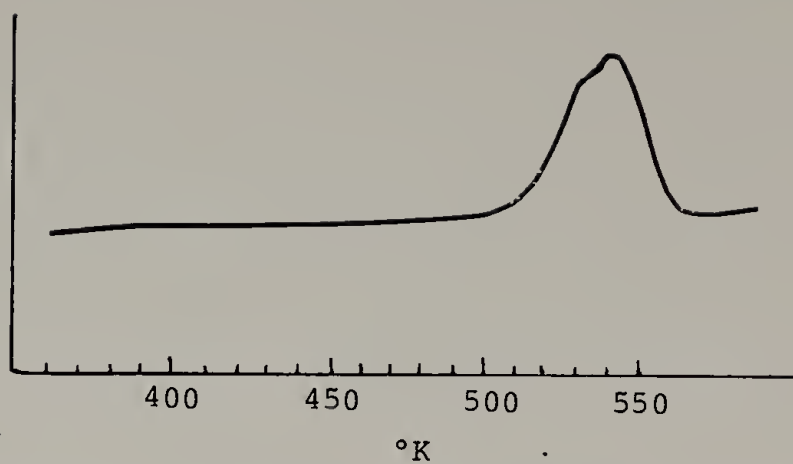


Figure 6. DSC of poly (oxy-2,6-dimethyl-1,4- phenylene)

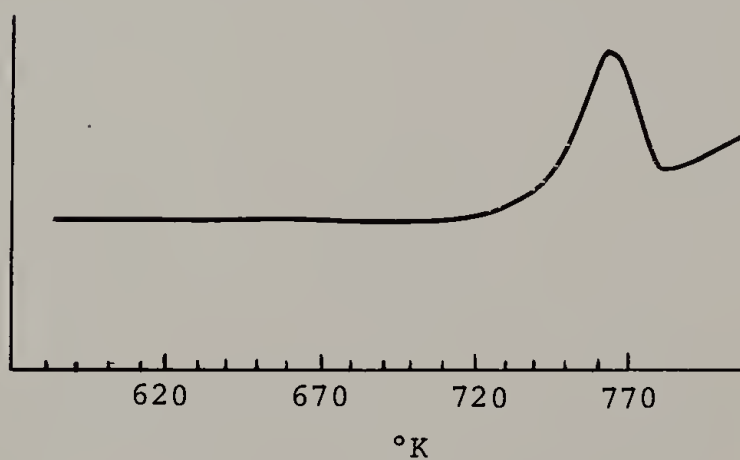


Figure 7. DSC of poly (oxy-2,6-dimethyl-1,4- phenylene)

Figure 8. WAXS photo of poly [oxy-2,6-bis (p-tolyl  
-1,4-phenylene)].

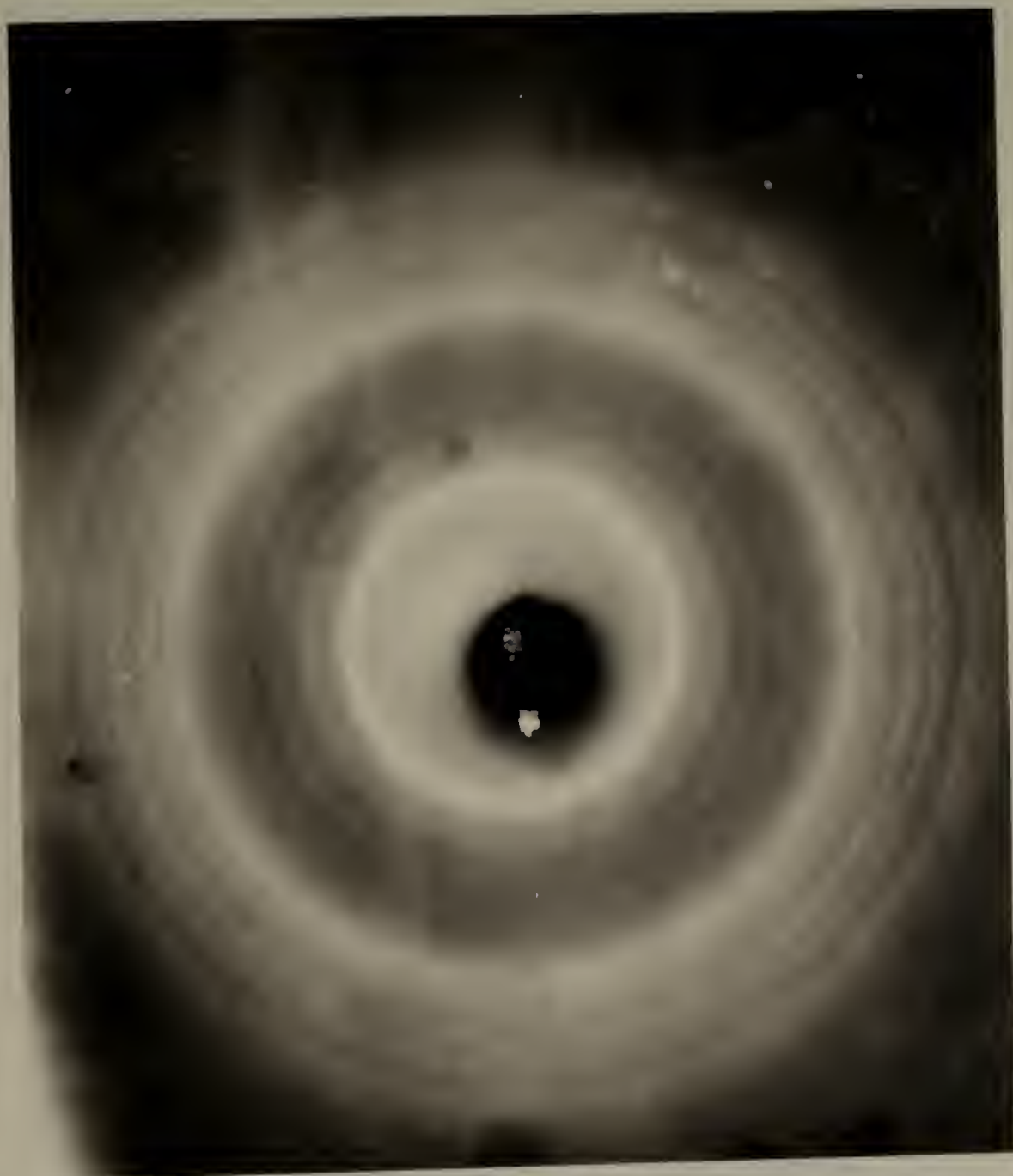


Figure 8

The thermal properties of PDAP proved to be somewhat different. Sample preparation and thermal history are as described in Chapter VI. The initial DSC scan (Figure 9A) of the sample of highest molecular weight, hereafter referred to as PDAP-I, produced no detectable  $T_g$  deflection or crystallization exotherm. The scan was marked by a significant endotherm with a maximum at 629°K (356°C), indicative of appreciable crystallinity. This was substantiated by the WAXS photo obtained for this raw sample (Figure 10). Calculating in the same manner as for PDTP gave a percent crystallinity of PDAP-I of 15% as synthesized. In all probability, it is this high degree of crystallinity which severely limits the solubility and does not allow the formation of high molecular weight homopolymer. Continued heating caused extensive degradation commencing at approximately 690°K (417°C), as indicated by a dramatic endothermic tailing of the baseline. The sample was therefore cooled rapidly from 670°K (397°C) to limit this degradation. Reheating PDAP-I from 400°K produced a  $T_g$  at 488°K (215°C) as the only significant feature. No crystallization exotherm was present, but a barely detectable, extremely broad endotherm was observed at 629°K (356°C) (Figure 9B). The sample was rapidly cooled once again to 473°C (270°C) and maintained at that temperature for 10 hours. The annealed material was cooled to 400°K and reheated at 40°/min. The resulting thermogram is shown

Figure 9. DSC scans of poly [oxy-2,6-bis (p-tolyl-1,4-phenylene)]  $R_{inh.} = 0.38$  dl./g.; (A) Initial scan, (B) Second heating after cooling rapidly from 670°K (C) Third heating after annealing at 540° for 10 hours.



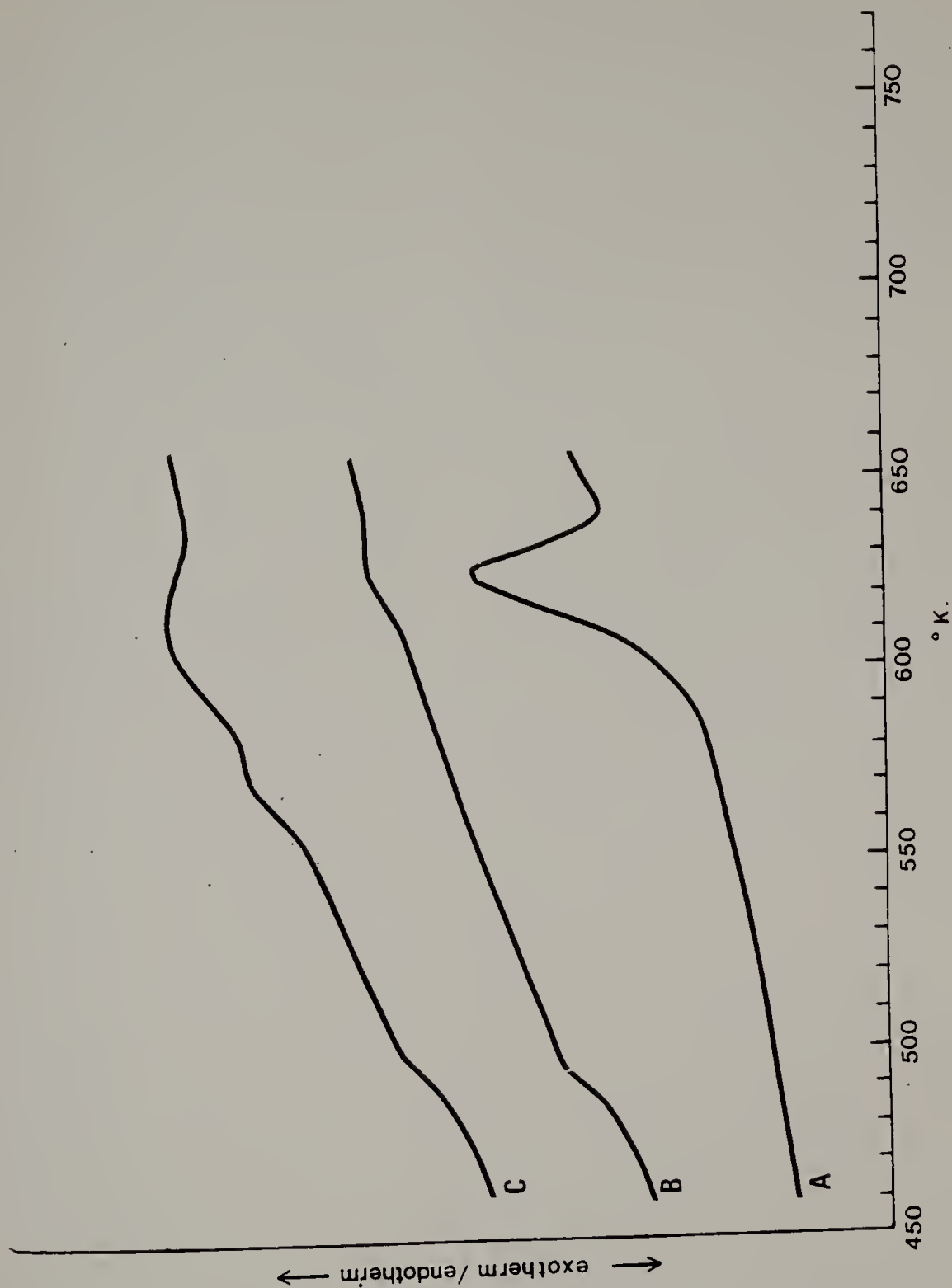


Figure 9

Figure 10. WAXS photo of raw poly [oxy-2,6-bis (p-methoxyphenyl-1,4-phenylene)].

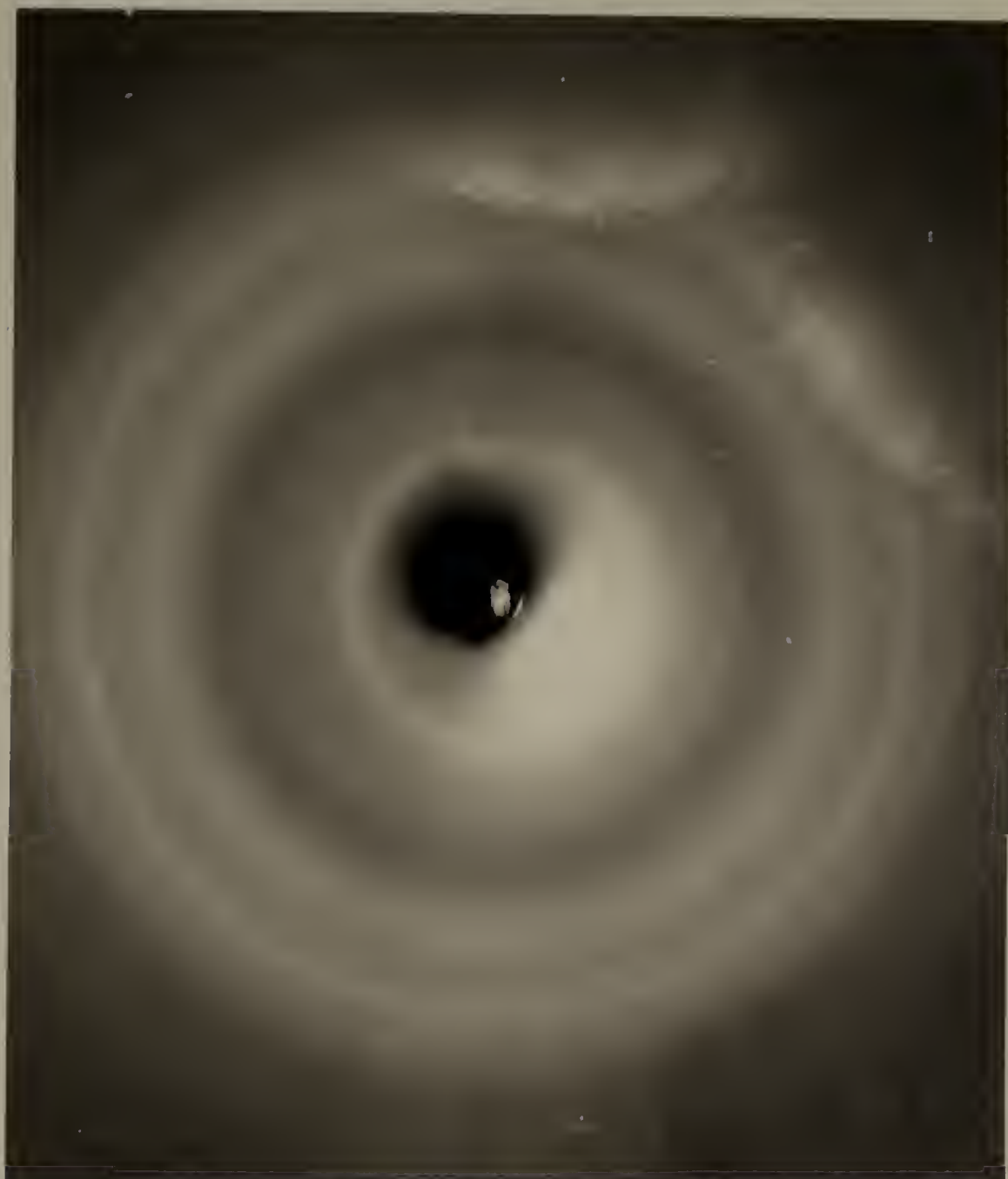


Figure 10

as Figure 9C. Annealing did not eliminate  $T_g$ , but the temperature of the transition was increased to 220°C. A broad endotherm was visible at 500°K (307°C), followed by a larger, still broader endotherm at 610°K (337°C). This endothermic profile, though considerably broader, resembles the thermogram obtained from the annealed sample of PDTP, implying a similar premelt behavior. The magnitude of the melting endotherms and therefore the degree of crystallinity is considerably less than that found in the sample during the initial scan. A contributing factor to this is probably the lack of adequate thermal stability. A certain amount of degradation undoubtedly occurs at the annealing temperature, which hampers crystallization. This is borne out by thermal gravimetric analysis of PDAP-I, to be discussed below.

Dramatically different results were obtained from the thermal analysis of PDAP of slightly lower molecular weight (0.32 dl/g), labeled PDAP-II. A sample subjected to the same pretreatment as PDAP-I was heated at 40°/min (Figure 11A). The shape of the initial scan closely paralleled that of PDAP-I, with a pronounced endotherm being the only feature. However, the peak maximum occurred at 649°K (376°C), or 20° higher than the higher molecular weight sample. The sample was then rapidly cooled from a maximum temperature of 670°K to 400°K. Reheating at the same rate as before (Figure 11B) gave the first appearance of a glass

Figure 11. DSC scans of poly [oxy-2,6-bis (p-methoxyphenyl) -1,4-phenylene],  $\eta = 0.32$  dl./g.; (A) Initial scan, (B) Second heating after cooling rapidly from 670°K.

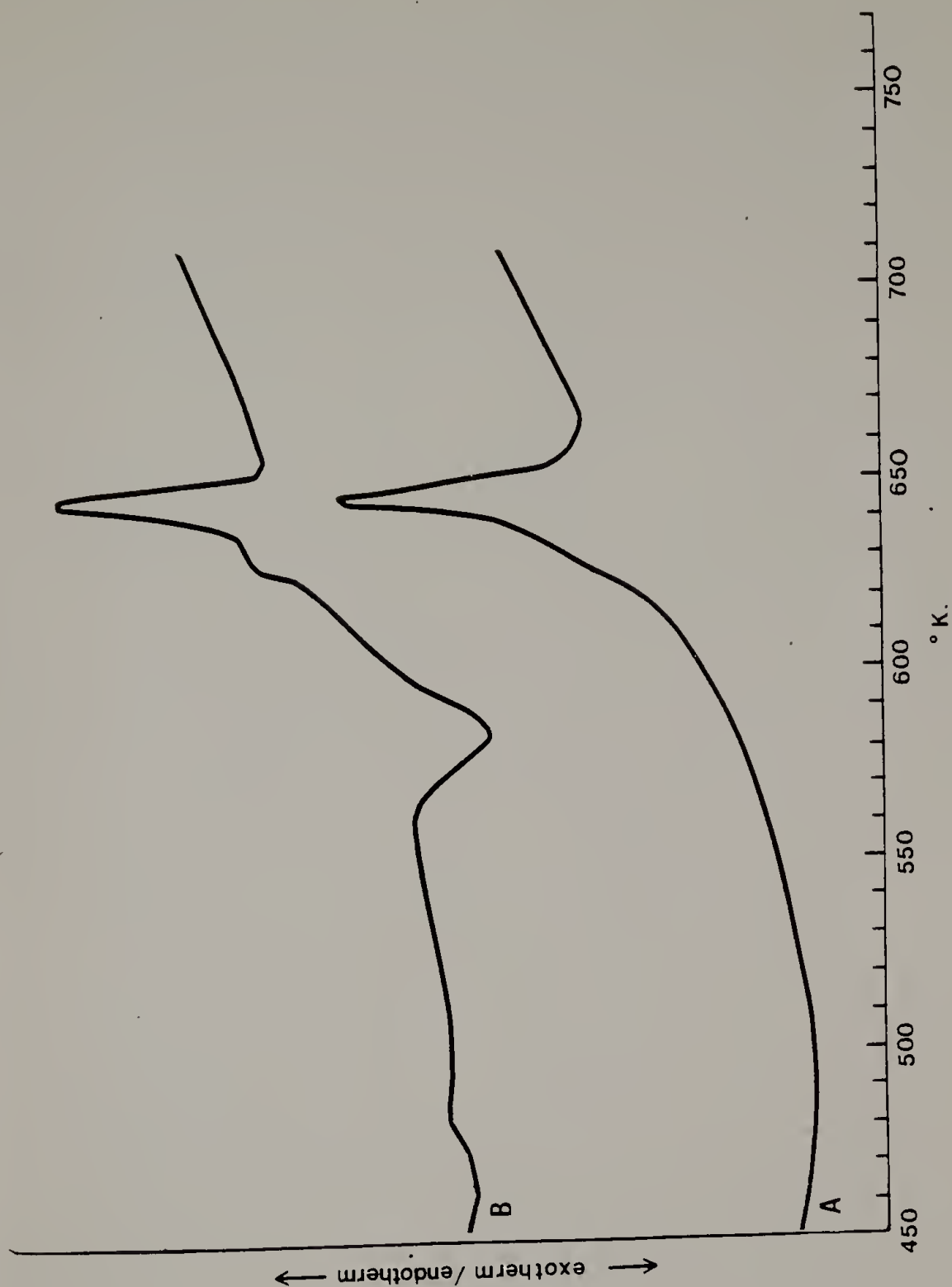


Figure 11

transition at 477°K (204°C), or 11° less than reported for PDAP-I. Continued heating at the same rate produced a pronounced exotherm with a maximum at 585°K (312°C), indicative of crystallization. This was followed at 633°K (360°C) by a minor endotherm which shouldered a sharp, strong endotherm at 649°K (376°C). The appearance of the two endothermic peaks is consistent with the observations of PDTP and PDAP-I. However, in the case of PDAP-II, the size of the low temperature peak is much smaller than the high temperature endotherm.

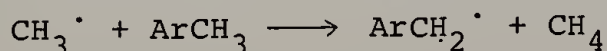
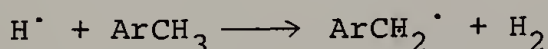
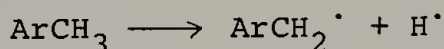
Somewhat surprising was the large increase in the temperature of both endotherms over those of PDAP-I. One might expect the higher molecular weight material to have the higher melting point. In this case, however, the observed values might be explained by the fact that PDAP-II crystallizes more rapidly, as indicated by the presence of an exothermic crystallization peak. This could imply the existence of larger or more perfect crystals and crystalline regions requiring higher melting temperatures. On further inspection of the results of the thermal analysis of these two PDAP samples, it appears that there exists a threshold molecular weight, below which facile crystallization can occur and above which long annealing times are necessary.



### E. Thermal Stability of Homopolymers

The thermal stability of PDTP and PDAP were measured by thermal gravimetric analysis.

The weight loss with respect to temperature for thermal and thermal oxidative degradation of PDTP are shown in Figures 12A and 13A, respectively. In the absence of oxygen, thermal degradation apparently occurs in two steps. There is an initial inflection at 490°C which is followed by a rapid drop in weight of approximately 28% over an 80° range. A second inflection at 570°C is followed by a slower decomposition rate with 58% of the original weight remaining at 800°C. This behavior is consistent with that reported for PDMP<sup>95</sup> and also PDPP.<sup>96</sup> In the case of PDMP, the rapid exothermic process led to the evolution of phenolic products, water and a black, highly crosslinked residue. The second step was referred to as a char forming process marked by the evolution of methane, carbon monoxide and hydrogen. The presence of small amounts of hydrogen and methane even at low pyrolysis temperatures suggests the Szwarc mechanism for pyrolysis of toluene:



Equation 59

Figure 12. Thermal degradation of homopolymers as detected by thermal gravimetric analysis; (A) poly [oxy-2,6-bis (p-tolyl) -1,4-phenylene] (B) poly [oxy-2,6-bis (p-methoxyphenyl) -1,4-phenylene].

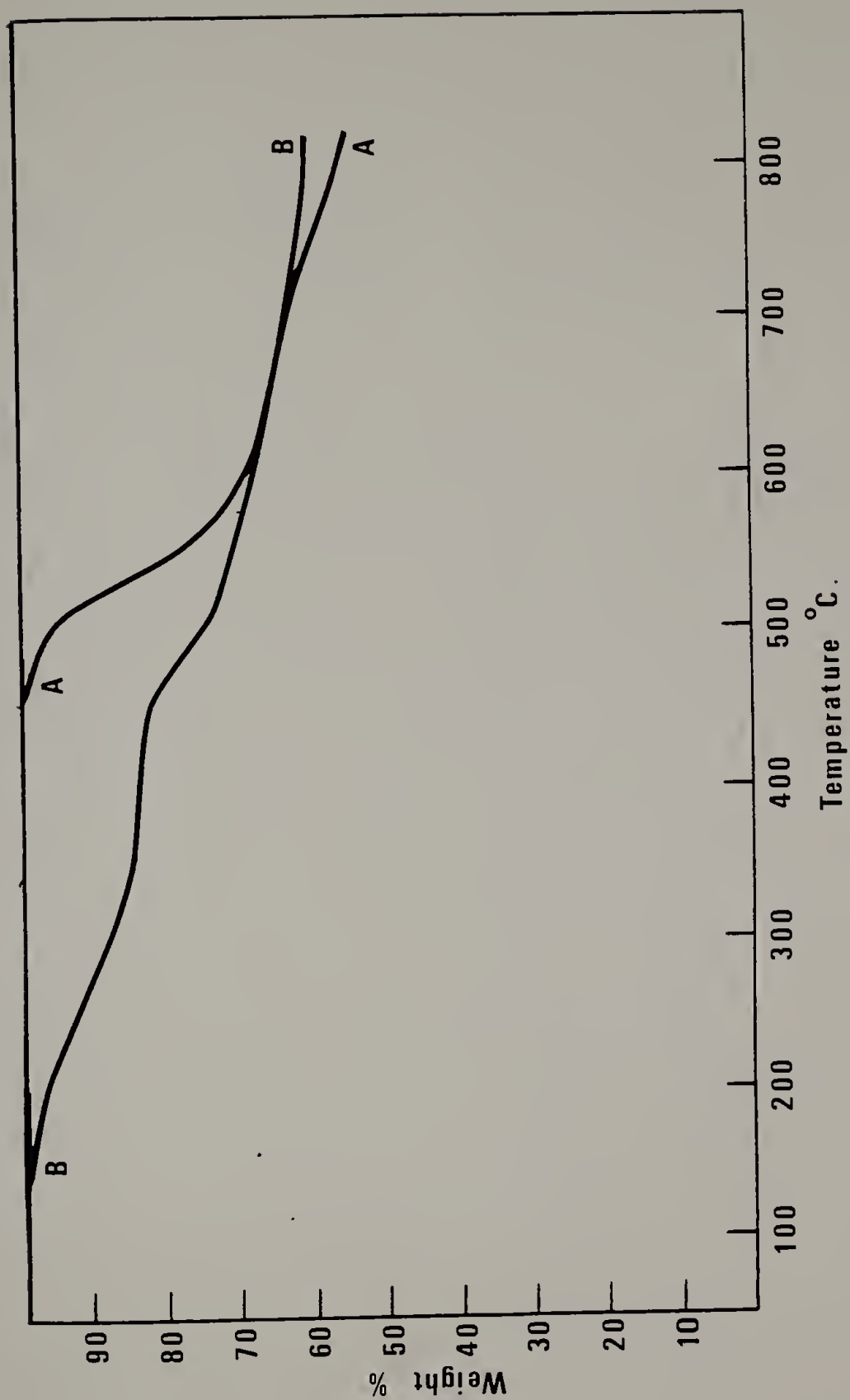


Figure 12

Figure 13. Thermal oxidative degradation of homopolymers as detected by thermal gravimetric analysis; (A) poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene] (B) poly [oxy-2,6-bis (p-methoxyphenyl)-1,4-phenylene].

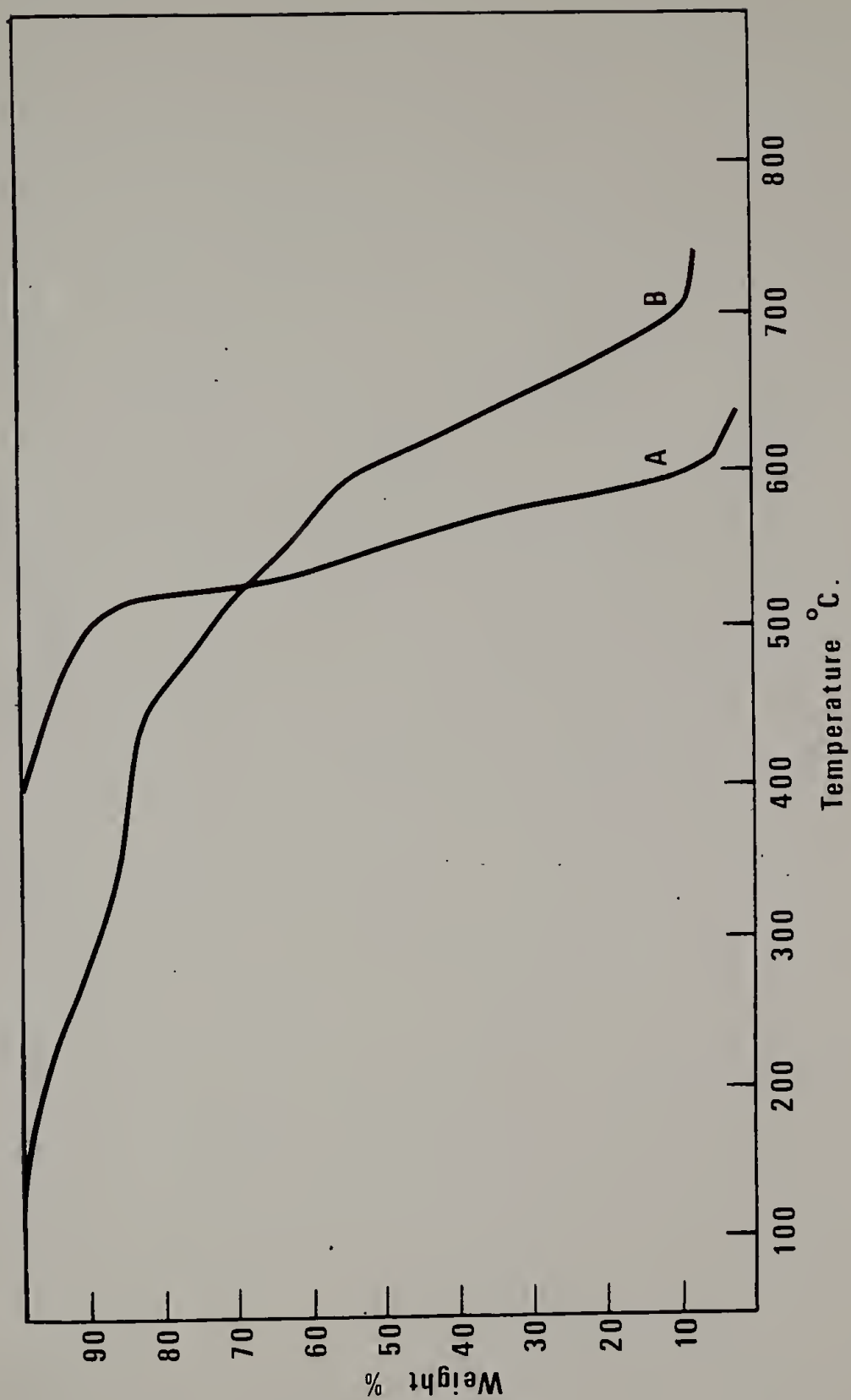
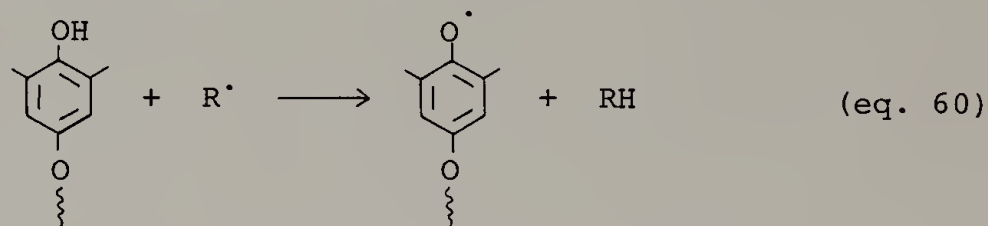
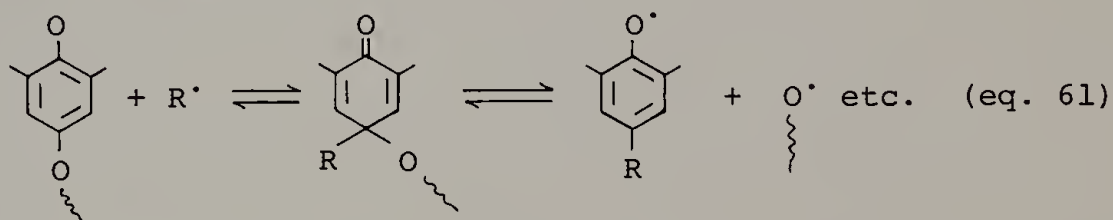


Figure 13

The first step in this sequence has an activation energy of 78 kcal/mole and at temperatures less than 600°C is probably aided by traces of oxidative polymerization catalyst. Radicals formed as above may explain the significant weight loss which occurs in the first phase of degradation if they are involved in an analogy of the quinol-ether redistribution. The first step in this process may be viewed as in equation 60.

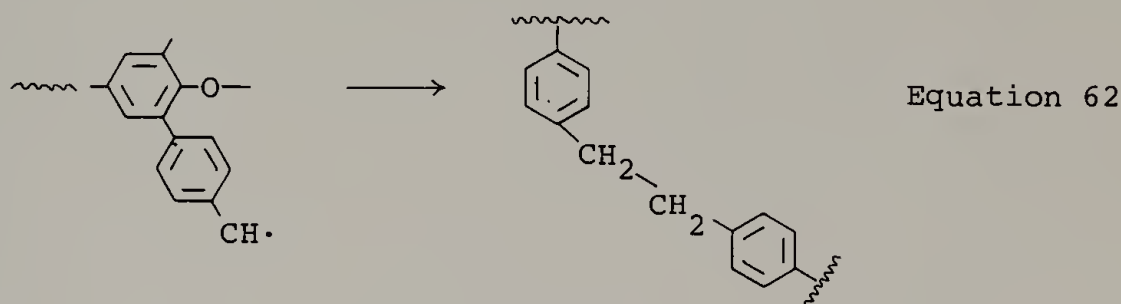


This hydride abstraction would be followed by the formation of the quinol-ether and then cleavage of the simple phenol fragments (equation 61).



In this manner, 60% of the original weight of PDMP may be volatilized. The remaining 40% is prevented from such degradation by extensive crosslinking. The likelihood that the predominant weight loss is due to scission in the main chain rather than by cleavage of pendant groups is reinforced by the similarity of the TGA profile for PDPP. In this case, rapid weight loss commences at 515°C, with

the second stage of degradation commencing at 575°C. From these observations, it can reasonably be assumed that thermal degradation of PDTP commences with the cleavage and volatilization of phenolic fragments. It appears that crosslink formation occurs more readily than with PDMP due to the fact that rapid weight loss ceases at 72% of original weight, as opposed to 40% for PDMP. Extension of benzyl radicals out from the main chain might explain the more facile crosslinking (equation 62).



Degradation of PDTP in the presence of oxygen proceeds differently. Weight loss commences at 400°C with a 5% loss at 475°C. This first phase of relatively slow decomposition continues up to 515°C, with a total weight loss of 8% at this point. A subsequent rapid loss of 32% then occurs in a span of 30°C. This latter stage of degradation parallels the first stage of the thermal degradation. This would tend to confirm the assumption that the main chain cleavage of phenolic fragments is not a thermal-oxidative process. The last stage or high temperature thermal-oxidative degradation shows virtually complete volatilization of the remaining material. This



implies preferential reactions of the benzyl radicals with oxygen in lieu of crosslinking.

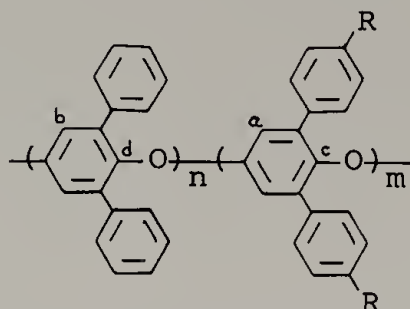
PDAP did not prove to be as thermally stable as PDTP. The most likely reason was the much lower molecular weight of the test sample (PDAP-I). Such molecular weight effects have been observed in the degradation behavior of PDMP.<sup>98</sup> Onset of thermal degradation of PDAP occurred at 100°C, with a 5% weight loss by 225°C (Figure 12B). A plateau was reached at 350°C, with 85% of the original weight remaining. A second stage of weight loss began at 450°C, with a decrease in rate at 500°. At this point, 75% of the original weight remained. As before, this must imply considerable crosslinking. In the presence of oxygen, the polymer behaved as under purely thermal conditions up to 500°C (Figure 13B). From this point, rapid weight loss continued with a maximum rate of 4.4%/min, until virtually complete volatilization.

#### F. Synthesis of Random Copolymers

The phenols DTP, DAP, and DBP were each copolymerized with DPP. To promote randomness, a 1:1 mixture of comonomers was polymerized with silver oxide as the oxidant at room temperature. Product yields, inherent viscosities, and molecular weights from gel permeation chromatography are tabulated in Table 12.

The preparation of these random copolymers was

TABLE 12  
RANDOM COPOLYMER SYNTHESSES



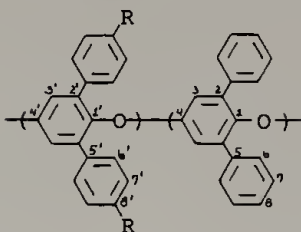
R =	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
Yield (%)	58	30	32
$\eta_{inh}$ (dl/g in CHCl <sub>3</sub> @ 25°)	0.75	0.53	0.53
Mn	$1.19 \times 10^5$	$7.23 \times 10^4$	$8.53 \times 10^4$
Mw	$1.89 \times 10^5$	$1.20 \times 10^5$	$5.98 \times 10^5$
MWD	1.59	1.66	1.45

undertaken for two reasons. The primary reason was to investigate their crystallization behavior. As mentioned earlier, the random copolymers prepared from mixtures of DMP and DPP proved completely amorphous. However, in contrast to that system, the copolymers prepared herein contain comonomers which both possess aromatic substituents in the 2,6 positions. It was believed that the greater similarity between the comonomers might allow more efficient packing, which would allow the polymers to crystallize. The second reason for the preparation of these copolymers is to provide a direct measure of the relative reactivities of these monomers with respect to DPP. This information would either substantiate or refute the hypothesis that the lower molecular weight obtained in the polymerization of DAP was due to reduced monomer reactivity.

G. Spectrometric Analysis of Copolymers:  
Determination of Copolymer Composition  
by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Table 13)

$^1\text{H}$  NMR analysis. The upfield aromatic peaks described earlier for the homopolymers are also present in the copolymers. As mentioned before, these are indicative of protons adjacent to the main chain meta carbon. The position of these peaks, set apart from the rest of the aromatic region, allowed them to be used to determine copolymer compositions.

TABLE 13  
COPOLYMER SPECTRAL DATA



R =	CH <sub>3</sub>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>
<u><sup>1</sup>H NMR (ppm from TMS)</u>			
C-3 proton	6.21/6.23	6.33-6.5 (m)	6.15-6.45 (m)
C-3' proton	6.29/6.32		
(R)	2.15 (s, CH <sub>3</sub> )	3.75 (s, CH <sub>3</sub> O)	
<u><sup>13</sup>C NMR (ppm from TMS)</u>			
C-1, C-1'	143.61, 143.05, 142.97	142.98, 138.01	144.17, 142.94, 140.75, 140.37, 140.23
C-2	*	*	*
C-2'	*	*	130.09
C-3, C-3'	117.99, 117.88, 117.73, 117.57, 117.44, 117.34	117.99, 117.87, 117.69, 117.56, 117.12	118.73, 118.58, 118.45, 118.30, 117.64, 117.51
C-4	155.47	155.44, 155.32	155.56
C-4'	155.09	155.07	155.07
C-5, C-5', C-6, C-6', C-7	*	*	*
C-7'	*	113.59	*
C-8	*	*	*
C-8'	*	159.17	*
(R)	20.98 (CH <sub>3</sub> )	55.12 (CH <sub>3</sub> O)	
<u>IR (cm<sup>-1</sup>) (films)</u>			
C-H (out of plane) stretch	869	860	870
C-O stretch	1190	1180	1190

\*unresolved

In this regard, the copolymer of DTP and DPP will be considered first. The homopolymer DPP exhibited a sharp singlet at 6.22 ppm, while that of DTP showed the corresponding peak at 6.28 ppm. Predictably, the spectrum of the copolymer showed a twin peak in this area of the spectrum, indicative of both units (Figure 14). In addition, each peak was split further, due, in all probability, to neighboring group effects. A DTP link, for example, may be bordered on either side by 2 DTP units, 2 DPP links, or one of each. Each peak appeared as a doublet, the peak furthest downfield occurring at 6.29 and 6.32 ppm, and the other occurring at 6.21 and 6.23 ppm. Based upon corresponding peak locations in the homopolymers, the downfield doublet can be assigned to the DTP segments and the other doublet to the DPP units. Integration of one doublet with respect to the other showed the copolymer to be composed of a 1:1 mixture of DTP to DPP. This implies equal reactivity under the conditions of the polymerization reaction.

The  $^1\text{H}$  NMR spectrum of PDAPcoDPP could not be resolved as easily (Figure 15). The peaks attributable to the main chain meta protons appeared as a multiplet ranging from 6.33-6.5 ppm. The individual peaks associated with each comonomer could not be distinguished. This may imply more extensive or longer range neighboring group effects than were apparent in the spectrum of PDTPcoDPP. In this case, the copolymer composition could only be derived

Figure 14.  $^1\text{H}$  MNR spectrum of poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene] co [oxy-2,6-diphenyl-1,4-phenylene], PDTP co DPP.

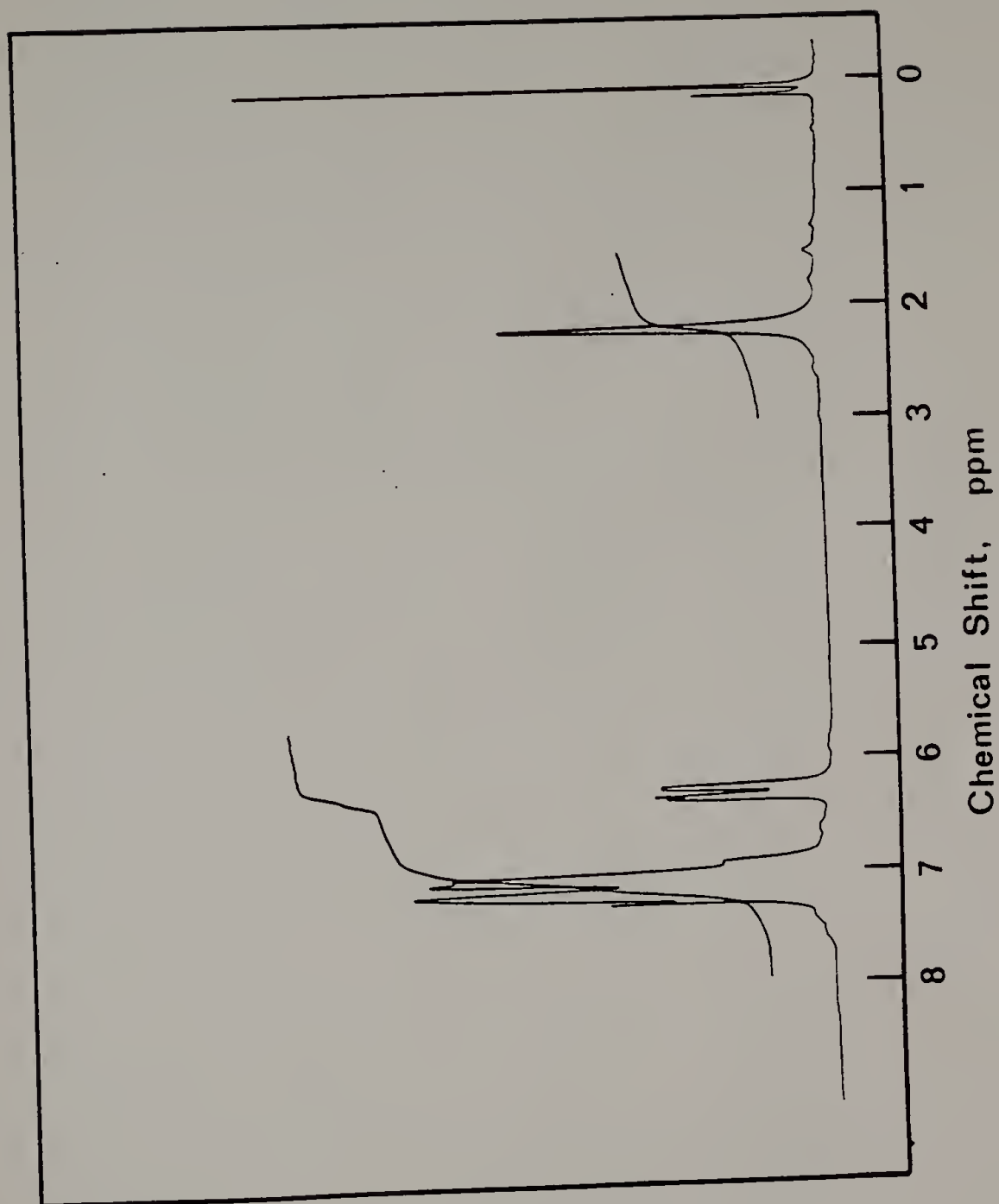


Figure 14



Figure 15.  $^1\text{H}$  NMR spectrum of poly [oxy-2,6-bis (p-methoxyphenyl)-1,4-phenylene] co [oxy-2,6-diphenyl -1,4-phenylene], PDAP co DPP.

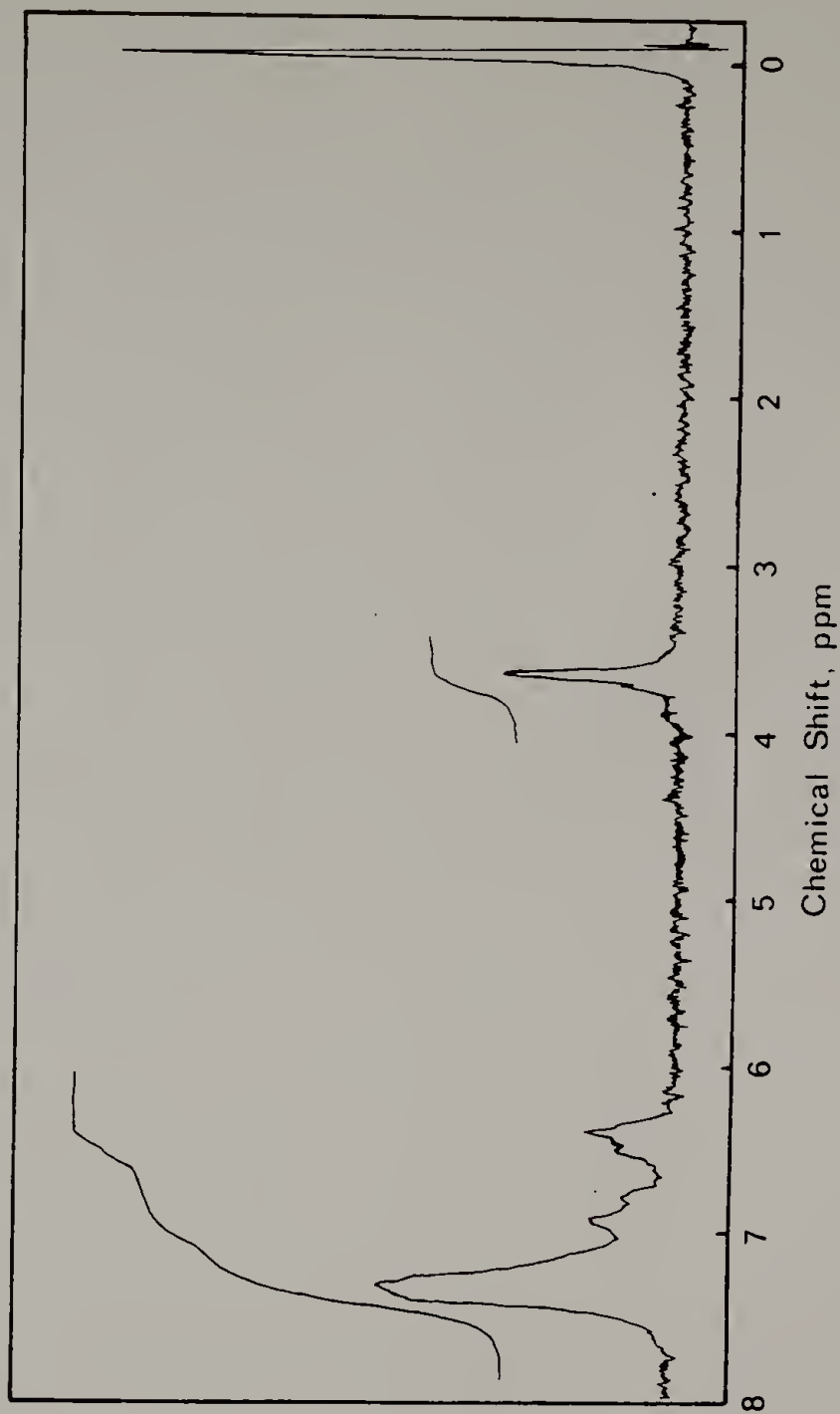


Figure 15

by comparison of the integrals of the above mentioned multiplet with respect to the methoxy singlet peak occurring at 3.75 ppm. For a 1:1 polymer, this ratio would theoretically be 4:6 and for the PDAP homopolymer, 2:6. The experimental value for the copolymer synthesized was 4.5:6, which means the copolymer contains 44% DAP units. The ratio of DAP units to DPP units can then be expressed as 0.8:1.

As in the case of PDAPcoDPP, the copolymer PDBPcoDPP could not be analyzed for copolymer composition simply by comparing the integrals of the meta proton peaks (Figure 16). These peaks appeared as a multiplet from 6.15 to 6.45 ppm. Unfortunately, unlike the previous case, there is no peak assignable to an aliphatic substituent enabling a derivation similar to the one described for PDAPcoDPP. This was circumvented by preparing a copolymer of DBP with DTP. The virtually identical reactivity of DTP to DPP allowed substitution of the former for the latter. This polymer, prepared the same way as all of the other polymers, exhibited the  $^1\text{H}$  NMR spectrum shown in Figure 17. The integrals of the multiplet at 6.4-6.8 ppm assigned to the meta protons was compared to the integral of the singlet representing the methyl protons found at 2.4 ppm. A ratio of 7:11 for these integrals corresponds to a DBP to DTP ratio of 0.9:1. This result indicates that DBP possesses comparable reactivity to DTP and

Figure 16.  $^1\text{H}$  NMR spectrum of poly [oxy-2,6-bis (p-biphenyl-1,4-phenylene) co [oxy-2,6-diphenyl -1,4-phenylene], PDBP co DPP.

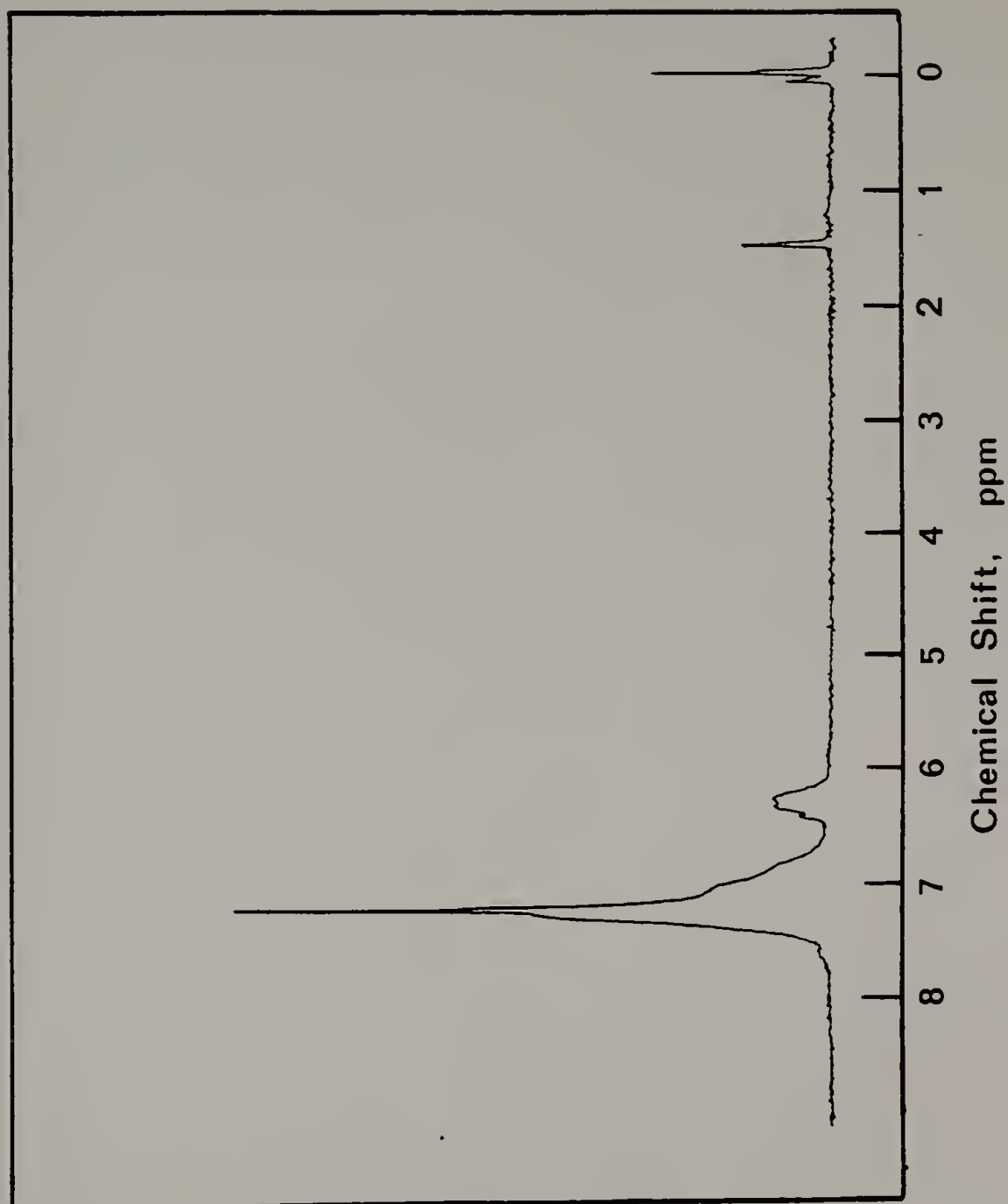


Figure 16

Figure 17.  $^1\text{H}$  NMR spectrum of poly [oxy-2,6-bis (p-biphenyl-1,4-phenylene) co [oxy-bis (p-tolyl) -1,4-phenylene], PDBP co DTP.

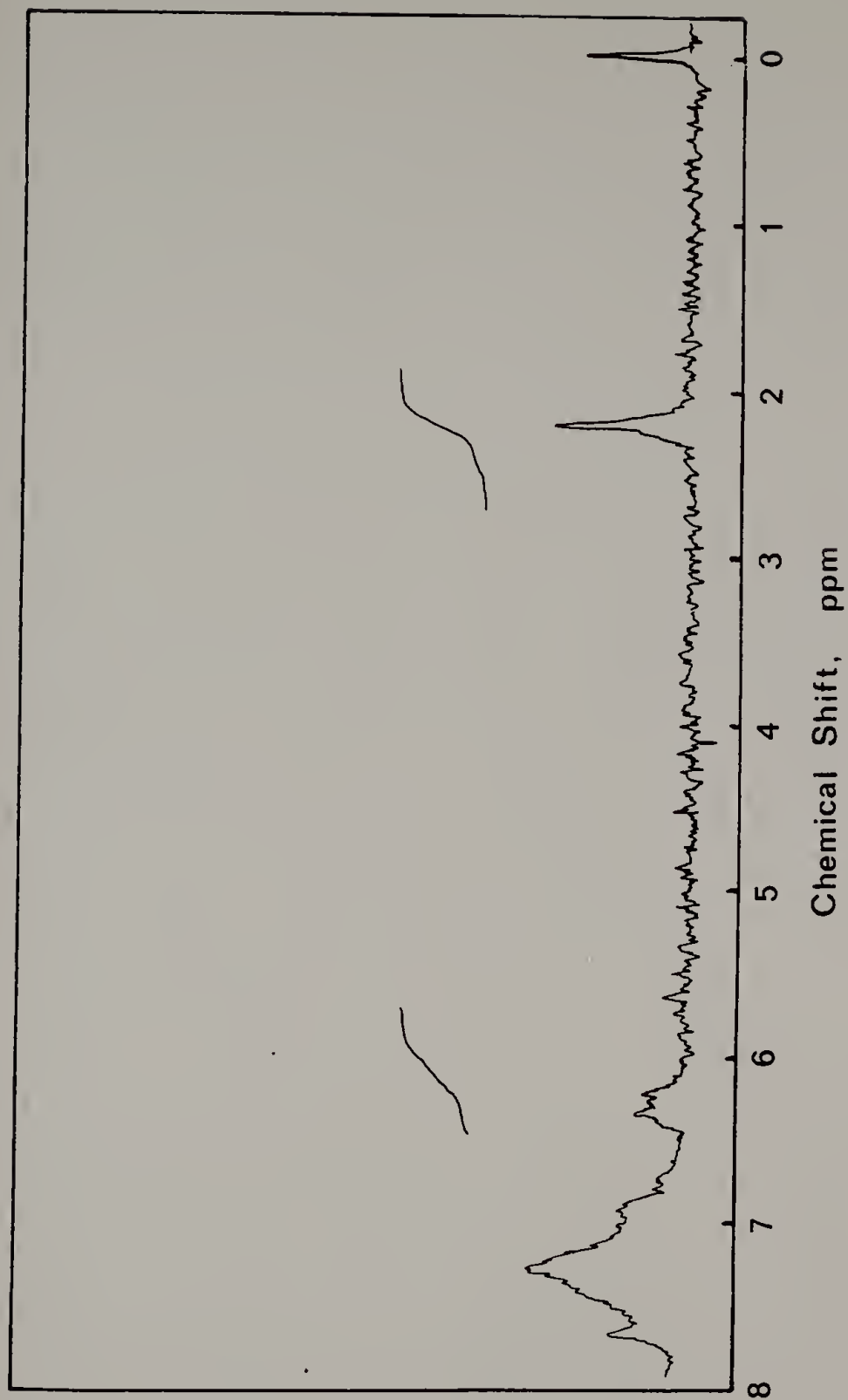


Figure 17



therefore DPP under these polymerization conditions.

$^{13}\text{C}$  NMR analysis. Peak locations and assignments where possible are listed in Table 13.

The  $^{13}\text{C}$  NMR spectra may also be used to determine ratios of the comonomers in the copolymers. The spectra of the copolymers are considerably more complicated than the homopolymers, even more so than anticipated. For example, the main chain meta carbons of the homopolymers appeared in the decoupled spectra as singlets at  $117.4 \pm 5$  ppm. However, the random copolymer, PDTPcoDPP, showed six peaks within this range (Figure 18). PDAPcoDPP provided 5 peaks ranging from 117.1 to 117.99 ppm (Figure 19), and PDBPcoDPP (Figure 20) also showed 6 peaks in this range. The close proximity of these peaks to each other and their multiplicity suggests long range effects where shifts are affected by groups 2 or 3 links removed. One peak which does not show this effect is the one assigned to the c-4 carbon, which is located in the homopolymers at 155.9 for PDPP, 155.08 for PDAP and 155.41 for PDTP. In copolymers PDTPcoDPP and PDBPcoDPP, there are two peaks in this region corresponding to each comonomer. The peak further downfield in each case is assigned to the c-4 carbon associated with the DPP unit. The comonomer ratios can therefore be calculated from the ratios of the peak heights. In the copolymer PDAPcoDPP, the c-4 carbon associated with

Figure 18.  $^{13}\text{C}$  NMR spectrum of PDTP co DPP.

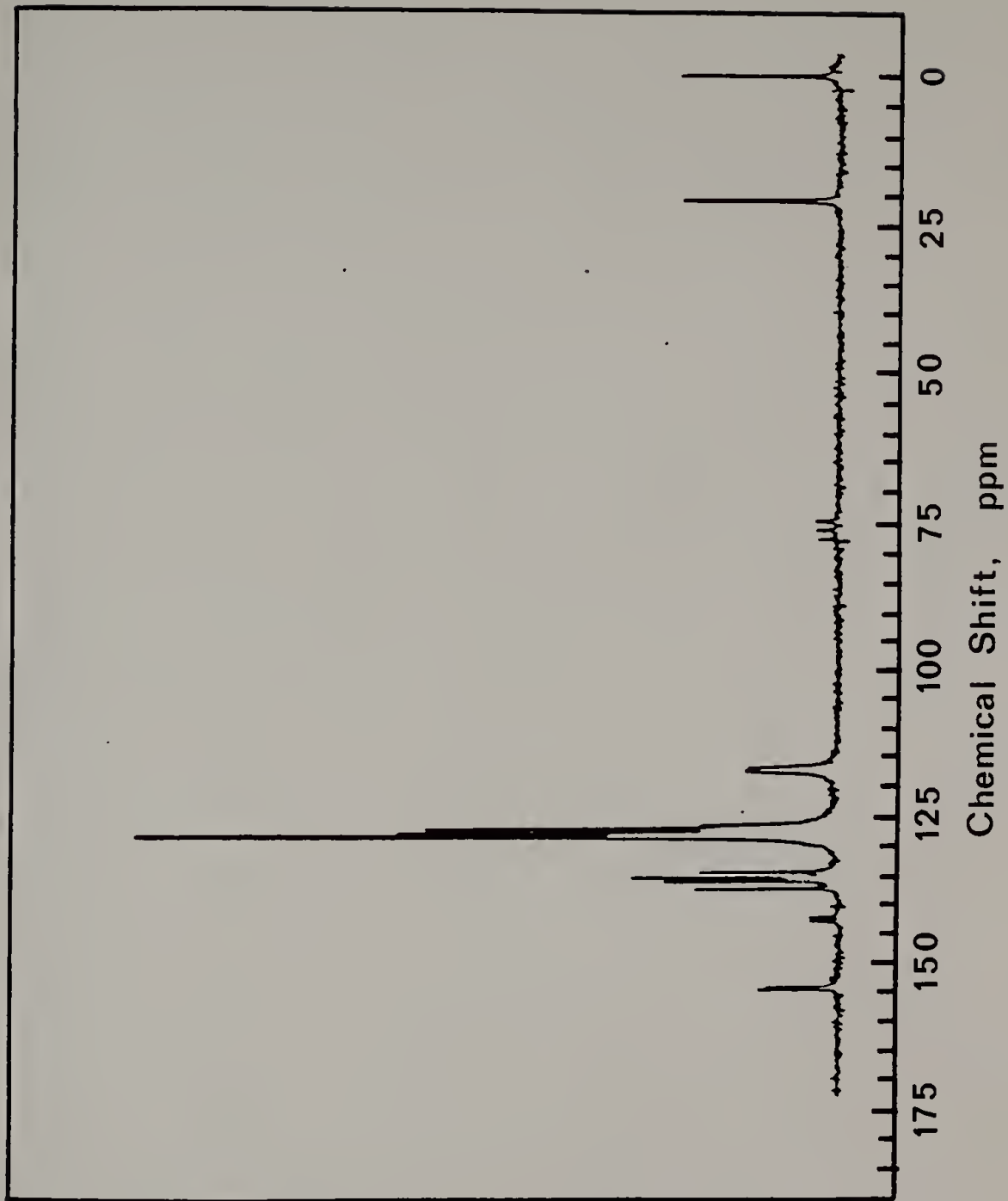


Figure 18

Figure 19.  $^{13}\text{C}$  NMR spectrum of PDAP co DPP.

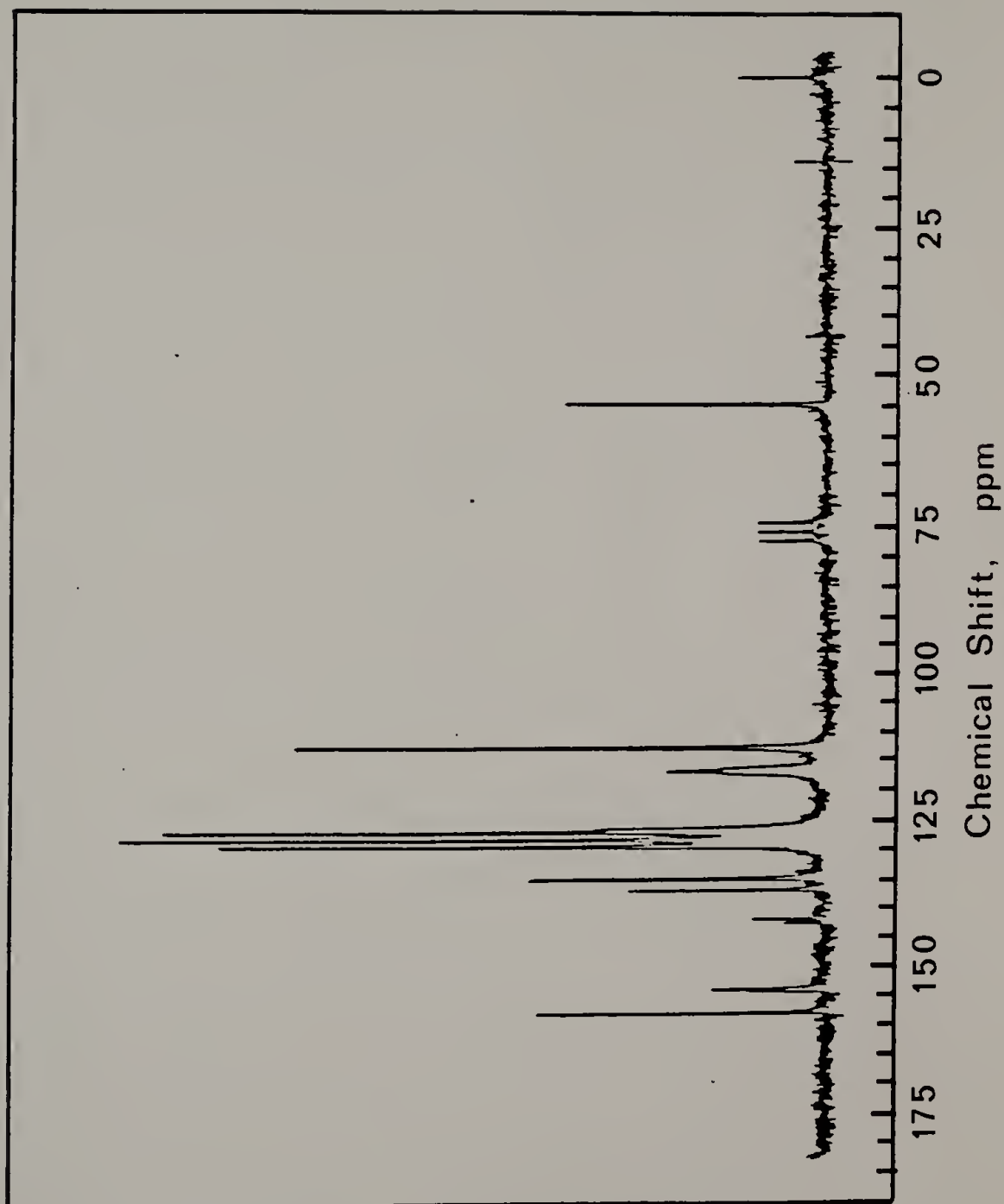


Figure 19

Figure 20.  $^{13}\text{C}$  NMR spectrum of PDBP co DPP.

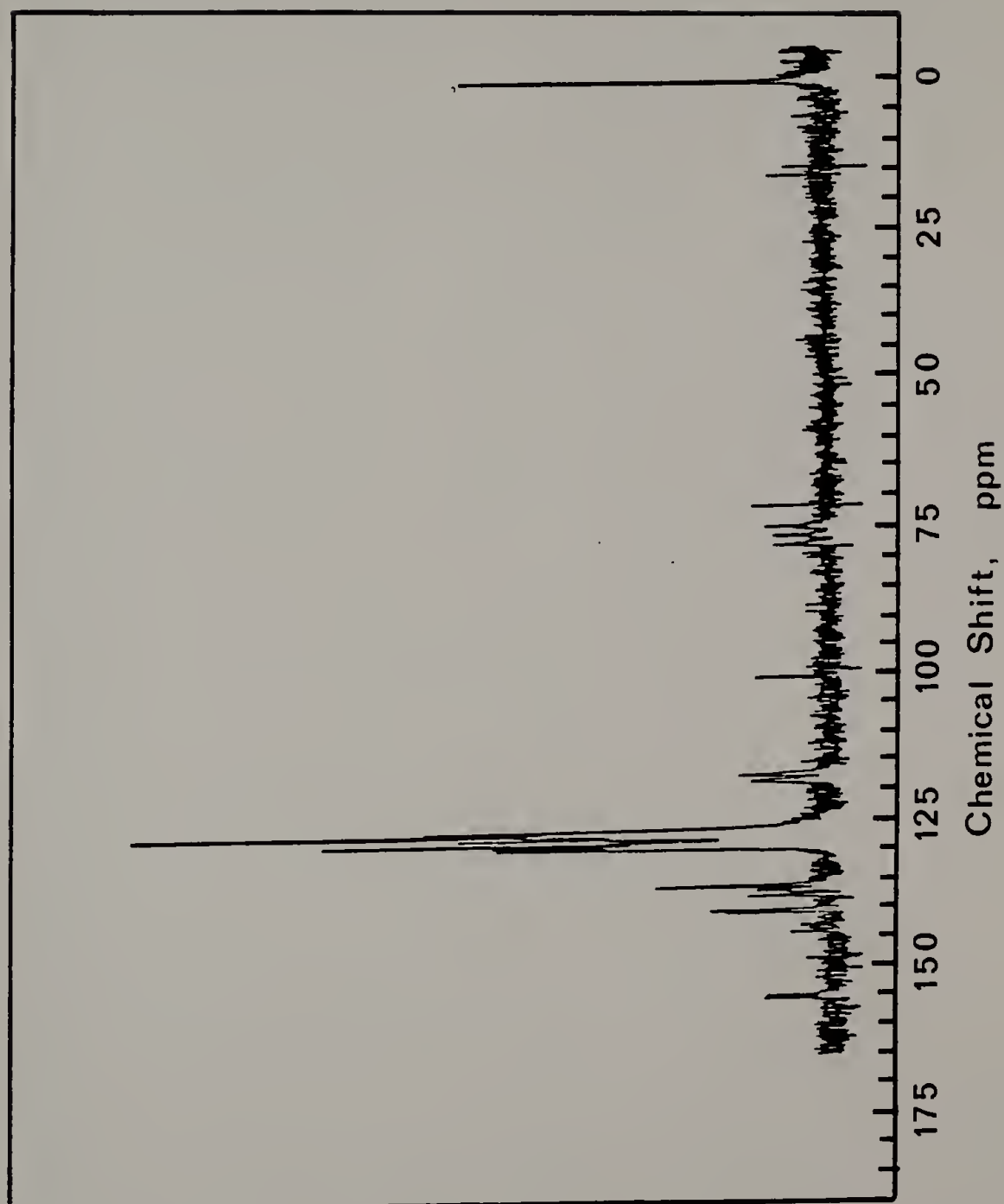


Figure 20



the DPP unit, for reasons which are not readily apparent, gives rise to 2 peaks at 155.44 and 155.32 ppm. The DPP portion in this material is therefore represented by the sum of these peak heights. Values calculated for the ratios of comonomer to DPP for each copolymer are listed below.

TABLE 14  
COMONOMER RATIOS FROM  $^{13}\text{C}$  NMR SPECTRA

	PDTPcoDPP	PDAPcoDPP	PDBPcoDPP
c-4 shift	155.47	155.44,+155.32	155.56
c-4 height	13	13+11=24	11
c-4' shift	155.09	155.07	155.07
c-4' height	11	18	11
c-4'/c-4	0.85:1	0.75:1	1:1

These values are in reasonable agreement to those derived from  $^1\text{H}$  NMR spectra. From these results, it can be concluded that the reactivities of DTP and DBP are quite similar to DPP under the reaction conditions utilized. Such is not necessarily the case when considering the calculated ratios for the PDAPcoDPP composition. Although the values in both determinations are less than 1:1, they are not low enough to say conclusively that DAP is significantly less reactive than DPP. The fact that these ratios are indeed

less than 1, coupled with the observation from Table 12 that the yield and molecular weight of PDAPcoDPP is less than that of PDTPcoDPP under virtually identical reaction conditions suggests that DAP may very well be less reactive and this may be a contributing factor in homopolymer production, which yields only low molecular weight polymer.

#### H. Thermal Analysis of Copolymers

As suggested earlier, these polymers could possibly be crystallizable. According to analyses by differential scanning calorimetry, such is not the case. In no instance did any of the copolymers exhibit either crystallization exotherms or melting endotherms even after long annealing times. Each sample when heated at 40°/min from 400°K to 770°K, showed a discontinuity in  $C_p$  indicative of  $T_g$  as its only feature (Figure 21). These observed  $T_g$  values are listed below.

TABLE 15

Copolymer	$T_g$
PDTPcoDPP	230°C
PDAPcoDPP	220°C
PDBPcoDPP	247°C

Particularly interesting is the value for  $T_g$  achieved for PDBPcoDPP. The value of 247°C is 17° higher

Figure 21. DSC scans of random copolymers (A) PDBP co DPP, (B) PDTP co DPP, (C) PDAP co DPP.

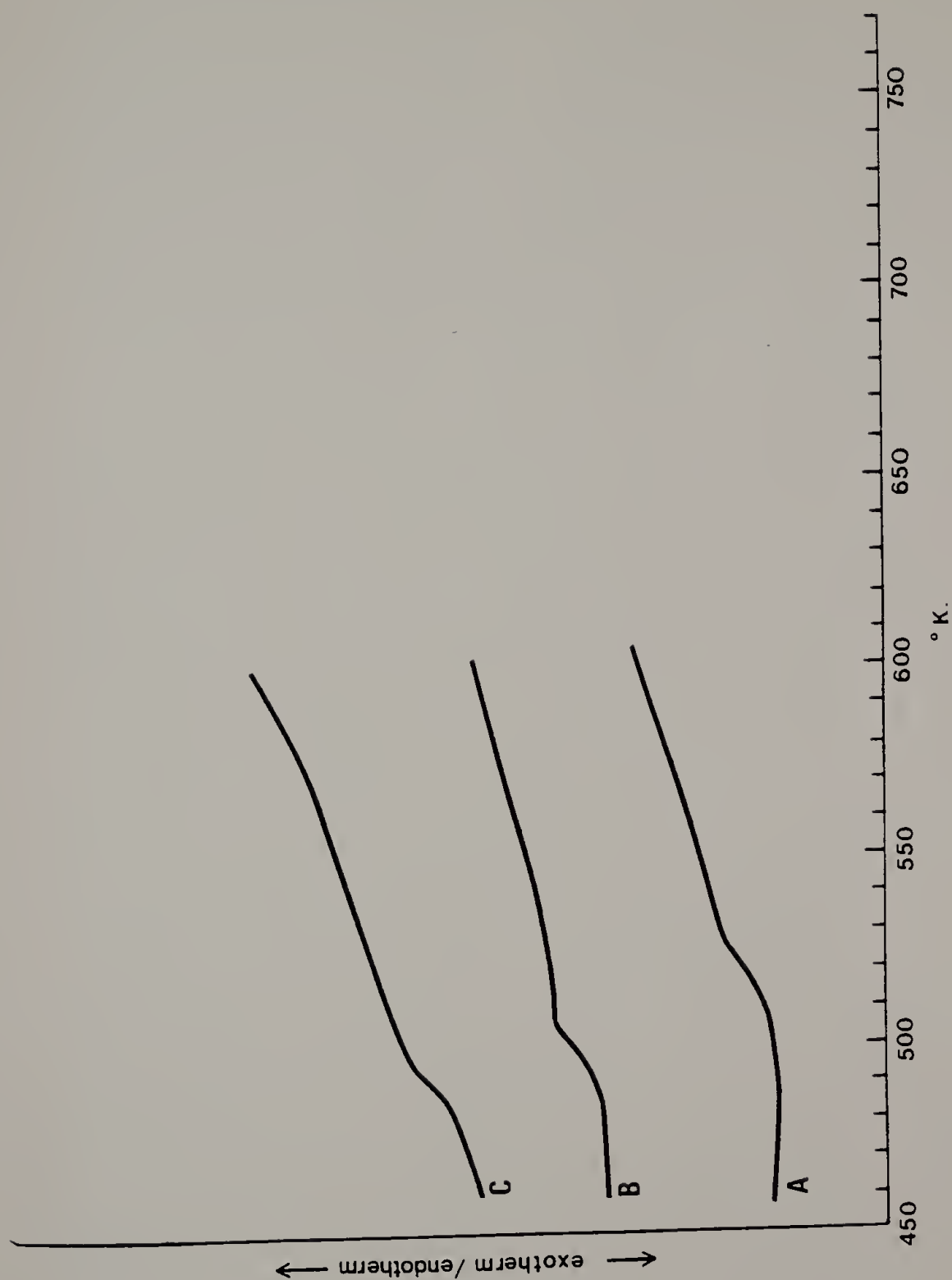


Figure 21

than that reported for PDPP. This is undoubtedly due to the added bulkiness of the extra phenyl group. Had the homopolymer been prepared in high molecular weight, a considerably higher  $T_g$  would have been observed. As preparation of this material was not possible, this value for  $T_g$  could only be approximated mathematically. A form of the Gordon-Taylor<sup>99</sup> (Equation 63) was used to do this.

$$\frac{1}{T_{g_c}} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \quad \text{Equation 63}$$

$w_1$  and  $w_2$  refer to the weight fractions of monomers 1 and 2 in the copolymer.  $T_{g_1}$  and  $T_{g_2}$  are the respective glass transition temperatures of the homopolymers, and  $T_{g_c}$  is the glass transition temperature of the copolymer. The results reported earlier allow the assumption that the ratio of DBP to DPP in the copolymer is 1:1 or  $w_1 = w_2 = 0.5$ . Substituting 503°K (230°C) for the  $T_g$  of PDPP homopolymer and 520°K (247°C) for the  $T_g$  of the copolymer produces a value of 265°C as the glass transition temperature of the hypothetical PDBP homopolymer.

### I. Thermal Stability of Copolymers

All copolymers behaved virtually the same upon thermolysis in the absence of oxygen. As with the homopolymers, the copolymers displayed an initial rapid loss in weight attributable to volatilization of phenolic fragments.

followed by a period of slower limited weight loss and extensive crosslinking (Figure 22). In all cases, complete volatilization occurred in the presence of oxygen (Figure 23). Pertinent data are listed in Table 16.

### J. Thermal Behavior of Blends

Blends of PDPP with the homopolymers of DAP and DTP were prepared by procedures described in Chapter VI. Upon preliminary examination, films of both blends were transparent and flexible. The blends were then subjected to thermal analysis by differential scanning calorimetry as with the homopolymers and copolymers. In both cases, the components of the blends acted independently. In other words, the thermal behavior of each component was identical to that of the respective homopolymer alone. A 1:1 blend of PDTP and PDPP when initially heated at 40°/min from 400°K (Figure 24A) displayed a  $T_g$  at 227°C, followed by a pronounced exotherm at 287°C., indicative of PDPP crystallization. Continued heating of the sample produced a melting peak with a maximum at 497°C. This first scan is almost the same as that for PDPP alone. A fresh sample was heated to 267°C and maintained at this temperature for 12 hours. Cooling to 127°C and reheating at 40°/min produced the profile shown in Figure 24B. In this case, there was apparently no  $T_g$ . Also not evident was the crystallization exotherm noted earlier, probably due to the

Figure 22. Thermal Degradation of Copolymers by gravimetric analysis; (A) PDTP co DPP (B) PDAP co DPP (C) PDBP co DPP.



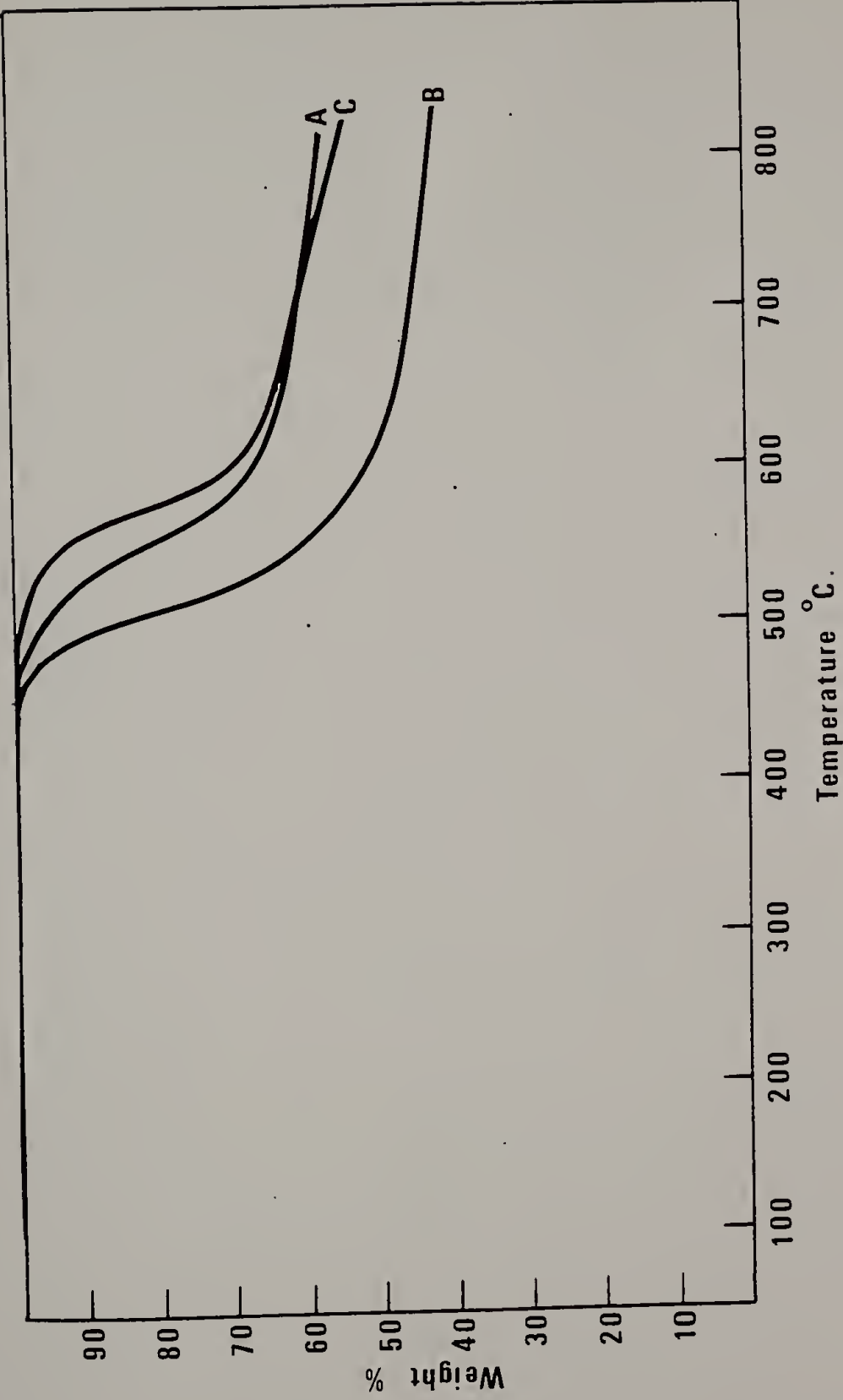


Figure 22

Figure 23. Thermal oxidative degradation of copolymers; (A) PDTP co DPP (B) PDAP co DPP, (C) PDBP co DPP. .

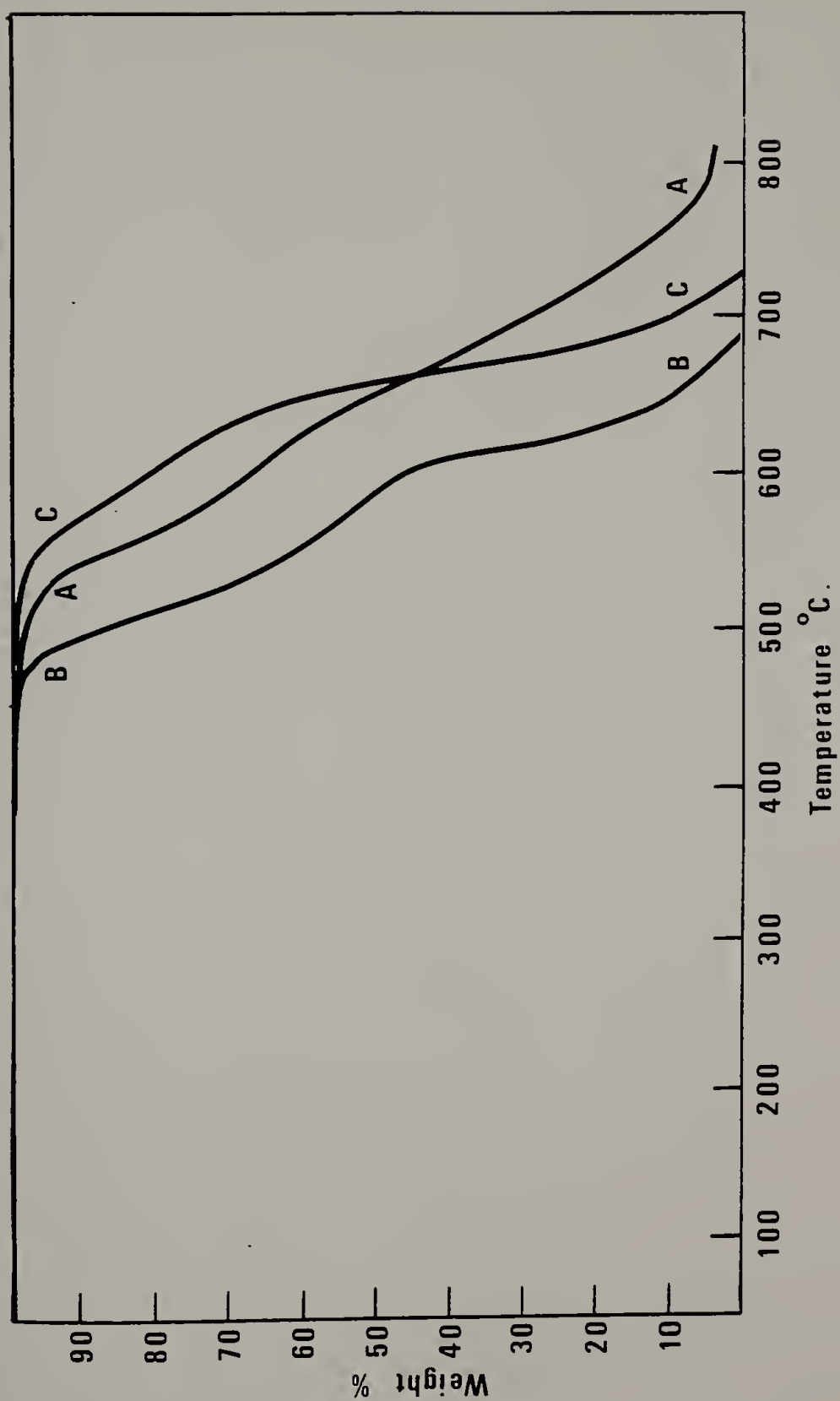


Figure 23

TABLE 16  
THERMAL AND THERMAL-OXIDATIVE  
DEGRADATION OF COPOLYMERS

	PDAPcoDPP	PDTPcoDPP	PDBPcoDPP
Commencement of wt. loss in N <sub>2</sub>	460°C	515°C	520°C
Commencement of wt. loss in Air	460	515	520
5% wt. loss N <sub>2</sub>	485	525	550
5% wt. loss Air	485	525	550
Commencement 2nd stage degradation (N <sub>2</sub> )	545	570	600
% of initial wt. remain. at commencement of 2nd stage degradation	55%	66%	66%
% initial wt. remaining at 800°C (N <sub>2</sub> )	44%	59%	55%

Figure 24. DSC scans of 1:1 blends of PDTP and PDPP;  
(A) Initial scan (B) Annealed 12 hours at 540°K.

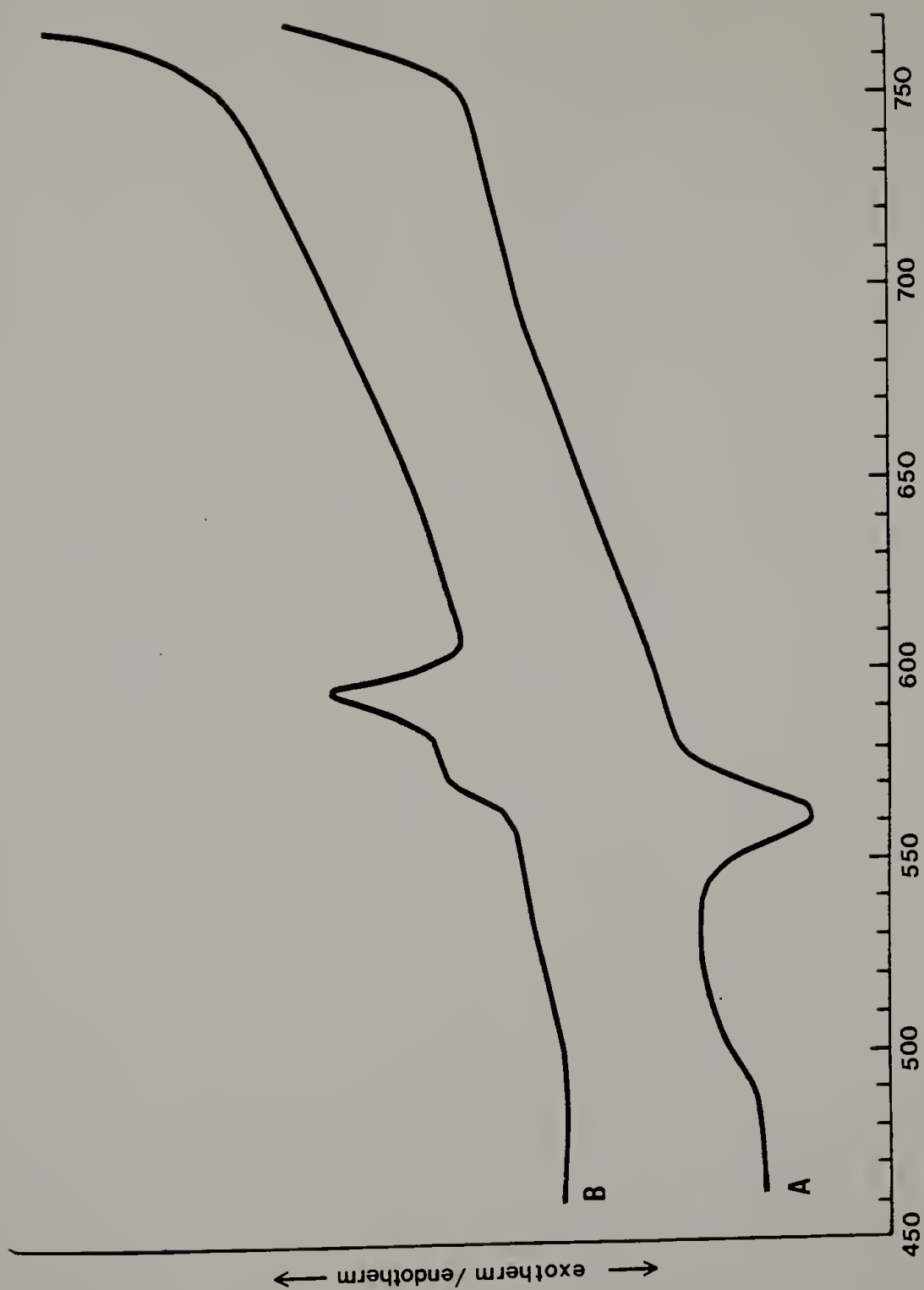


Figure 24

fact that all possible crystallization of the PDTP portion was confirmed by the characteristic melting profile with maximum at 321°C. The PDPP portion melted as before, commencing at 480°C with a maximum at 497°C.

The lower molecular weight sample PDAP-II was used in lieu of PDAP-I to prepare blends of PDAP and PDPP. This was done to observe the effects of blending on the crystallization exotherm observed for this homopolymer. The initial heating of this sample at 40°/min produced the trace shown in Figure 25A. A  $T_g$  was recorded at 231°C, followed by a sharp exotherm at 278°C. An endotherm with maximum at 367°C signified the melting of the crystalline PDAP. The sample was cooled rapidly from a maximum temperature of 380°C to prevent extensive decomposition of the PDAP fraction. Reheating from 127°C (Figure 25B) caused a  $C_p$  discontinuity at 207°C. As the PDPP portion crystallized in the first heating and was not allowed to melt, no  $T_g$  was detected at 230°C. Continued heating at the same rate produced a broad exotherm with a maximum at 276°C, which indicated crystallization of the PDAP fraction. Melting of this fraction occurred at 366°C. An endothermic curvature of the baseline following this melting was indicative of some degradation. An endothermic maximum was detected at 494°C for PDPP melting.



Figure 25. DSC scans at 1:1 blends at PDAP ( $\eta_{inh}$  0.32 dl./g.) and PDPP; (A) Initial scan (B) Second scan after cooling rapidly from 653°K.

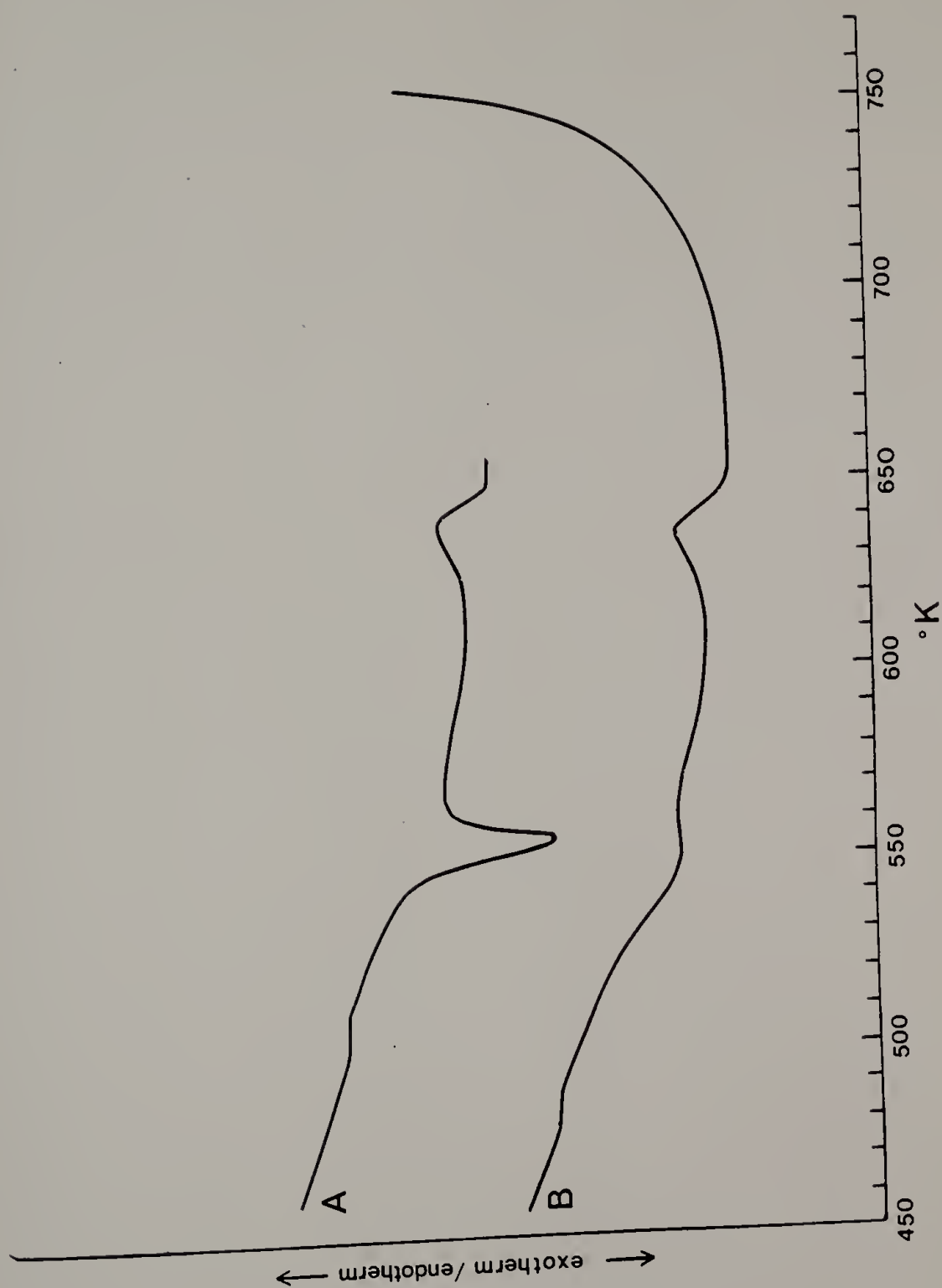


Figure 25

## CHAPTER VI

### EXPERIMENTAL

#### A. Purification of Monomers, Solvents and Reagents

All monomers were purified by repeated recrystallizations as described in Chapter III. Purity was monitored by melting points and elemental analyses. Prior to polymerization, the monomers were dried in vacuo for twenty four hours in the presence of phosphorous pentoxide and at 100°C.

Solvents used in polymerization reactions were purified as follows: Benzene (Fisher Scientific Co. spectrophotometric grade cat. #B-411) was used as received.

o-Dichlorobenzene was distilled in the presence of nitrogen, retaining the fraction boiling at 86°C at 18 mm pressure. Pyridine was distilled from potassium hydroxide in a nitrogen atmosphere at 115-115.5°C.

Polymerization agents and catalysts were purified as follows:

Silver oxide (Fisher Scientific cat. #5-184) was used as received.

CuCl was purified by dissolution in concentrated hydrochloric acid followed by precipitation in methanol.

The colorless granular solid was dried in vacuo in the presence of  $P_2O_5$ .

N,N,N',N'-tetramethylethylenediamine (TMEDA) was distilled from KOH at a boiling range of 120-122°C.

### B. Polymer Spectroscopic Analysis

Infrared spectra were obtained from films or KBr pellets on the Perkin-Elmer model 283 spectrophotometer.

$^1H$  NMR spectra were obtained in  $CDCl_3$  solutions containing tetramethylsilane as a standard. The Varian T-60 or FT-80 was used for this purpose.

$^{13}C$  NMR spectra were obtained in  $CDCl_3$  solution with tetramethylsilane standard on the Varian CFT-20 spectrophotometer. All samples were run in the decoupled mode.

### C. Molecular Weight Determinations

Values for  $M_n$ ,  $M_w$ ,  $M_z$ , and molecular weight distribution were derived from gel permeation chromatography of chloroform solutions of polymers using the Waters model 244 Liquid chromatograph.

### D. Inherent Viscosities

Inherent viscosity values were obtained from chloroform solutions of 0.5% polymer concentration at 25°C using a Cannon-Fenske viscometer.

### E. Polymer Syntheses

Poly(oxy-2,6-diphenyl-1,4-phenylene). 2,6-Diphenylphenol (2.0 g,  $8.1 \times 10^{-3}$  mole) was combined with 10 g silver oxide and 50 ml benzene in a 150 ml screw capped bottle. The bottle was shaken overnight (16 hr.). Excess silver oxide was removed by filtration and the polymer precipitated from the red benzene solution by dropwise addition to 500 ml of methanol. The fibrous polymer was redissolved in chloroform (20 ml) and the solution filtered through celite. The polymer was reprecipitated in methanol and dried in vacuo at 110°C for 3 hours. The yield of off-white fibrous polymer was 84% with an inherent viscosity of 0.74 dl/g.

Poly(oxy-2,6-bis(p-tolyl)-1,4-phenylene). Poly(oxy-2,6-bis(p-tolyl)-1,4-phenylene) was prepared by a similar technique. The polymer, after initial isolation by precipitation in methanol, was fibrous and red-violet in color. Purification was effected by dissolving previously isolated polymer in benzene and passing through a dry bed of neutral alumina. The resulting yellow benzene eluate was added dropwise to methanol generating off-white fibrous material, after drying as above, in a 60% yield of inherent viscosity 0.74 dl/g. Analysis: calculated for  $C_{20}H_{16}O$ ; C, 88.24%; H, 5.88%. Found: c, 88.21%; H, 5.88.

Poly(oxy-2,6-bis(p-methoxyphenyl)-1,4-phenylene). This was prepared by several methods, as described below.

The first method utilized the same procedure used in the preparation of PDTP described above. The yield of purple flakes isolated by dropwise addition of the benzene solution to methanol was 10% with an inherent viscosity of 0.05 dl/g.

Repeating this procedure replacing benzene as the polymerization solvent with o-dichlorobenzene produced brittle purple flakes in a 25% yield with an inherent viscosity of 0.16 dl/g.

The third attempt utilized CuCl and TMEDA as catalysts at elevated temperatures. To a 100 ml test tube partially immersed in an oil bath set at 60°C was added freshly distilled o-dichlorobenzene (10 ml), N,N,N',N'-tetramethylethylenediamine (TMEDA) (6.2 ml, 41.3 mole), CuCl (8.2 mg, .083 mmole), and anhydrous magnesium sulfate (0.4 g). The solution was stirred and oxygen bubbled through a gas dispersion tube at a rate of approximately 0.2 ft<sup>3</sup>/min. After 15 minutes, 1 gram (3.27 mmole) 2,6-bis(p-methoxyphenyl)phenol in 5 ml o-dichlorobenzene was added dropwise to the green solution. Oxygen addition and stirring were continued at 60°C for twenty four hours. The purple mixture was filtered and the polymer precipitated in methanol. The yield of purple brittle material was 60%. The polymer was purified by dissolution in 1,1,2,2-tetra-

chloroethane followed by precipitation by the slow addition of acetone. The latter procedure was repeated six times or until no further color removal was evident. The yield of pale brown polymer obtained after drying in vacuo for twenty four hours at 100°C was 24%. After purification the polymer was found to form brittle films when cast from tetrachloroethane solution. Inherent viscosity was determined by an indirect procedure described below. Analysis: calculated for  $C_{20}H_{16}O_3$ ; C, 78.95%; H, 5.30%. Found: C, 77.87%; H, 5.19%.

The latter procedure was repeated using 0.083 mmole tetramethylethylenediamine, which provided a Cu:nitrogen ratio of 1:2. In this case a crude yield of 68% was obtained. Purification as in the previous case produced a yield of 26% of purified pale brown polymer, which also demonstrated the ability to form brittle films. Analysis: calculated for  $C_{20}H_{16}O_3$ ; C, 78.95%; H, 5.30%. Found: C, 78.10%; H, 5.16%.

Because these polymers are insoluble, determination of viscosity and molecular weights of these products required perbromination to impart solubility in chloroform. This involved dissolution of the purified polymers in large excesses of liquid bromine. The resulting solutions were stirred overnight or approximately 12 hours. The bromine solution was then diluted to four times its volume with chloroform. The polymer was then precipitated by dropwise



addition to methanol. After isolation by filtration, the brominated polymer was dried in vacuo for 24 hours at 100°C. The dried samples were analyzed for bromine content. Inherent viscosity determinations were then performed in chloroform solution. From these results, the inherent viscosity of the nonbrominated material was calculated using the relationship:

$$\eta = \eta_{\text{Br}}/(1-x) \quad (\text{Equation 64})$$

where  $\eta_{\text{Br}}$  refers to the inherent viscosity of the brominated polymer and  $x$  is the fraction, by weight, of bromine in the brominated polymer. Values obtained for the products of the latter two polymerizations are tabulated below.

TABLE 17

Cu:N	x	$\eta_{\text{Br}}$ (dl/g)	$\eta$ (dl/g)
1:1	0.568	0.14	0.32
1:2	0.562	0.17	0.38

Preparation of PDAP was also attempted using 4-bromo-2,6-bis(p-methoxyphenyl)phenol (BrDAP). This monomer was synthesized as follows.

2,6-Bis(p-methoxyphenyl)phenol (2 g, 6.5 mmole) was dissolved in 50 ml ether. To this was added, at once,



dioxane dibromide (1.62 g, 6.5 mmole) and the mixture stirred for 2 hours. During this time, moderate evolution of HBr gas was noted. The ether was evaporated to leave a pale violet solid weighing 2.5 g or 99% of the theoretical yield. The crude melting point was 103-110°C. The phenol was recrystallized from absolute ethanol and decolorizing charcoal to give white needles in an overall yield of 85%. The melting point of the pure material was 114-115°C. Analysis: calculated for  $C_{20}H_{17}BrO_3$ ; C, 62.35%; H, 4.41%; Br, 20.76%. Found: C, 62.53%; H, 4.60%; Br, 21.05%.

Two methods were used to polymerize this monomer.

The first method involved the use of stoichiometric amounts of CuCl oxidation catalyst. The brominated phenol (1 g, 2.6 mmole) was combined with CuCl (0.26 g, 2.6 mmole), TMEDA (1.17 ml, 7.8 mmole) and 100 ml pyridine in a flask partially immersed in a 60°C oil bath. Oxygen was bubbled through the system at approximately 0.2 ft<sup>3</sup>/min and the mixture stirred for eight hours. The green solution was then cooled and filtered. The filtrate was added slowly to methanol producing a pale violet nonfiber forming precipitate. After isolation by filtration and drying in vacuo at 100°C, the yield was determined to be 85% with an inherent viscosity of 0.19 dl/g.

The second method involved a two phase system. In a 50 ml test tube were combined potassium hydroxide (0.22 g, 3.8 mmole), water (10 ml), cuprous sulfate (1 mg),

sodium lauryl sulfate (5 mg) and BrDAP (1 g) in two ml benzene. Oxygen was added via a gas dispersion tube at the same rate as above for a period of 15 minutes. Then, at 15 minute intervals, 3 portions of ammonium persulfate totaling 4.6 mg ( $2 \times 10^{-5}$  mole) in 0.2 ml water were added and the mixture was stirred under continuous  $O_2$  addition for fifteen hours. The phases were separated and the aqueous phase washed with benzene. The combined benzene phases were added to methanol to effect precipitation of the polymer. A pale pink nonfibrous precipitate resulted which, upon drying as in previous cases, weighed 0.27 g or 20% of the theoretical yield. The inherent viscosity was determined to be 0.06 dl/g.

Poly(oxy-2,6-bis(p-biphenyl)-1,4-phenylene). CuCl (0.031 g, 0.31 mmole), TMEDA (0.0475 ml, 0.315 mmole) were combined with 30 ml benzene in a 100 ml test tube partially immersed in an oil bath held at 60°C. Oxygen was bubbled through the system at a rate of 0.2 ft<sup>3</sup>/min. After fifteen minutes, DBP (1 g, 2.5 mmole) in 30 ml benzene was added dropwise over a thirty minute period. The purple mixture was then stirred under a steady stream of oxygen at a constant temperature for twenty four hours. It was noted that considerable precipitation of a purple granular solid occurred very soon after addition of monomer solution. After the prescribed period, the mixture was added to

methanol and filtered to isolate a dark purple granular solid which, when dried, weighed 0.9 g, or 90% of theoretical weight of a polymeric product. The isolated product was cleaned by soxhlet extraction with methylene chloride for twenty four hours or until no further color was removed by solvent. The yellow solid was dried in vacuo at 100°C to give 0.71 g (70%) of product which was insoluble in all common organic solvents. Analysis: calculated for  $C_{30}H_{20}O$ ; C, 90.15%; H, 5.05%. Found: C, 88.93%; H, 4.86%.

Perbromination of this product, as in the case of PDAP, was conducted to induce solubility in chloroform. The brominated product was found to contain 53.3% bromine by weight. The inherent viscosity of the brominated material was found to be 0.039 dl/g, which converts at 0% bromine to 0.084 dl/g.

Poly(oxy-2,6-diphenyl-1,4-phenylene)co(oxy-2,6-bis(p-tolyl)-1,4-phenylene). This was prepared by combining 5 mmole DPP and 5 mmole DTP with 5 g  $Ag_2O$  and 50 ml benzene in a 150 ml screw capped bottle. The bottle was shaken overnight (16 hours) and the reaction mixture filtered to remove silver and excess silver oxide. The red benzene filtrate was passed through a bed of neutral alumina and the yellow benzene eluate added dropwise to methanol. The white fibrous precipitate was filtered and dried in vacuo

at 100°C for three hours. The yield was 58% of a polymer with an inherent viscosity of 0.75 dl/g.

Poly(oxy-2,6-diphenyl-1,4-phenylene)co(oxy-2,6-bis(p-methoxyphenyl)-1,4-phenylene). This was prepared as above with a few modifications. In this case, benzene was replaced with o-dichlorobenzene as the polymerization solvent. Purification was accomplished by dissolution in benzene followed by slow addition of acetone to the benzene solution. This was repeated until no further color removal was detected. The yield of fibrous polymer after drying, as in the previous cases, was 30% with an inherent viscosity of 0.53 dl/g.

Poly(oxy-2,6-diphenyl-1,4-phenylene)co(oxy-2,6-bis(p-biphenyl)-1,4-phenylene). This was prepared as in the case of PDPPcoPDTP. After purifying by passing a benzene solution through neutral alumina, filtering and drying, the yield of off-white fibrous polymer was calculated to be 32% with an inherent viscosity of 0.53 dl/g.

F. Determination of Weight Percent Diphenoquinone as Side Product in Homopolymerizations

In order to accurately determine the percentage of diphenoquinone as side product in the homopolymerizations, it was necessary to prepare these diphenoquinones in their pure form. The description of these syntheses follows.

3,3',5,5'-Tetraphenyldiphenoquinone. DPP (2.0 g, 8 mmole) was dissolved in 50 ml n-butyronitrile. To this was added CuCl (0.70 g, 8 mmole). The mixture was heated at 100°C with stirring and continuous addition of oxygen at a moderate rate. The red solution was cooled and metallic green crystals appeared. The solid diphenoquinone was filtered and dried to give a yield of 1.6 g, or 81%. After recrystallization from n-butyronitrile a melting range of 278-280°C was achieved.

3,3',5,5'-Tetra(p-tolyl)diphenoquinone. This was prepared by an identical procedure in a yield of 53%. After recrystallization from n-butyronitrile, the melting range was 284-286°C. Analysis: calculated for  $C_{40}H_{32}O_2$ ; C, 88.24%; H, 5.88%. Found: C, 88.39%; H, 5.78%.

3,3',5,5'-Tetra(p-methoxyphenyl)diphenoquinone. This was prepared as above in a yield of 69% with a melting point after recrystallization of 290-292°C. Analysis: calculated for  $C_{40}H_{32}O_6$ ; C, 78.95%; H, 5.26%. Found: C, 78.13%; H, 5.30%.

3,3',5,5'-Tetra(p-biphenyl)diphenoquinone. This was prepared as above in a yield of 45%. The charcoal colored material did not melt at temperatures up to 500°C. Purification was effected by recrystallization from methylene chloride. Analysis: calculated for  $C_{60}H_{40}O_2$ ; C, 90.91%; H,



5.05%. Found: C, 91.98%; H, 5.76%.

The absorption maxima for the pure diphenoquinones were obtained in  $\text{CHCl}_3$  utilizing the Beckman uv/visible spectrophotometer. From the value of absorbance  $A$  obtained at this wavelength, the molar absorptivity  $\epsilon$  was calculated from the Lambert-Beer law,<sup>92</sup>

$$A = \frac{\epsilon bc}{M}$$

where  $b$  is the path length, in this case 1 cm,  $c$  is the concentration of absorbing species, diphenoquinone, in g/l, and  $M$  is the molecular weight of the diphenoquinone.

Having established the molar absorptivity for pure diphenoquinone, the proportion of this compound in the polymerization product mixtures could now be determined as follows:

After cessation of the polymerization, the product solution was filtered to remove insoluble catalysts and other reagents. The solvent was then evaporated from the filtrate, leaving a crude solid mixture consisting of polymer and quinone. This material was dried for 12 hours at  $100^\circ\text{C}$  in vacuo. A solution of the solid mixture and spectrograde  $\text{CHCl}_3$  was prepared in a precisely known concentration, designated here by  $c'$ . The absorbance of this solution was obtained at the wavelength of the respective diphenoquinone maxima. From this absorbance and the

previously determined molar absorptivity, the actual concentration,  $c$ , of the diphenoquinone in the solution was calculated. The percentage of diphenoquinone produced in the polymerization reaction was then derived from  $100 \times c/c'$ .

#### G. Thermal Analyses of Polymers

Polymers and copolymers were subjected to thermal analysis via differential scanning calorimetry. The Perkin-Elmer model DSC-2 was used for this purpose.

All polymers, after preparation and purification as described earlier, were dried for 24 hours in vacuo at 100°C prior to thermal analysis. The fibrous samples, PDTP, PDTPcoDPP, PDAPcoDPP, PDBPcoDPP required compacting prior to thermal analysis. A minipress pelletmaker was used for this purpose. PDAP did not form fibers and was used in a powdered form.

All samples were brought rapidly to an initial temperature of 400°C prior to scanning. Heating was at a rate of 40°/min, and all scans were conducted in a nitrogen atmosphere.

#### H. Determination of Percent Crystallinity

The percent crystallinities of PDTP and PDAP were estimated from the MacBeth TD 528 microdensitometer intensity measurements of WAXS photos (Figures 8 and 10,

respectively). From a plot of intensity values versus diameter, the crystalline fractions were measured as the area under the peaks attributable to crystalline regions divided by the area under the entire curve.

### I. Thermal Stability

The thermal stability of the polymers and copolymers was measured by monitoring weight loss with respect to temperature on the DuPont model 951 thermogravimetric analyzer.

### J. Preparation of Blends

A blend consisting of a 1:1 mixture of PDPP and PDTP was prepared by dissolving equal weights of both polymers in chloroform. Films were made by casting the resulting solution on glass plates and evaporating the solvent. The blend was obtained in fibrous form by adding the chloroform solution slowly to methanol.

Similarly, a 1:1 blend of PDPP and PDAP was prepared, in this case the solvent was 1,1,2,2-tetrachloroethane.

Both blends were then subjected to differential scanning calorimetry as described for the homopolymers and copolymers.



## C H A P T E R   V I I

### CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The double nucleophilic displacement reaction involving 1,3-dibromopropane and 1,3-diarylpropanone has proven to be a general route to 2,6-diarylcyclohexanones and hence 2,6-diarylphenols. Phase transfer catalyzed systems contain many variables such as solvent, catalyst, concentrations of reagents, temperature and reaction time. Minimum effort was expended in optimization of this ring forming reaction, since the principal goal of this thesis was obtaining these phenol precursors.

The procedures described in Chapter I for the synthesis of the diaryl propanones can be extended to the synthesis of other ketones which could lead to the preparation of polymers with different property profiles.

Of the polymers prepared, only poly[oxy-2,6-bis(p-tolyl)-1,4-phenylene] (PDTP) achieved the desired crystallizability and melting temperature. There are indications that poly[oxy-2,6-bis(p-methoxyphenyl)-1,4-phenylene] (PDAP) would also have these properties but it could not be produced in high molecular weight due to crystallization during polymerization. A detailed study of the conditions of polymerization might overcome this.

It is apparent that random copolymerization of 2,6-diarylphenols will always produce amorphous products. Future work might include the preparation of block copolymers. As indicated by the behavior of blends, a copolymer containing blocks of DTP or DAP and DPP of sufficient length would likely have two crystalline phases with two melting points.

Another area not investigated in this thesis is the compatibility behavior of the homopolymers with poly(oxy-2,6-dimethyl-1,4-phenylene). The latter polymer forms compatible mixtures with polymers such as polystyrene, while poly(oxy-2,6-diphenyl-1,4-phenylene) does not. It would therefore be of some interest to see if the added substituents would change the compatibility of the arylsubstituted polyphenylene ethers with other polymers such as polystyrene.

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A P P E N D I X    A

Infrared Spectra

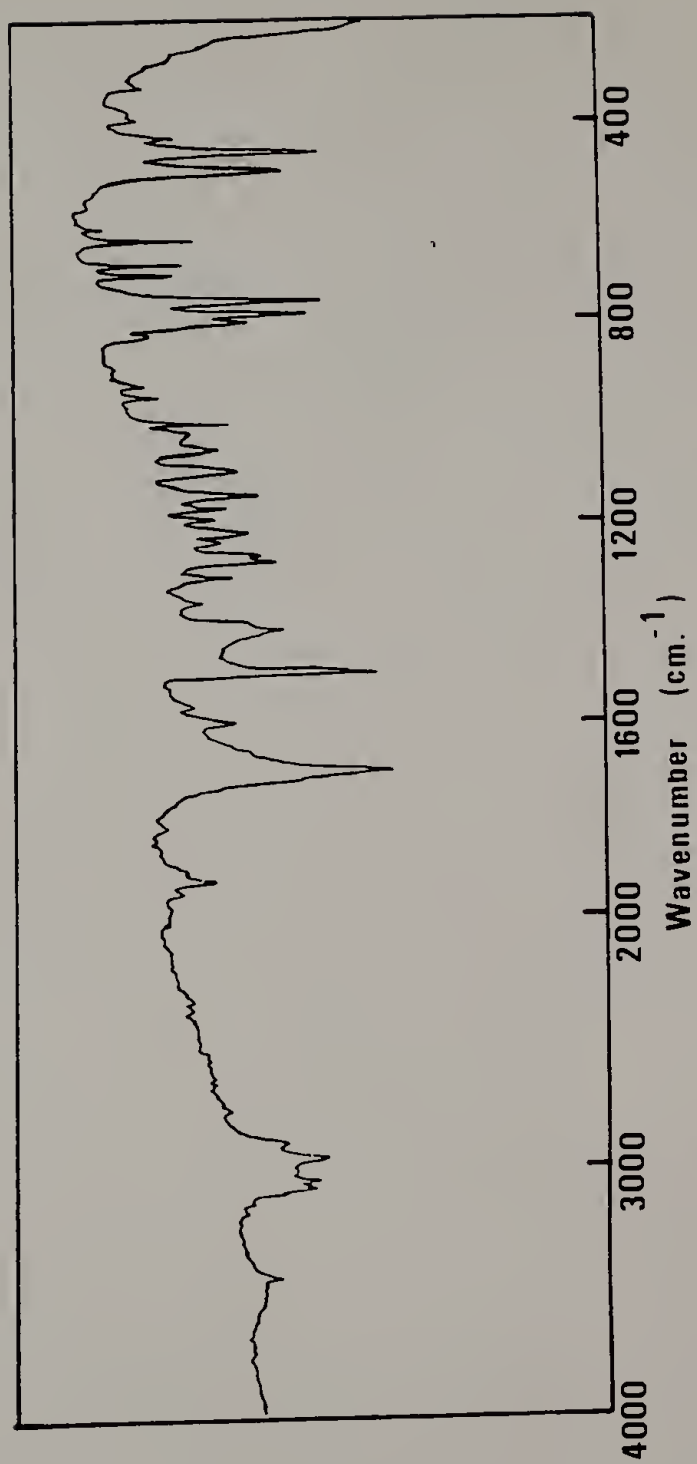


Figure 26. 1,3-Bis (p-tolyl)-2-propanone

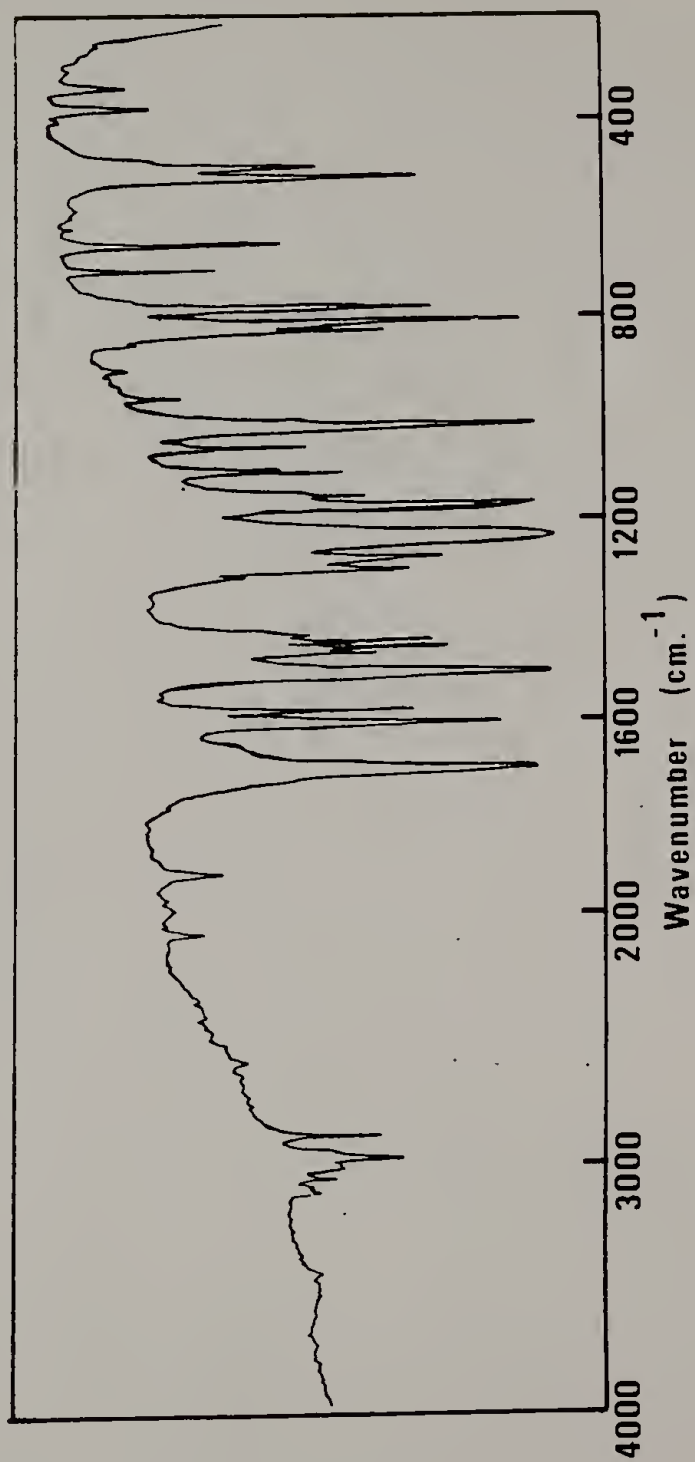


Figure 27. 1,3-Bis (p-methoxyphenyl)-2-propanone.

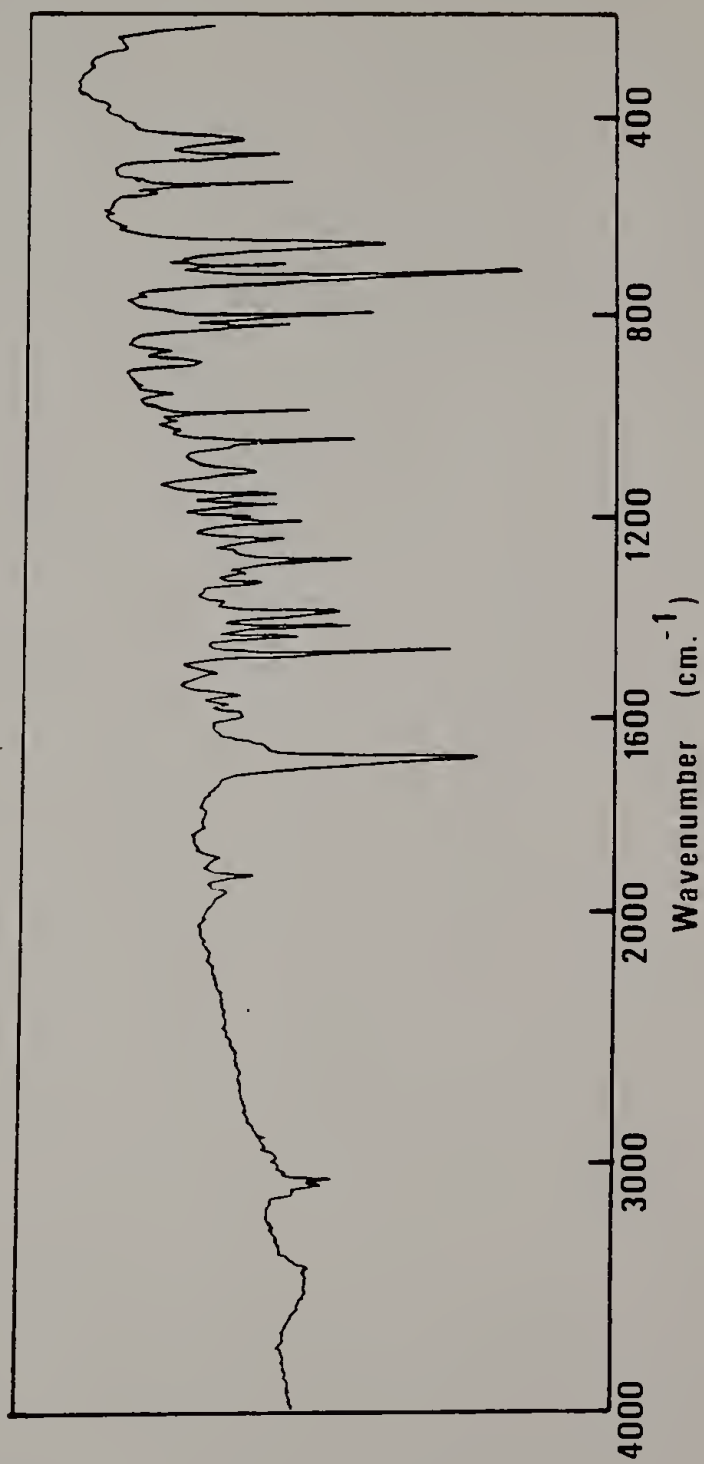


Figure 28. 1,3-Bis (p-biphenyl)-2-propanone.

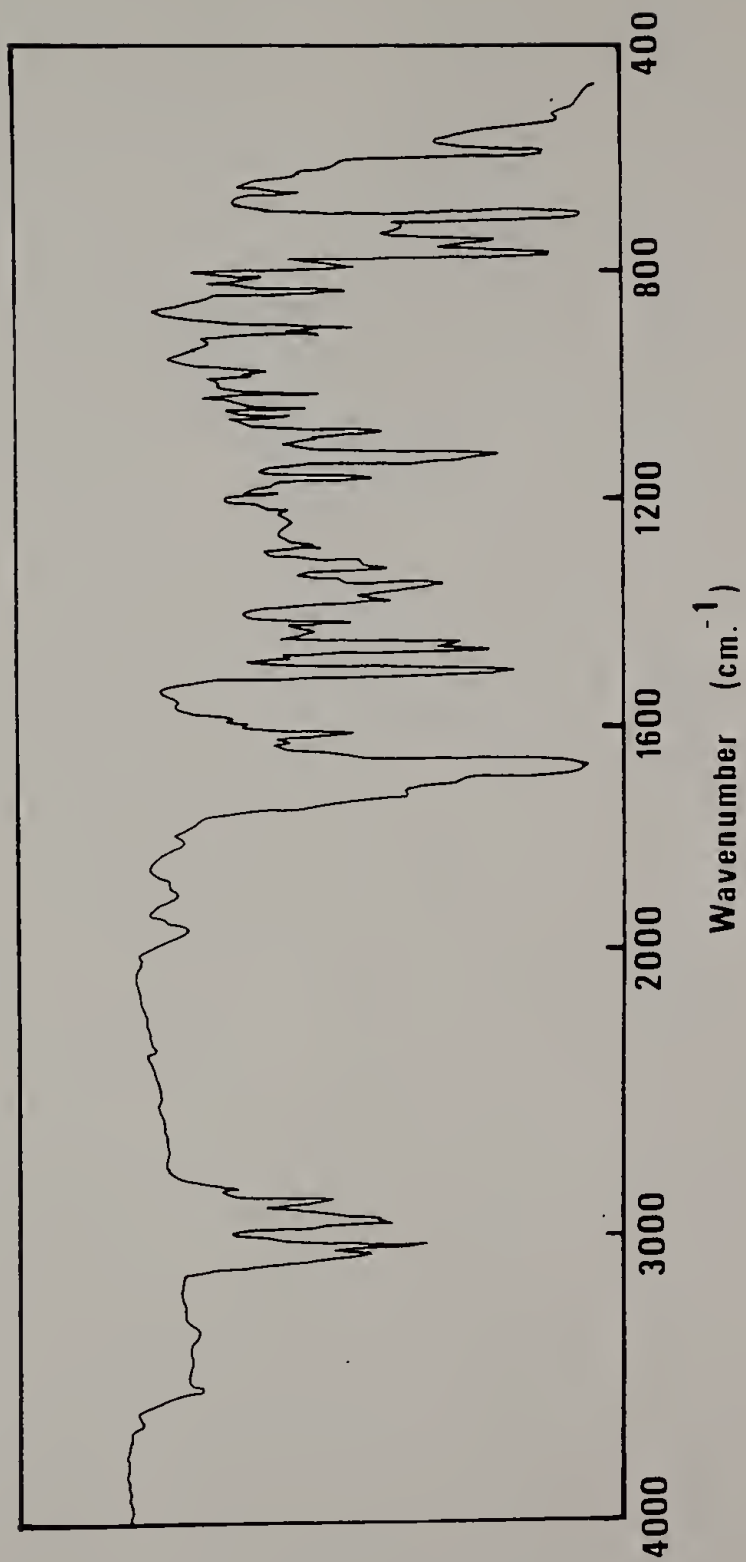


Figure 29. 2,6-Diphenyl-2-cyclohexenone.

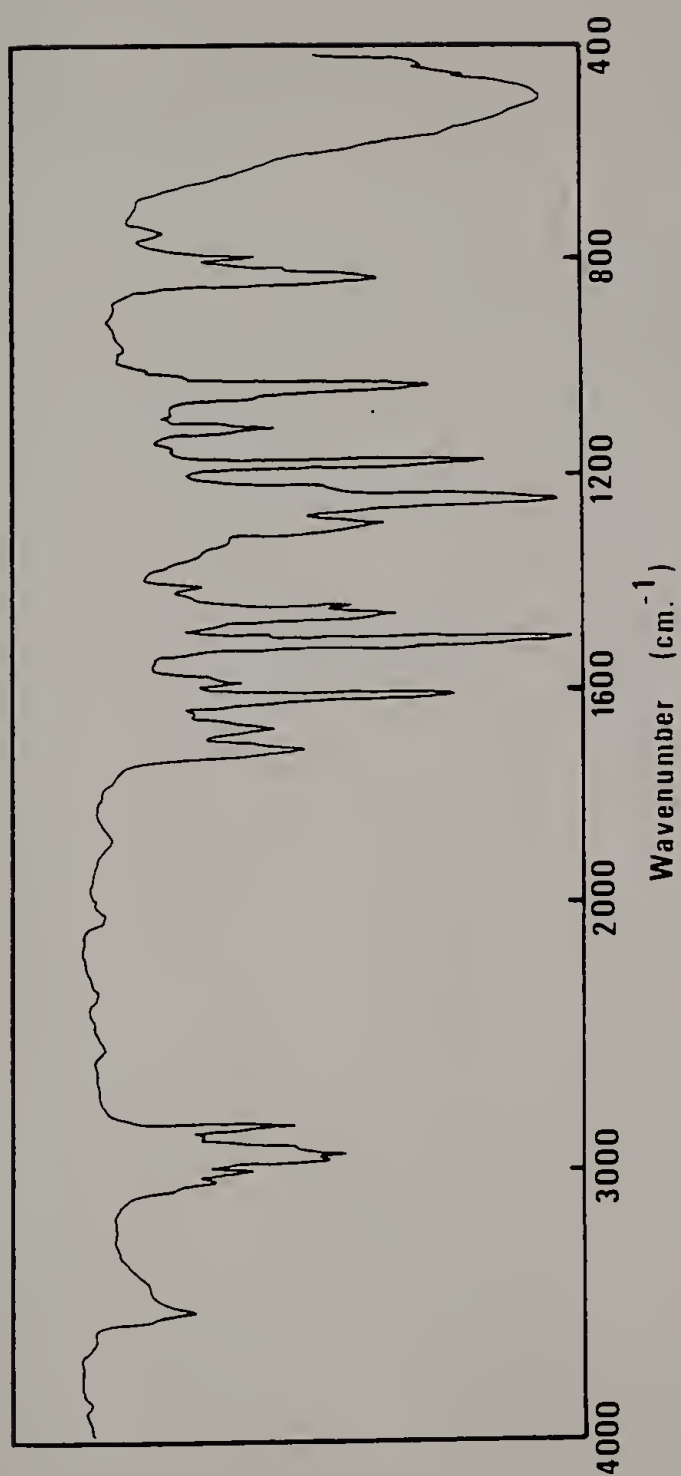


Figure 30. 2,6-Bis (p-methoxyphenyl)-2-cyclohexenone.



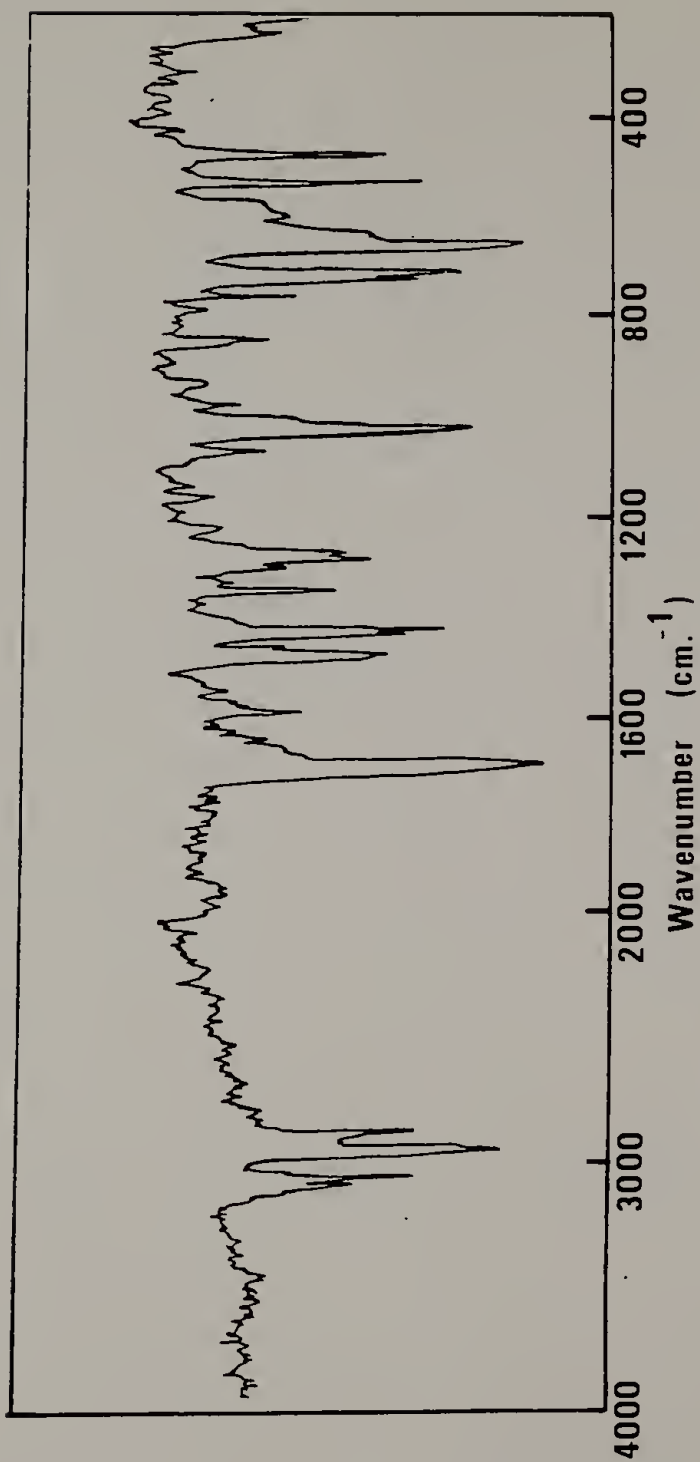


Figure 31. 2,6-Diphenylcyclohexanone.

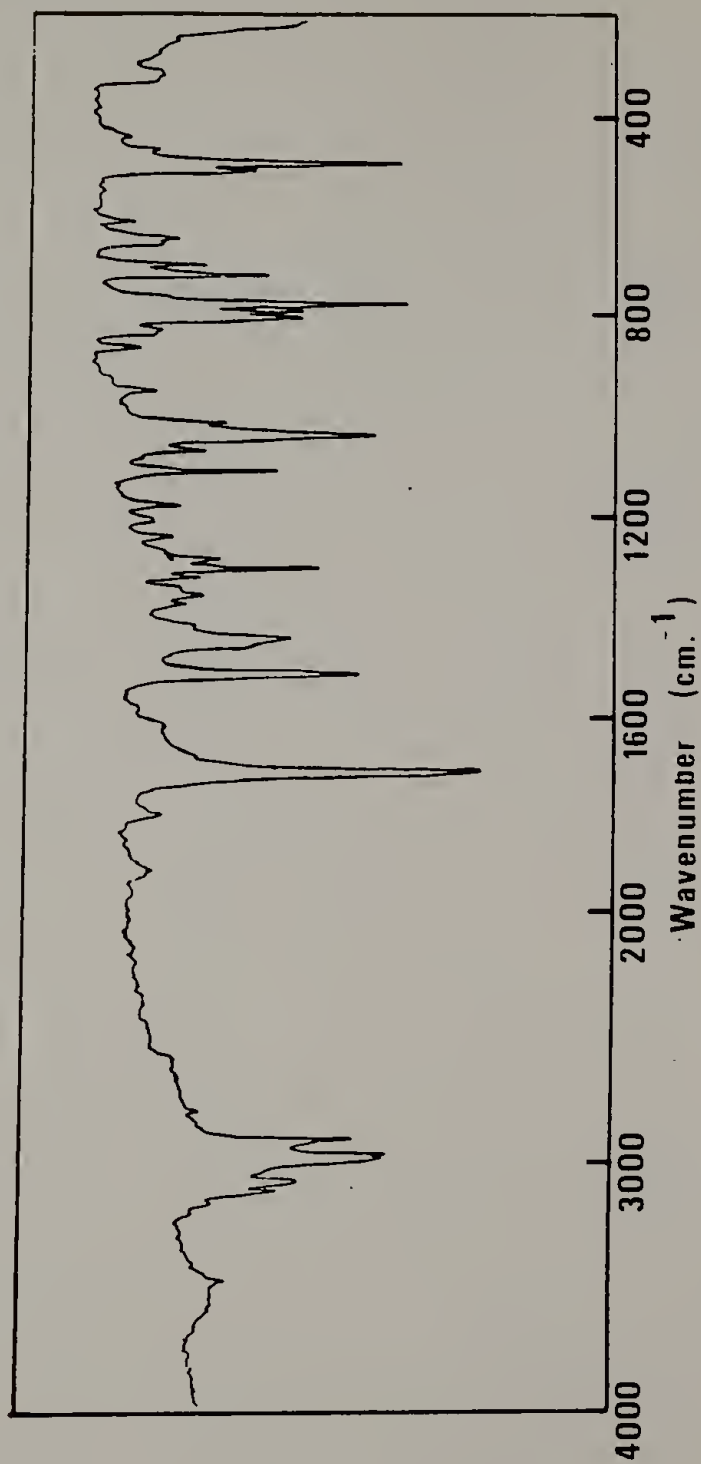


Figure 32. 2,6-Bis (p-tolyl) cyclohexanone.

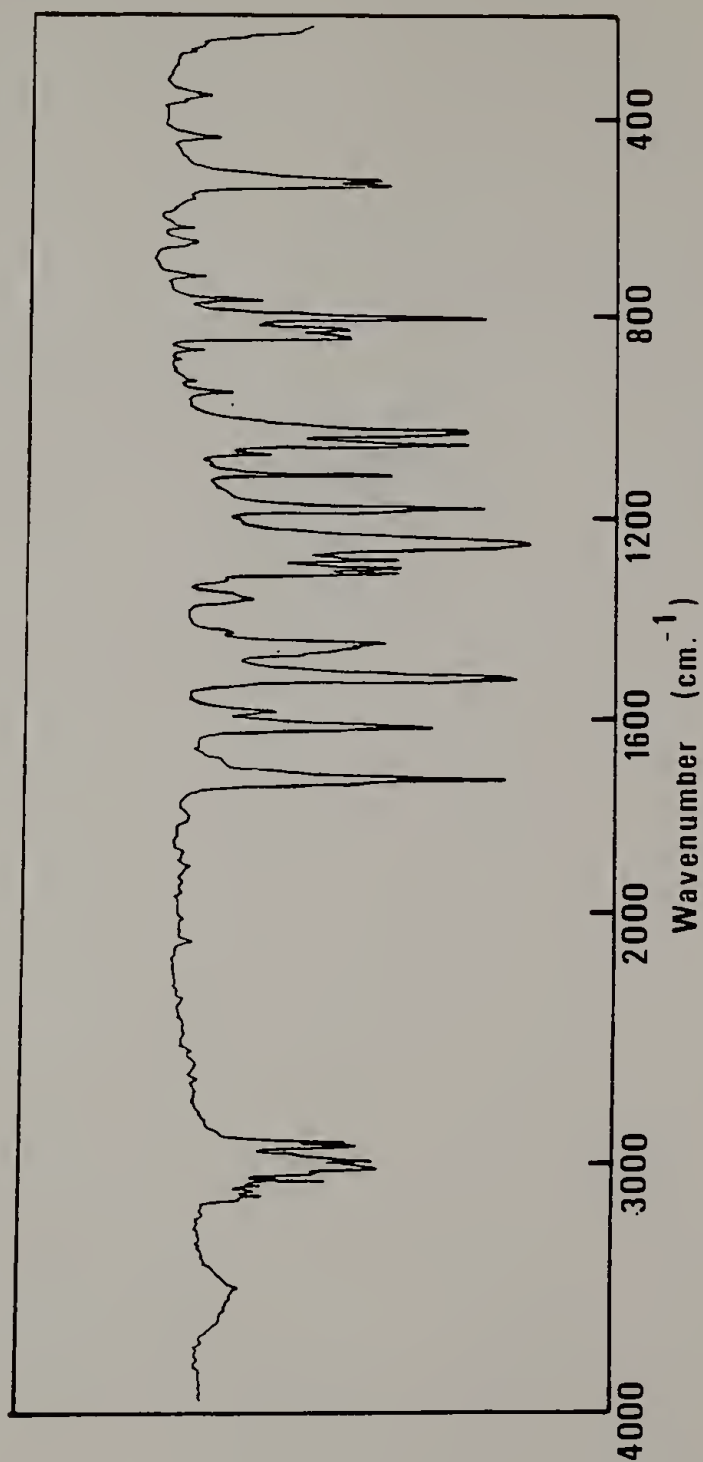


Figure 33. 2,6-Bis (p-methoxyphenyl) cyclohexanone.

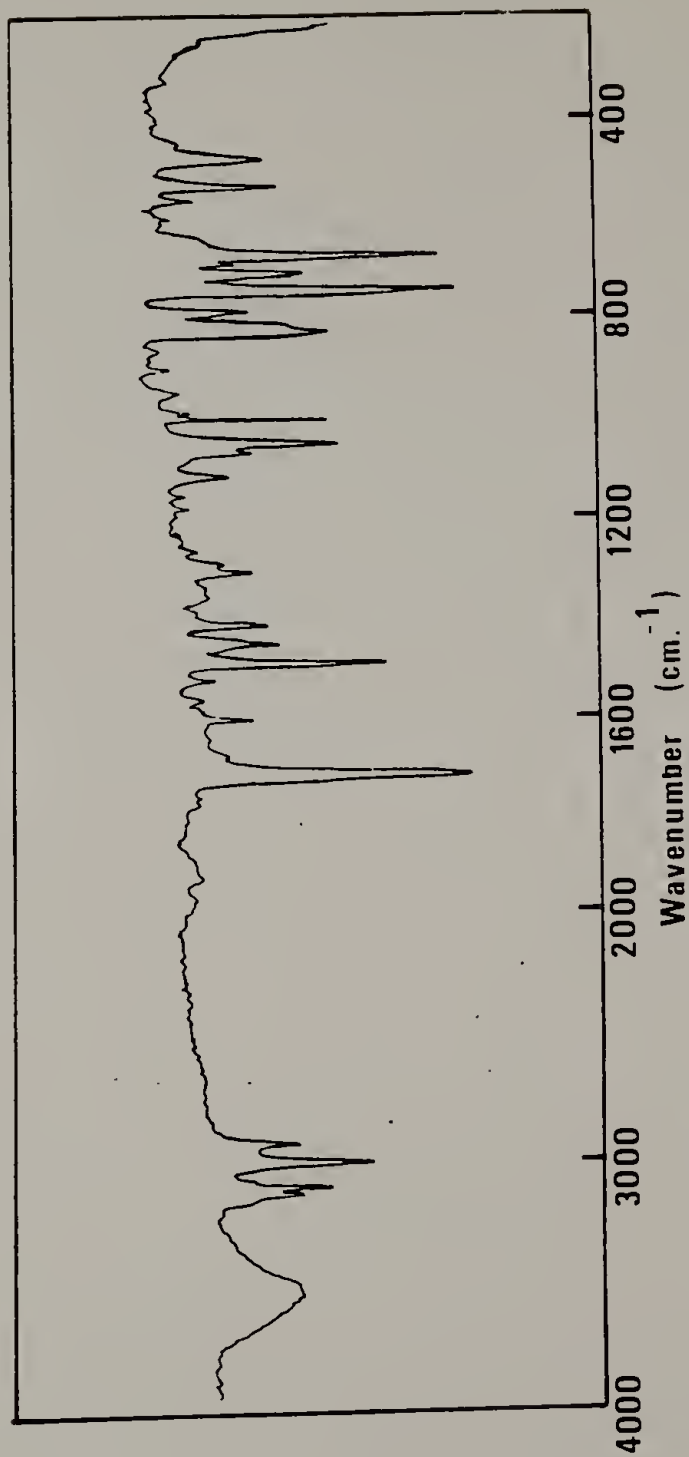


Figure 34. 2,6-Bis (p-biphenyl) cyclohexanone.

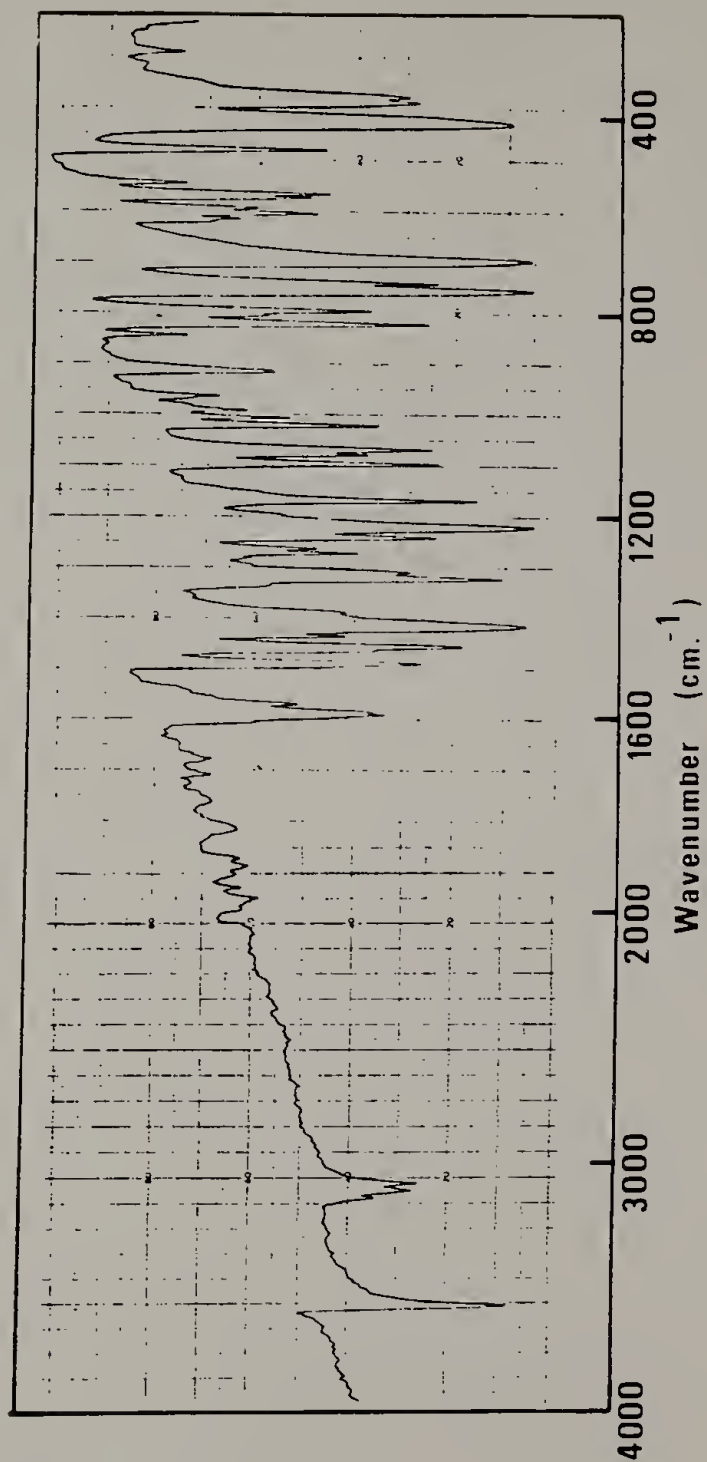


Figure 35. 2,6-Diphenylphenol.

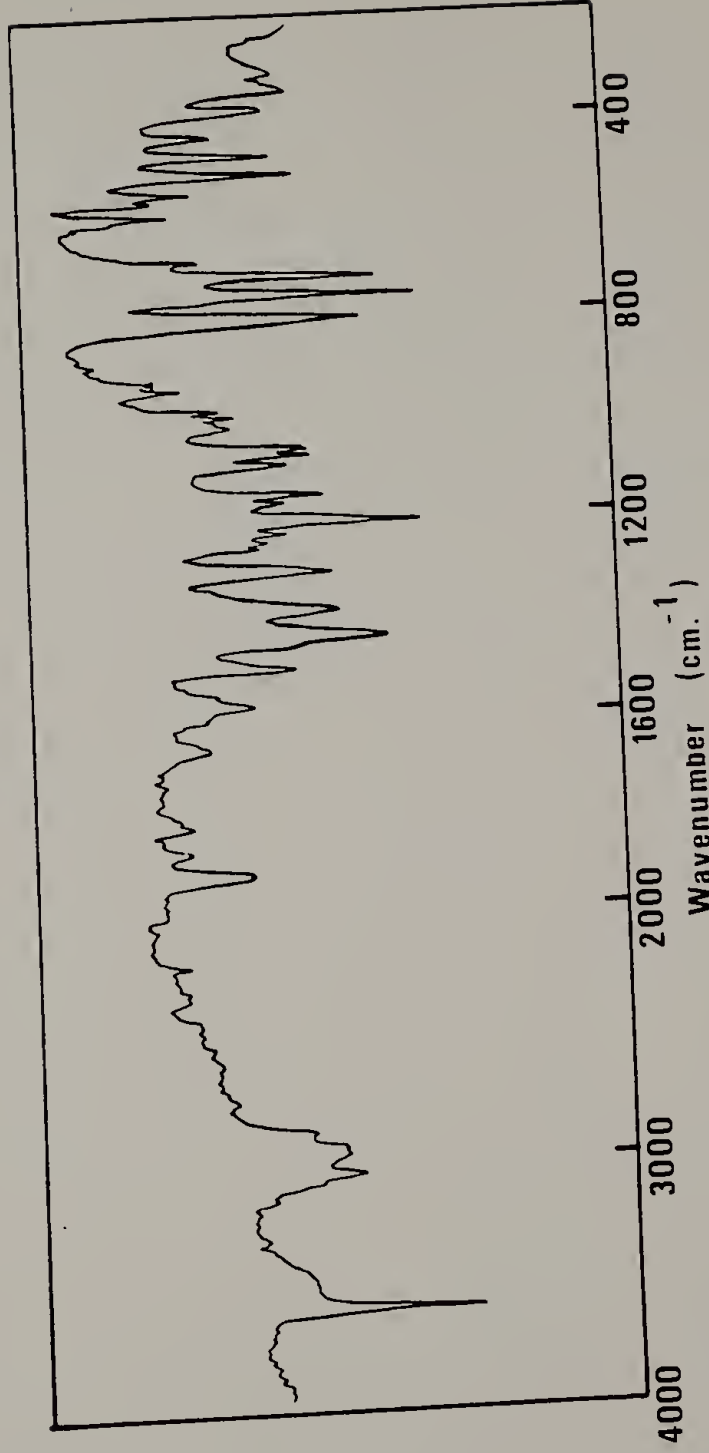


Figure 36. 2,6-Bis (p-tolyl) phenol.

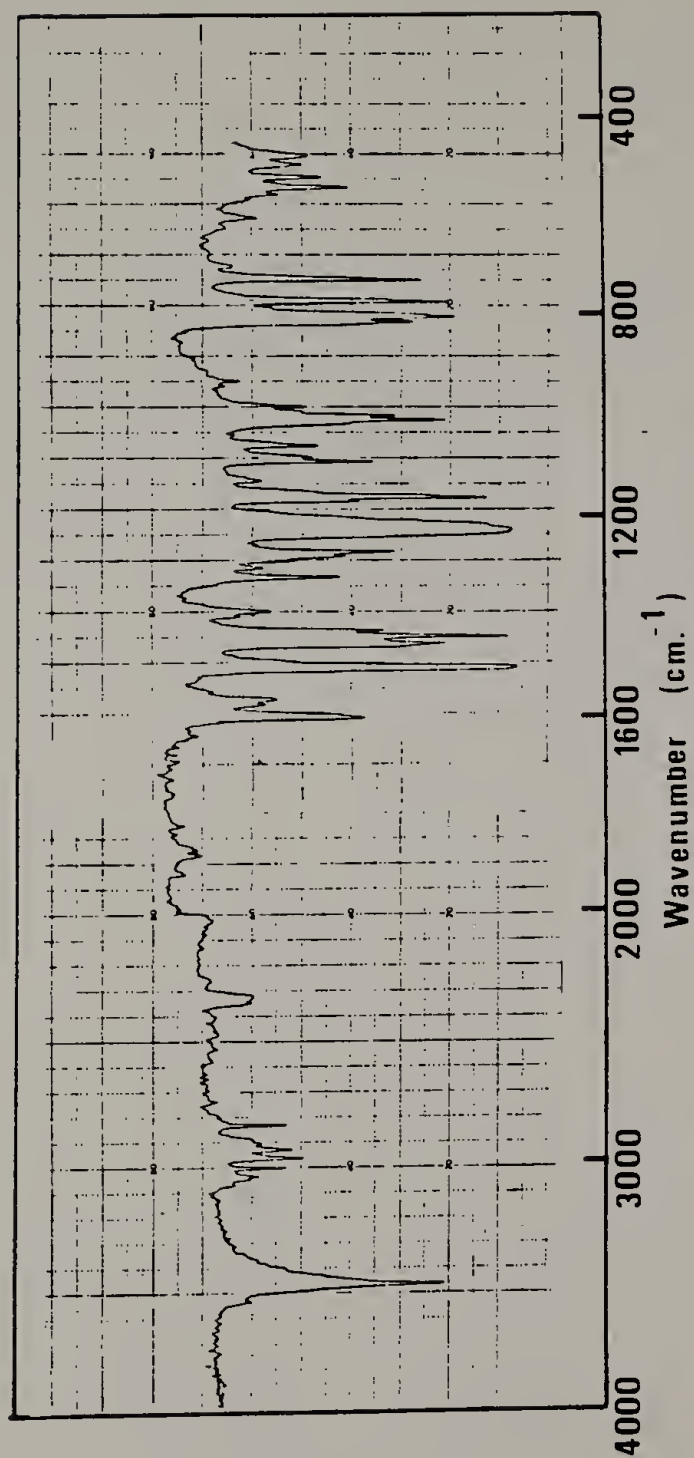


Figure 37. 2,6-Bis (p-methoxyphenyl) phenol.

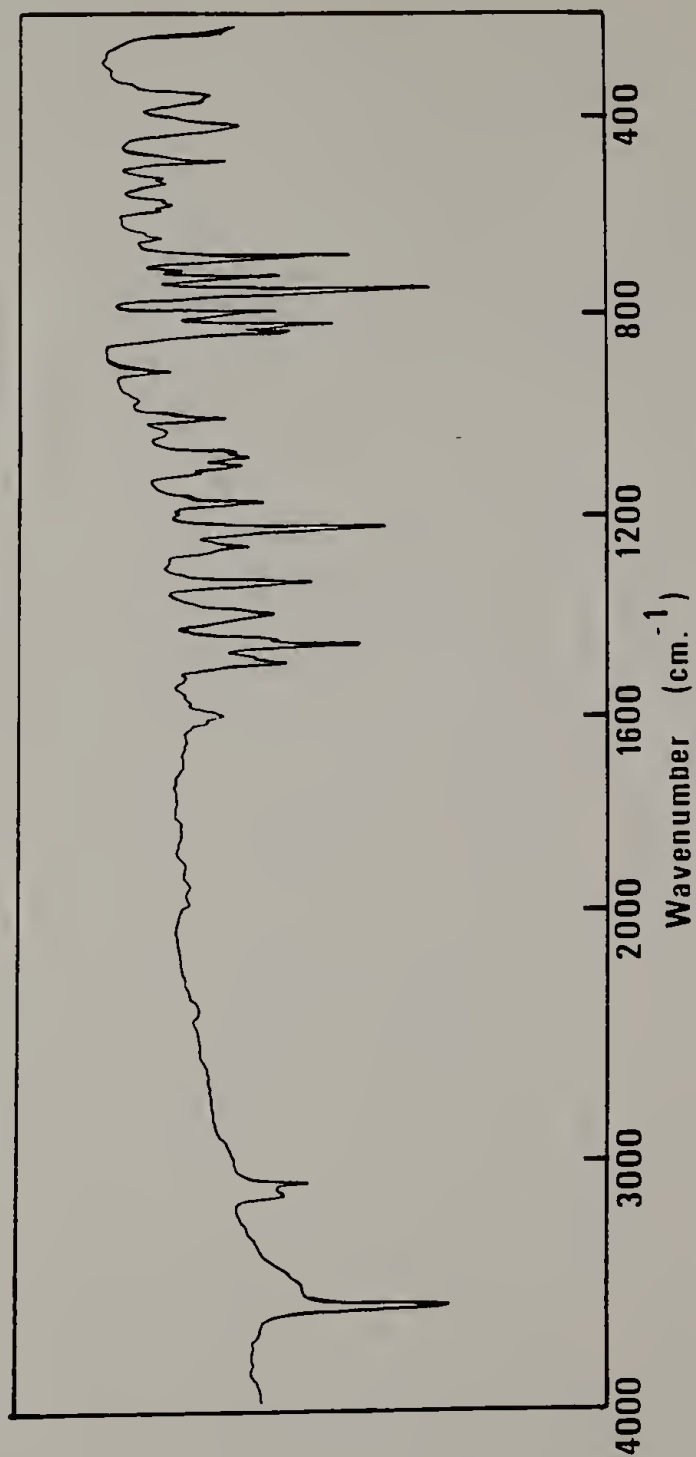


Figure 38. 2,6-Bis (p-biphenyl) phenol.



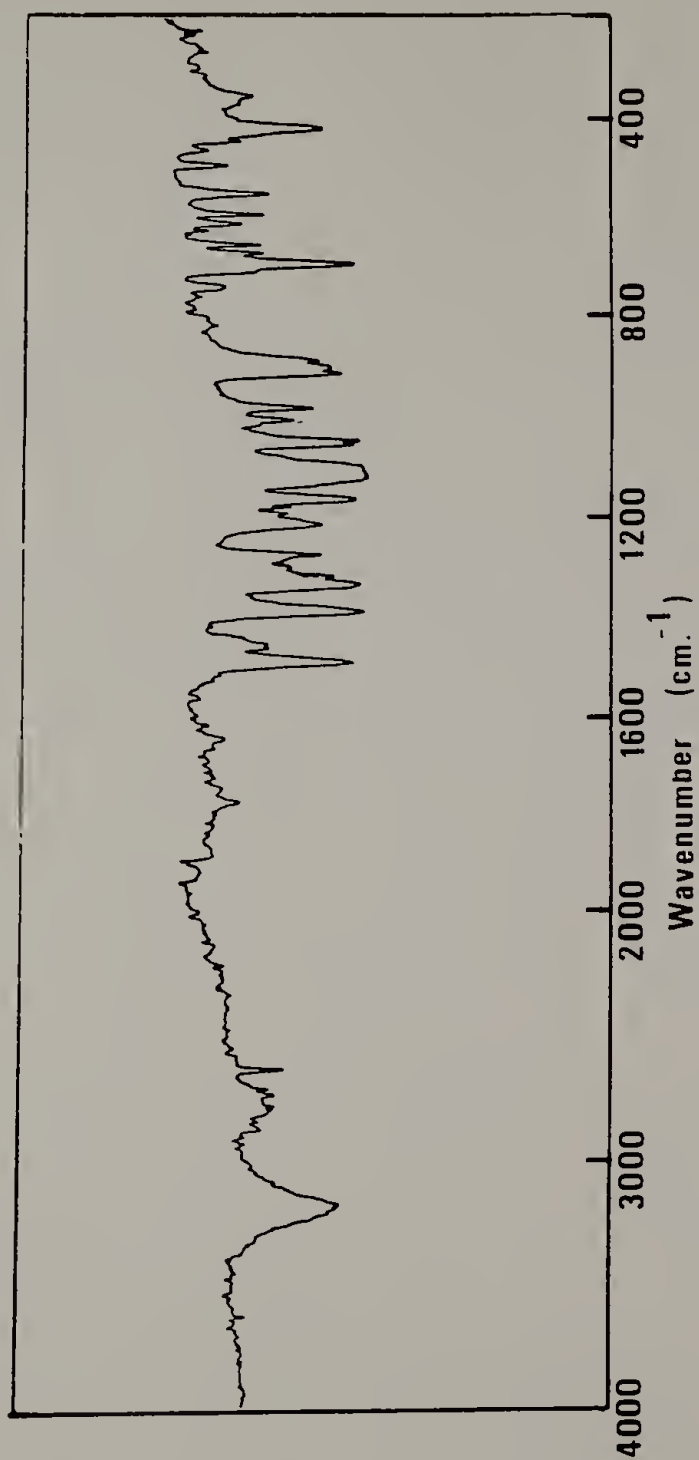


Figure 39. 4-Bromo-2,6-bis (p-methoxyphenyl) phenol.

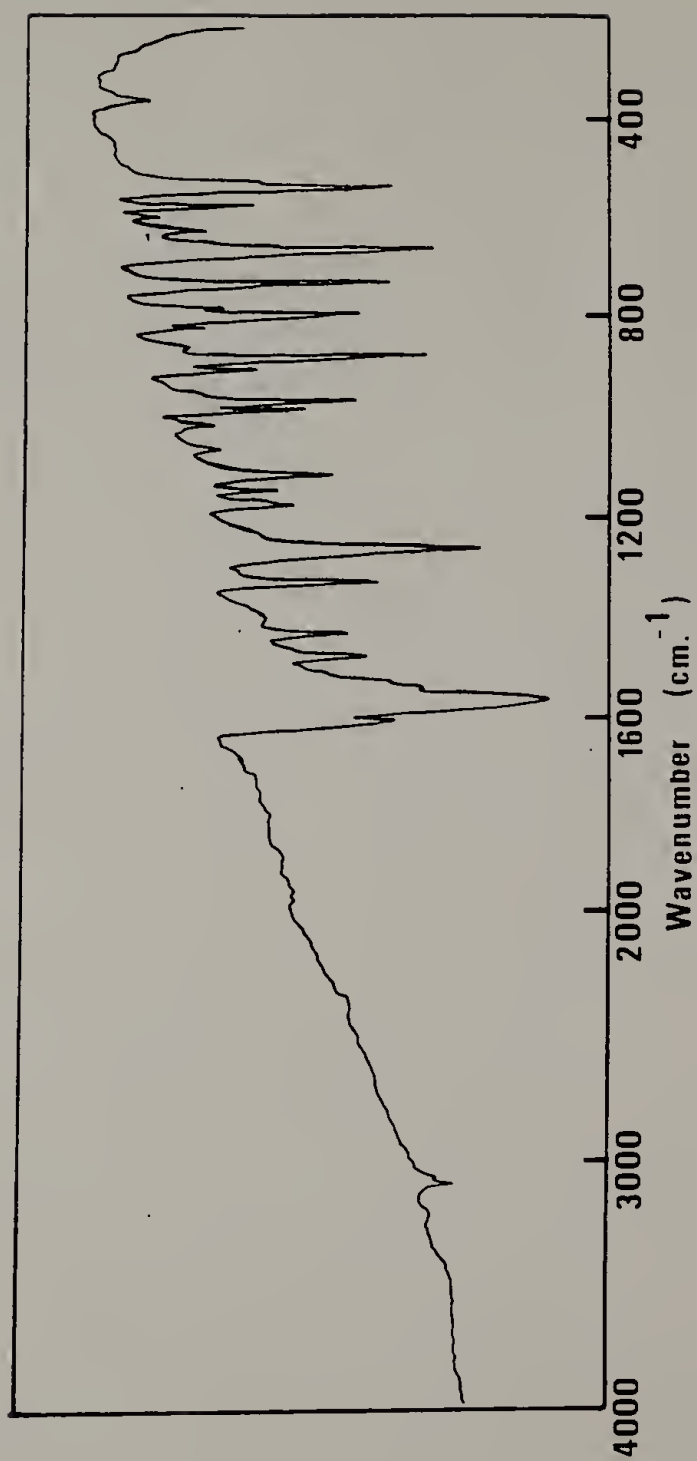


Figure 40. 3,3',5,5'-Tetra (p-tolyl) diphenoquinone.

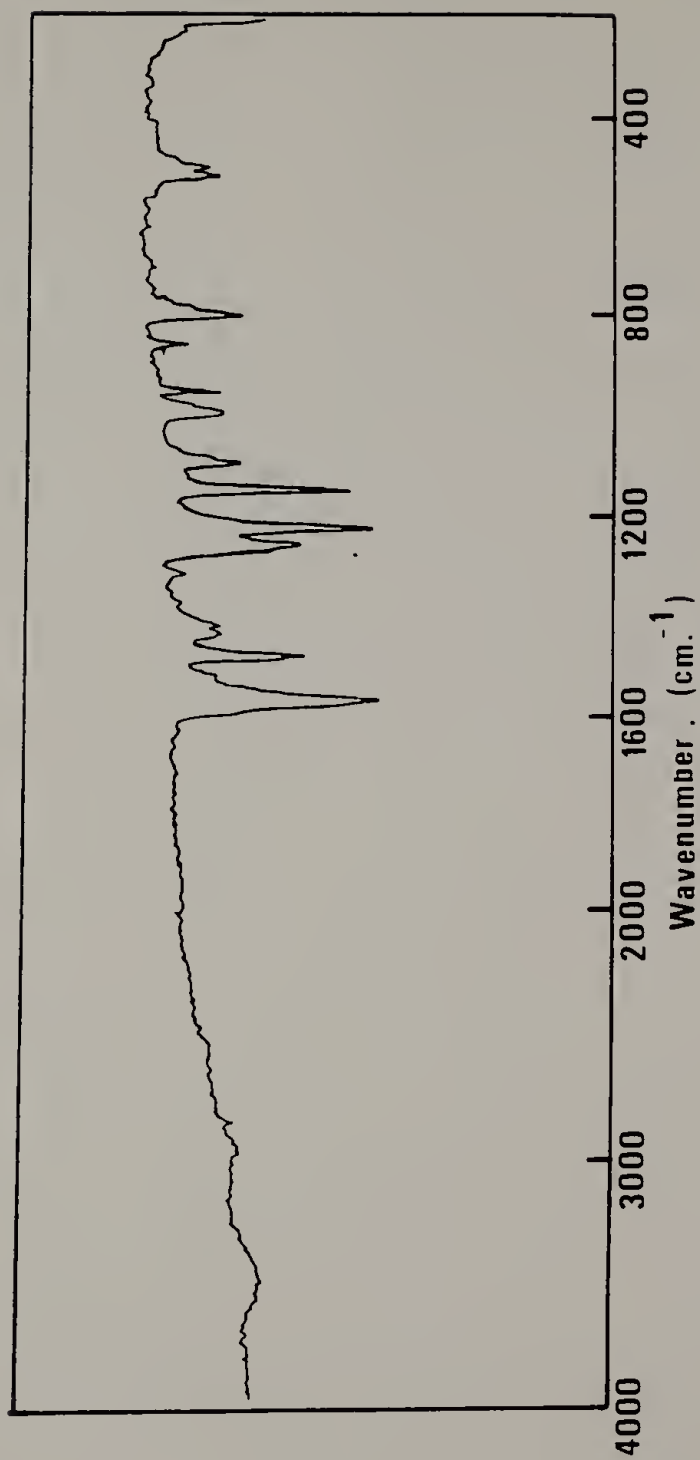


Figure 41. 3,3',5,5'-Tetra (p-methoxyphenyl) diphenoquinone.

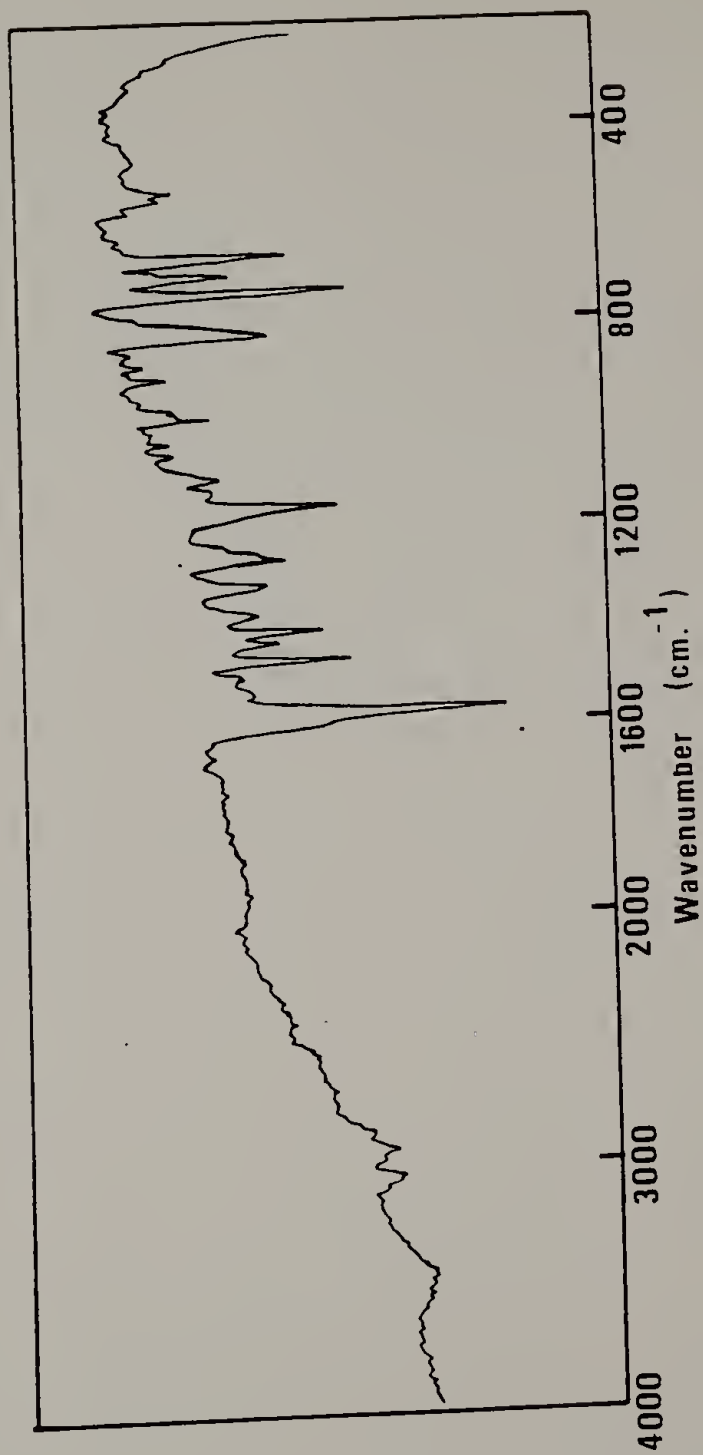


Figure 42. 3,3',5,5'-Tetra (p-biphenylyl) diphenoinone.

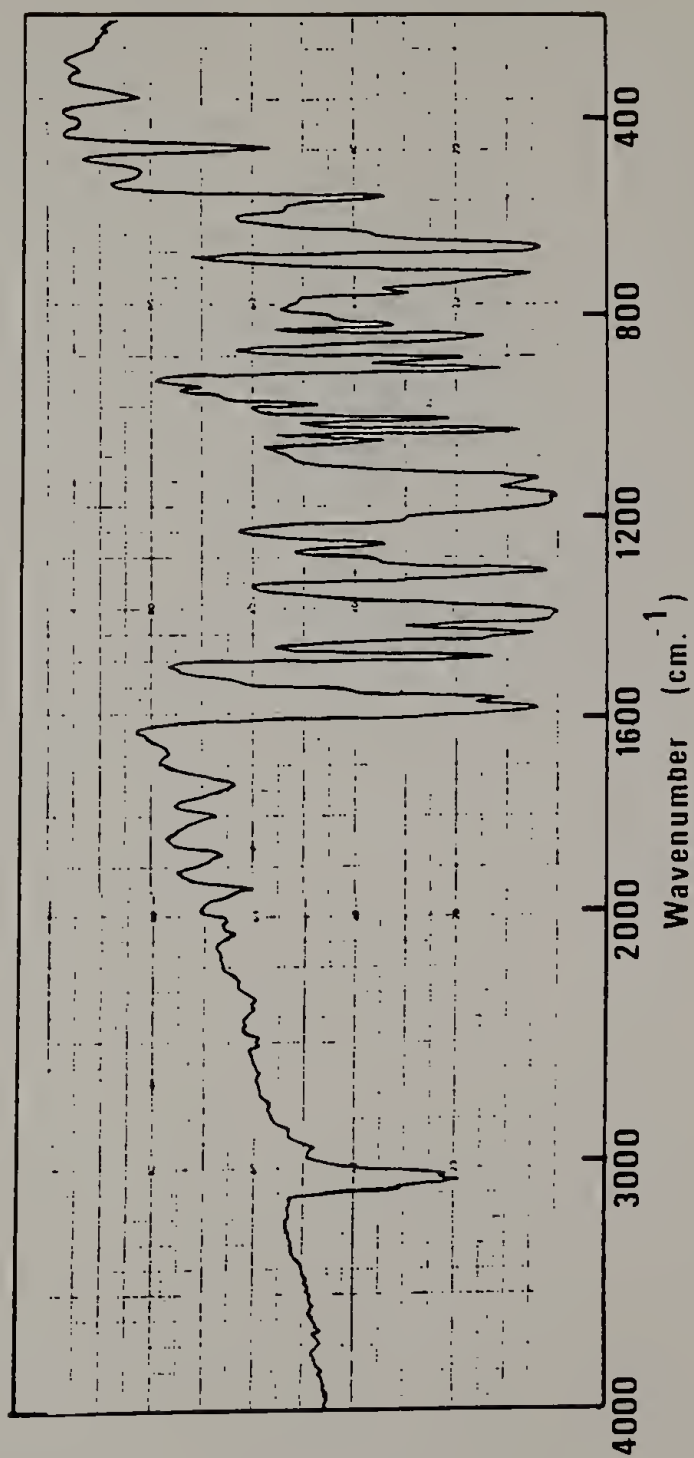


Figure 43. Poly (oxy-2,6-diphenyl-1,4-phenylene).

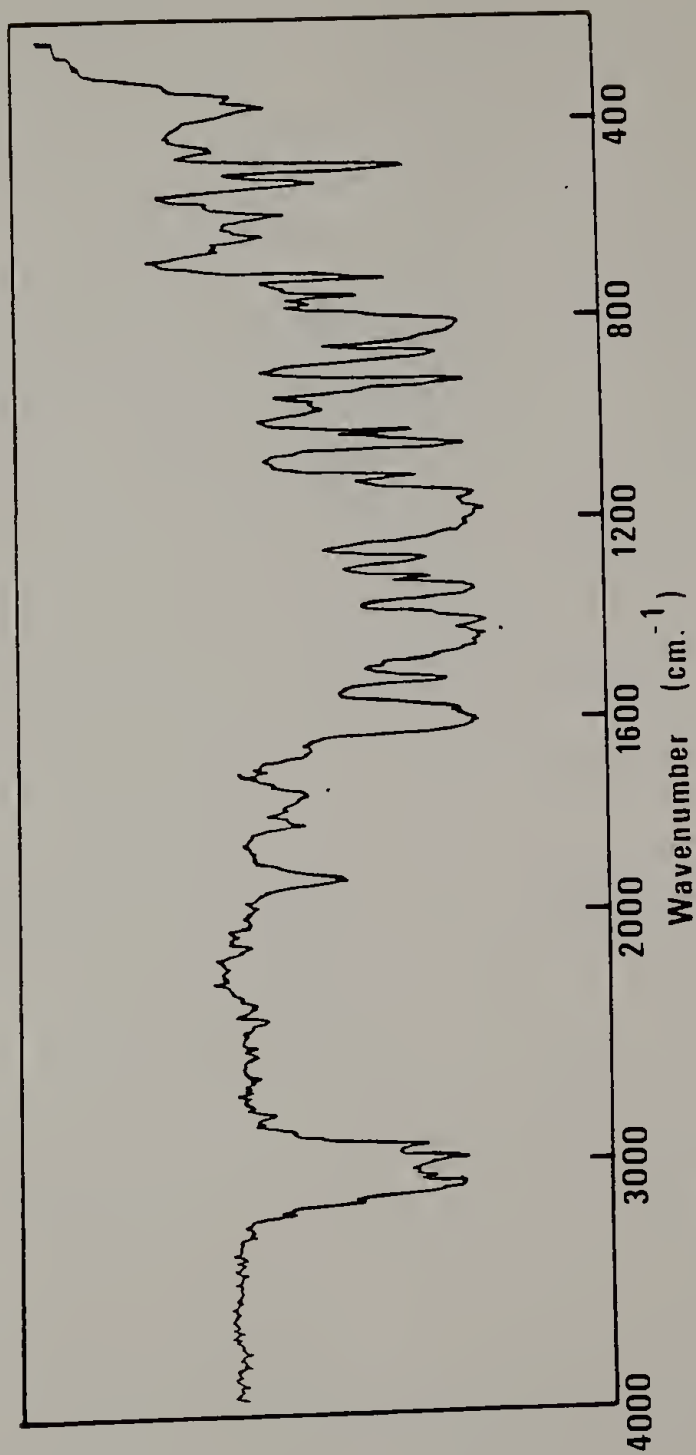


Figure 44. Poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene].

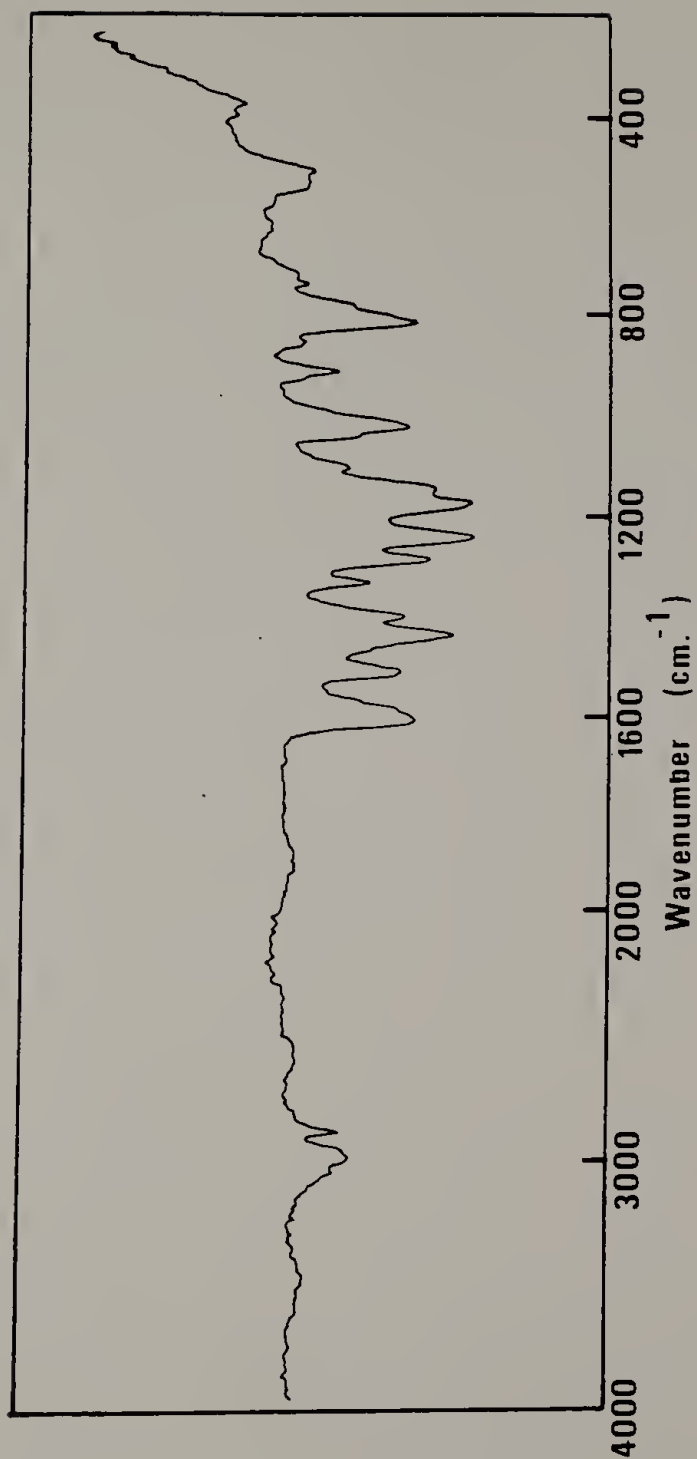


Figure 45. Poly[oxy-2,6-bis(p-methoxyphenyl)-1,4-phenylene].

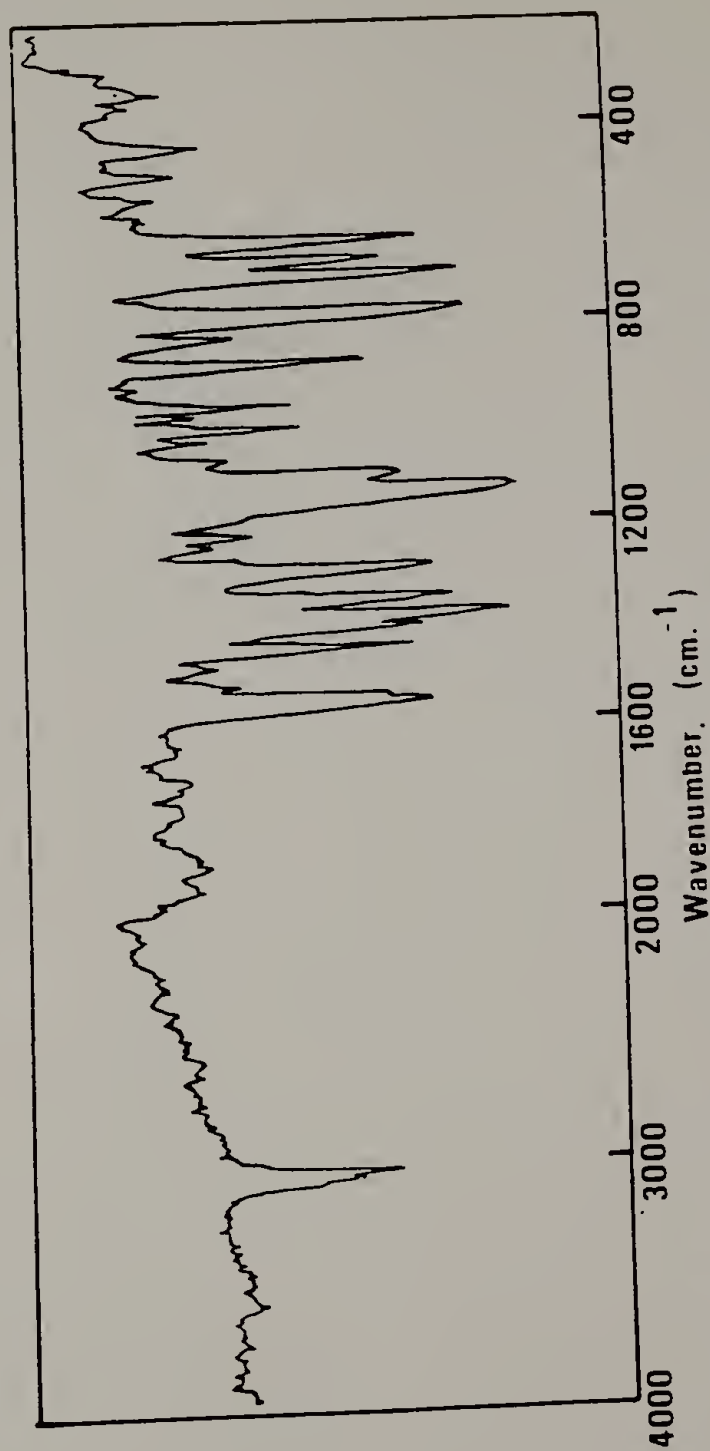


Figure 46. Poly[oxy-2,6-bis(p-biphenyl)-1,4-phenylene].



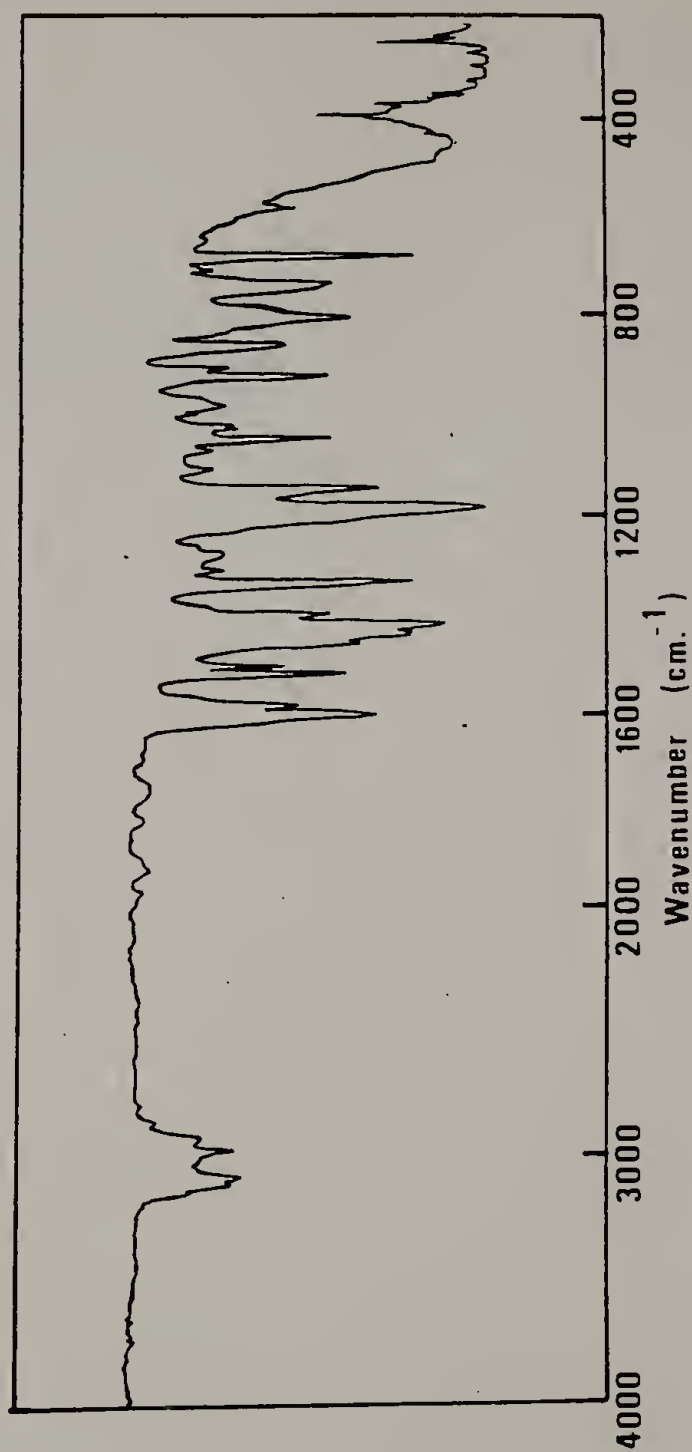


Figure 47. Poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene]  
co [oxy-2,6-diphenyl-1,4-phenylene].

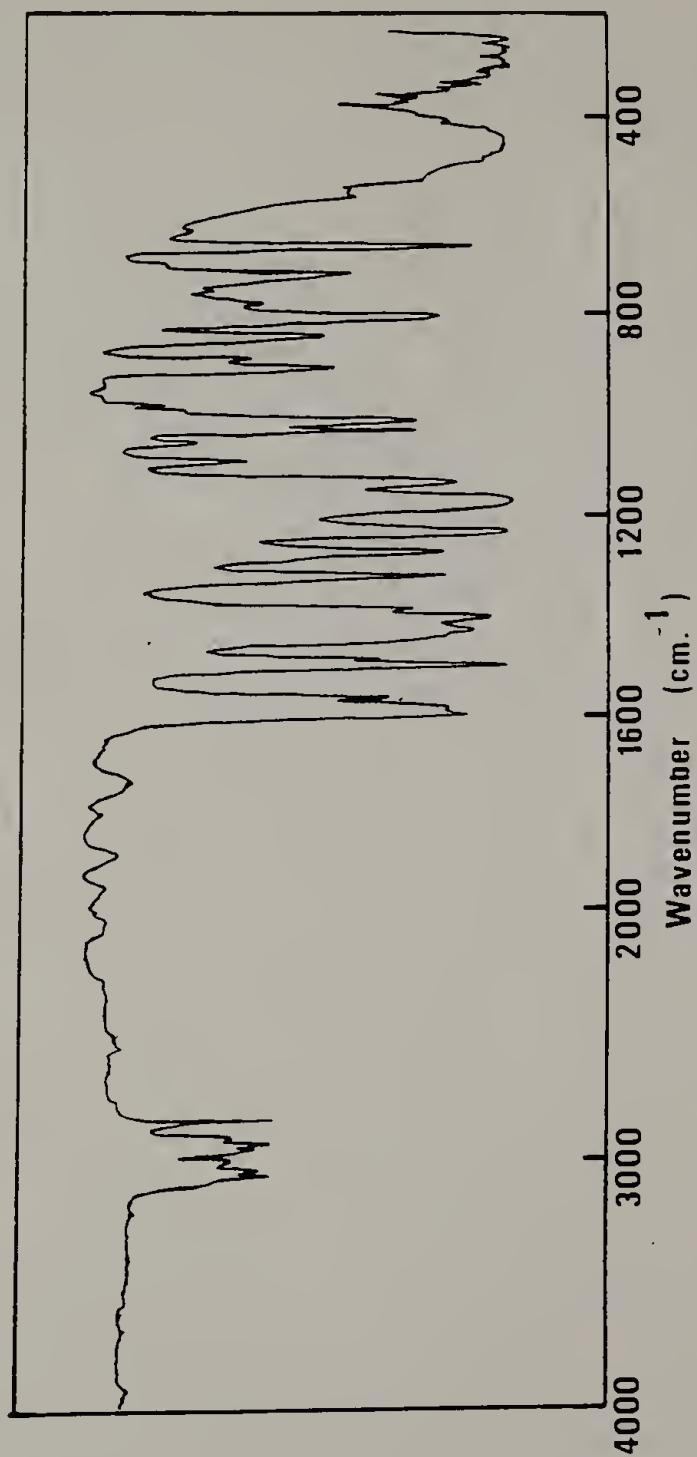


Figure 48. Poly [oxy-2,6-bis (p-methoxyphenyl) -1,4-phenylene] co [oxy-2,6-diphenyl-1,4-phenylene].

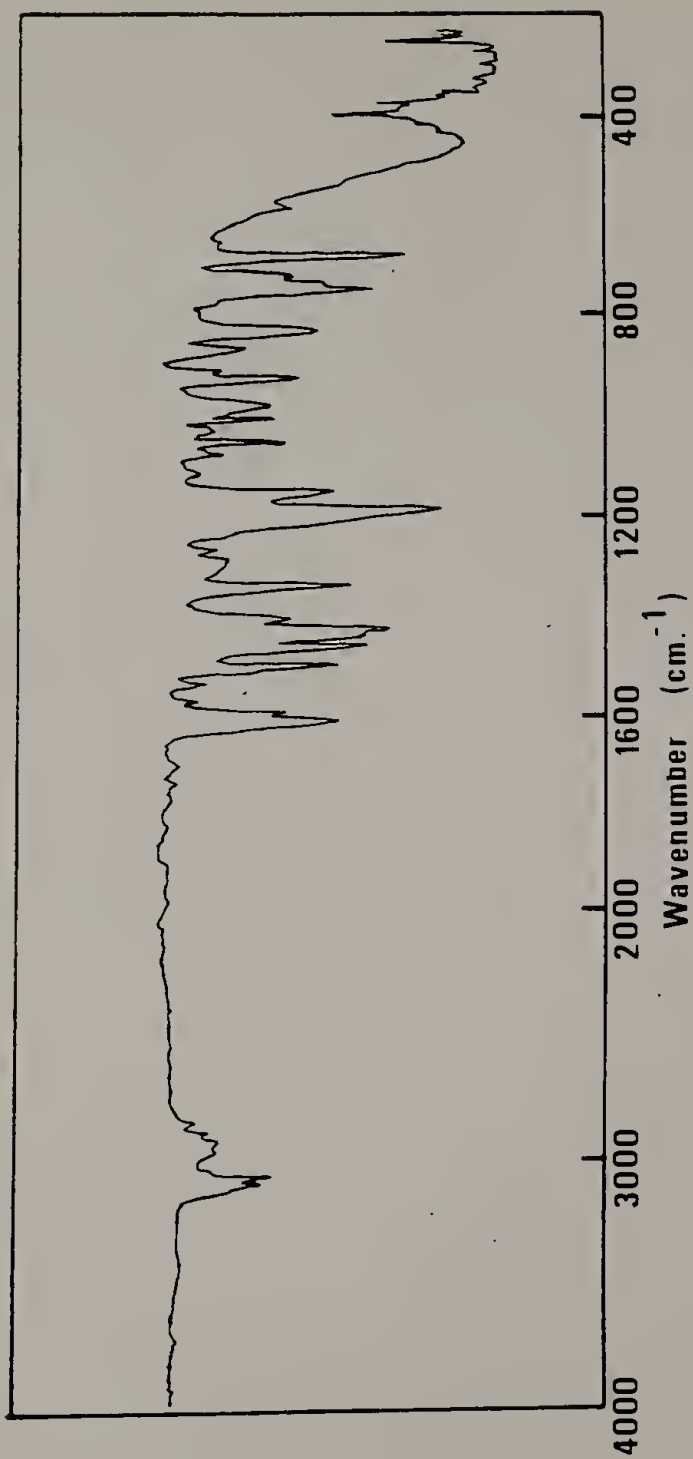


Figure 49. Poly [oxy-2,6-bis (p-biphenylyl) -1,4-phenylene] co oxy-2,6-diphenyl-1,4-phenylene].

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<sup>1</sup>H NMR SPECTRA

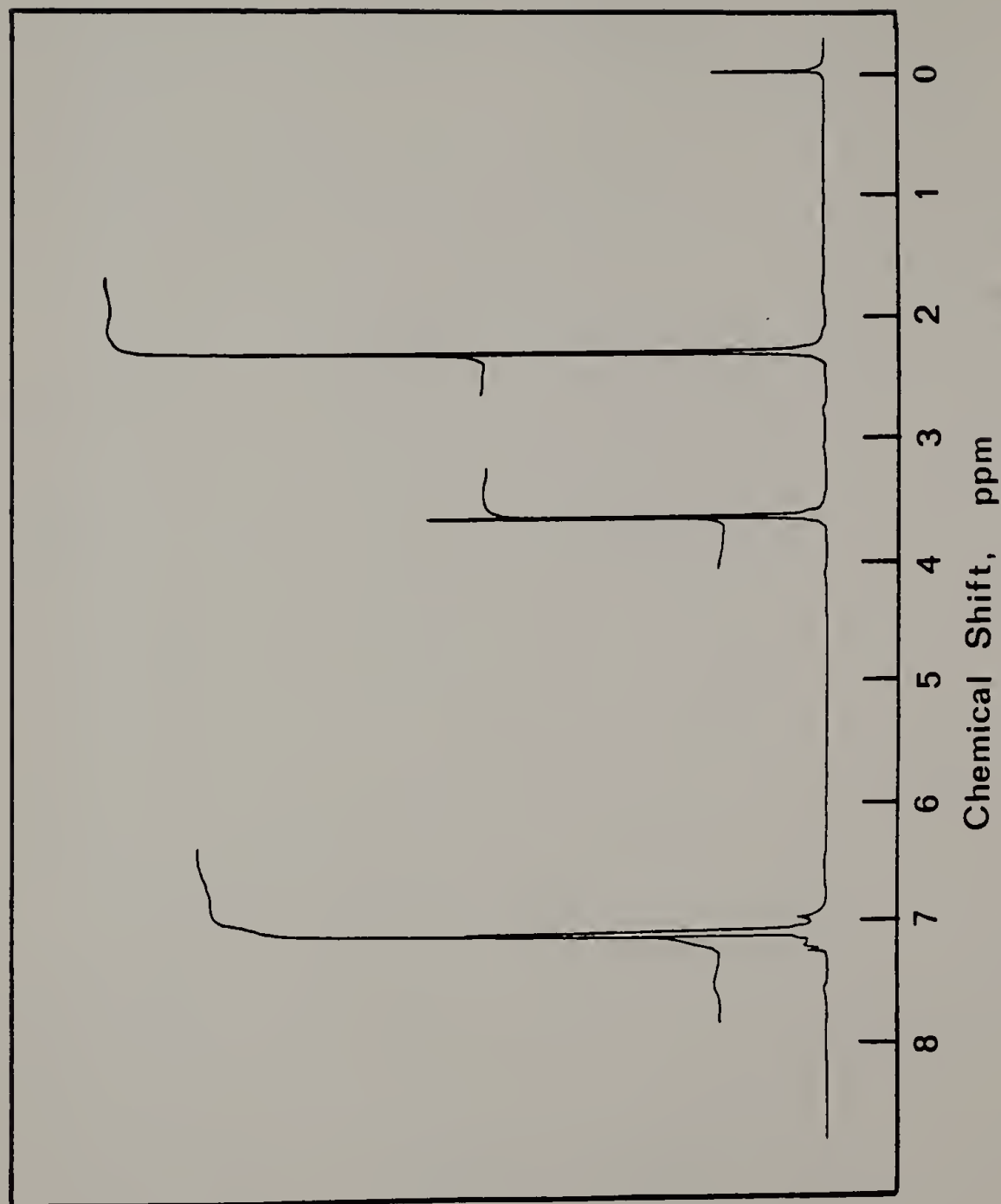


Figure 50. 1,3-Bis (p-tolyl)-2-propanone.

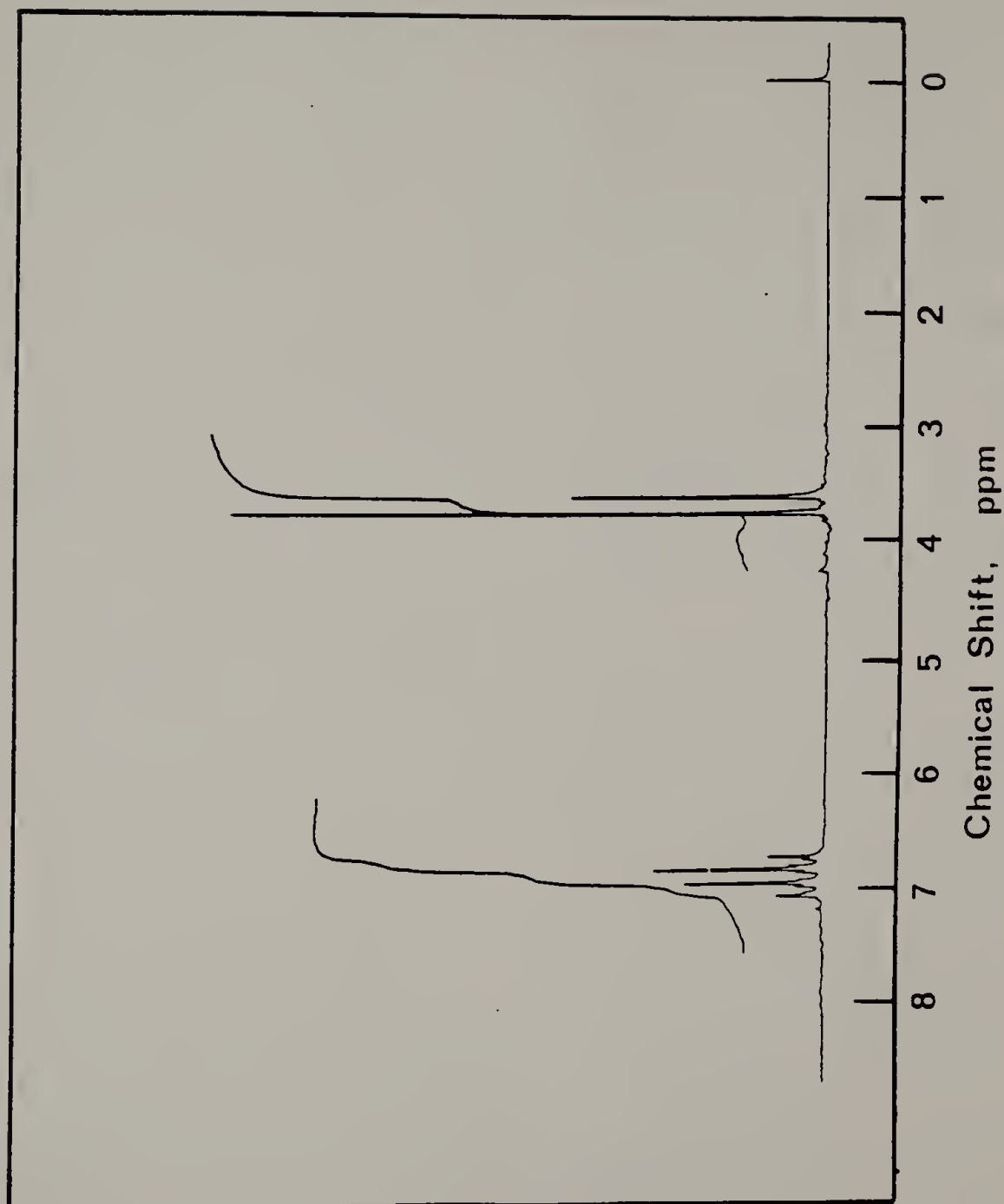
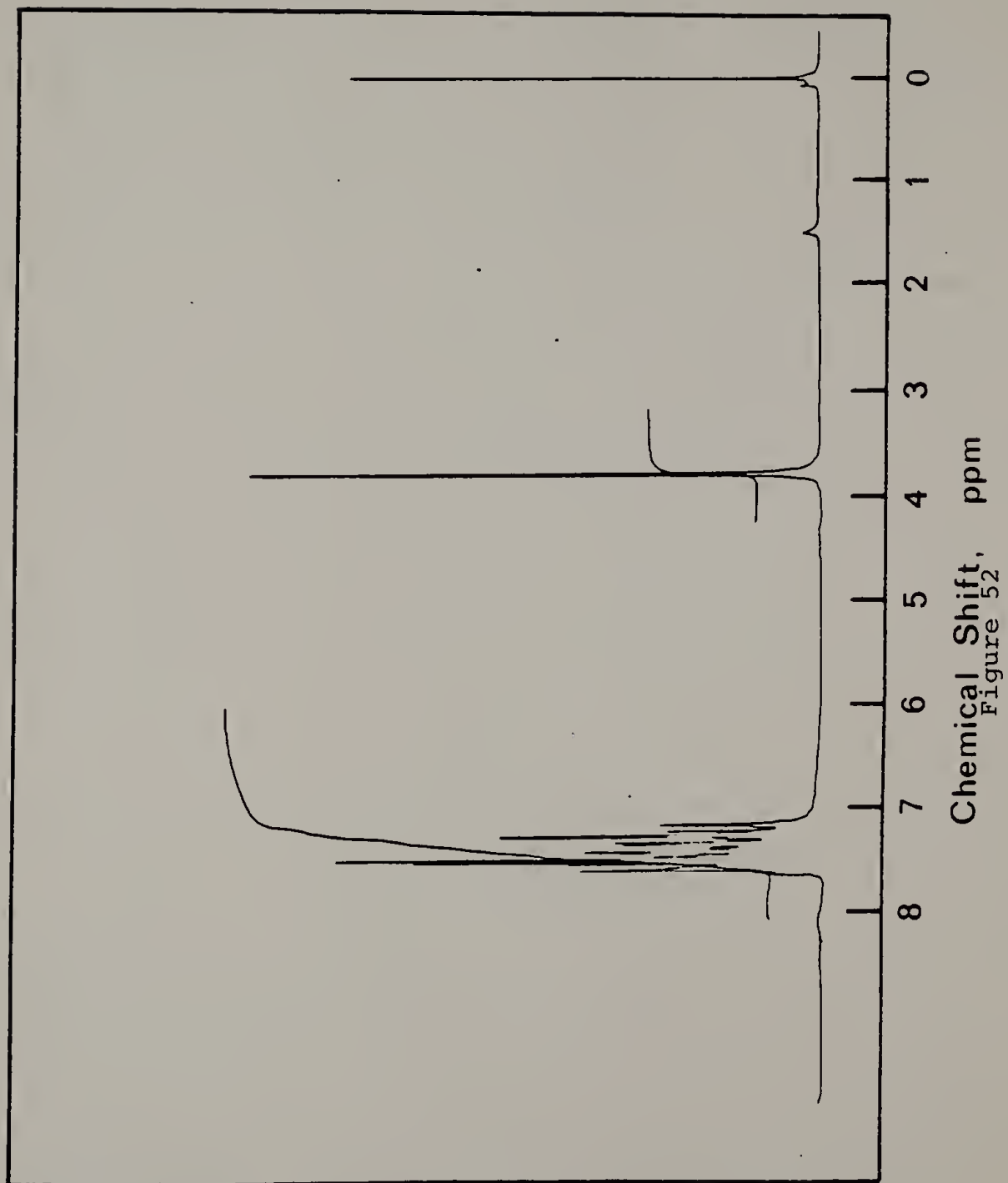
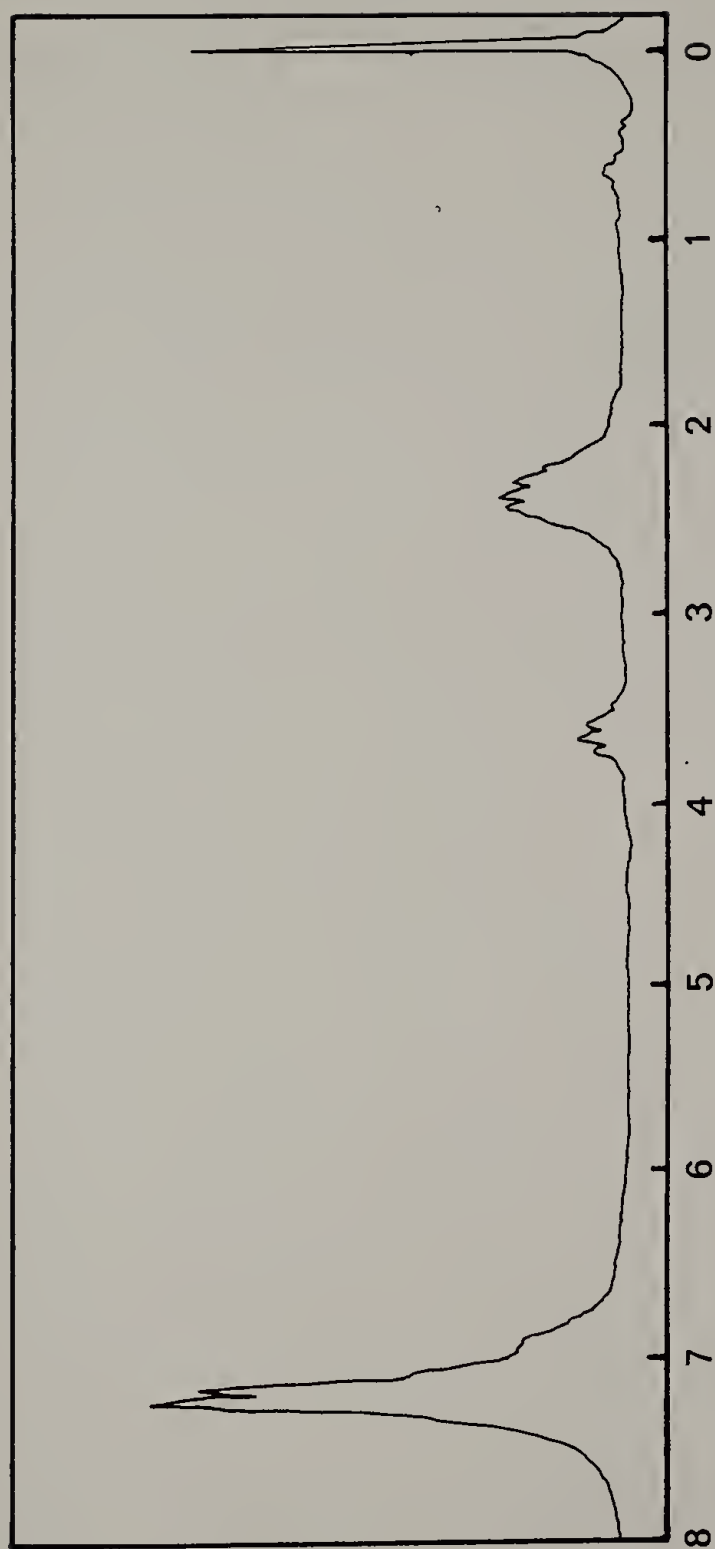


Figure 51. 1,3-Bis (p-methoxyphenyl)-2-propanone.

Figure 52. 1,3-Bis(p-biphenylyl)-2-propanone.

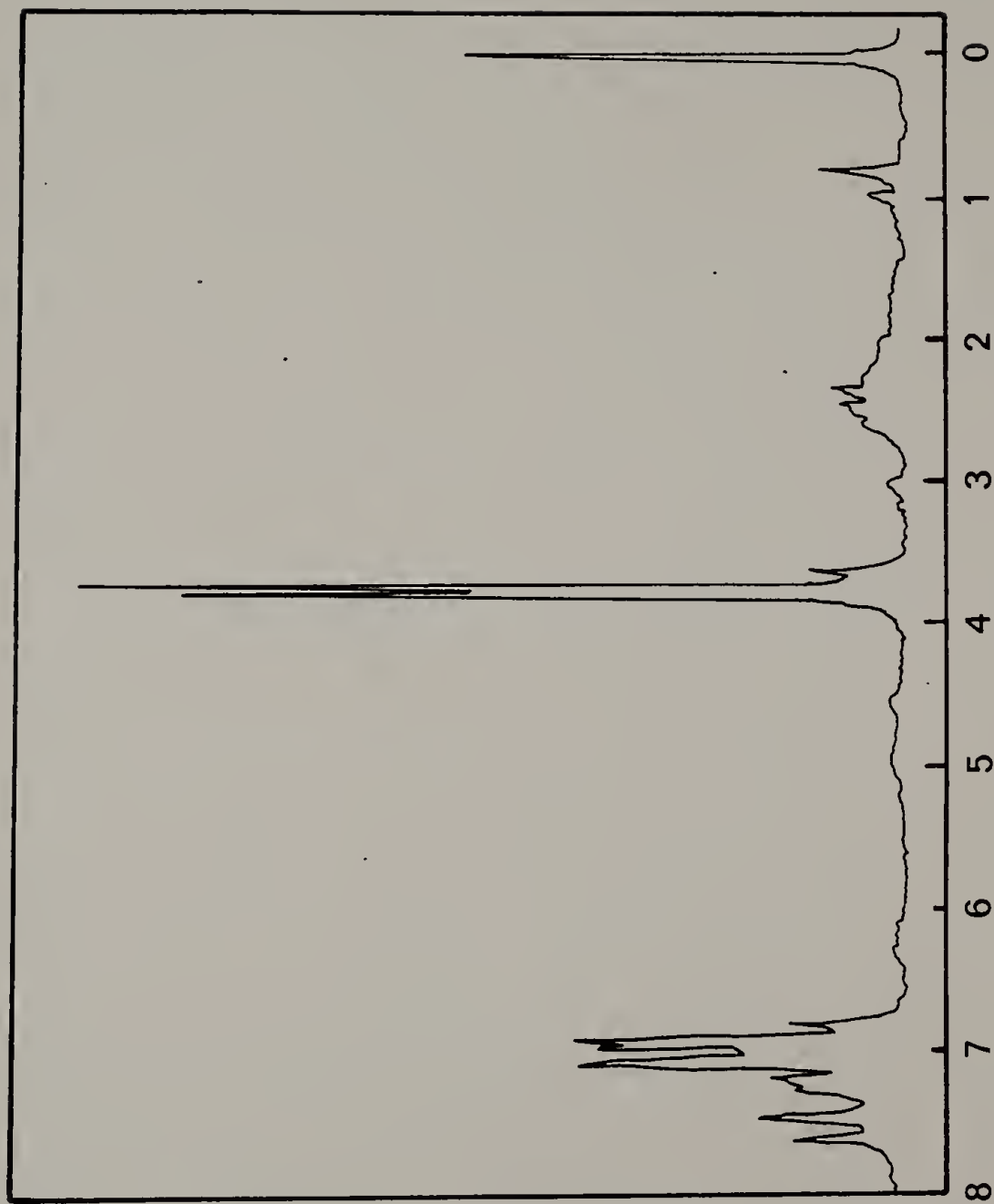






Chemical Shift, ppm

Figure 53. 2,6-Diphenyl-2-cyclohexenone.



Chemical Shift, ppm

Figure 54. 2,6-Bis (p-methoxyphenyl)-2-cyclohexenone.

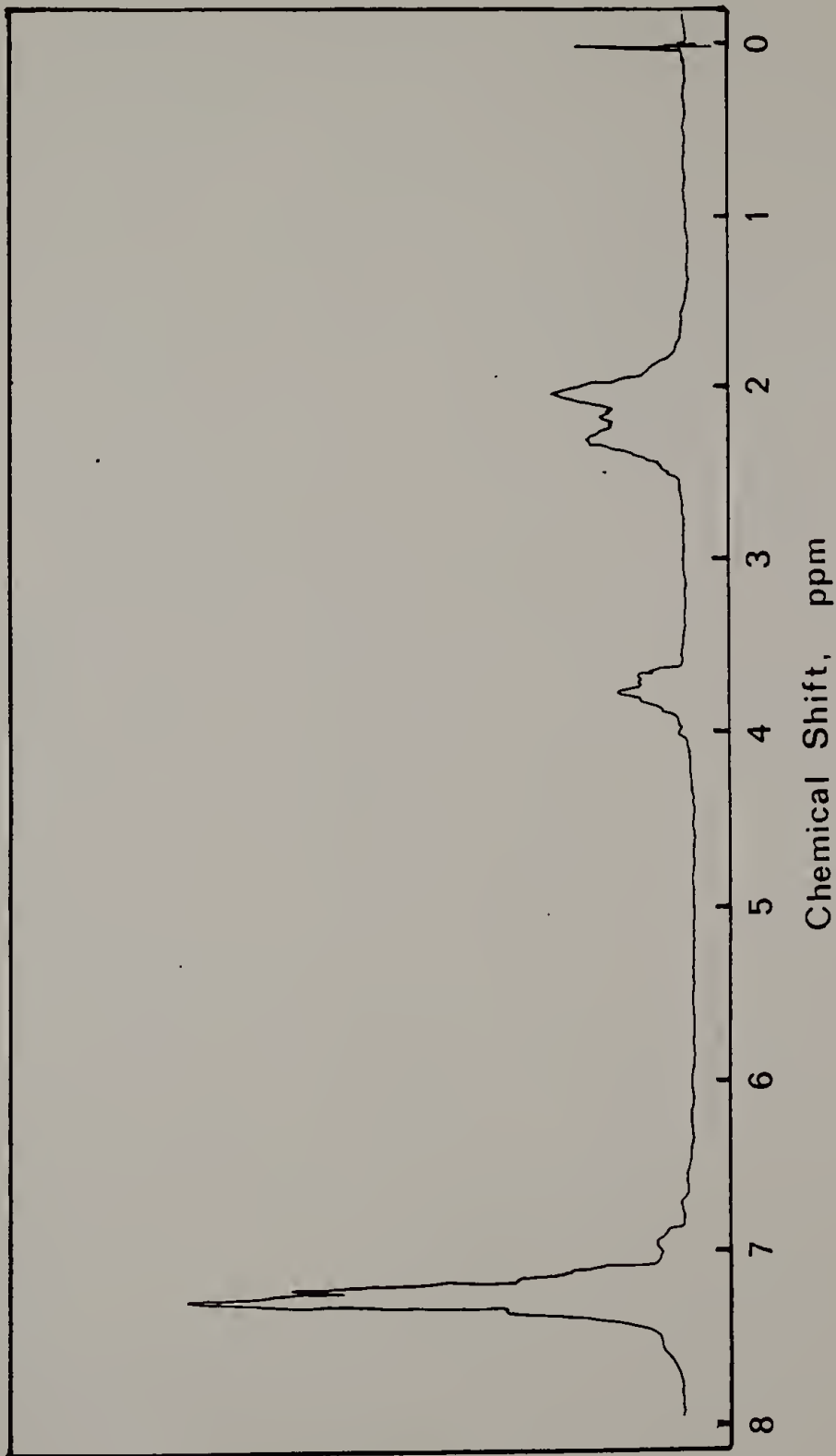


Figure 55. 2,6-Diphenylcyclohexanone.

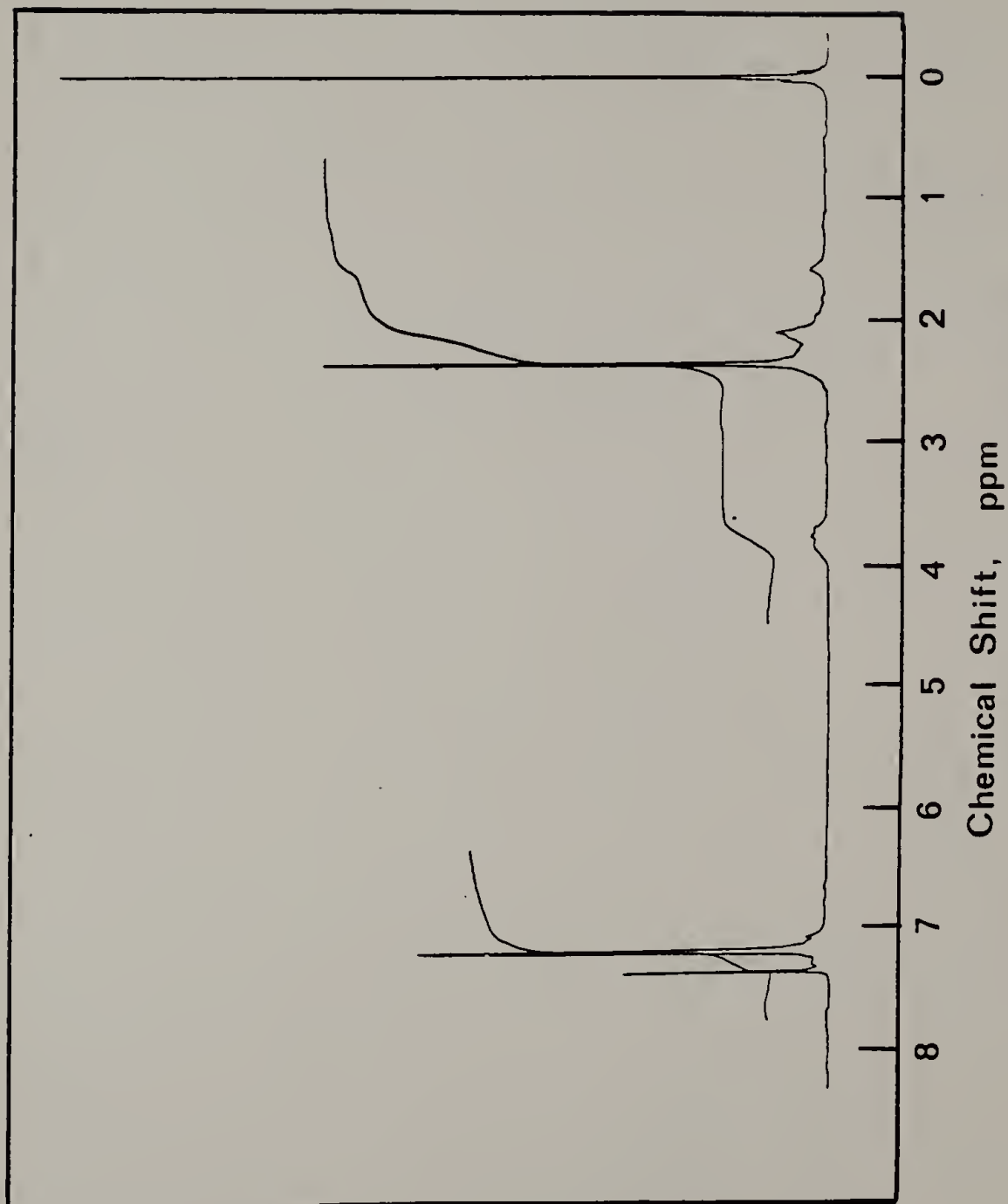


Figure 56. 2,6-Bis (p-tolyl) cyclohexanone.

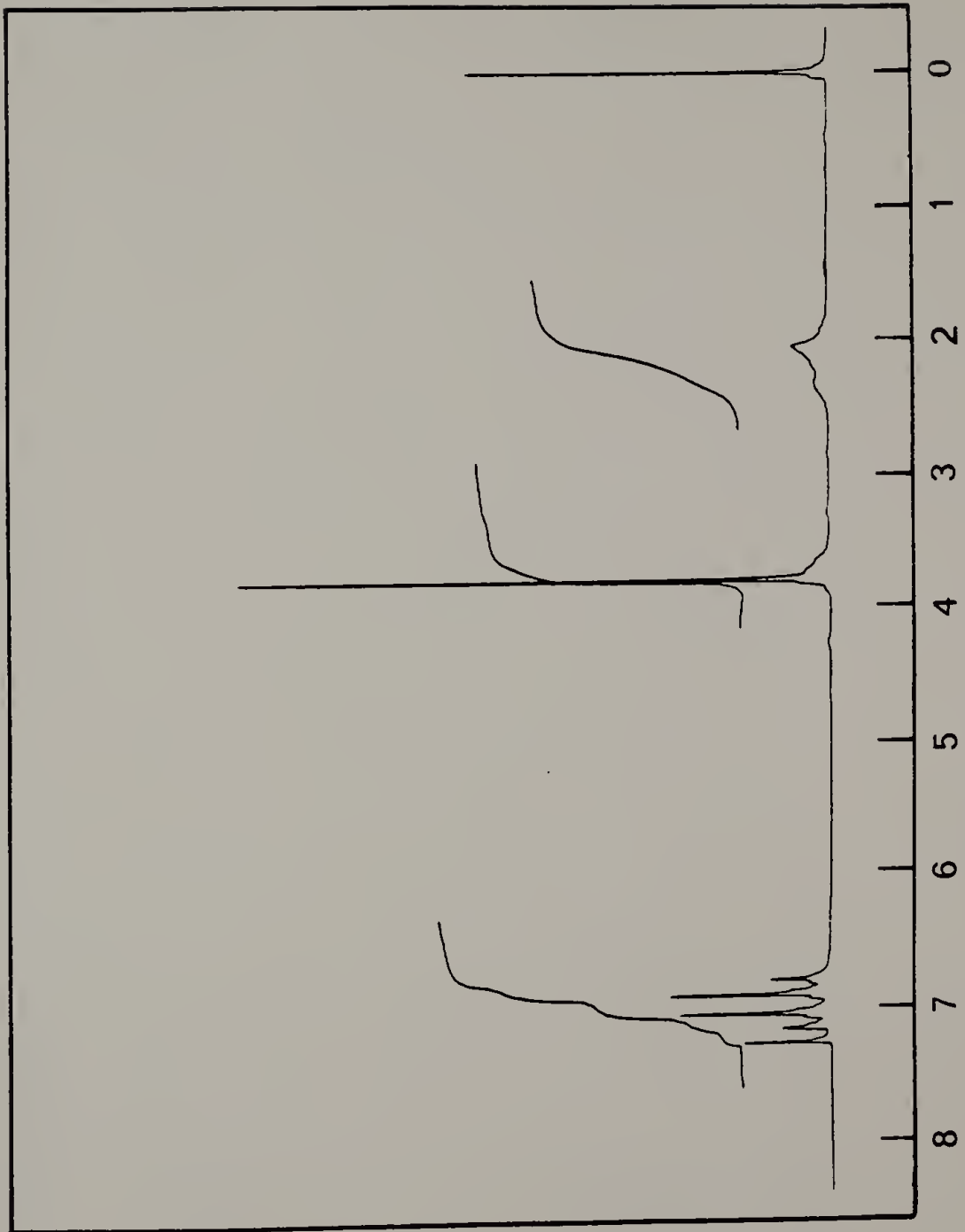


Figure 57. 2,6-Bis (p-methoxyphenyl) cyclohexanone.

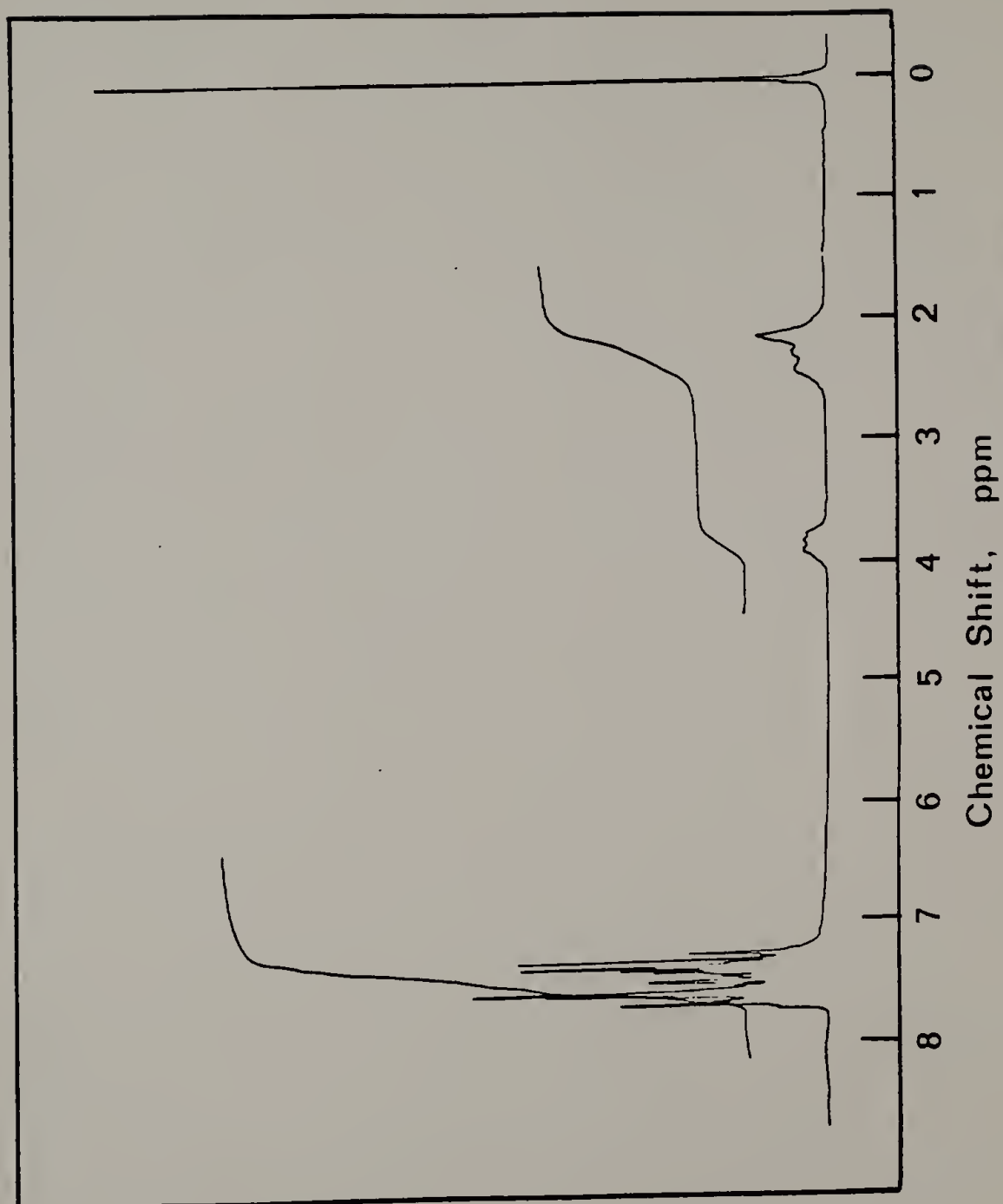


Figure 58. 2,6-Bis (p-biphenyl) cyclohexanone.

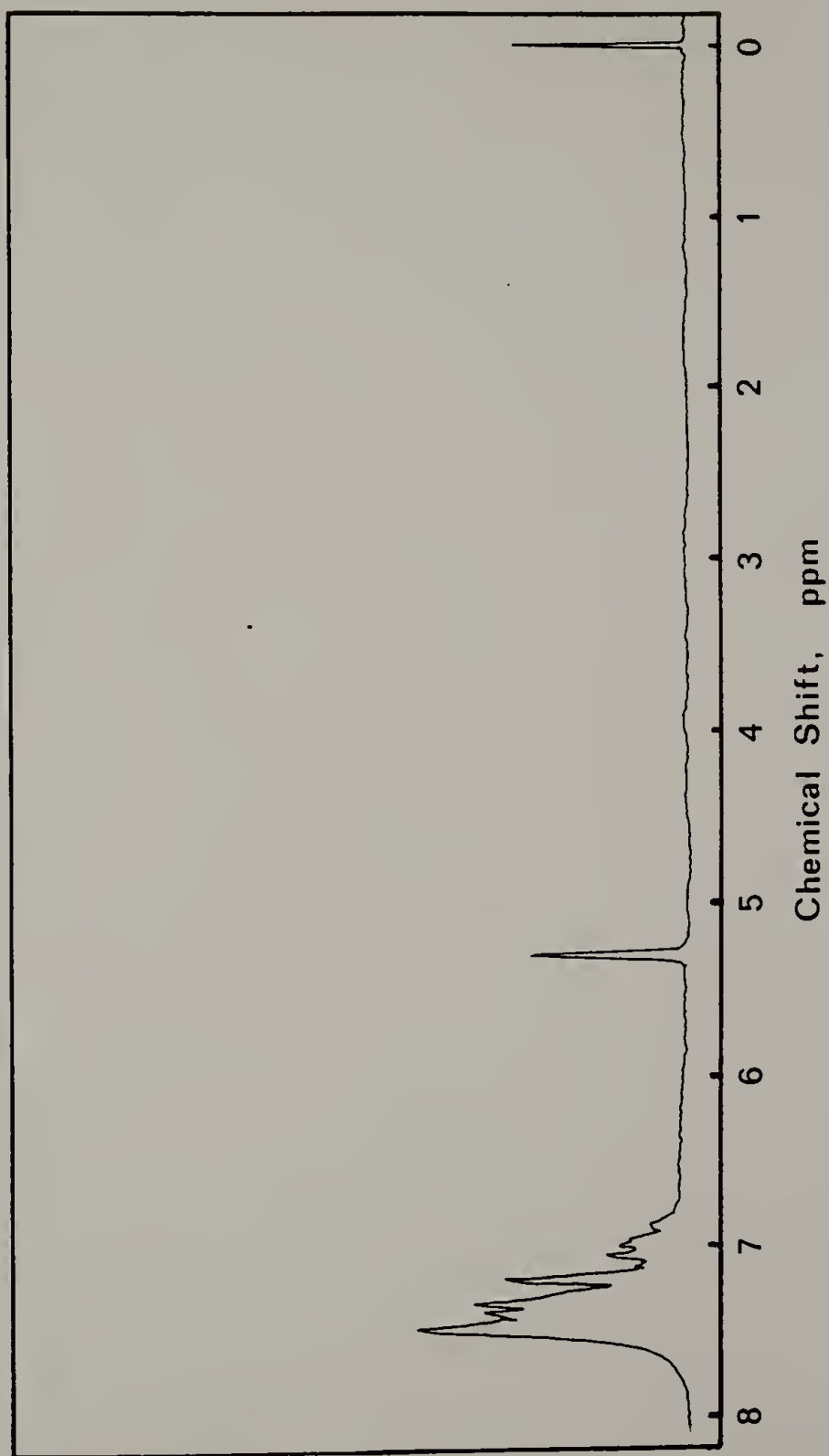
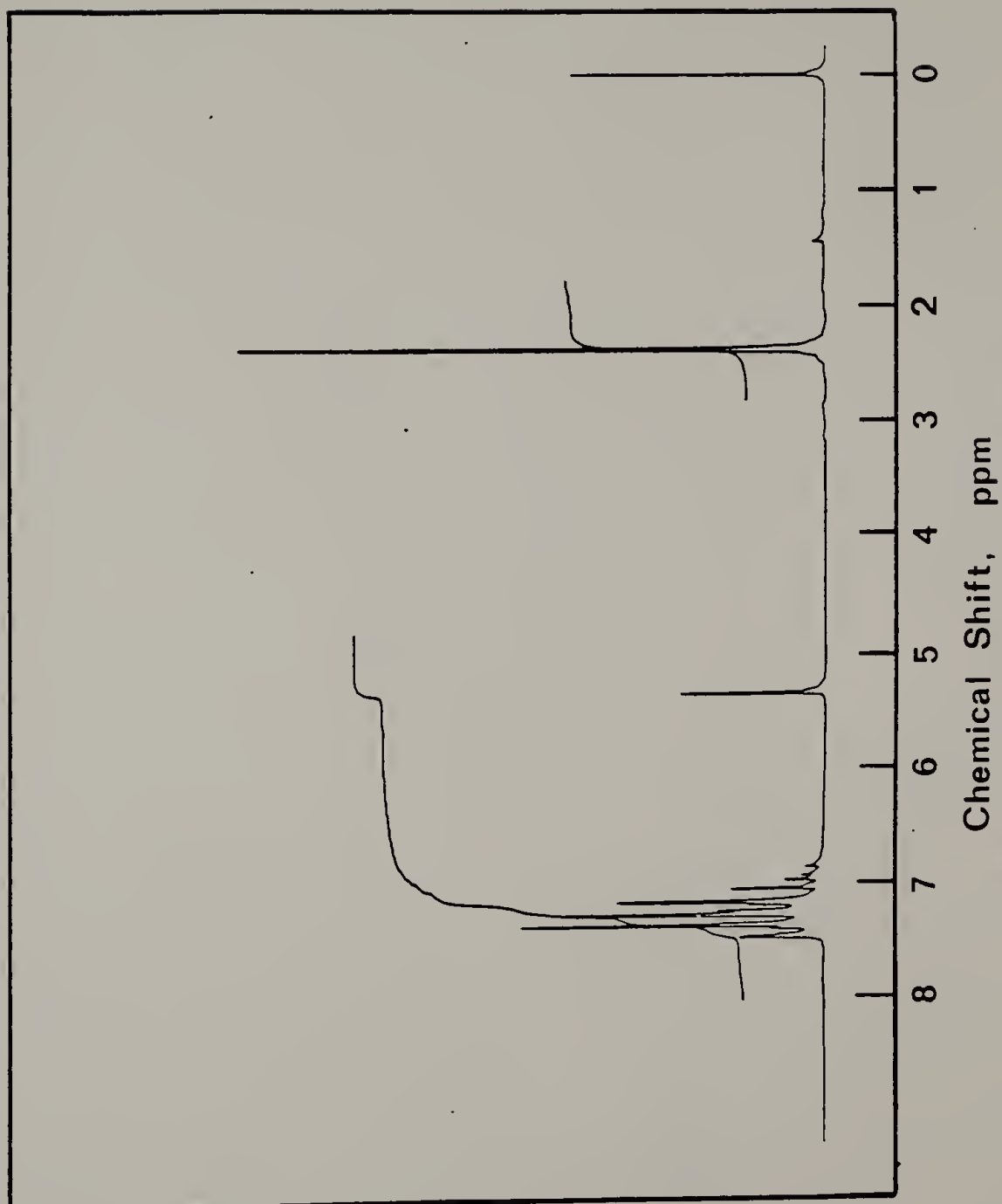


Figure 59. 2,6-Diphenylphenol.



Chemical Shift, ppm

Figure 60. 2,6-Bis (p-tolyl) phenol.



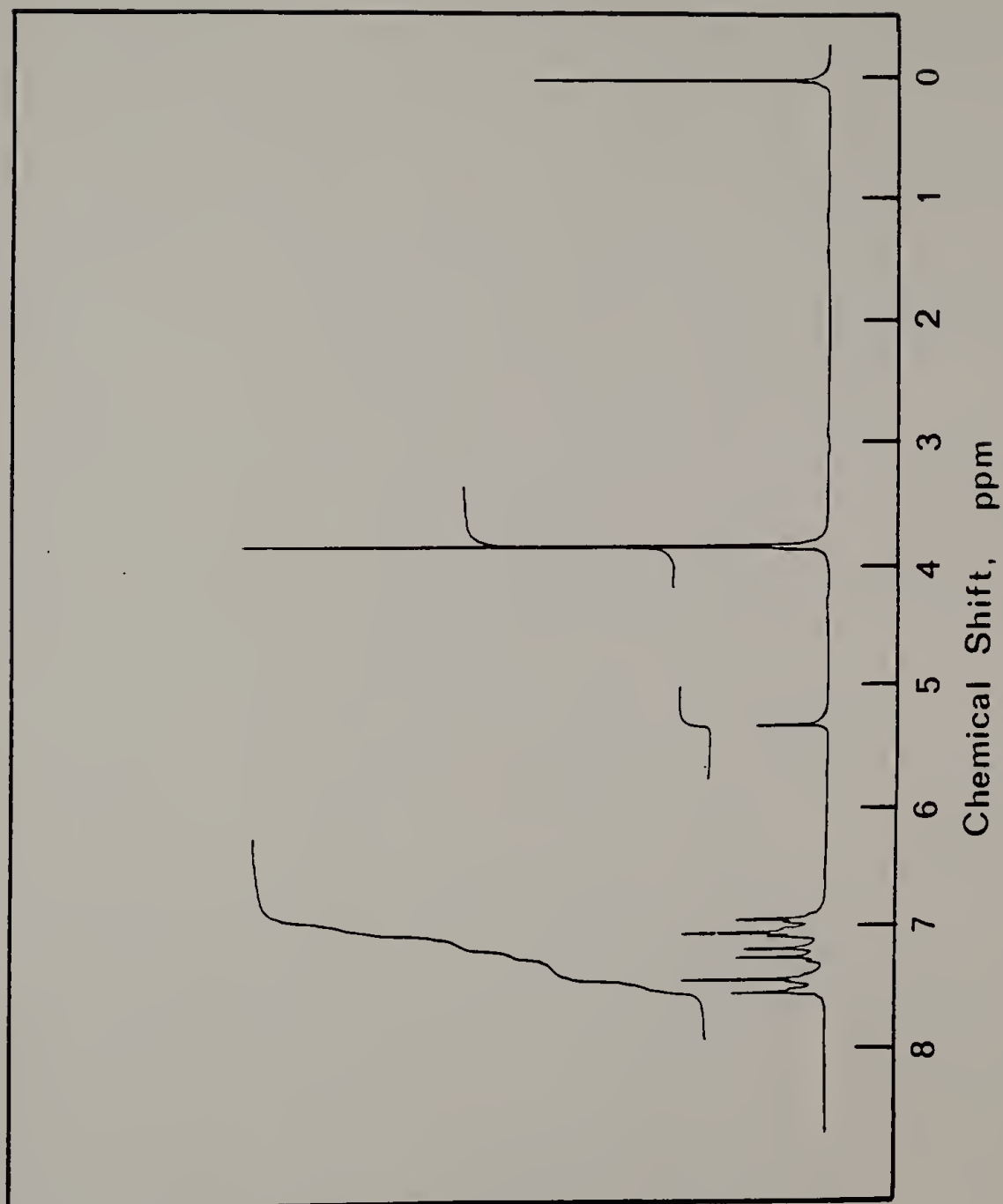


Figure 61. 2,6-Bis (p-methoxyphenyl) phenol.

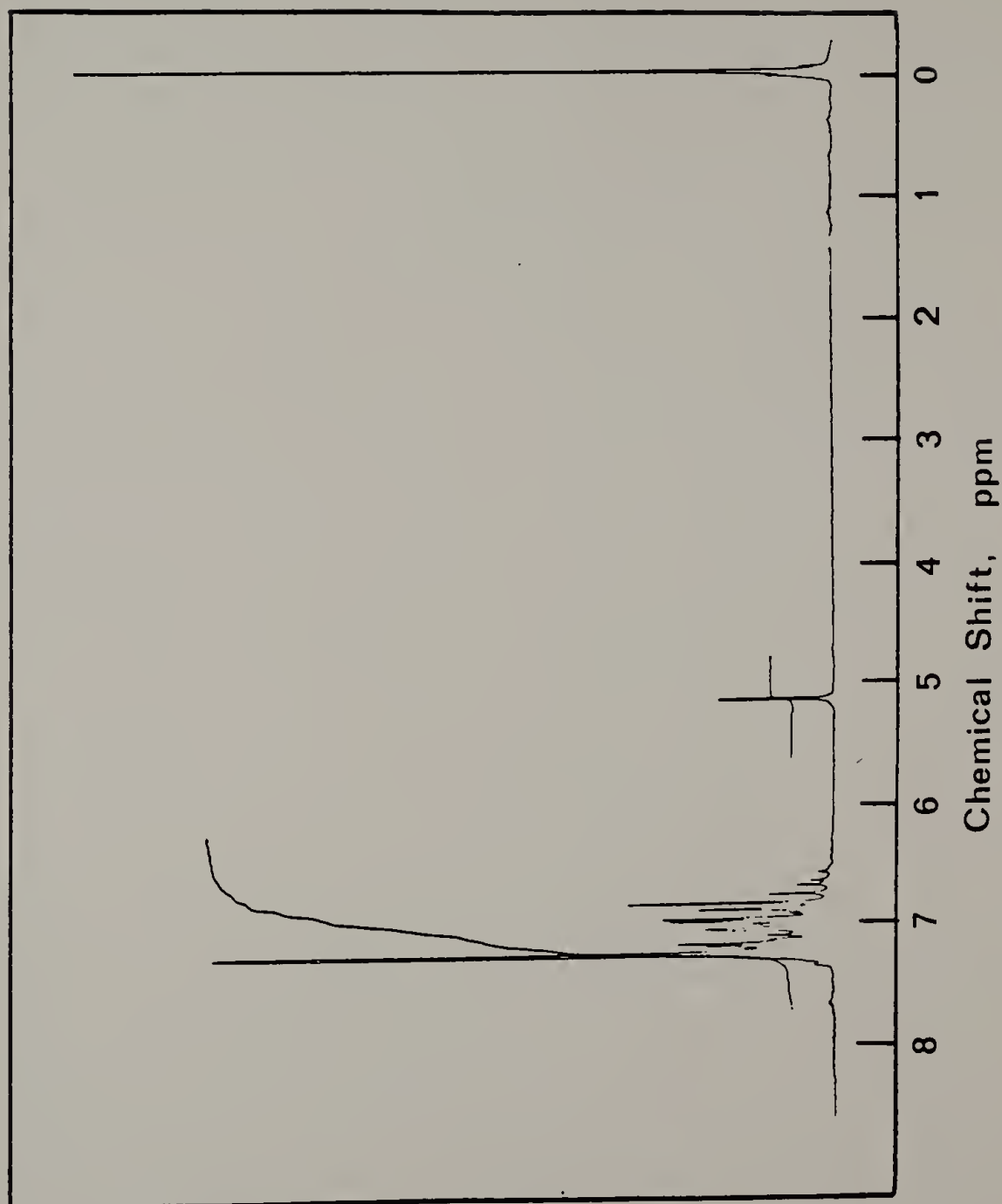


Figure 62. 2,6-Bis (p-biphenyl) phenol.

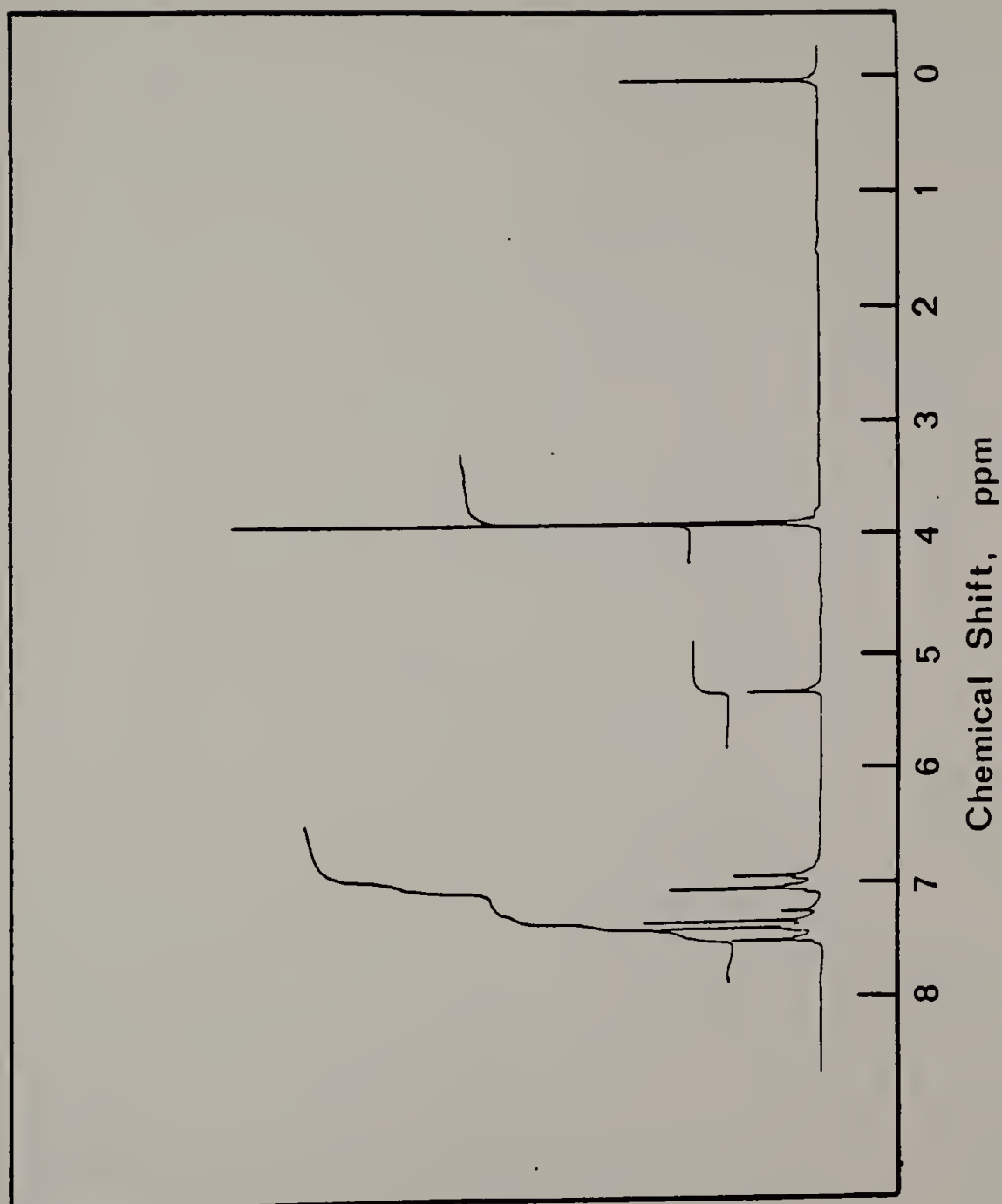


Figure 63. 4-Bromo-2,6-bis (p-methoxyphenyl) phenol.

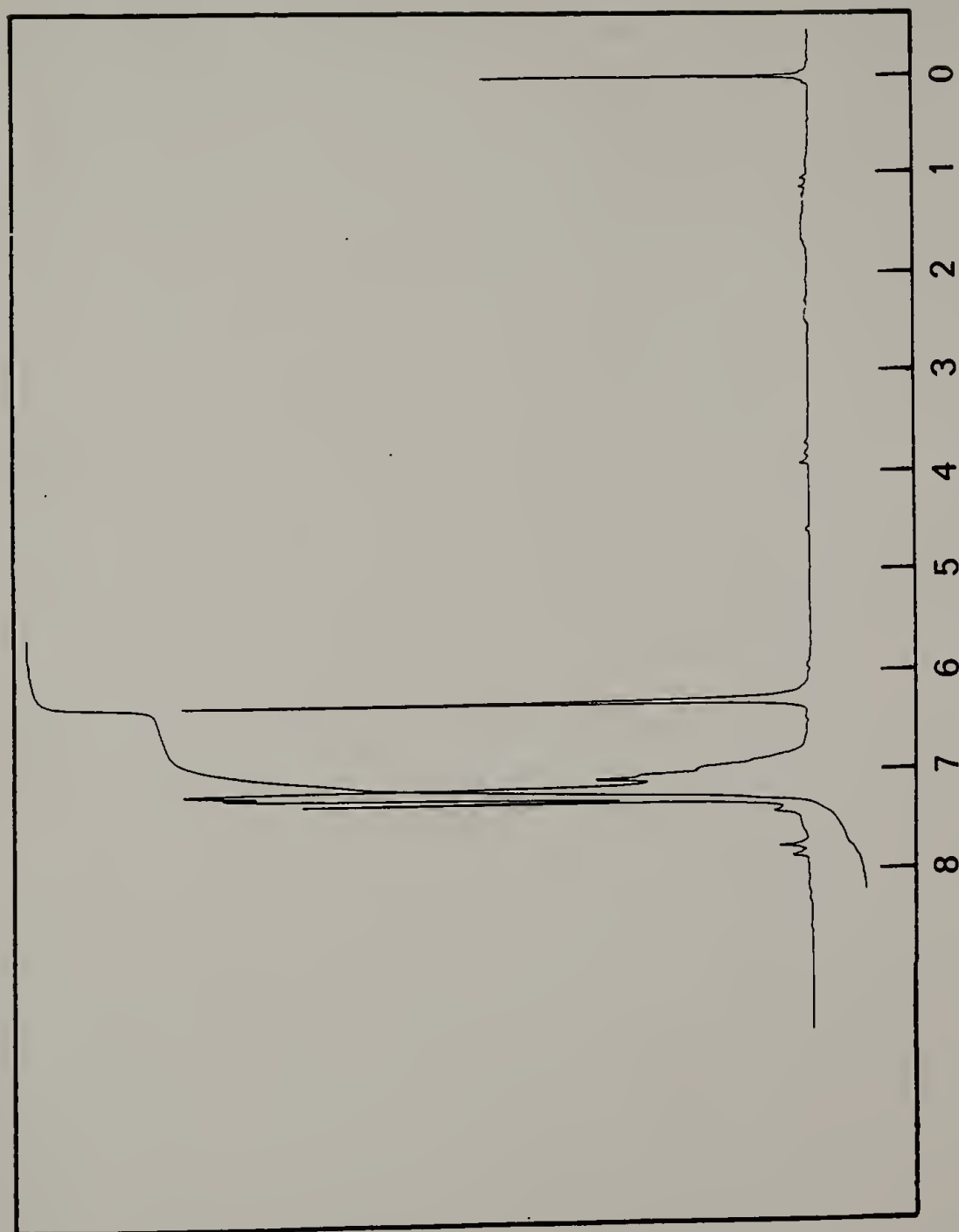


Figure 64. Poly (oxy-2,6-diphenyl-1,4-phenylene).

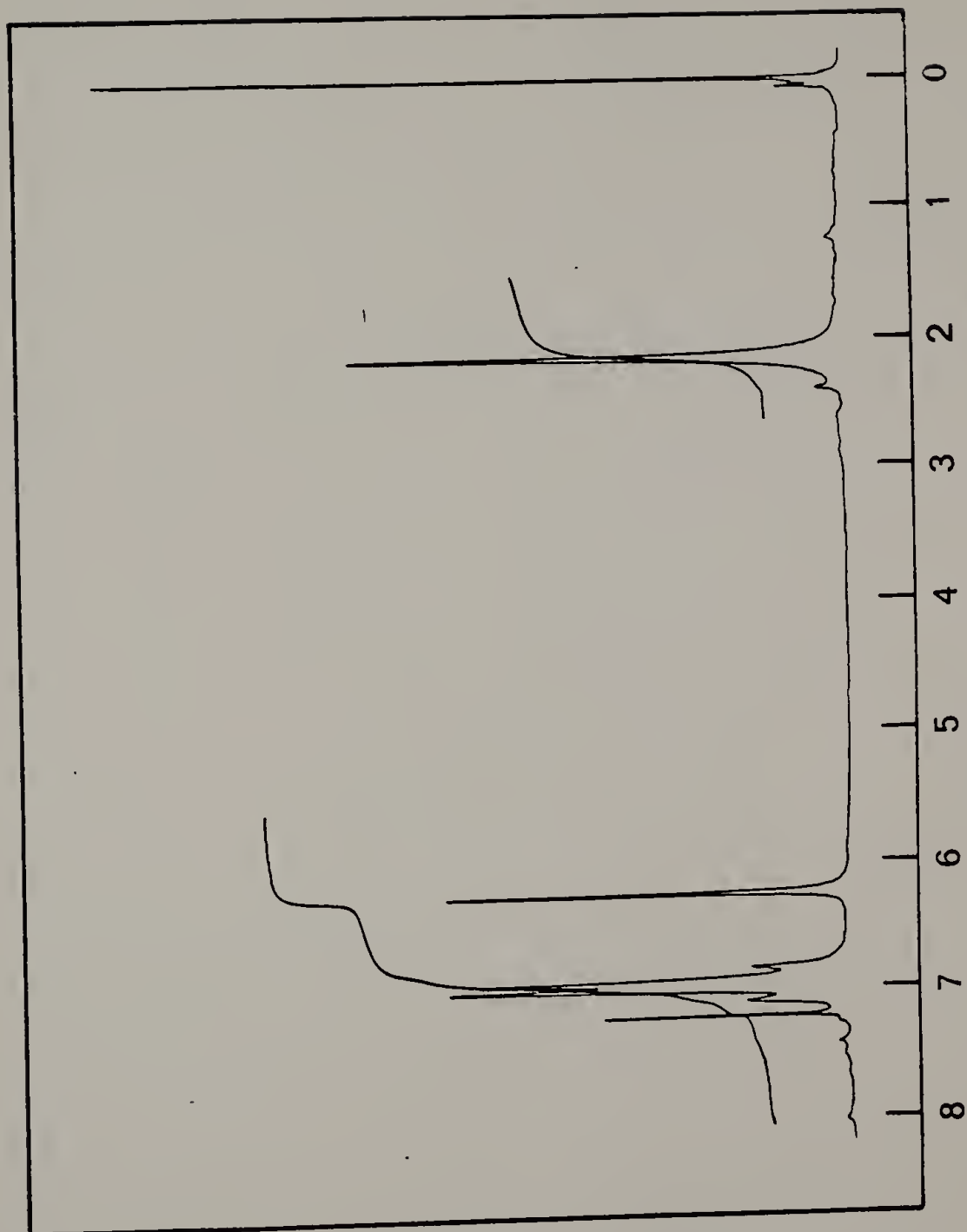


Figure 65. Poly [oxy-2,6-bis (p-tolyl)-1,4-phenylene].

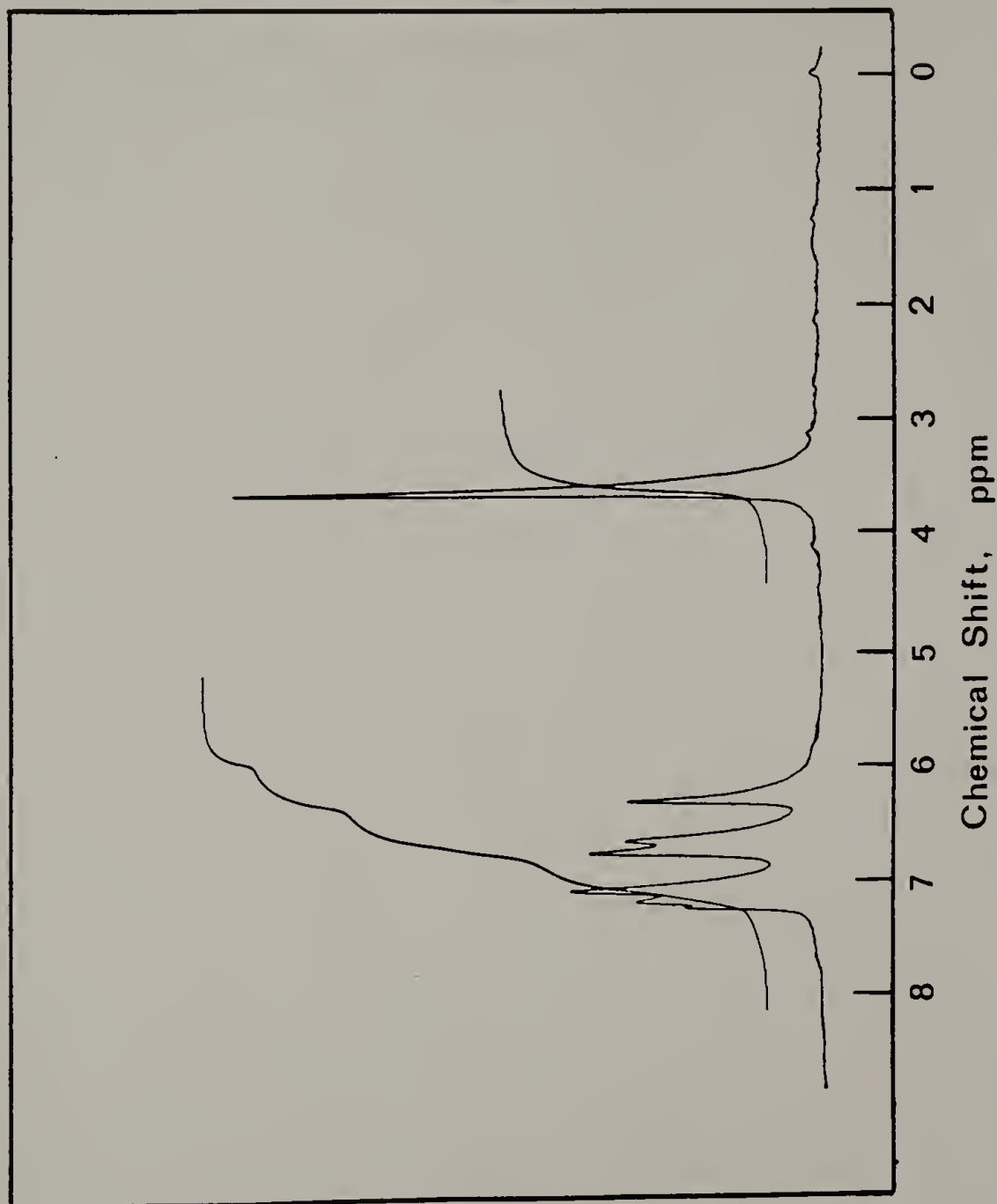
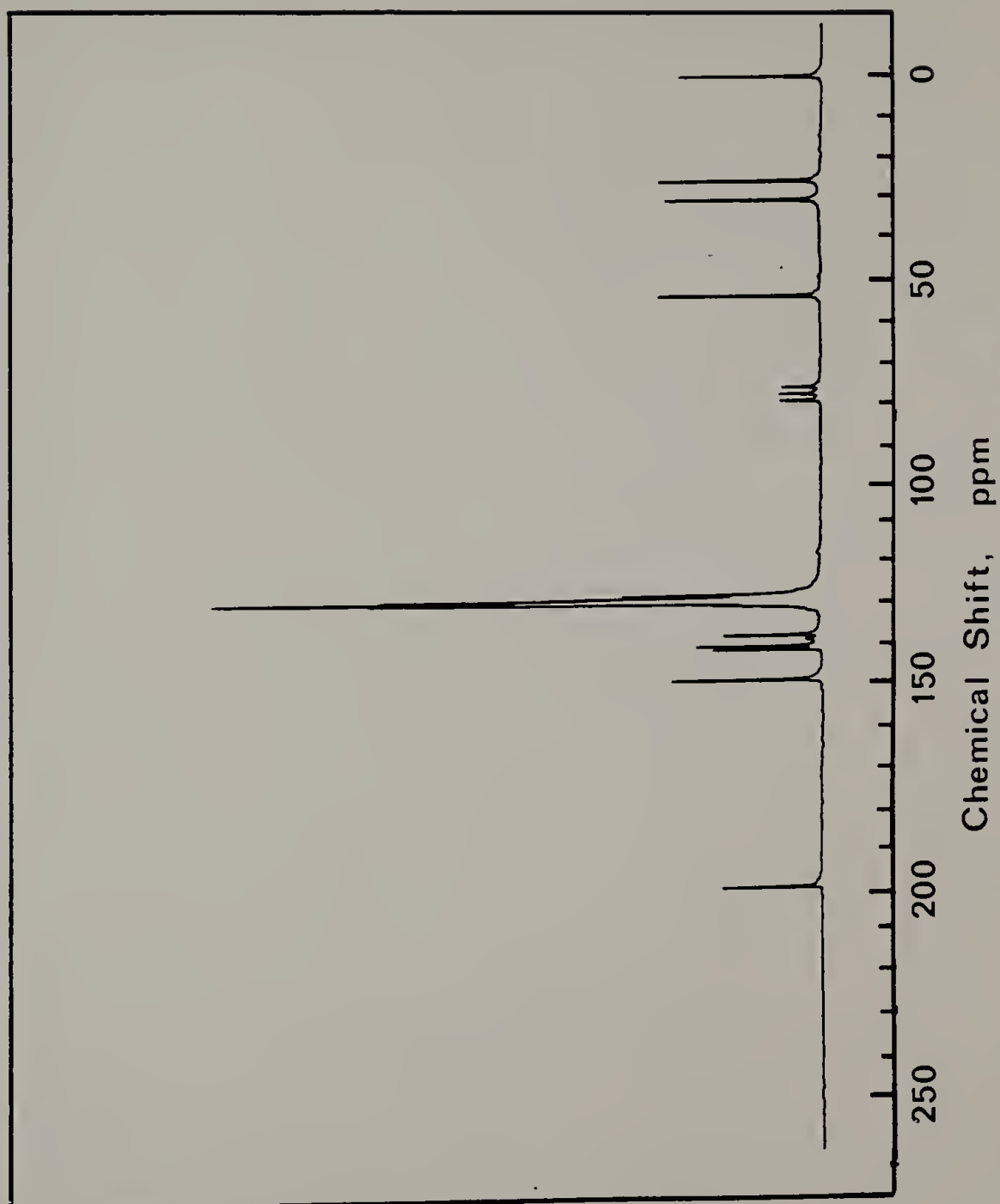


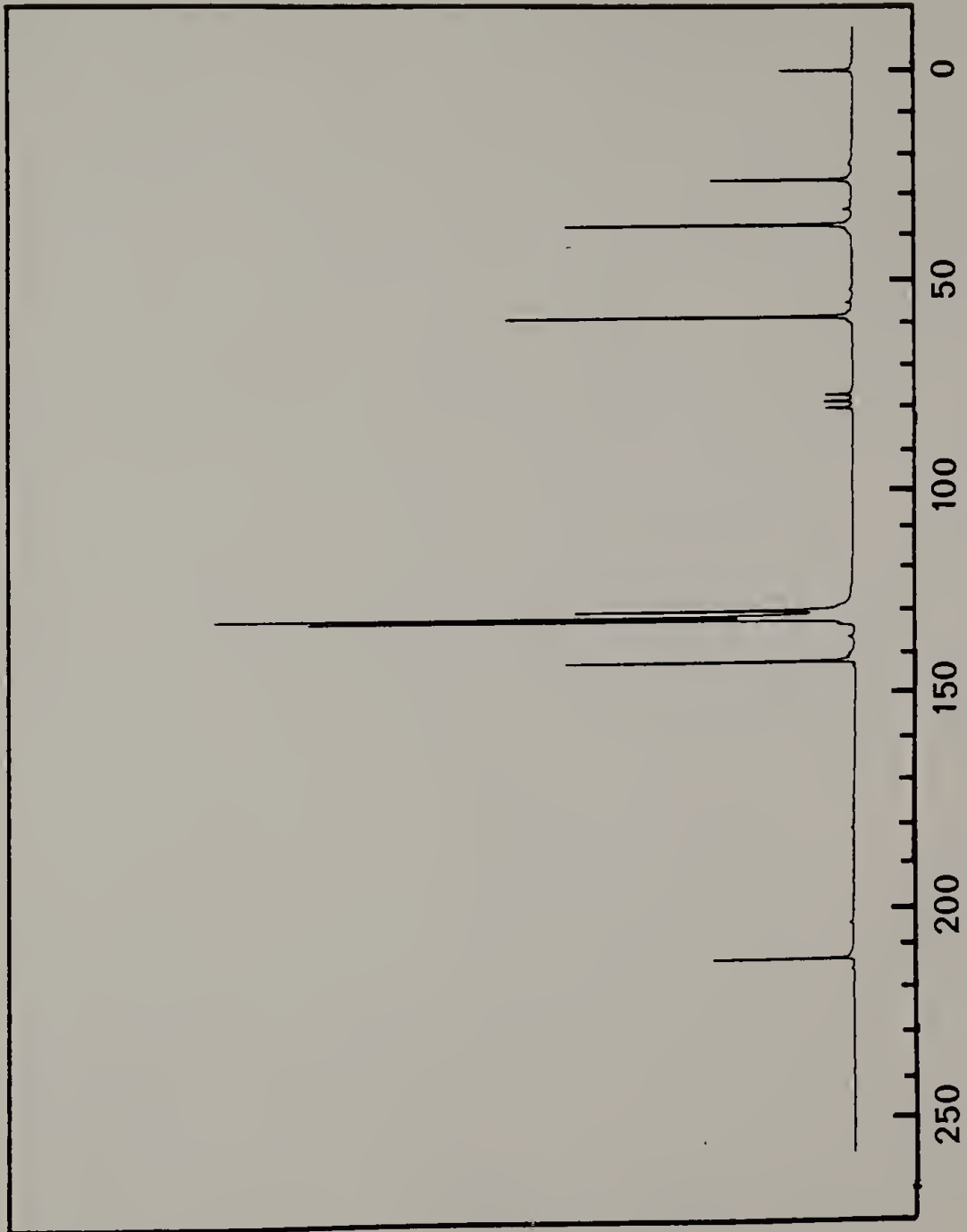
Figure 66. Poly[oxy-2,6-bis(p-methoxyphenyl)-1,4-phenylene].

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$^{13}\text{C}$  NMR SPECTRA

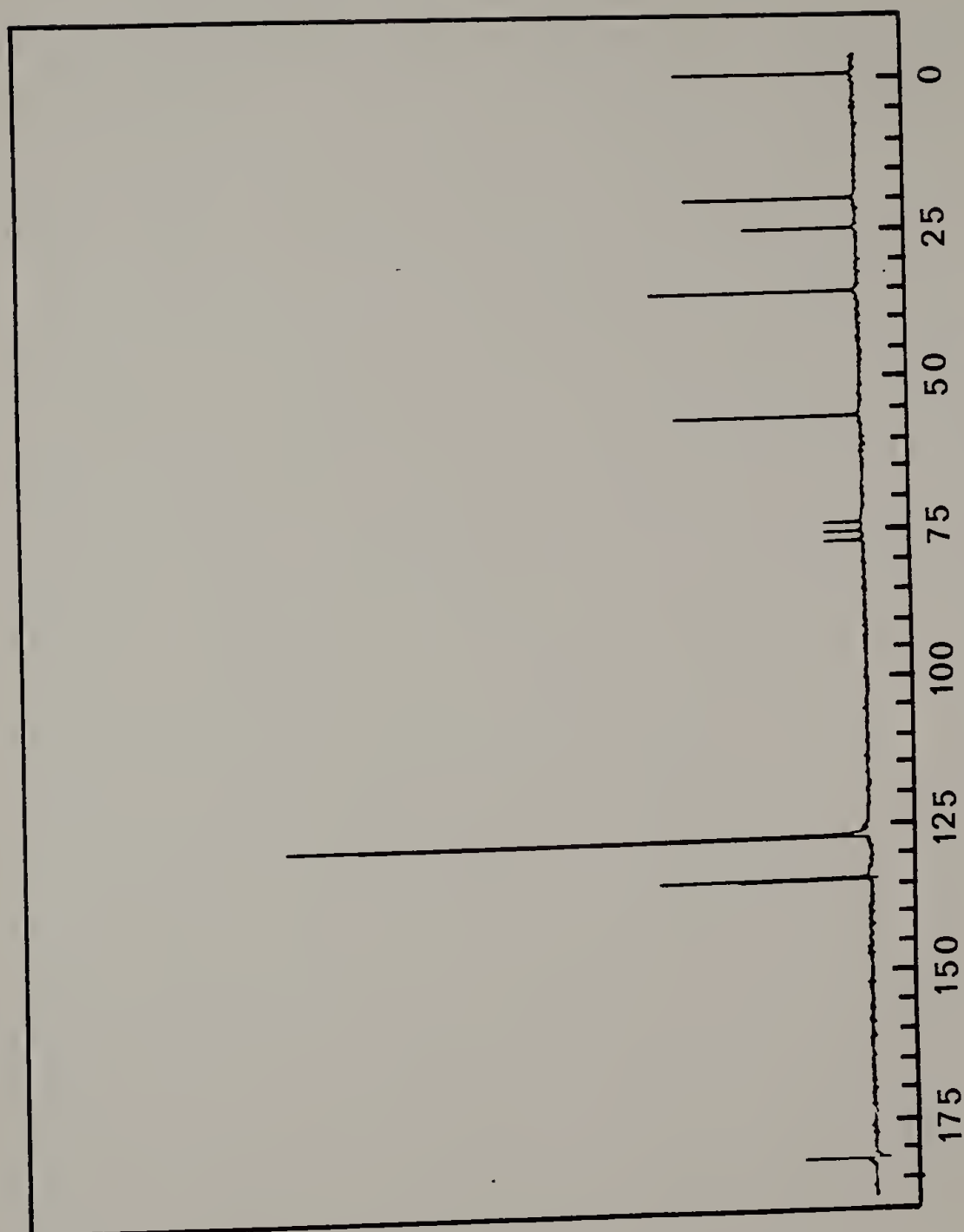






Chemical Shift, ppm

Figure 68. 2,6-Diphenylcyclohexanone.



Chemical Shift, ppm

Figure 69. 2,6-Bis (p-tolyl) cyclohexanone.

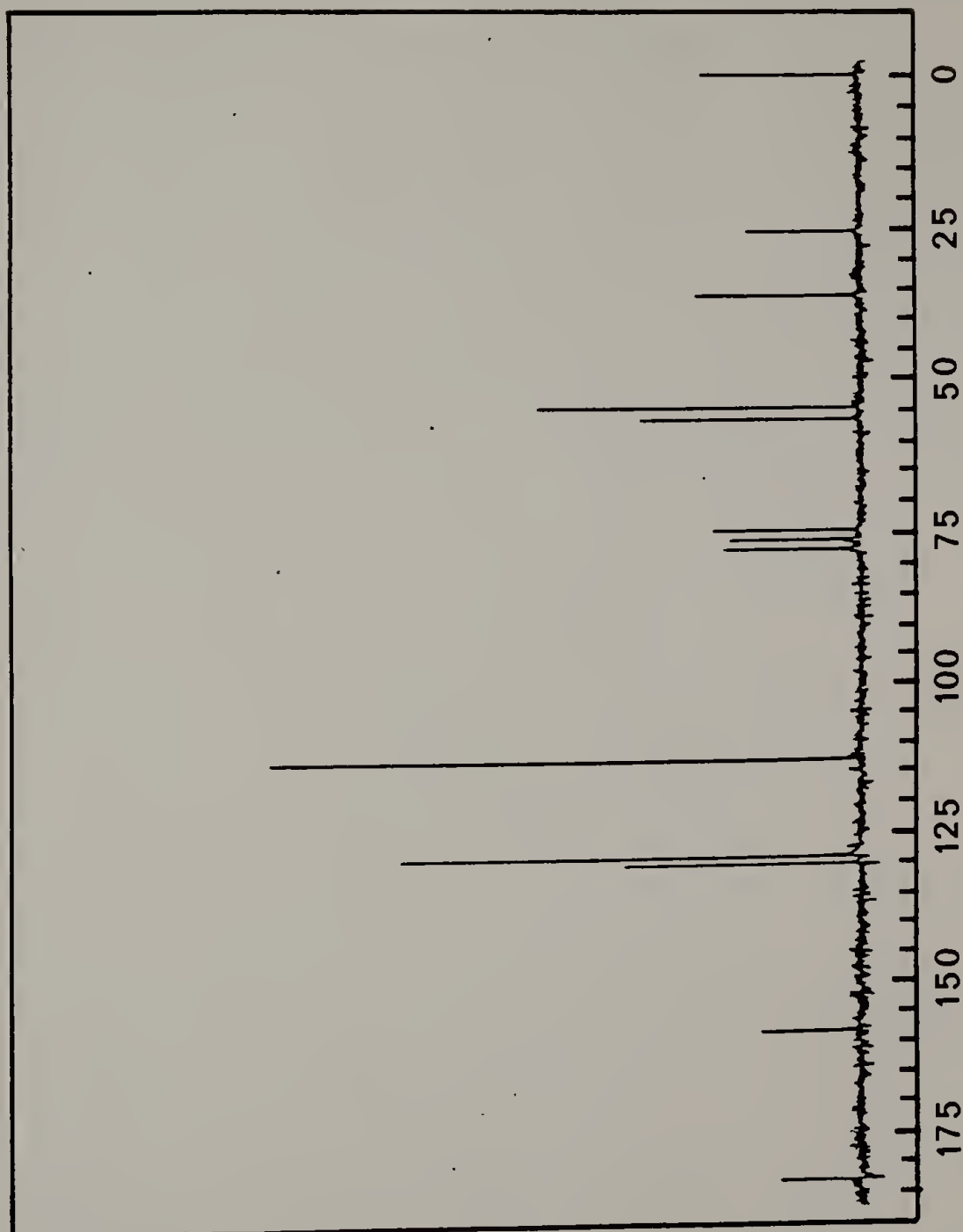
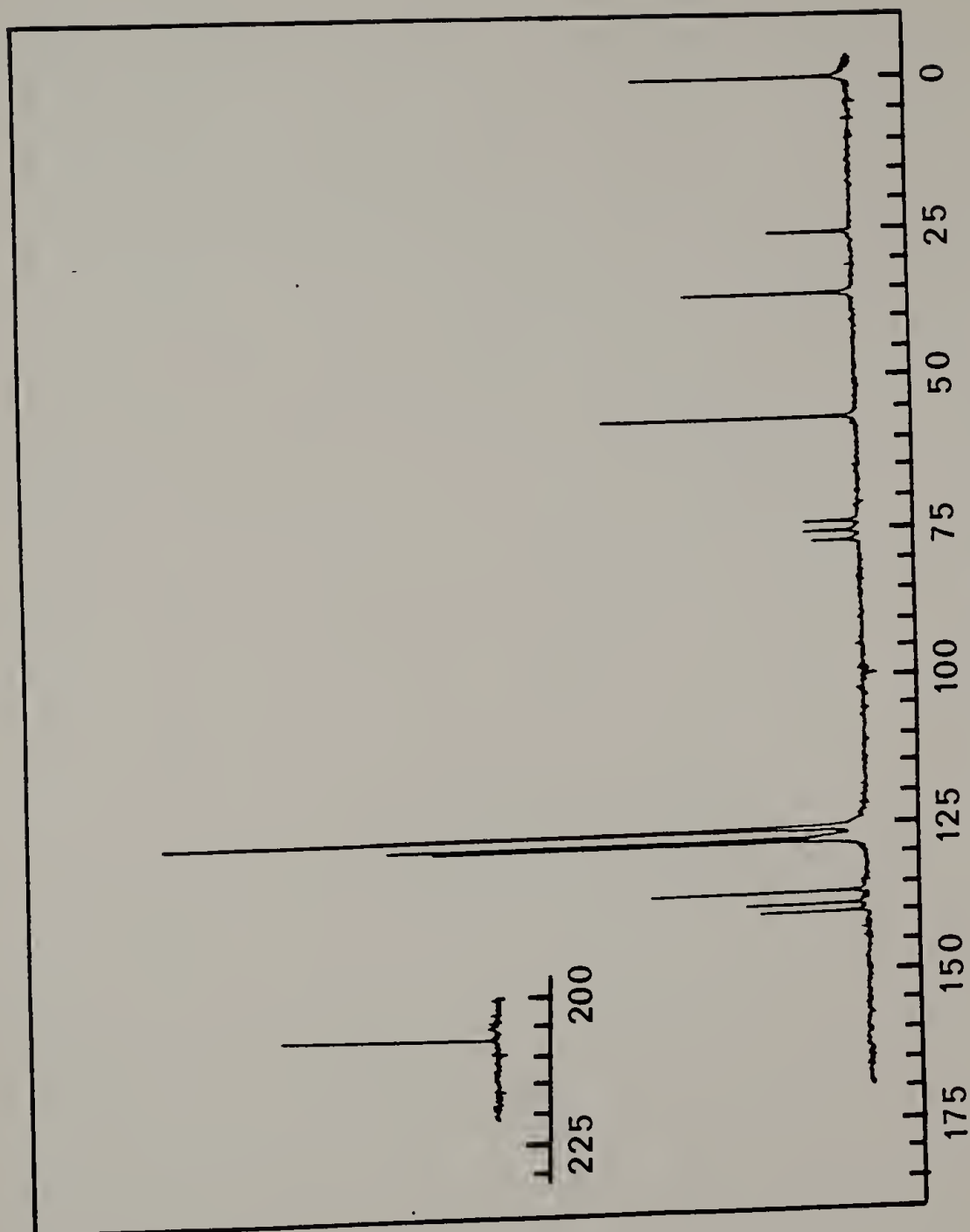
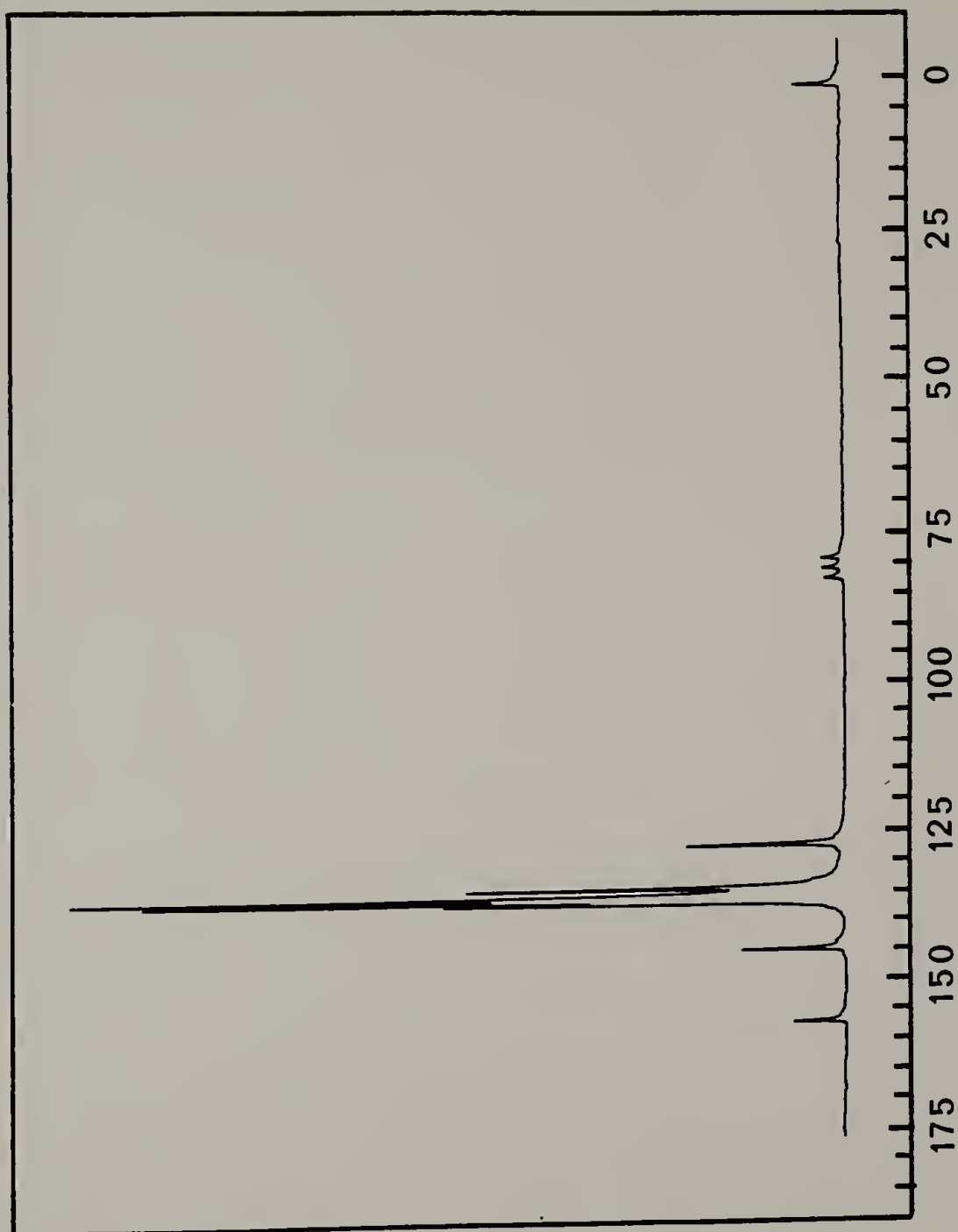


Figure 70. 2,6-Bis (p-methoxyphenyl) cyclohexanone.

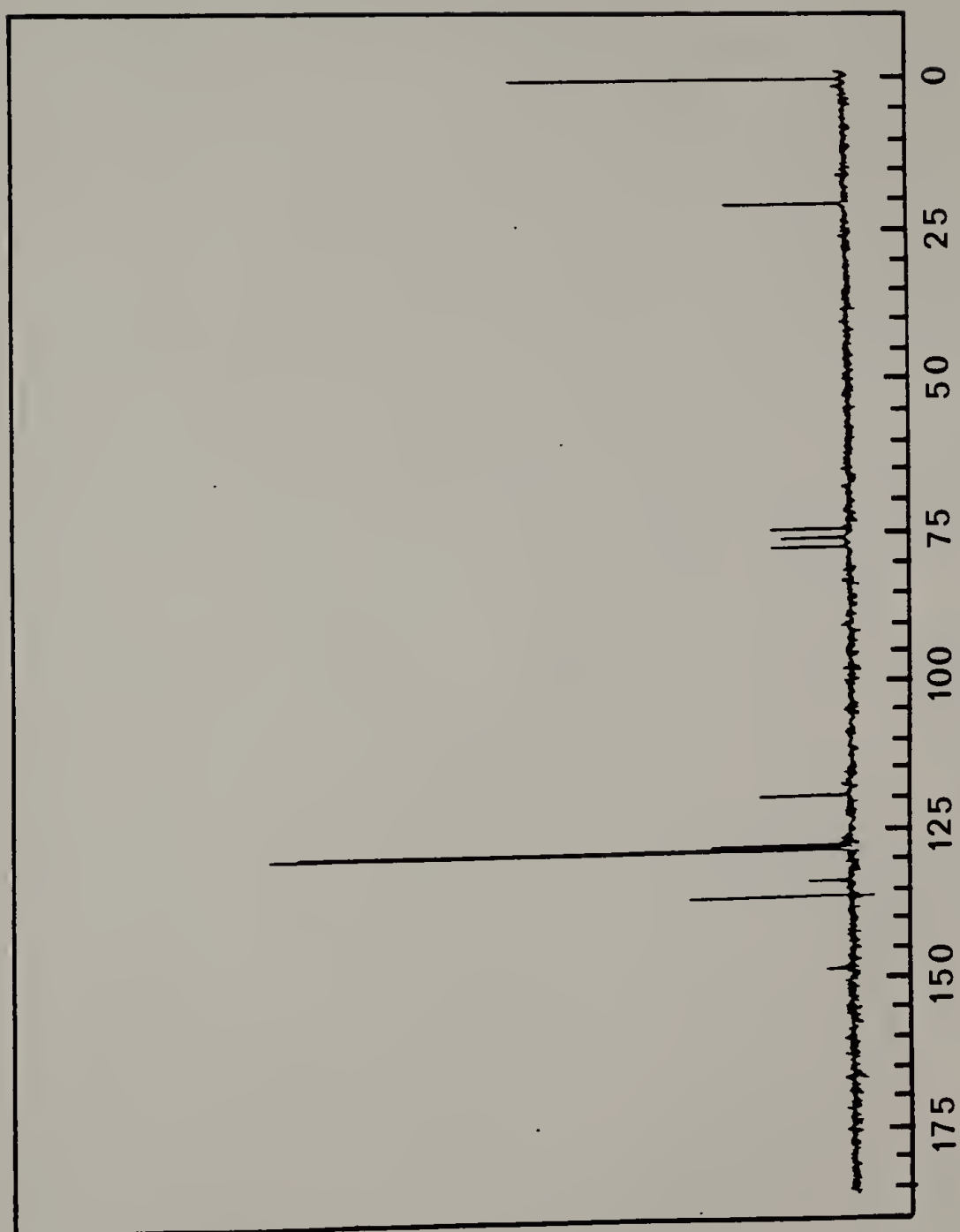


Chemical Shift, ppm  
Figure 71. 2,6-Bis (p-biphenylyl) cyclohexanone.



Chemical Shift, ppm

Figure 72. 2,6-Diphenylphenol.



Chemical Shift, ppm  
Figure 73. 2,6-Bis (p-tolyl) phenol.

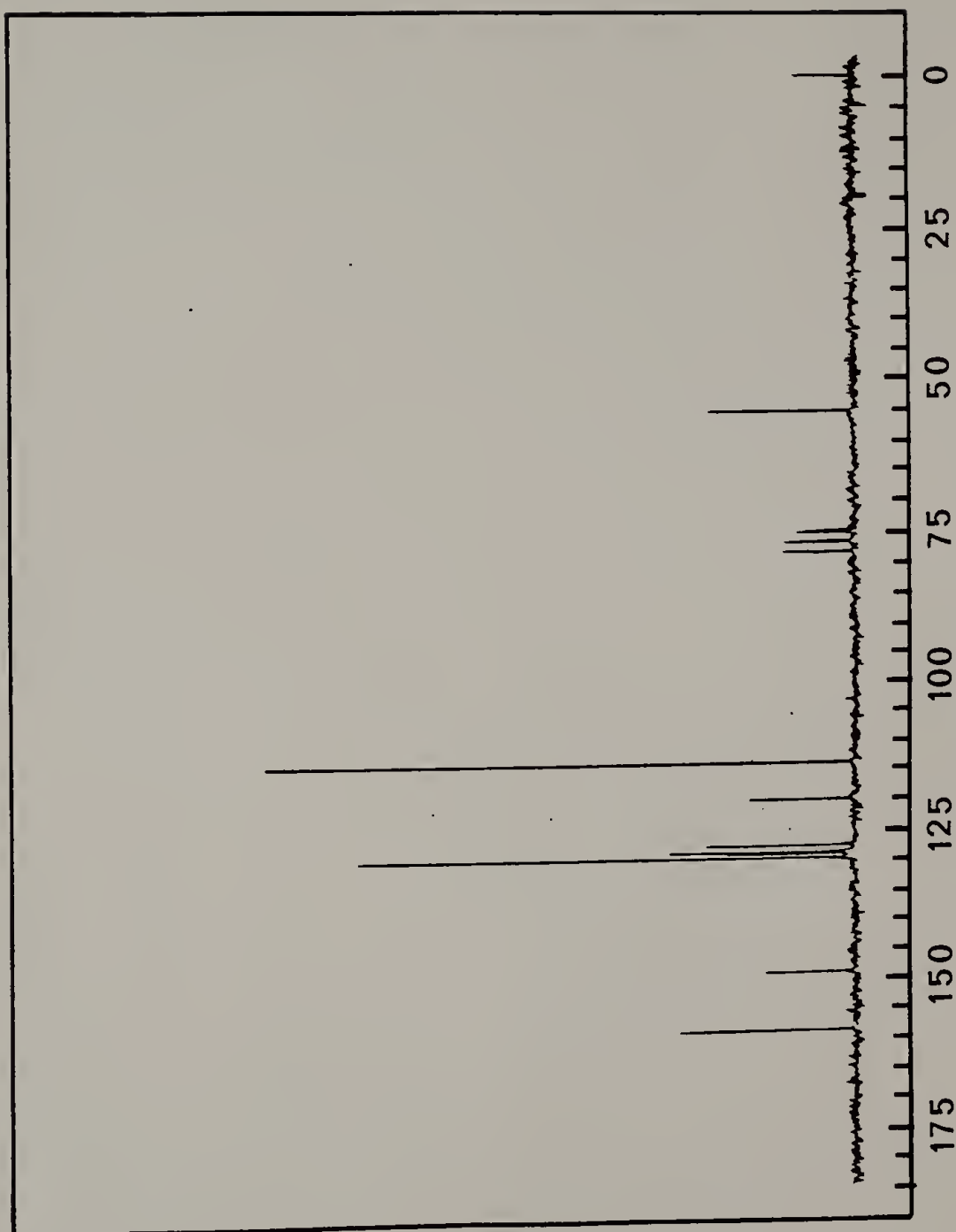


Figure 74. 2,6-Bis (p-methoxyphenyl) phenol.

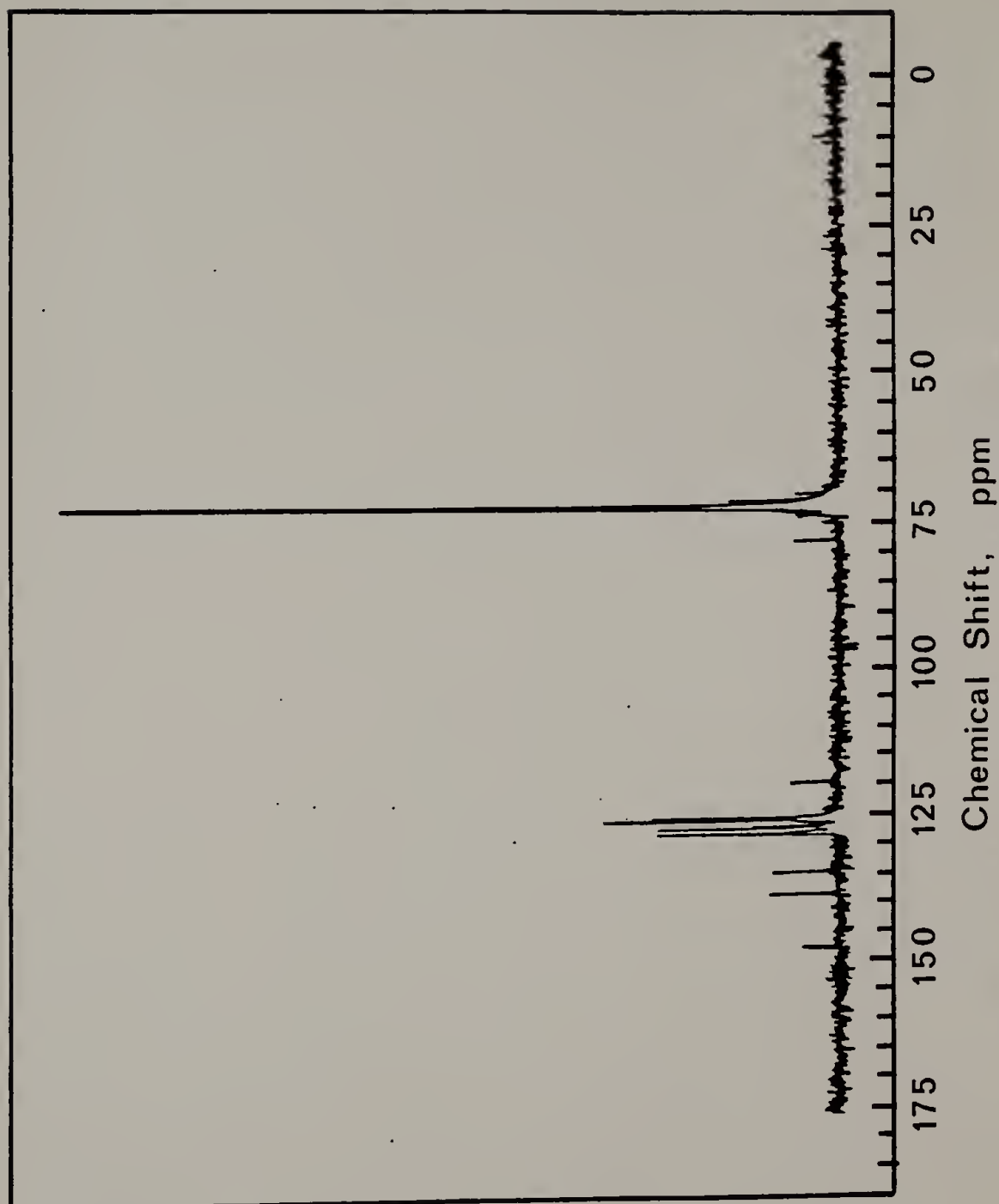


Figure 75. 2,6-Bis (p-biphenyl) phenol.



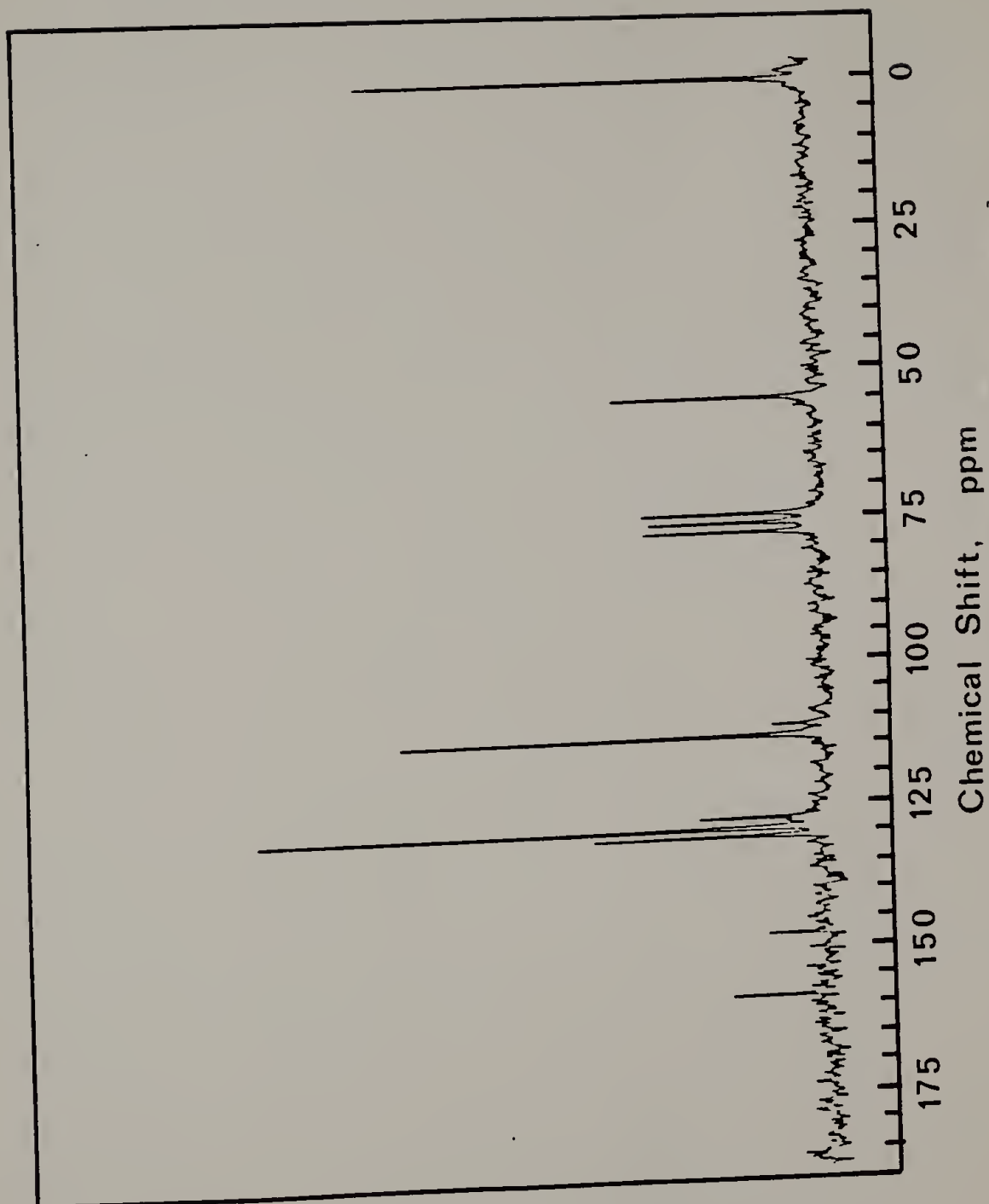


Figure 76. 4-Bromo-2,6-bis (p-methoxyphenyl) phenol.

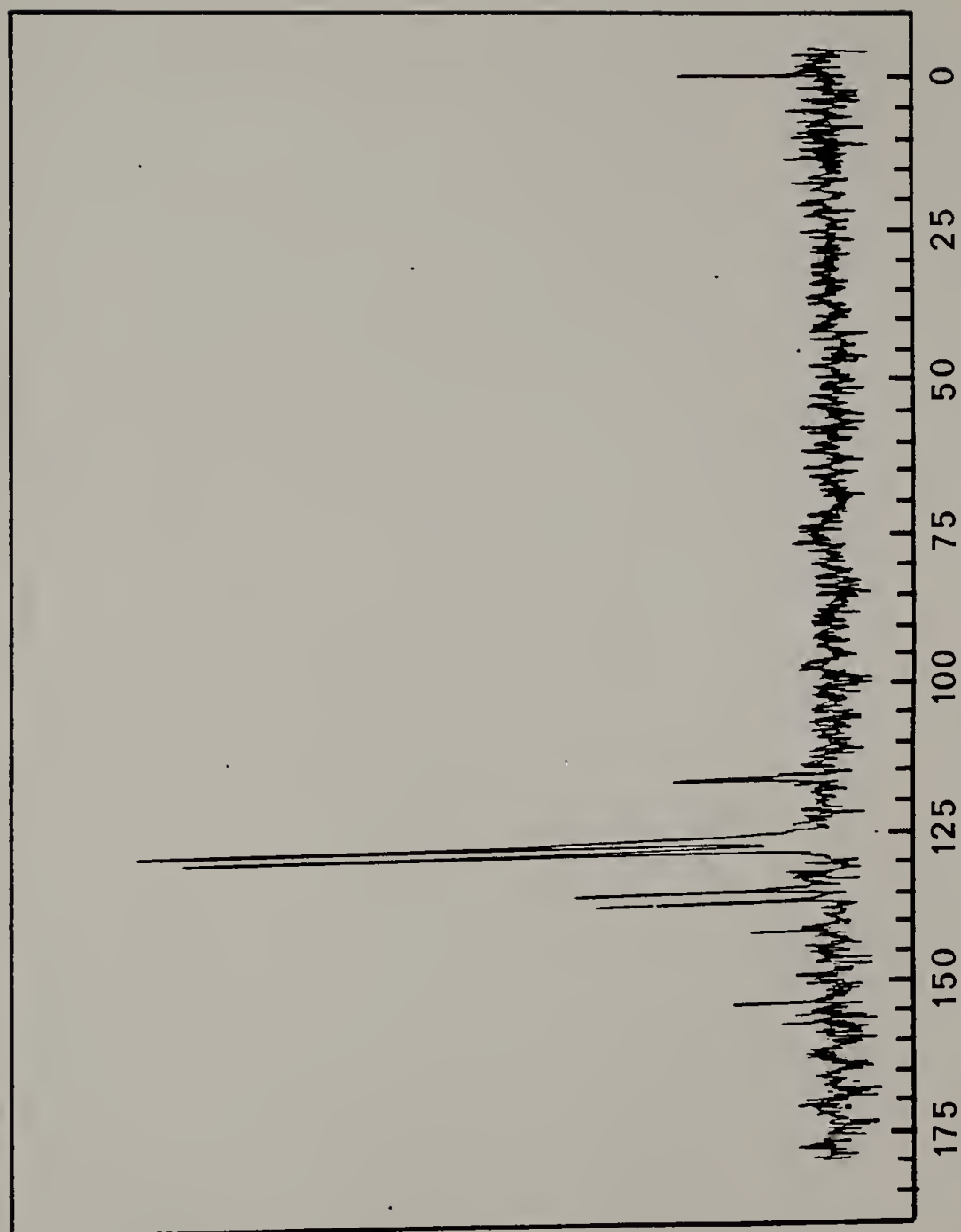


Figure 77. Poly (oxy-2,6-diphenyl-1,4-phenylene).

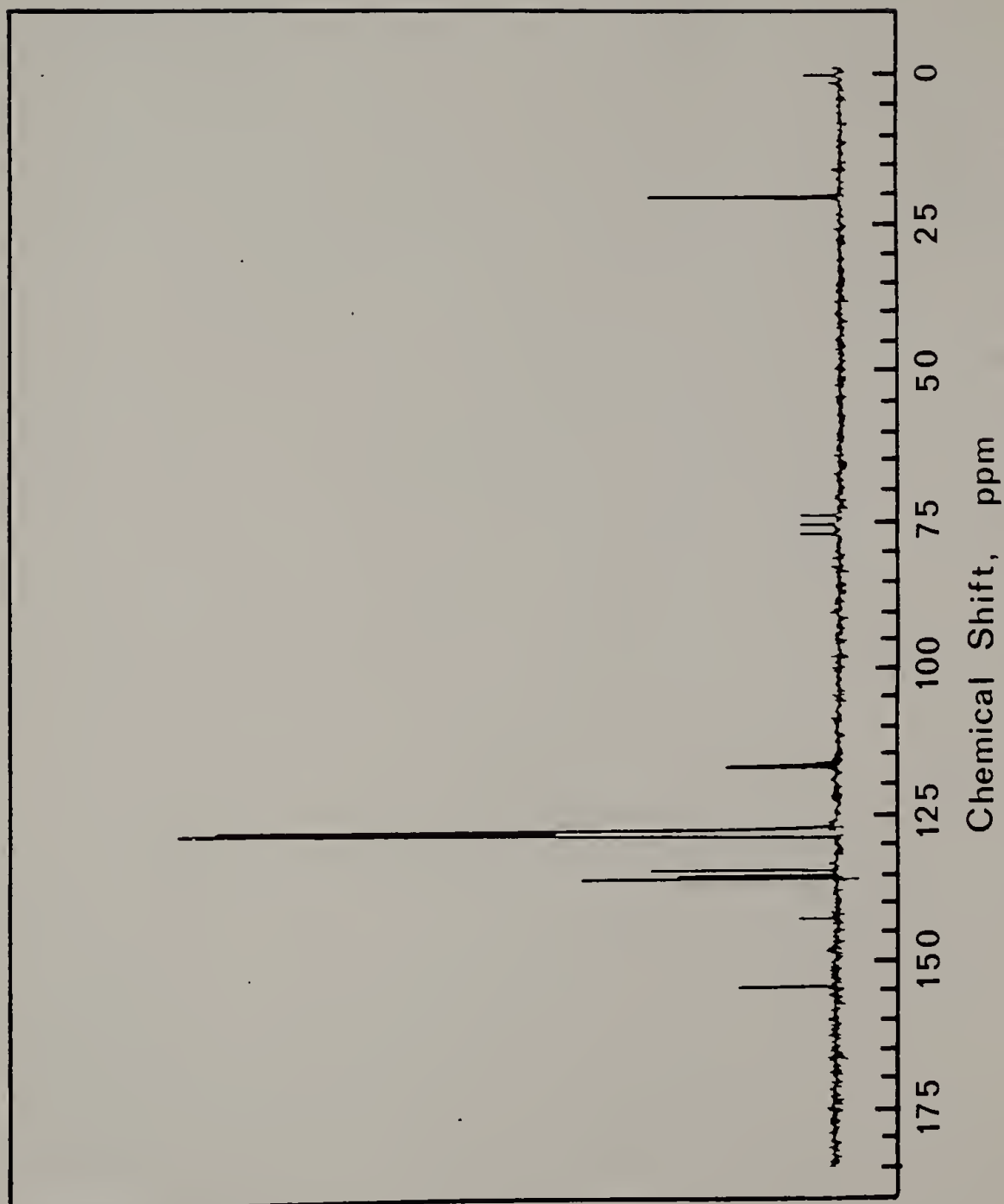


Figure 78. Poly[oxy-2,6-bis(p-tolyl)-1,4-phenylene].

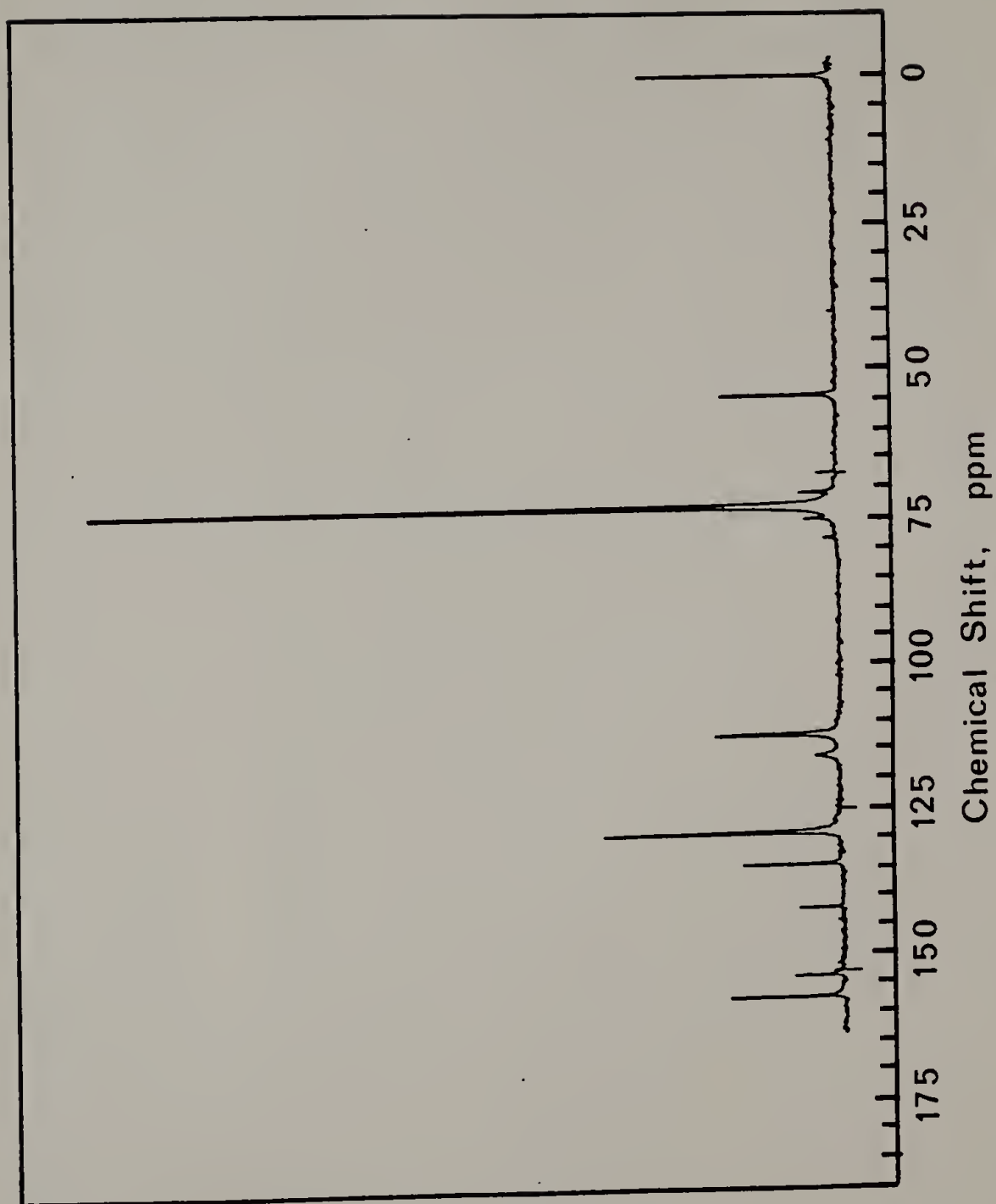


Figure 79. Poly [oxy-2,6-bis (p-methoxyphenyl)-1,4-phenylene].

