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The physical properties of organic polymers containing ions.

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THE PHYSICAL PROPERTIES OF ORGANIC POLYMERS CONTAINING IONS

A Dissertation Presented
By
LAWRENCE W. MCKENNA, JR.

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

September 1970

Polymer Science and Engineering
THE PHYSICAL PROPERTIES OF ORGANIC POLYMERS CONTAINING IONS

A Dissertation

By

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September 1970
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CHAPTER I
INTRODUCTION

Objectives of the Investigation

The physical and chemical interactions between polymer chains are of fundamental importance to the macroscopic properties of these materials. Physical interactions, e.g., entanglements, contribute to the high strength and viscosity of polymers relative to low molecular weight compounds of similar structure.\(^1,2\) The role of chemical interactions is of equal importance. These may involve one, or all, of the following three general types of forces:

1. London Dispersion and van der Waal's forces, very short range with energies of the order \(10^0\) kcal/mole;
2. hydrogen bonding forces, longer range with energies of the order \(10^1\) kcal/mole;
3. primary covalent crosslinks, very strong bonds with strengths of the order \(10^2\) kcal/mole.

Chemical interactions of the first type are present in all polymers and in the case of polyolefins, for example, are the only kind of interchain force operating.
Bonds of the third type lead to rubber-like properties and have been the subject of extensive research. Interchain associations through bonds of the second type lead to a large number of important polymers with interesting properties, e.g. poly(vinyl alcohol), polyacrylonitrile and polyamides. In the work described here, a study was made of the effects of bonds of this type on the mechanical properties and crystallization behavior of a unique polyethylene copolymer containing a relatively minor molar fraction of pendant, ionizable acid groups. Such polymers are known as "ionomers".

By ionizing the acid groups and varying both the degree of neutralization and the type of cation, effects of hydrogen and ionic bonding could be observed and compared in samples of polymer with the same basic composition and structure. Since the polymer is primarily ethylene, the "matrix" in which these interchain forces operate is of low dielectric constant. This would be expected to lead to some unusual effects not ordinarily seen in polyethylene homopolymers. This work was done to examine the properties of the copolymers and describe the complex nature of the system.
"Ionomer" as a Generic Term

The term "ionomer" was derived and used first by R. W. Rees to describe a new class of thermoplastic polymers (the suffix "-mer") containing strongly interacting ionic groups (the prefix "ion-`). In theory, then, the term can be applied to many polymer systems which have electrostatically charged groups attached to the chain. However, common usage in the past few years has limited "ionomer" to a stricter sense and the definition has been made more precise by Rees and co-workers at E. I. du Pont de Nemours and Company. To avoid eventual misunderstanding and confusing application of this term, an operational definition is developed in this section.

Current use of the name "ionomer" now generally implies a series of \( \alpha \)-olefin copolymers, based on ethylene as the major component, and a minor amount of carboxylic acid, typically acrylic or methacrylic, partially ionized with Groups I or II metal cations. While variations in polymer molecular weight, type and concentration of acid comonomer, type of ion and degree of neutralization may be made, gross changes in composition result in products outside the operational definition of an ionomer. Thus, a
salt of poly(styrene-co-methacrylic acid), for example, is not an ionomer. Similarly, poly(acrylic acid-co-ethylhexyl acrylate)\textsuperscript{8} should not be termed an ionomer as was recently reported.\textsuperscript{9}

In the discussions which follow, an ionomer is understood to meet the following three compositional criteria:

1. ethylene as a major component;
2. acrylic or methacrylic acid as a minor component, (generally about 1-10 mole \%) either in the chain backbone or as grafted side chains;
3. at least partial ionization of the acid groups with Group I or II metal cations.

Other composition variations might be made within the ionomer class. For example, sulfonyl groups have been claimed as a substitute for carboxyl groups in ionomer-type materials.\textsuperscript{10} Ionization of ethylene-acrylic acid copolymers with organic amines has also been described.\textsuperscript{11} However, these polymers have not been reported outside the patent literature, their properties are not well defined and they are not included in the usually accepted sense of ionomers. It is, in fact, the unique properties which ionization of pendant carboxyl groups confers on semi-
crystalline olefin polymers that makes ionomers so distinctly different and interesting. Thus, the operational definition used here refers only to ethylene copolymers containing minor amounts of metal carboxylate groups.

Survey of Commercial Development of Ionomers

Ionomers are a result of need-oriented industrial research. Their unique properties were not completely predictable and, while various end-use applications were immediately realized, a real understanding of the nature of the system required a more intensive, basic approach to their study. Thus, ionomers are an illustration of the close relationship between polymer technology, which provides synthetic products with useful properties, and polymer science, which defines and predicts the relationship between molecular architecture and properties. The methods of preparation and some of the interesting end-use properties and applications of ionomers are surveyed in this section to serve as background for the discussion of basic properties and structure upon which this thesis is based.

1. Preparation methods. Synthesis of the ethylene-carboxylic acid copolymer is always done using free radical
methods but the techniques differ and lead to polymers of two different types of general structure: random copolymers (from copolymerization of the two monomers) and graft copolymers (from the polymerization of the acid-functional monomer in the presence of polyethylene). One of the first ionomers was prepared by Tanner\textsuperscript{12} at Du Pont in an interesting variation of the usual graft technique: maleic anhydride was grafted onto polyethylene film without significant homopolymerization. The grafted film was then treated to give pendant dicarboxylate groups randomly distributed along the backbone. A more conventional grafting technique was used by Tanner in preparing polyethylene film grafted with side chains of poly(acrylic acid).\textsuperscript{13} The films were then converted to the ionomer by soaking in Na\textsubscript{2}CO\textsubscript{3} solution. However, most of the work at Du Pont has been concentrated on synthesis of random copolymers via copolymerization of both monomers.\textsuperscript{14} Generally, the process involves elevated temperature and pressure, using a peroxide catalyst, often in solution. A number of patents have been issued to Du Pont\textsuperscript{15-23} for this method of producing the copolymers and making ionomers from them. The techniques for ionizing the acid group vary. One of the earliest and most extensive
description is given by Rees,\textsuperscript{15} who claims that uni-, bi-
and trivalent metal cations from Groups I, II, III, IVA and
VIII may be used. Preferred compositions use alkali metal
salts and bases to ionize 10-50\% of the acid groups present
in the polymer. The neutralization may be done by mechani-
cally mixing the ionizing agent with the copolymer or by
treatment in solution or dispersion. Techniques using
monoamines,\textsuperscript{20} diamines\textsuperscript{16} and mixtures of amines and metal
salts\textsuperscript{19,22} have also been described. An innovative method
uses Portland cement (\textasciitilde{}3\% CaO)\textsuperscript{21} or hydrolyzable co-
crystallized oxides\textsuperscript{23} admixed with the polymer and then
treated with water to form the ionized groups after fabri-
cation.

Copolymerization has been done in emulsion systems at
Gulf,\textsuperscript{24} and Spencer,\textsuperscript{25} or the dried, solution-made copolymer
simultaneously ionized and emulsified, as at Bayer.\textsuperscript{26} Other variations of the method of random copolymer synthe-
sis include terpolymerization of an ethylene/acrylic acid/
sodium acrylate mixture to produce ionomers directly,\textsuperscript{27,28}
continuous copolymerizations,\textsuperscript{29,30} and low temperature and
pressure reactions.\textsuperscript{31,32}

Graft copolymerizations have been extensively investi-
gated at Dow, where both high and low density polyethylene were grafted using preirradiation of the backbone or peroxides as the free radical sources. Other work using irradiation to initiate grafting has been done on polyethylene fibers in Russia, and on films in France and Japan. Ionomers can be prepared by the same techniques as discussed before; for example, by treating the grafted film with base. Graft copolymers and ionomers have also been prepared at Union Carbide, where an interesting approach to ionization of the acid groups is the use of organometallic compounds, such as the alkanoates and acetates of Al and Sn. Although not classified as an ionomer, a terpolymer which may be converted to a product having ionomer properties merits attention because of the synthetic route devised by Carbide. An ethylene/alkyl acrylate random copolymer is hydrolyzed to give a predominantly ethylene chain containing acrylic acid and some small amount of residual alkyl acrylate.

The two main synthetic routes, random and graft copolymerizations, result in ionomers of quite different structure and, thus, some of the properties may differ. A graft copolymer will be "blocky" because monomer units of the same
type are always adjacent to each other. Random copolymers, on the other hand, will tend to have a random distribution of comonomer units although the exact nature of this sequence distribution is not known. The usual synthetic routes are run to low conversion and often have monomer delays thus improving the composition distribution.

2. Applications and end-use properties. Ionomers may be considered as modified polyethylenes from the standpoint of both chemical structure and physical properties. There has been an enormous amount of work reported on modifying polyethylene through copolymerization with other vinyl monomers, but the ionomer structure is unique in its combination of properties.

One of the most obvious influences of ionization is the optical clarity. For example, the per cent haze measured on a 20 mil plate of a typical ionomer is about 5.0% versus 57% and 100% for low and high density polyethylene, respectively. Another outstanding difference when compared with polyethylene is the improved toughness over a wide temperature range. Ionomers are typically three to four times as tough as polyethylene because of the combination of moderately high tensile strength and
elongation. Brittleness temperature is unusually low (ca. -105°C.) and, as might be expected, tensile impact strength is quite high.

For a polymer with such remarkable properties, melt processing becomes an important question. The ionomers can be processed using conventional polyethylene equipment, and even offer advantages in terms of melt strength and resistance to pinholing and puncture during processing. Melt viscosity is generally higher than polyethylene at the lower processing temperatures but since the activation energy is also higher, viscosity versus temperature curves have a steeper slope. At higher temperatures, ionomer viscosity is equal to or less than conventional polyethylenes.

There are several other interesting modifications of typical polyolefin properties which make ionomers useful. Adhesion to paper, metals and other polymers is often improved; permeability of oils, greases and organic solvents is reduced, and excellent corona resistance (or resistance to electromechanical stress cracking) is observed.

Ionomers have been suggested for use in many areas where the combination of transparency and optimal mechani-
The electrical properties are utilized in wire coatings and cable constructions. The toughness and resiliency of ionomers are amply demonstrated by its use in that frequently abused object of man's inner frustrations, the golf ball.

Finally, an example of the effect of ionization on the microphase behavior of ionomers is illustrated by a patent which claims improved compatibility of polymeric blends. Ethylene-acid copolymers give heterogeneous blends with poor properties when mixed with other vinyl monomer-acid copolymers but compatibility and physical properties are improved after ionization.
Review of Studies on Ion Containing Organic Polymers

Organic polymers containing ionized groups first received attention following the discovery of the high tensile strengths of synthetic carboxylic elastomers reacted with divalent metal ions. Since then, there have been many studies of the structure and properties of polymers containing ionic groups and a number of theories developed to describe their unusual behavior. A review of this work is given in this section, divided into two parts: (1) salts of strictly amorphous systems, usually either butadiene or styrene copolymers with (meth)acrylic acids, and (2) the ionomer-type copolymers. Although outside the scope of this review, the elegant work of Eisenberg on salts of inorganic polymers is mentioned here because of its treatment of the effects of ions on polymeric properties.

1. Salts of amorphous organic polymers. In a survey of earlier work, Brown refers to the impressive physical properties of carboxylic synthetic elastomers "crosslinked" by metal ions. These polymers differed from conventional vulcanizates in that they had high tensile strength, self-
reinforcement without the need for fillers and high resistance to sudden stress coupled with high relaxation under tension and high compression set, as manifested by plasticity at elevated temperatures and poor flexure. For example, a butadiene-methacrylic acid copolymer showed increasing tensile strength as the interchain association was increased by ionization:

<table>
<thead>
<tr>
<th>Carboxylate Group</th>
<th>Maximum Tensile Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>100</td>
</tr>
<tr>
<td>Na Salt</td>
<td>1700</td>
</tr>
<tr>
<td>Zn Salt</td>
<td>6000</td>
</tr>
</tbody>
</table>

While the nature of this association was not discussed in detail, most of the early work seemed satisfied with describing it simply as "crosslinking".

Cooper was the first to apply the concept of interchangeable bonds to these systems. His work suggested that the associated ionic groups are labile and capable of interchange reaction with each other under the influence of imposed stress. Thus, high tensiles were obtained because of a network relaxation process preventing premature failure. Corresponding unionized copolymers vulcanized with sulfur to form true crosslinks were observed to be
much weaker. Furthermore, while the sulfur vulcanizates were insoluble, the salts of low molecular weight butadiene copolymers were soluble so long as there was less than eight carboxyl groups per chain. Cooper attributed this to the ability of the solvent to separate the ionic groups and, in fact, in dilute solution, osmotic pressure measurements showed no significant change in the apparent molecular weight of the chains upon ionization with divalent salts. However, the viscosity of the polymers in the solid state was observed to increase dramatically depending on the degree of ionization and the valence of the cation. Thus, the concept of true crosslinks appeared to be less reasonable than one invoking some sort of thermal- and stress-sensitive association between ionic groups of different chains.

Supporting this concept of bond interchange, Otocka and Eirich studied stress relaxation in similar copolymers. They refined the ionic associative complex idea and described it as intermolecular, quadrupolar linkages, in which ion pairs of pendant metal carboxylates are themselves paired in the rubbery state. These groups dissociate under thermal or mechanical influences and then reform,
relaxing the network stresses. Hakozaki, in his study of the tensile and viscous flow properties of a butyl acrylate-acrylic acid salt, also provides this explanation.

Disputing bond interchange as a mechanism to explain the properties of salts of butadiene elastomers, Halpin and Bueche claim that ionization, per se, has little to do with the observed behavior. Their tensile and creep data, and theoretical treatment of it, suggests that the unique strength properties are a natural consequence of a very low crosslink density network in which the usual viscoelastic relaxations occur. In their view, any elastomeric network would show the same general properties, regardless of the nature of crosslinking, if the network density and glass transition temperatures were the same.

It is worthwhile, at this point, to review additional evidence from studies made on salts of styrene copolymers. Erdi and Morawetz showed that the rigidity and tensile viscosity of the plasticized salts increased with degree of ionization and valence of the cation. When compared at temperatures corresponding to the same compliance, samples with a divalent cation had the lowest irrecoverable, viscous flow. Their experiments were interpreted as show-
ing that ionization is more effective in reducing viscous creep than in reducing elastic compliance. They concluded that the ionic groups thus serve as crosslinks but, since the compliance greatly exceeded theoretical predictions, the crosslinks were weak and of low efficiency. In contrast, work by Fitzgerald and Nielsen\textsuperscript{69} suggests that the increase in glass transition temperature must be taken into account when interpreting properties of polymers with inter-chain associations. Thus, viscoelastic behavior may be quite similar when observed at the same temperature difference above $T_g$.\textsuperscript{62}

In view of all these disparate theories, it is, perhaps, not surprising that Tobolsky, Lyons and Hata\textsuperscript{70} took a somewhat different approach to the nature of ionic association in carboxylic elastomers. In their studies of the effect of temperature on modulus and stress relaxation, they concluded that the ionized groups "clustered" together in a separate phase and act somewhat as reinforcing fillers. Modulus curves showed an enhanced and extended "rubbery plateau" region above the glass transition of the polymer. This region never is completely horizontal, as in the case of unionized copolymers vulcanized with sulfur, but decreases
slowly with increasing temperature. The data suggest that the clusters maintain at least some of their integrity up to at least 180°C. Stress relaxation curves, on the other hand, show no plateau region. In this respect, they behave as the two-phase elastomeric block copolymers\textsuperscript{12} where styrene segments form discrete microphases in a butadiene matrix. The modulus and stress relaxation results argue against the previously postulated ideas of true cross-linking,\textsuperscript{63} low crosslink density,\textsuperscript{67} or chemical exchange mechanisms\textsuperscript{64,65} as being entirely satisfactory explanations. Furthermore, selective plasticization experiments seem to support the cluster concept. Ionized elastomers swollen with acetic acid gave modulus curves in which the rubbery plateau was reduced by a factor of three while the major transition temperature was only slightly affected. Plasticization with xylene shifted the transition temperature downwards but had a negligible effect on the enhanced rubbery plateau modulus. Thus, Tobolsky and his co-workers conclude that the properties of ionized elastomers are due to a two-phase structure reinforced by hard, ionic clusters.

This review illustrates the divergence of opinion on the nature of ionic effects in organic polymers. Ionomers
offer a new class of materials with which to explore this question.

2. Ionomers. The work on ionomers described in this thesis was started in 1966 and has been described in part in several recent publications from this laboratory. Additional studies have also been done, most of them concurrently with this work, at Du Pont, Bell, Princeton, and Union Carbide. Since reference will be made later to these results, it is sufficient at this point to briefly outline them and state the important conclusions.

In early work by Rees and co-workers, the effects of ionic bonding on fine structure were examined. Progressive ionization eventually destroyed visible spherulitic structure and lowered the total level of crystallinity. The ionomers had much higher melt viscosities than the acid copolymer and increased flow activation energy. At temperatures below the melt state, the metal ion valency seemed to have little influence on properties but in the melt, divalent metal ions gave much higher viscosities. Later Longworth et al. obtained evidence from X-ray diffraction, electron microscopic and dynamic mechanical
studies which suggested that the ionic groups reside in separate phases, or domains, in the amorphous matrix. This conclusion was also made by Tobolsky and his group on the basis of stress relaxation experiments. They suggested that the behavior of ionomers depends more on the degree of ionization than on the valence of the ion and is dominated by the existence of ionic clusters interspersed throughout a predominantly amorphous matrix. Tobolsky made reference to a model of this type developed by Bonotto who studied the effects of ion valency on the physical properties of ionomers. Potts et al. studied copolymers with no free acid groups, prepared by direct copolymerization with sodium acrylate, and compared them with conventional ionomers which are usually only partially ionized. They concluded that, in the ionomers, acid and carboxylate moieties interact to give stronger moduli than polymers without free acid groups. However, this interaction does not persist in the melt where dipole-dipole interaction of the ionized groups is the only strong interchain force. Eisenberg deduced from the theoretical considerations the existence of multiplets in the melt which collapse to form clusters below a certain characteristic temperature. His calculations pre-
dicted ionic domains of sizes and spacings reasonably close to that suggested by the experimental data of Longworth and work done by others in this laboratory. Results from NMR studies done by Read in cooperation with this laboratory also suggest that ionic domains are formed in the ionomers, and work by Sakamoto et al. also at this laboratory, gives melt rheology results which coincide with this view.

On the other hand, Otocka et al. give results from dynamic mechanical, calorimetric and NMR work which they suggest argue against phase separation. They conclude that the ionic groups are relatively uniformly dispersed throughout the amorphous matrix with dipole-dipole coupling defining the limit of interaction.
CHAPTER II

EXPERIMENTAL DETAILS

Sample Preparation

A commercial sample of poly(ethylene-co-methacrylic acid) ionomer (Surlyn A1552) was obtained from W. F. Brondyke of Du Pont. The molecular weight was reported by him to be about $3 \times 10^5$ and the sample was co-polymerized by a high pressure and temperature, free radical method. A strong absorption in the infrared at about 1550 cm.$^{-1}$ showed that a portion of the acid groups were ionized. To prepare the unionized starting material, a technique was developed to convert the salt groups back to the original acid state. This purified polymer was then characterized further with regard to comonomer concentration and approximate methyl branching and was used to prepare all of the salts discussed in this work.

1. Preparation and purification of the unionized co-polymer. A number of solvents were examined; most were non-solvents or merely swelling agents. Best results were obtained with mixtures of xylene and tetrahydrofuran (THF) at high (>80°C.) temperatures. Solubility of the partially
ionized commercial material appears to be critically dependent on temperature and polymer concentration and less so on the ratio of the two solvents. It appears that true solutions can be obtained in mixtures of xylene and THF only when the polymer concentration is less than 7% weight/volume (w/v) and the temperature greater than about 75-80°C.

The polymer was first reduced to a fine particle size by grinding in a Cumberland mill. To avoid gumming in the mill and possible heat effects on the polymer, it was necessary to pre-cool the polymer particles first with dry ice. Thus, the polymer was shaken for about 10 minutes in a jar with powdered dry ice and more dry ice was added during the grinding. In preparation of the unionized co-polymer, the xylene was minimized to 5% volume/volume (v/v) of the solvent mixture. At a polymer concentration of 6% w/v, the mixture was heated to reflux while stirring in glass equipment. A solution of concentrated hydrochloric acid (HCl) in THF (1:2 volume ratio) was added slowly. The polymer solution, originally hazy, was observed to quickly clear at about the same time an amount of HCl stoichiometrically equal to the carboxylate groups had been added. A slight excess of HCl was added and the system reacted for
about 0.5 hours. Distilled water was then added to precipitate the polymer as a white flocculant mass and the mixture cooled. The supernatant was decanted (a check for dissolved polymeric solids was negative) and the solids washed thoroughly in hot methanol (MeOH) and water (5:1 volume ratio) to extract salt and residual HCl. The polymer was then air dried on a vacuum filter, redissolved in pure THF and the precipitation and washing steps repeated twice. Final drying was in vacuum at 80°C. for 1.0 hour. The resultant material was a white very fine floc.

2. Characterization of the unionized copolymer. Complete conversion to 100% acid groups was checked by determining the absorption of molded films in the infrared at 6.4 microns. This band is very strong and characteristic. No hint of an absorption was found for materials properly prepared.

The methacrylic acid content was determined by oxygen analysis at Galbraith Laboratories. The samples were re-dried for one hour at 80°C., then 0.5 hour at 110°C. under nitrogen. Duplicate results gave 4.30 and 4.39% oxygen. Thus, the per cent methacrylic acid (assuming all oxygen to be present in acid groups) is 4.13 mole per cent.
To characterize the degree of chain branching, an estimate was made of methyl groups per 1000 backbone carbon atoms. These groups were determined by comparing the absorbency of the infrared peak at 1378 cm$^{-1}$ with that in three different samples of branched polyethylene. The latter polymers were purified by precipitation from hot xylene, dried, and their methyl group content estimated from melting point depression and per cent crystallinity (calorimetric) in well annealed samples.$^{95,96}$ By this technique the poly(ethylene-co-methacrylic acid) copolymer was found to have about 67 methyl groups per 1000 carbon atoms. Subtracting the methyl group contribution due to the methacrylic acid present gives a degree of branching of about 26/1000 C. atoms. This value is in the range of low density polyethylene (LDPE) prepared by similar high pressure, free radical techniques.

In summary, a description of the average chemical composition along the chain can now be made. In an average chain segment 100 monomer units long, there is about 90 ethylene units, four pendant acid groups and five pendant branches. Thus, the ratio of potentially crystallizable methylene units to branch points is about eleven to one.
3. Preparation of the polymeric salts. While the acid copolymer and some of the salts appear to be completely soluble in mixtures of THF/xylene at high temperature, it was impossible to maintain solution homogeneity during neutralization, probably because of the addition of polar solvents used to dissolve the neutralizing bases and salts. To improve this somewhat, most polymeric salt preparations were done in refluxing THF in which the unionized copolymer is soluble at about 5% w/v.

The monovalent salts were prepared using lithium and sodium hydroxides dissolved in distilled water and diluted to about 10% with either methanol or THF. These mixtures were added slowly to the refluxing polymer solutions under good agitation in all glass equipment. Usually, especially at high ionization levels, the solution became quite hazy after a certain volume of the neutralizing base solution had been added. At low and intermediate levels of ionization, the stoichiometric amount of base added was the controlling variable in determining the per cent ionization. At high levels of neutralization, when the formation of a fine, flocculant dispersion was observed, time was the controlling factor. This suggests that higher levels of ioni-
zation (>50%) were diffusion controlled in a heterogeneous system. The maximum per cent ionization ever obtained was about 87%.

At less than about 50% ionization, about 1.5 to 2.0 times the stoichiometric amount of base was used to obtain a given level of per cent ionization in 20 minutes of reaction time. At higher levels about 3.0 times the base was required and progressively longer reactions times (up to 1.5 hours) were needed. The polymers were purified of excess base by adding distilled water to the reaction flask, cooling to complete precipitation, and extracting several times in hot, aqueous methanol. Both the supernatant and the washes tested negative for dissolved polymer. Drying was done in vacuum at 100°C. and the samples were stored in a desiccator.

The calcium salts were more difficult to prepare because of their intractibility. For low degrees of ionization (<30%) a solution of calcium acetate was used in the same procedure as described above. Larger amounts of salt and longer times were necessary than in the preparation of the monovalent salts. Calcium salts of stronger acids (CaCl₂) did not appear to work at all. For higher degrees
of ionization, it was necessary to run the reaction in a very dilute dispersion (~2%) for long times (ca. 3.0 hrs.). Even then, it was impossible to obtain ionization levels higher than 80%. No further attempts were made in this direction since the highly ionized polymers were so intractable and difficult to press into films for property studies.

4. Measurement of per cent ionization of the polymeric salts. The integrated absorbency per cm. sample thickness of the 1700 cm.\(^{-1}\) carbonyl band was used to determine the degree of ionization. Figure 1 shows the infrared spectra of four samples ionized to different levels with sodium. The absorbency, \(A\), is defined as \(\log_{10} \frac{I_0}{10I}\), where \(I_0\) is the incident, and \(I\) the transmitted intensity. The integrated absorbency corresponds to the area beneath plots of \(A\) against wave number (cm.\(^{-1}\)). For the 1700 cm.\(^{-1}\) band, the ratio \(S/\Delta \nu_{\frac{1}{2}}\), where \(S\) is the spectral slit width and \(\Delta \nu_{\frac{1}{2}}\) the absorption band half-width, was found to vary from about 0.13 for the acid copolymer to about 0.06 for the most highly ionized copolymer. Since the peak absorbencies did not exceed 0.8, the correction for instrument resolving power (about 1%) was considered negligible.

The success of the present technique for measuring degree
of ionization depends on the lack of overlap of neighboring bands and on accurate film thickness measurements. The intensity of the carbonyl absorption for the unionized acid copolymer is such that it is necessary to use a film of approximately \(1.27 \times 10^{-3}\) cm. thickness in order to get this absorption on scale. The following procedure was developed to measure the thickness accurately. A band was selected with an absorbency that could be measured from film thicknesses of about \(2.54 \times 10^{-2}\) cm. to thicknesses of less than \(1.27 \times 10^{-3}\) cm. An appropriate band for this is the \(935\) cm\(^{-1}\) band in the case of the unionized acid copolymer. This band is assigned to the out of plane deformation modes of the hydroxyl groups. Its absorbency should thus be proportional to the number of acid groups within the beam and should be independent of the thermal history of the sample. A plot was made of peak absorbency (\(A_{\text{max}}\)) versus thickness for this band. Thicknesses in the range of \(2.54 \times 10^{-2}\) to \(7.62 \times 10^{-3}\) cm. could be satisfactorily measured by a micrometer. This plot yielded a straight line which extrapolated through the origin. Thus it was established that Beer's law was obeyed. From this plot, the thickness of the films was determined, thus enabling the evaluation of
the integrated absorbency of the 1700 cm\(^{-1}\) band per unit sample thickness. In the case of the ionized samples a similar procedure was followed except that at the higher degree of ionization it was not necessary to employ very thin films and the thicknesses could be measured directly by the micrometer. The per cent ionization was then calculated using the relationship

\[
\% \text{ Ionization} = \left[ 1 - \frac{\text{integrated absorbency per cm. (ionized)}}{\text{integrated absorbency per cm. (Unionized)}} \right] \times 100.
\]

Table I lists the integrated absorbencies and the per cent ionization for the four sodium samples.

**Property Measurements**

1. **Preparation of films.** Films for property measurements were prepared by compression molding, generally at 150°C. for the acid copolymer and monovalent salts and 180°C. for the calcium salts. Mold pressure was usually about 10,000 psi for five minutes. The films were always prepared between two sheets of 10 mil Mylar backed by 25 ml steel plates. This was necessary in order to separate the polymer from the mold surface without tearing or straining
it, but was also done to prevent any unusual surface crystallinity effects resulting from cooling in contact with high energy metal surfaces. In some cases, especially for the mechanical and some infrared studies, thicker samples were required. Aluminum stock of suitable thickness was prepared by surface grinding and cavities cut through the stock. Thermal history was carefully controlled. For quenched samples the mold was removed from the press and immediately quenched in a large volume of dry ice-acetone. Annealed samples were prepared by heating in an oven at various temperatures and times, always under a flow of nitrogen. For the calorimetric study, the film samples were crimped into the DSC pans. Annealing was done in nitrogen purged containers in a silicone oil bath controlled at ±0.1°C. Quenching was done in liquid nitrogen.

2. Infrared absorption measurements. A Beckman spectrophotometer, Model IR-10 was used for determination of methyl branches, per cent ionization and the temperature-dependent behavior of the acid groups. The latter studies were made using a temperature enclosure constructed for this purpose. Temperatures were measured using a calibrated copper-constantan thermocouple which rested against the
polymer film surface.

A Perkin-Elmer grating spectrophotometer, Model 457 was used for determinations of crystallinity. In this method the degree of crystallinity of the acid copolymer is estimated from the extinction coefficients, $\epsilon_{1894}$ and $\epsilon_{2016}$ of the bands at 1894 cm.$^{-1}$ (associated with the crystalline phase) and 2016 cm.$^{-1}$ (containing both crystalline and amorphous components) respectively. The extinction coefficients are here defined as the peak absorbency per cm. sample thickness, where absorbency is defined as before. The volume fraction of crystallinity is given by:

$$X_c = \frac{\epsilon_{1894}}{6.4}$$

and

$$X_c = \frac{(\epsilon_{2016} - 2.1)}{6.0}$$

For the acid copolymer, the two values estimated by these equations were usually in fairly close agreement, but $X_c$ from $\epsilon_{1894}$ was always lower.

For the ionized polymers, the 1894 cm.$^{-1}$ peak was submerged beneath a broad peak centered at about 1940 cm.$^{-1}$. However, the band at 2016 cm.$^{-1}$ was fairly well resolved and the crystalline fraction was determined.

Since these absorptions are fairly weak ones, thick
samples were required. In this study, samples of about 0.07 cm. were used. Partly because of the thickness, the samples became heated in the beam and initial results were poor. A thermocouple molded into the sample showed that temperatures were about 60°C. It is possible that this could affect results since these absorptions have been shown to be temperature sensitive. To minimize the temperature effect, the samples were cooled while in the beam by directing a slow flow of precooled nitrogen on them and by scanning only that portion of the spectrum of interest to this study. In this way, sample temperatures never exceeded 30°C. "Slow" scanning speed (100 cm.⁻¹ per minute above 2000 cm.⁻¹ and 50 cm.⁻¹ per minute below 2000 cm.⁻¹) gave the best results.

3. Dynamic mechanical properties measurements. Two types of apparatus were sued in this study. Initial work was done on a torsion pendulum at the Monsanto Co. This apparatus was constructed by D. M. Sullivan from the design by Nielsen. A sketch of the apparatus is given in Figure 2. Samples were rectangular with nominal length, width and thickness dimensions of 3.0 inch, 0.35 inch and 0.05 inch, respectively. Determinations were made over a
wide temperature range, typically -150° to +100°C., at a nominal frequency of 1 Hz. The oscillations were recorded on a Sanborn 321 oscillograph.

The torsion pendulum measures shear modulus. The complex shear modulus is given by:

\[ G^* = G' + iG'' \]

Here, \( G' \) is the elastic or storage component; \( G'' \) is the nonelastic or loss component. The real part of the complex shear modulus, \( G' \), is calculated using the following equation:

\[ G' = \frac{(38.54)(L)(I)}{(c)(d^3)(\mu)(p^2)} \]

where, 
- \( L \) = sample length, inches
- \( c \) = sample width, inches
- \( d \) = sample thickness, inches
- \( \mu \) = dimensionless shape factor, function of \( c/d \)
- \( I \) = moment of inertia of the disc, gms.-cm.²
- \( p \) = period of oscillation, seconds.

Thus, \( G' = K/p^2 \), where \( K \) is a constant for a given sample.

The logarithmic decrement, \( \Delta \), is a function of the ratio of the imaginary to the real part of the complex shear modulus:
\[ \Delta = \pi \left( \frac{G''}{G'} \right) \]

It is calculated by taking the logarithm of the ratio of amplitudes of two successive oscillations. Thus,

\[ \Delta = \ln \frac{A_n}{A_{n+1}} \]

where \( A_i \) = the amplitude of the \( i \)th oscillation. In practice, several values of \( \Delta \) can be calculated from the oscillatory damping curve at each temperature point. The values are then averaged to increase precision.

Additional work was done on a Vibron Dynamic Visco-elastometer (Toyo Measuring Instrument Co.), Model DDVII. The temperature range for these measurements was from -190\(^o\)C to about +90\(^o\)C. Measurements were made at a constant frequency of either 3.5, 11 or 110 Hz.

The Vibron measures the complex tensile, or Young's, modulus:

\[ E^* = E' + iE'' \]

where, \( E' \) = the elastic modulus, and \( E'' \) = the loss modulus.

The damping function \( \tan \delta \) is simply:

\[ \tan \delta = \frac{E''}{E'} \]
The tan $\delta$ is read directly from the Vibron; the real and imaginary parts of the complex modulus are calculated as follows:

$$E' = E^* \cos \delta$$
$$E'' = E^* \sin \delta$$

4. X-ray measurements. Crystallinities were determined by an X-ray radial scan method using both copper and molybdenum targets. The instrument used was a North American Philips, water-cooled, X-ray Diffraction Unit, Type 1205. The per cent crystallinity was calculated by decomposition of the peaks in a plot of intensity versus Bragg angle into crystalline and amorphous contributions.\(^{102}\)

5. Calorimetric measurements. Measurements of crystallinity were carried out on a Differential Scanning Calorimeter (DSC, Perkin Elmer Model IB). The instrument\(^{103}\) and the technique\(^{104}\) of measuring heats of fusion have been described in detail. Samples were cut from films with a cork borer to a size which would just fit into the aluminum cup provided by the instrument maker. The samples (3-6 mg.) were weighed accurately on a micro-analytical balance to $10^{-5}$ gms. and the cover sealed on with a crimping device. The samples were then melted in a nitrogen
atmosphere at 150°C. for one hour. Quenched samples were removed from the oven and immediately placed in liquid nitrogen. Annealed samples were removed from the oven and placed in small vials containing silicone oil which had been equilibrated in a bath at the annealing temperature. These vials were immediately placed back in the bath and if long annealing times were involved, purged with a stream of nitrogen before sealing the cap. After annealing, the cups were removed and quenched in liquid nitrogen.

Samples were run on the DSC immediately after quenching or annealing. Rate of heating was 10°C./min. from room temperature to 150°C. The melting endotherms are usually observed starting at about 50°C. to about 105°C., depending on the nature of the sample. The samples were then cooled at 10°C./min. to observe the crystallization exotherm.

The DSC temperature scale was calibrated for a given set of instrument settings and using a heating rate of 10°C./min. A set of four Fisher Calorimeter Standards was used for calibration in the temperature range of interest. All temperatures reported are corrected according to the calibration.
Apparent heats of fusion $\Delta H_f^*$, were determined by comparing the area under the experimental curve with the area for a known amount of indium. The following equation was developed for these calculations.

$$\text{% Crystallinity} = \frac{(W_I) (\Delta H_f^I) (A_S) (R_S)(100)}{(W_S) (\Delta H_f^{PE}) (A_I) (R_I)}$$

where, $W$ is the weight of material in mg., $\Delta H_f$ is the heat of fusion millicalories/mg., $A$ is the area under the melting curve, $R$ is the recorder range, and the $I$ and $S$ refer to indium and sample, respectively.

The $\Delta H_f^I$ of indium was taken as 6.8 mcals./mg. The $\Delta H_f^{PE}$ of 100% crystalline polyethylene was estimated as 66 mcals./mg. Since, for a given calibration run, $W_I$, $A_I$ and $R_I$ are constants, the formula becomes:

$$\text{% Crystallinity} = \frac{K(A_S)(R_S)}{W_S}$$
CHAPTER III

INFRARED STUDIES ON THE NATURE OF THE CARBOXYLIC GROUPS

Temperature Dependence of Hydrogen Bonding

The results of the temperature dependent infrared studies on the unionized copolymer are shown in Figure 3. Of interest are the appearance of a band at 3540 cm\(^{-1}\) which increases in magnitude with increasing temperature, and the appearance of a shoulder at 1750 cm\(^{-1}\) on the main 1700 cm\(^{-1}\) carbonyl band which also increases with increasing temperature. Such behavior is characteristic of low molecular weight carboxylic acids in non-polar solvents and is interpreted on the basis of a monomer-dimer equilibrium. Thus the 3540 cm\(^{-1}\) band is attributed to the free hydroxyl stretching vibration, the 1750 cm\(^{-1}\) band to the monomeric carbonyl stretching vibration, and the 1700 cm\(^{-1}\) band to the dimerized carbonyl stretching vibration. Figure 4 shows the peak absorbance per cm. film thickness for the 3540 cm\(^{-1}\) absorption as a function of temperature. From this plot it is evident that free hydroxyl groups are first detected by infrared at about 30°C. The above results lead to a structure for the copolymer in which the acid groups
are dimerized to form interchain links. The dimerization is essentially complete at room temperature. This structure may be schematically represented as

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{O} \\
\text{O} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

The dissociation constant, \( K \), is defined by

\[
K = \frac{[\text{COOH}]}{[\text{COOH}]^2}
\]

where \([\text{COOH}]\) is the concentration of monomeric carboxyl groups and \([\text{COOH}]^2\) is the concentration of dimerized carboxyl groups. \( K \) was evaluated from the spectra in Figure 3. This was accomplished by measuring the peak absorbencies of the 1700 cm.\(^{-1}\) and 3540 cm.\(^{-1}\) bands at each temperature (54°-99°C.). At 99°C., the 1750 cm.\(^{-1}\) band was sufficiently well resolved so that its peak absorbency could be measured using a baseline determined as indicated in Figure 3. The ratio of this absorbency to that of the 3540 cm.\(^{-1}\) free hydroxyl band was obtained at 99°C. This ratio was assumed independent of temperature and thus the
absorbencies of the 1750 cm.\(^{-1}\) band at the other temperatures could be derived from the measured absorbencies of the 3540 cm.\(^{-1}\) band at these temperatures. If the peak absorbencies are expressed as absorbencies per centimeter, the following relationships can reasonably be assumed to apply:

\[
A_1 \text{ max} = \epsilon_1 C_1 \quad (1)
\]
\[
A_2 \text{ max} = \epsilon_2 C_2 \quad (2)
\]
\[
\epsilon_2 = 2\epsilon_1 \quad (3)
\]

where \(A_1 \text{ max}\) is the peak absorbency per centimeter of the 1750 cm.\(^{-1}\) band, \(\epsilon_1\) is the molar extinction coefficient of the 1750 cm.\(^{-1}\) band in cm.\(^2\) mole\(^{-1}\), \(C_1\) is the concentration in moles per cm.\(^3\) of the monomeric carboxyl groups, \(A_2 \text{ max}\) is the peak absorbency per centimeter of the 1700 cm.\(^{-1}\) band, \(\epsilon_2\) is the molar extinction coefficient of the 1700 cm.\(^{-1}\) band in cm.\(^2\) mole\(^{-1}\), and \(C_2\) is the concentration in moles per cm.\(^3\) of the dimerized carboxyl groups. Equation (3) is justified by the work of Chang on the model system pivalic acid in benzene. It was found that the molar extinction coefficient for the dimer in this system is almost exactly twice the molar extinction coefficient for the
monomer.  Using equations (1), (2) and (3), the expression for the dissociation constant becomes

$$K \text{ (moles/cm.}^3\text{)} = \frac{(A_{1, \text{ max}})^2}{(A_{2, \text{ max}}) \epsilon_2} \quad (4)$$

$\epsilon_2$ can be determined using equation (2), substituting the value of the peak absorbance per cm. of the 1700 cm.$^{-1}$ band at room temperature and the known concentration of the methacrylic acid groups in the copolymer. It is interesting to note that the value thus obtained, $9.14 \times 10^5$ cm.$^2$ mole$^{-1}$, compares quite favorably with the value of $12.6 \times 10^5$ cm.$^2$ mole$^{-1}$ obtained for the pivalic acid-benzene system. Small differences would be expected, of course, between values obtained from different spectrometers owing to differences in resolving power, scanning speed, etc.

The logarithms of the dissociation constants are plotted as a function of reciprocal temperature in Figure 5. The open circles are the experimental points while the cross represents the value for the dissociation constant of unconjugated carboxylic acids in carbon tetrachloride measured by Wenograd and Spurr. The heat of dissociation of 11.6 kcal. mole$^{-1}$ obtained from the slope of the van't Hoff plot in Figure 5 also agrees well with literature
values for low molecular weight carboxylic acids in non-polar solvents. Thus, it may be concluded that the association of the acid groups of the copolymer is quantitatively comparable to the dimerization of low molecular weight carboxylic acids in non-polar solvents. It was further established that the peak absorbency of the 3540 cm.\(^{-1}\) free hydroxyl band is in inverse proportion to the degree of ionization. This means that the monomer-dimer equilibrium of the remaining carboxyl groups is unaffected by ionization of a portion of the carboxyl groups.

**Infrared Dichroism in the Acid and Ionized Copolymers**

The results of the infrared dichroism studies are presented in Figure 6. Attention is directed to the 720-730 cm.\(^{-1}\) region. In the case of the unionized copolymer, the unpolarized band in this region consists of a doublet with absorption maxima at 720 and 730 cm.\(^{-1}\). Such behavior is characteristic of polyethylene and it has been shown\(^{110}\) that the 720 cm.\(^{-1}\) band is due to both the amorphous and crystalline phases, the crystalline component being polarized along the a crystallographic axis. On the other hand, the 730 cm.\(^{-1}\) band is due entirely to the crystalline phase.
and is polarized along the b crystal axis. Both the 720 cm.\(^{-1}\) and 730 cm.\(^{-1}\) bands thus show perpendicular dichroism when the polymer is extended. Turning to the 70\% ionized copolymer, it can be seen that the 730 cm.\(^{-1}\) band has entirely disappeared in the parallel polarized spectrum but appears as a shoulder on the main 720 cm.\(^{-1}\) band in the perpendicularly polarized spectrum. It is thus apparent that even at 70\% ionization, a significant amount of crystallinity remains. It can also be seen that the shoulder around 2650 cm.\(^{-1}\) characteristic of the hydrogen bonded hydroxyl group shows perpendicular polarization. This indicates that the transition moment of the hydrogen bonded hydroxyl group is perpendicular to the main chain and is thus evidence for the presence of intermolecular hydrogen bonds in the acid dimers present. In this connection it is interesting to note that the parallel dichroism of the hydrogen bonded 3350 cm.\(^{-1}\) hydroxyl band in isotactic polyvinyl alcohol has been cited as evidence for intramolecular hydrogen bonding in this polymer.\(^{111}\)

Figure 7 shows a plot of the dichroic ratio (defined as \(D = \frac{A_{||}}{A_{\perp}}\)) versus per cent extension for three bands of the 70\% ionized copolymer. The 720 cm.\(^{-1}\) band shows rela-
tively large perpendicular dichroism, emphasizing the significant crystalline contribution to this band. Both the 1700 cm$^{-1}$ and 1560 cm$^{-1}$ bands show relatively small perpendicular dichroism. This is consistent with the presence of the carboxyl groups and carboxylate ions in the amorphous phase since they would be expected to be too large to be incorporated into the polyethylene crystal lattice. The perpendicular dichroism of the 1560 cm$^{-1}$ band indicates that the carboxylate ions have a preferred orientation out of the plane of the main chain. This can be seen schematically as

\[ \begin{array}{c}
\text{C} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \]

As shown, the transition moment direction for the asymmetric stretching mode would be parallel to the main chain if the carboxylate groups were in the plane of the main chain. The out-of-plane orientation of the carboxylate ions may be due to steric hindrance arising from neighboring carboxylate or carboxyl groups. Work to be discussed later suggests that the carboxylate groups do segregate together. Thus, even though the polymer probably has a random composition distribution, in the ionized state the
carboxylate groups may well have an out-of-plane orientation due to their interaction.
CHAPTER IV
THE CRYSTALLIZATION BEHAVIOR

Introduction

The bulk crystallization behavior of polyethylene has been studied extensively by many authors, but much of this work has been on linear or only slightly branched homopolymer. The crystallization of more highly branched homopolymer and semi-crystalline copolymer systems is not as well described. A theoretical treatment by Flory\textsuperscript{144} shows that irregularities in the polymethylene chain (e.g. comonomer units) have a depressing effect on the melting temperature of the crystalline phase. Various studies\textsuperscript{145} have shown that branch points and comonomer units also result in a reduction in the degree of crystallinity and increase the breadth of the melting curve. Much of the theory developed in work on linear polyethylene has been applied to the bulk crystallization of branched and copolymerized ethylene polymers. However, because of the generally non-equilibrium thermodynamic state, and often unusual kinetics, theoretical treatments are viewed with caution and the application of such treatments is difficult.
As the present studies will indicate, the ionomers are no exception to the last statement. The crystallization behavior of ionomers was first described briefly by Rees.\textsuperscript{76} He showed that progressive ionization increased the optical clarity, apparently by reduction of spherulites. Samples of quenched and annealed acid copolymer (similar in composition to the samples used in this work) and the annealed sodium salt had about the same level of crystallinity (ca. 30\%, X-ray) but the quenched salt was low (ca. 10\%). In a similar copolymer, Otocka and Kwei\textsuperscript{82,83} found low levels of crystallinity by DSC (ca. 10\%) even after annealing. They also observed that as the acid content increased, the T_m decreased, with ionization decreasing the melting points still further.

In this thesis, the crystallization behavior was examined to help elucidate the morphology of the polymer. Crystallinity was generally determined by DSC techniques but an infrared method and X-ray were also used.

**Calorimetric Studies**

1. **Discussion of errors.** The apparent heat of fusion, \( \Delta H_f^* \), was determined from the areas under the melting
curves. It proved to be quite difficult to do this with high precision in most cases, partly because of the low degrees of crystallinity but particularly because of the broad endotherms. Others $^{82,83}$ have made this observation when examining ionomers and arbitrarily chose a temperature of 60°C as the onset of melting. The baseline was then constructed from this point. This method appears to introduce error, however, since the initial melting point changes significantly depending on the sample and its thermal history. In this work, the baseline was constructed in the following manner: the slopes of the recorded trace, well before and well after any melting, were approximated with a straight edge and a line drawn. The slopes before and after melting were distinctly different, probably due to the change in heat capacity of the sample. The points of departure of the recorded trace from the drawn lines were taken as the initial and final melting temperatures. A straight line was then drawn between these two points to serve as the baseline for the melting region. While this technique is probably a good approximation to the real baseline, it is recognized that some error is introduced, especially for samples of low crystallinity and broad endotherms. A limited study of
reproducibility and the errors involved indicated the range of probable error in $\Delta H_f^*$ measurements to be about $\pm 10\%$ for samples with $X_C < 0.10$ ($X_C =$ weight fraction crystallinity) and $\pm 8\%$ for samples with $X_C > 0.10$. The errors are believed to be in the following order of decreasing importance:

a. construction of the baseline,

b. measurement of the area,

c. weight of sample.

In all but a few cases, event temperatures could be estimated from the curves with a good degree of accuracy. $T_m$ (the temperature at maximum excursion from the baseline), $T_f$ (the temperature of final melting), and $T_C$ (the temperature at the maximum in the recrystallization exotherm) are all good to $\pm 1^\circ C$. $T_i$ (the temperature of initial melting) was, in many cases, more difficult to determine precisely and was only approximated in this work. When stated, the estimated error range of $T_i$ is included, e.g. $T_i$ ($\pm 2^\circ$).

2. The melting curves. The melting curves for quenched and annealed samples could be classified into three types, depending on the number of peaks present. An example of each of these types is shown in Figure 8. Type A endotherms have one peak; all quenched samples and
samples annealed above the $T_m$ were of Type A. The breadth of the peaks increased with increasing degree of ionization and were especially skewed towards the low temperature side.

Type B endotherms have two peaks; these occur in samples of acid and low degrees of ionization when annealed at temperatures near or somewhat (ca. 10°C.) below the main $T_m$. The lower temperature peak increased in temperature with annealing, tending to merge with the main peak at long annealing times.

Type C endotherms have multiple (generally three) peaks and occurred when annealing was done at high degrees of supercooling (ca. 20°C.) in samples of the acid and low degrees of ionization. Longer annealing times tended to merge the lower peaks into the main melting peak.

Data on the quenched samples are given in Table II. In the calcium samples, only that of low ionization was studied since higher degrees of neutralization produced samples with $\Delta H_f^*$ so low and endotherms so broad that they could not be measured with satisfactory precision.

The data given in Table II show some interesting features of the ionomer system. There is very little difference between the unionized sample and those contain-
ing monovalent cations, with regard to both degree of crystallinity and \( T_m \). The acid polymer has a slightly higher crystalline content; inspection of the melting ranges suggests that this is due to the additional formation of more low melting crystals when compared with the sodium salts. The calcium salt is seen to have both a significantly lower crystallinity and lower \( T_m \).

Annealing produces some interesting results in these copolymers. The annealing procedure is diagrammed in Figure 9. As described in the Experimental section, all samples were melted in sealed DSC cups under nitrogen at 150°C. The samples were then placed in a bath at the annealing temperature. After the specified time, these samples were quenched in liquid nitrogen and run on the DSC. The melting curves for the acid and highly ionized sodium salt annealed for various times at 85°C. are shown in Figures 10 and 11. Table III gives data on the melting behavior after 70 hours of annealing at 85°C. (ca. 10° supercooling). The \( T_m \) is observed to increase slightly in all cases with a significant reduction in the melting range. Since \( T_f \) is approximately the same as in the quenched samples, this smaller melting range obviously involves only the
lower melting crystalline regions. This is confirmed by comparing the $T_i$'s for the quenched and annealed samples. A significant increase in $T_i$ is seen for all samples, with the acid having the largest increase.

A most unusual effect is seen for the change in crystallinity on annealing. With the exception of the acid, which is about the same, all samples show lower degrees of crystallinity. This is especially remarkable in view of the increase in $T_m$. To investigate the effect of annealing further, the crystallinity was calculated for samples annealed for various times at 85°C. The results are shown in Figure 12. Here, the surprising nature of the annealing process is seen clearly. Crystallinity of all samples actually decreases to some minimum value with increasing annealing time. In the case of the sodium salts, the crystallinity at the minimum decreases with increasing ionization. At longer times, the crystallinity begins to slowly increase except for the calcium salt. This is in distinct contrast to the behavior of branched polyethylene and other crystallizable polymer systems which have always been found to increase in crystallinity when annealed at temperatures below the melting point. Since the crystal-
lizable portion of the ionomers are, in fact, polyethylene segments, this behavior suggests that the acid and ionic groups in the melt and amorphous phase have a profound effect on the crystallization kinetics.

To characterize the crystallization behavior further, the effect of annealing temperature was studied. Annealing was done above the melting point (110°C.), near the melting point (95°C.), and at a low temperature (75°C.) corresponding to a supercooling of about 20°C. Annealing at 110°C. gave curves similar in all respects to the quenched samples. Very little change in degree of crystallinity was found. Samples annealed near the melting point were generally of Type A and showed a continuous decrease in crystallinity with annealing time. The only exceptions were the acid and 21% ionized sodium samples. In these, the crystallinity started to increase with longer annealing times similar to the observations made at 85°C. In addition, these samples showed a gradual increase in a separate crystalline peak at 102°C. at long annealing times. This was not found in any other samples or under any other conditions. Samples annealed at 20°C. supercooling developed additional peaks on the low temperature side of $T_m$ (Type C). These peaks
increased slightly in magnitude and moved to higher temperatures as annealing time increased. Otherwise, the effect of annealing time was similar to that observed at 85°C., i.e. crystallinity decreased initially followed by a slow increase at longer time. In all of these studies, annealing at different temperatures had a negligible effect on the $T_m$ of the major melting exotherm. This is shown by the tabulation of data in Table IV. The most important effect of annealing is on the shape of the curve on the low temperature side of $T_m$. The low temperature melting crystallites are progressively reduced and the main melting peak sharpened. The effect of annealing temperature on degree of crystallinity is very small, if not negligible, in comparison with the effect of time. However, maximum crystallinity and observed $T_m$ seem to occur at annealing temperatures of about 85°C., i.e. at about 10°C. supercooling.

Finally, recrystallization exotherms were observed. In the DSC runs, the samples were heated to 150°C., then immediately cooled to room temperature at 10°C./min. The recrystallization temperature, $T_c$, depended only on the cation and ionization level and not on the previous thermal histories of the samples. These data are shown in Table V.
and are considered very accurate since the values in each case are based on averages of dozens of values and the range is within $\pm 0.5^\circ C$. It is interesting to note that $T_c$ increases slightly with a low degree of ionization with monovalent sodium, but then drops rapidly with increasing ionization levels. The divalent calcium salts show an even more drastic effect in decreasing $T_c$, even at a low ionization level.

3. Discussion of the crystallization behavior. The $T_m$ for both the acid and salts was found to be in the range 96-99$^\circ C$. for samples annealed below $T_m$. As pointed out in the discussion on errors, it may well be that this range represents error only since the deviation from the mean value is expected to be 97.5$\pm$1.0$^\circ C$. This value seems quite low for a polymer containing 96 mole per cent ethylene. Flory has treated the case of melting point depression in semicrystalline polymers. An equation was developed which depends on the distribution of the noncrystallizable comonomer units in the polymer chain:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R}{\Delta H_f} \ln p$$
where $T_m^0$ is the equilibrium melting point of the pure crystallizable monomer units, in this case polyethylene = 415°K, $T_m$ is the equilibrium melting point of the copolymer, $R$ is the gas constant, $\Delta H_f$ the heat of fusion of the crystallizable component, and $\ln p$ is defined as the probability that an ethylene unit will be succeeded by another ethylene unit regardless of the previous sequence composition. If the copolymer is strictly random (a good assumption for the ionomer) then $p$ can be identified with $X$, the mole fraction of crystallizable $-\text{CH}_2-$ units. Thus,

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_f} \ln X.$$

This equation was used to estimate the theoretical equilibrium melting point of the ionomer for comparison with the observed melting points. The assumption that the acid groups are totally excluded from the crystals is justified by the works of Otocka and Wunderlich. Two separate calculations were made which took into account the two different ways branches (other than comonomer units) may affect the results. It has been shown that branched polyethylene does not follow the Flory equation exactly when branch points are considered as comonomer units in the
calculation. Presumably, some of the branches rather than acting as noncrystallizable "comonomer" units are small enough to be incorporated in the lattice without interruption of crystal growth. For this reason the Flory equation was applied to two cases:

Case A. Branch points considered as noncrystallizable comonomer units;

Case B. Branch points capable of being cocrystallized.

The results of these two calculations will then represent a minimum and maximum theoretical $T_m$, respectively, depending on the effect of branches. The calculated values are

Case A = 118°C.

Case B = 127°C.

These values are significantly higher than both the observed melting temperatures, $T_m$, and final melting temperatures, $T_f$. Since the $T_m$ is dependent on the lamella thickness, this means that acid and ionic groups in some way interfere with the development of the expected lamella growth. Furthermore, the data in Tables II - IV show that annealing affects mainly the lower melting (smaller)
crystallites. The effect is most noticeable in the acid, becoming less as the ionization level increases. This can be interpreted as a reduction in the number of metastable, small crystallites in favor of crystal sizes of equilibrium size. Since this happens more readily at lower degrees of ionization than at the higher levels, it must be concluded that transport of the material necessary for lateral growth of equilibrium crystals is made more difficult by ionization. It is important to note that the reduction in smaller crystallites follows a trend in reduction in crystallinity with annealing (Figure 12).

The minima observed in the curves of crystallinity versus isothermal annealing time are a principal result of this study and require explanation. The first point to be emphasized is that rapid quenching from the melt produces a relatively high level of crystallinity and many small crystals. Secondly, interruption of the quenching at some temperature and then isothermally annealing for a given time produces generally lower crystallinity but many fewer small crystals. Thirdly, recrystallization temperatures tend to decrease with increasing ionization and are markedly lower for the divalent salts. All of these features can
be accommodated by a mechanism involving competing phase separation and its effect on secondary crystallization. In the melt at 150°C., the association between acid groups and ionic groups is of low order. This has been well established for the acid copolymer by the temperature dependent infrared work. In the case of the ionized groups, melt rheology work suggests a rapidly decreasing order of association above 100°C. In the solid state at room temperature, the acid groups are dimerized and the ionic groups associated in some way. In this thesis, it is proposed that ions segregate into domains as a thermodynamic state more favorable than their existence as isolated entities in the amorphous region. This proposal has also been made by others, and confirmed in a theoretical treatment. In a later section, dynamic mechanical data will also support this argument.

This means that at the annealing temperature there are two competing exothermic processes: one is the association of acid groups to form dimers (\(-\Delta H = 5.9 \text{ kcal/mole acid groups}\)), or ionic groups to form phases (\(-\Delta H > 10 \text{ kcal/mole ionic group}\)); the second is crystallization of the ethylene groups onto a crystal surface (\(-\Delta H = 1.85 \text{ kcal/mole}\).
Thus, strictly on the basis of enthalpy change, the formation of one acid dimer would be favored over the crystallization of six ethylene units and the association of two ionized carboxylate groups would be favored over crystallization of more than ten ethylene units. Since, for a random copolymer with only 4 mole % co-monomer groups, ionic phase segregation will no doubt involve long range diffusional motions of the chains, rapid quenching minimizes the extent of acid dimerization and ionic phase segregation. Crystallization, on the other hand, can occur very rapidly and, although it may lead to many small crystallites, can develop to moderately high levels. Thus, the quick quenched samples are found to have significant levels of crystallinity including a large population of smaller size. When the cooling process is interrupted and isothermal annealing conducted, long range diffusion of the chains can then take place to perfect the highly stable phase segregation. When this occurs, the ethylene units are placed in a more highly strained state and somewhat restricted in their ability to move to the surface of growing crystals. In thermodynamic terms, this can also be viewed as a decrease in entropy of the amorphous chains, resulting
in decreased driving force for crystallization. Therefore, when these samples are quenched, the smaller crystallites are unable to form in the time scale available. Thus, an annealed sample may have a lower level of crystallinity because of the reduction in entropy and transport velocity of the ethylene segments restricted by perfected phase segregation.

An interesting apparent exception to this mechanism is the sodium salt of low ionization. This sample always has a degree of crystallinity, $T_m$, and $T_c$ similar to the acid which, at first glance, might be unexpected based on the proposed mechanism. This behavior may be readily explained by considering that low degrees of ionization are not sufficient to cause favorable rates of phase segregation. However, the reduction in the number of potential acid dimers by virtue of neutralization, allows greater mobility to the neighboring ethylene segments in the chain, leading to the observed effects. The divalent calcium salts are probably much more effective in reducing segmental mobility since they may serve as pseudo-crosslinks. Thus, crystallinity increases only very slowly, even at long annealing times, and the crystallization process has been slowed considera-
bly as evidenced by the low $T_c$.

Some further comments may be made with regard to the crystallization process. Because of the relative constancy of the main $T_m$ for all samples, regardless of whether quenched or annealed, these crystals are regarded as being of equilibrium thickness. This size is governed by the number of defects in the chain (constant in all samples) and can be considered the result of primary nucleation and growth. The smaller crystals which melt at lower temperatures, however, are greatly affected by ionization and annealing conditions and are considered the result of secondary crystallization. This has been shown by Schultz and Scott\textsuperscript{148} to be due to heterogeneous nucleation in the amorphous zone of polyethylene followed by diffusion controlled growth. This explanation fits with the observations that higher ionization levels depress the crystallinity on annealing, and that calcium salts have very low rates of secondary crystallization, since the salts have higher melt viscosities and, presumably, lower rates of segmental diffusion.

Finally, this proposed mechanism can now be compared with the morphological behavior found by others in the
ionomers. As mentioned earlier, others\textsuperscript{76,80} found that the haze level was reduced considerably on ionization and spherulitic structure was eventually destroyed even for annealed samples. In view of the results presented here, this must mean that the significant effect of ionization is reduction in the radial growth of the folded chain lamella in a continuous twisted strand necessary for spherulite formation. This again fits with the idea that ionization reduces the diffusion of chains sufficiently to prevent long range growth especially during secondary crystallization.

In this picture, the ethylene segments can form fairly thick lamella of some equilibrium thickness, given sufficiently long times of annealing to account for the reduced rate of diffusion in the amorphous phase. However, lateral or radial growth of the lamella is limited due to the restrictions in order imposed by the ionic domains.

\textbf{Crystallinity Determination by Infrared}

Read and Stein\textsuperscript{99} developed a technique for determining the volume fraction of crystallinity, $X_v$, in polyethylene which was later applied by Read\textsuperscript{91} to the acid and ionized copolymers from this study. The procedure was described in
the experimental section. Since the degrees of crystallinity found by calorimetry were so low, and since X-ray measurements (to be discussed in the next section) gave much higher values, it became important to determine crystallinity by another method. The results are shown in Table VI and compared with crystallinity determined by DSC. For the acid copolymers of varying thermal history, the results are in fair agreement. In the case of the ionized copolymers, there is a significant difference when the samples are quenched. For annealed samples there is fairly good agreement. It is possible that the discrepancy is due to the relatively high fraction of smaller sized crystalline regions in the quenched salts and the inaccuracies inherent in determining the absorbency of the small 2016 cm\(^{-1}\) peak.

Crystallinity by X-ray*

In an early part of this work, crystallinity was determined by X-ray. The procedure involves analysis of plots of scattering intensity versus Bragg angle. The crystalline

*The author is grateful to Dr. Tisato Kajiyama for these calculations.
contribution to the peak area was estimated after drawing a baseline representing amorphous scattering. The masses of the amorphous and crystalline regions are obtained by integration.

\[ m_a = k_a \int_{2\theta_1}^{2\theta_2} I(\theta_a) \, d\theta \]

where \( m_a \) is the mass of the amorphous region and \( I(\theta_a) \) the amorphous scattering intensity.

\[ m_c = k_c \int_{2\theta_1}^{2\theta_2} I(\theta_c) \, d\theta \]

where \( m_c \) is the mass of the crystalline region and \( I(\theta_c) \) the crystalline scattering intensity. These equations are, of course, only valid if the two-phase model for the structure of a semicrystalline polymer is applicable. In addition, if it is assumed that the ratio of the proportionality constants \( k_a/k_c \) is unity, the weight fraction crystallinity is
The results are given in Table VII. The samples studied were both quenched and annealed (90°C., 24 hrs., slow cooling over 8 hrs. to room temperature) at various levels of ionization. Three major differences are observed when these data are compared with DSC and IR methods: the level of crystallinity is much higher, there is a much larger difference between the quenched and annealed samples and the annealed samples may increase slightly with ionization. The data are shown in Figure 31. At the present time the reasons for this difference are unknown and deserve further work. It could be speculated that relative to DSC, the X-ray technique is not measuring "more" crystallinity but, in fact, "less" amorphous scattering. This is possibly a reasonable hypothesis because phase segregation and acid dimerization at the measurement temperature may affect the order of at least part of the polyethylene segments in the amorphous state. That ionization leads to some ordering has been shown by low angle X-ray measurements. 90 Thus,
estimation of the amorphous scattering by measurements in the melt may not truly represent that scattering at room temperature.
CHAPTER V

STUDIES OF THE DYNAMIC MECHANICAL RELAXATIONS

Introduction

Considering the low acid content and the number of branches in these copolymers, it might be expected that the mechanical relaxations of the material would be similar to those observed in low density polyethylene at the same frequency. The latter polymer exhibits three loss peaks below its melting region.\textsuperscript{112} The $\alpha$ relaxation at about 50°C, the $\beta$ relaxation at about -20°C, and the $\gamma$ relaxation at about -140°C. These relaxations have been investigated by numerous authors.\textsuperscript{113} The $\alpha$ peak seems to be due in part to motion in both the amorphous and crystalline phases.\textsuperscript{114-117} The magnitude of the $\beta$ relaxation in branched polyethylene definitely depends on the concentration of branches present and is thus associated with them. On the basis of the results of several authors\textsuperscript{118-120} the motion responsible for the $\beta$ peak seems to be microbrownian segmental motion involving the branches and occurring only in the amorphous phase. In other words, it is a type of glass transition and may be thought of as the glass transition of the co-
polymer consisting of ethylene sequences and branches. The \( \gamma \) relaxation has been attributed to motions of short methyl-ene sequences but there is considerable confusion in the early literature as to the phase in which it originates. With this discussion as a basis, it is now possible to turn to the relaxation observed in the acid copolymer and its salts.

The Dynamic Mechanical Relaxation Spectra

Curves of the effect of temperature on storage modulus, \( G' \), for the acid copolymer and progressively ionized sodium salts are shown in Figures 13 and 14 for quenched and annealed samples, respectively. For these samples, annealing was done at 95°C. for 3.5 hours followed by slow cooling to room temperature over a period of 7-8 hours. Figure 13 shows that the moduli for the quenched samples at any given temperature are depressed with increasing degree of ionization. Annealed samples, however, do not show as big a difference except in the region of 0°C. This indicates that there is an energy absorption occurring around the 0°C region, it being particularly pronounced in the annealed samples, and that the energy absorption appears to grow
stronger with increasing ionization. To examine polymer absorption mechanisms in more detail, the mechanical damping function, or logarithmic decrement, $\Delta$, is plotted in Figures 15 and 16. The effect of ionization is clearly seen for the quenched samples in Figure 15. The unionized acid copolymer exhibits a single, strong loss peak at about $25^\circ C$. As ionization increases, an additional loss peak, designated $\beta$, starts to develop at about $-10^\circ C$. It is clear that the $\beta$ peak increases in magnitude with increasing ionization. Furthermore, the higher temperature peak appears to increase in both magnitude and temperature. In all cases, the onset of a low temperature loss peak at about $-130^\circ C$ may be seen. This is clearly due to the so-called $\gamma$ relaxation, observed also in polyethylene. However, the temperature range of these experiments was insufficient to resolve the $\gamma$ relaxation; this will be dealt with more fully later.

Turning to the annealed samples, Figure 16 shows that the high temperature peak for the unionized acid copolymer splits into two peaks with maxima at $50^\circ C$ and $25^\circ C$, designated $\alpha$ and $\beta'$, respectively. The $\alpha$ relaxation moves to higher temperatures with increasing ionization, as in the quenched samples. The reason for splitting of the $\alpha$
peak in the 78% ionized sample is not understood but may be due to the inadvertent presence of a small amount of absorbed moisture. Water pickup is difficult to prevent in highly ionized samples; its effect on the α peak will be discussed later. The β' relaxation decreases in magnitude with increasing ionization and has virtually disappeared at 60% ionization.

The loss moduli, G'', are plotted as a function of temperature for these same two sets of polymers in Figures 17 and 18. Owing to the decrease of G' with increasing temperature, these plots have the usual effect of de-emphasizing the magnitude of the α peak and enhancing that of the γ peak relative to the Δ plots, since

\[ G'' \sim \left( \frac{G'}{\pi} \right) \Delta \]

Otherwise the same trends are noted with the β and β' peaks as in the case of the Δ plots except that a small β peak appears as a low temperature shoulder on the main β' peak of the unionized acid copolymer.

The relaxation behavior was examined further using the Vibron (dynamic tensile modulus). Plots of the damping function, tan δ, are shown in Figures 19 and 20 for
quenched and annealed lithium salts and in Figures 21 and 22 for the corresponding calcium salts. These curves confirm the general behavior observed on the torsion pendulum (dynamic shear modulus). The temperature of the peak maxima are almost exactly the same for comparable samples despite the differences in test methods. The test frequency for the data plotted in Figures 19-22 was the lowest available, 3.5 Hz, to facilitate comparison with the torsion pendulum data.

Test temperatures were low enough to scan the low temperature $\gamma$ peak completely. This relaxation was observed in all samples and its existence at about the same temperature as in polyethylene was confirmed in these tests. Examination of the quenched samples again shows that the $\beta$ relaxation is absent in the unionized samples but appears at low ionization levels, increasing in magnitude with the percent neutralization. This behavior is common to both the mono- and divalent cations. The higher temperature peak shifts to higher temperatures although the maximum in the peak is difficult to define because of experimental difficulties due to the severe drop in $E'$ in this region. The splitting of the high temperature peak is observed
again; this is prominent in the case of lithium, but less in the calcium.

The annealed samples also have the same general behavior as seen in the logarithmic decrement plots. The $\alpha$ and $\beta^\prime$ relaxations are clearly observed in the acid copolymer. The $\alpha$ peak appears to move to higher temperatures and increase in magnitude with increasing ionization and the $\beta^\prime$ peak eventually disappears. The $\beta$ relaxation, again at about $-10^\circ$C., grows in magnitude with ionization. No special difference in behavior due to cation valence is observed.

The $\alpha$ Relaxation

A completely satisfying interpretation of the $\alpha$ relaxation in these polymers cannot yet be made. The $\alpha$ relaxation in polyethylene has been attributed to motions in the crystal fold surface\textsuperscript{134} and in the crystal interior.\textsuperscript{116} These conclusions are based on the observed decrease in peak intensity and upward shift in peak temperature on annealing. Others\textsuperscript{117} have proposed origins in the amorphous phase due to interlamellar slip. In the ionomers, the $\alpha$ relaxation has been attributed to motions due to ionic
groups and, working with samples from the present study, Read et al. suggested a similar origin from dielectric measurements.

None of these explanations seem appropriate when considering the overall nature of the copolymers. The fact that the \( \alpha \) relaxation is observed in acid copolymers means that ionic groups are not necessary contributors to the motion. Furthermore, the increase in peak temperature and magnitude with ionization rules out origins in the crystalline phase, since these modifications have been shown to reduce both crystallinity and average crystallite size slightly. However, comparison of the damping curves for quenched and annealed samples show that annealing obviously has some influence on the \( \alpha \) peak.

The proposed mechanism which accommodates all of these facts is based on long range diffusional motions of the chains. This motion is restricted, perhaps severely, by the crystallites and the ionic groups. However, as the crystallites start to melt in this temperature region, their effect as tie points is diminished and the \( \alpha \) relaxation signals onset of long range chain diffusions. Thus, annealing, by virtue of perfecting crystallinity, should indirectly pro-
duce a more prominent $\alpha$ relaxation as is observed. If this viscous flow process is indeed the mechanism, then it is not surprising to see that ionization raises the temperature of the peak. Studies of melt rheology on these polymers have shown that ionization dramatically increases polymer viscosity at temperatures above the melting point. Thus ionization may provide sufficient restriction to long range diffusion of chains in the amorphous phase to raise the temperature of the $\alpha$ peak. Indeed, if the ionic phase segregation as proposed earlier is correct, this should certainly raise the temperature of the $\alpha$ peak.

The results of Read's dielectric measurements can also be accommodated by this mechanism. That the $\alpha$ peak is dielectrically active should not be surprising since, even in the most highly ionized samples, there are still free acid groups in the amorphous phase. At low frequencies, at least, the magnitude of the $\alpha$ relaxation is seen to increase considerably with increasing water content in the ionized copolymer. This might be explained as "plasticization" of the ionic groups, making them less effective as tie points in the amorphous network and thereby allowing greater long range diffusional flow. In addition, the $\alpha$ peak is found to
decrease in temperature with water content, which means that the "plasticized" ionic phase is a "looser" structure allowing an earlier onset of flow. The same effect of water on the peak was found by Longworth. This may also help to explain the occasional $\alpha$ peak splitting observed occasionally in ionized samples.

The $\beta'$ Relaxation

The $\beta'$ peak is uncovered in the dynamic mechanical damping plots ($\Delta$ and tan $\delta$) by annealing, which has the effect of shifting (increasing) the temperature of the $\alpha$ relaxation. The behavior of the $\beta'$ relaxation which is especially significant is that it decreases in magnitude in direct proportion to the decrease in the concentration of the unionized acid groups. This immediately indicates that the molecular motion responsible for the $\beta'$ relaxation involves the carboxylic acid groups. The temperature dependent infrared studies (Chapter III) showed that the unionized acid groups exist almost entirely in the form of interchain hydrogen-bonded dimers in the temperature range of the $\beta'$ relaxation. Since the enthalpy of dissociation of these dimers was measured as 11.8 kcal. mole$^{-1}$, they may
be classified as labile, quasi-crosslinks. Such interchain association would be expected to provide restriction on motions in the amorphous phase. Ionizing the acid groups decreases the number of interchain dimers and, thus, restrictions on segmental motions. When this is done, the \( \beta' \) peak is observed to decrease in magnitude, finally disappearing at higher ionization levels, with a concomitant appearance and growth of the \( \beta \) peak at about \(-10^\circ C\). It is proposed, then, that the \( \beta' \) relaxation involves micro-brownian segmental motions of the chain in the amorphous phase similar to that occurring in the \( \beta \) relaxation of low density polyethylene, but at a higher temperature due to the restrictions imposed by the acid dimers. This relaxation can be viewed as a glass transition of amorphous, branched polyethylene. This interpretation is in accord with the views of Andrews\(^{123} \) who explains amorphous relaxations in terms of the thermal breakdown of intermolecular secondary bonding of various types.

Confirmation of this proposed mechanism has been provided by the work of Otocka and Kwci.\(^{82} \) These authors worked with ethylene-acrylic acid copolymers containing varying amounts of acid units. In their study it was found
that the temperature of the \( \beta' \) relaxation is a function of the concentration of acid units and that the difference in temperature of the \( \beta' \) relaxation and the \( \beta \) relaxation in branched polyethylene is linearly dependent on the density of dimer units present. The calculation is carried out assuming that all dimer units are in the amorphous phase which they undoubtedly are since, among other things, they would not be expected to fit into the polyethylene crystal lattice for steric reasons.

It is important to stress that the proposed mechanism for the \( \beta' \) relaxation views the effect of the acid groups in terms of quasi-crosslinks. The presence of this type of intermolecular association accounts for the shift in peak temperature from \(-20^\circ C\) in ordinary branched polyethylene to \(+20^\circ C\) in the acid copolymers. It could be disputed that this shift may be a simple \( T_g \) effect without invoking the idea of segmental restriction, i.e. the acid groups merely raise the \( T_g \) in the amorphous phase. However, both the infrared work and a calculation of copolymer \( T_g \) argue against this interpretation. The acid copolymer, on which these mechanical studies were done, had a weight per cent crystallinity of about 10% as measured by DSC. Knowing the compo-
sition of the copolymer, the composition in the amorphous phase can be calculated:

$$\text{Wt. \% MAA (amorphous phase)} = \frac{\text{Wt. \% MAA (copolymer)}}{100 - \% \text{Crystallinity}}$$

$$\text{Wt. \% MAA (amorphous phase)} = \frac{11.7}{100 - 10} = 13.0\%$$

where MAA is methacrylic acid comonomer.

The $T_g$ of the amorphous material can be calculated assuming the $T_g$ of amorphous, branched polyethylene is $-20^\circ C.$, the $T_g$ of poly(methacrylic acid) is $+130^\circ C.$, and using the simplified copolymer $T_g$ equation as given by Meares:

$$\frac{1}{T_g} = \frac{W_1}{T_g^1} + \frac{W_2}{T_g^2}$$

Thus, the $T_g$ for the copolymer in the amorphous phase is calculated to be $-7^\circ C.$, well below the observed $\beta'$ peak temperature.

The $\beta$ Relaxation

The $\beta$ relaxation is either completely absent or has a very minor contribution in the unionized acid copolymer. It is clear, however, that the peak arises and increases in magnitude as acid groups are ionized, i.e. as the number of
dimers decreases. The temperature of the peak maximum is approximately the same for the sodium, lithium and calcium salts and, of special significance, the temperature is very close to that for the $\beta$ relaxation of branched polyethylene when measured at the same frequency. Furthermore, changes in the crystallinity produced by annealing have no significant effect on the temperature of the peak maximum.

It is, of course, somewhat unexpected that ionization should produce a $\beta$ relaxation at a lower temperature than is found in the acid copolymer, and that the valence of the cation should have no significant effect on the temperature of the $\beta$ relaxation. Several authors $^{65,68,77}$ have expressed the opinion that ionization with both monovalent and divalent cations in ethylene-methacrylic acid copolymers and other systems leads to increased interchain bonding due to the introduction of ionic interchain links. However, the present results cast doubt on this interpretation, at least in the case of the ethylene-methacrylic acid copolymers, since the relaxation occurs at a lower temperature than the $\beta'$ relaxation associated with the interchain hydrogen bonds.

For these reasons, the proposed mechanism of the $\beta$ relaxation in salts of ethylene-methacrylic acid copolymers
is identical to that for the $\beta$ relaxation in branched polyethylene. The polymer chain motions occur in the amorphous phase involving segments of the chain around branched points. These motions are the same as those observed at the $\beta'$ peak in the unionized copolymer but occur at a lower temperature, having been freed from the restrictions due to acid interchain dimerization. Thus, the increase in the magnitude of the $\beta$ peak with increasing ionization is a result of the greater number of branched polyethylene-like chain segments free to move at the lower temperature. There may also be some contribution due to the fact that ionized salts tend to have a lower crystallinity and, therefore, greater amorphous phase.

In Figures 23 and 24 the loss modulus, $E''$, is plotted for the quenched and annealed salts, each at about the same, high ionization level. Inspection of these figures uncovers some other interesting aspects of the $\beta$ relaxation which add to the proposed mechanism and suggest other features of the micromorphological state of ionomers. In the case of the quenched salts, Figure 23, it can be seen that although the temperature of the relaxation is about the same for each sample, the breadth of the relaxation differs, with the
divalent cation having the most narrow distribution. When these samples are annealed, Figure 24 shows that the relaxation distribution narrows considerably, with calcium again having the narrowest breadth, but the magnitude of $E''$ increases. It appears, then, that the ionized groups in some way affect the chain motions responsible for the $\beta$ relaxation. If they were directly involved, the peak temperature would be much higher than it is, even from a simple copolymer $T_g$ calculation, and the divalent cation should show a dramatic effect. Since this behavior is not observed, an alternate explanation for the effect of the cations on the $\beta$ relaxation is necessary. This explanation invokes the concept of phase segregation where the salt groups, being thermodynamically in a very high energy state as isolated entities in a medium of low dielectric constant, "prefer" to segregate into separate phases. Phase separation of this kind would obviously be diffusion-controlled since it depends on chain segments rearranging to provide conformations suitable for segregation of the attached ionized groups. Thus, the effect of annealing on sharpening and increasing the magnitude of the $\beta$ relaxation is due to more perfect phase segregation during the annealing process. Moreover,
at a given level of ionization the calcium salts would be expected to form separate phases much more readily than the monovalent salts since the former is associated with at least twice as many carboxylate groups. Thus, the narrow breadth of relaxations in the calcium salts would be expected.

As was pointed out in the section on crystallinity, there is a growing body of evidence supporting this proposed phase segregation. Static mechanical measurements by Bonotto and Bonner, x-ray and electron microscopy by Longworth and Vaughn, low angle x-ray work by Delf and MacKnight and theoretical calculations of Eisenberg all lend evidence to a separate ionic phase concept. It should be pointed out, however, that other workers, notably Otocka and Davis disagree, favoring the idea of separate dipole associations as apposed to phase segregation.

The $\gamma$ Relaxation

Despite the considerable amount of reported work, there is no completely satisfactory explanation for the low temperature ($T \approx -120^\circ C.$) relaxation in semicrystalline ethylene polymers. Schmieder and Wolf, Oakes and
Robinson and Woodward and collaborators all observed the \( \gamma \) relaxation in polyethylene of varying crystallinity and attributed it to short range motion in the amorphous areas. Wilbourn demonstrated that the \( \gamma \) transition is more general, occurring in polymers of widely differing types containing at least four methylene sequences. Schatzki then proposed his now famous "crankshaft" model for \( \gamma \) relaxations in the amorphous regions. Boyer summing up the work done to 1963, favored this model and concluded that the \( \gamma \) peak does indeed arise in the amorphous areas, a conclusion also reached by Bohn. More recently, Andrews and Hammack presented a new model for the \( \gamma \) transition, assigning it to amorphous phase motions. Iwayonagi and Sakurai have given additional support to a local mode amorphous motion but discount the Schatzki model. On the other hand, Pechold et al., Sinnott, Illers and Takayanagi have all presented evidence for a \( \gamma \) relaxation mechanism involving defects in the crystalline regions. Peterlin and co-workers have given evidence which they suggest shows that the relaxation is related to crystallinity, not through internal defects, but due to disordered regions in the chain fold plane. This is
also claimed by Wada et al.\textsuperscript{138} for single crystals.

The available evidence thus leads to the reasonable hypothesis that in semicrystalline systems the $\gamma$ relaxation may, in fact, consist of contributions from both the amorphous and crystalline regions. This suggestion was first made by Cole and Holmes\textsuperscript{139} and later by Boyer.\textsuperscript{140} Sinnott\textsuperscript{134} pointed out an unresolved shoulder on the low temperature side of the $\gamma$ peak for both melt-crystallized and solution grown single crystals of high density polyethylene and suggested that the $\gamma$ region may be a superposition of two peaks. Hoffman et al.\textsuperscript{116} have shown that the $\gamma$ relaxation in poly(chlorotrifluoroethylene) can be decomposed into $\gamma_a$ and $\gamma_c$ regions which are associated with the amorphous and crystalline phases respectively, and suggest that polyethylene should show similar behavior. Matsuoka and co-workers\textsuperscript{141} have proposed that the $\gamma$ relaxation in polyethylene may arise in either, or both, the crystalline or amorphous regions, depending on the method of preparation of the sample.

As discussed in previous sections, the progressive ionization of an ethylene-methacrylic acid copolymer with monovalent and divalent salts results in significant
changes in the properties of the polymer. The acid and ionized groups exist exclusively outside the crystal lattice and show their influence on mechanical relaxations arising in the amorphous regions. Thus, their presence allows a unique opportunity for distinguishing processes which may depend on both amorphous and crystalline contributions. The samples used in this work were characterized for crystallinity by the X-ray method.

Plots of log $E''$ versus $1/T$ in the $\gamma$ relaxation region are given in Figures 25a and 25b for quenched and annealed samples of the unionized polymer and a sodium-ionized derivative. These plots are typical of all the samples studied. It can be shown that the strength of the relaxation mechanism taking place in the $\gamma$ region should be proportional to the area under the curve, assuming the process is of the Arrhenius type. In this case, the relaxation times are described by the following equation:

$$\tau = \tau_0 \exp\left(-\frac{\Delta H_a^*}{RT}\right)$$

Then the relaxation strength, $\Delta E$, is given by the equation:

$$E'_i - E'_f = \Delta E = \frac{2\Delta H_a^*}{n R} \int E'' d(1/T)$$
where, $E'_i$ and $E'_f$ are the storage moduli immediately before and after the relaxation region, 
\[ \Delta E \] is the relaxation magnitude, 
and, $E''$ is the loss modulus as a function of $1/T$.

$\Delta H_{a*}$ is the apparent activation energy. In this treatment it is assumed constant throughout the relaxation region. Dielectric determinations,\textsuperscript{91} coupled with the mechanical data presented here, confirm that the $\gamma$ relaxation processes have an Arrhenius dependency and that $\Delta H_{a*}$ has about the same value for each process.

If the relaxation process takes place in either the crystalline or amorphous regions exclusively, there should be some straightforward relationship between the peak area, as given by the value of the integral, and either $\chi$, the degree of crystallinity, or $1-\chi$. Analysis of the areas and comparison with crystallinities did not uncover any such relationship. Moreover, since the $\gamma$ peak is far removed from the perturbing influence of any other transitions, one would also expect a symmetrical distribution of relaxation times if only one mechanism is involved. It is clear, however, that the peaks are asymmetric and, in fact, show
a prominent shoulder on the low temperature side. These features suggest that the \( \gamma \) relaxation is, in reality, two closely related mechanisms partially superimposed on each other.

The \( \gamma \) peak was then decomposed into two separate peaks by assuming symmetry around a line drawn through the high temperature peak maximum and constructing the second peak by differences. The method is illustrated in Figure 26 for the unionized polymer. This procedure results in two separated peaks, which are designated as \( \gamma_a \), the high temperature peak, and \( \gamma_c \), the low temperature peak. The maximum in \( \gamma_c \) coincides with the shoulder on the undecomposed curve.

The area of \( \gamma_c \) for all the samples is plotted in Figure 27 as a function of \( \chi \). The area increases linearly with a slope directly proportional to \( \chi \) only, and does not depend on level of ionization, type of cation or thermal history, except insofar as the latter affects the overall degree of crystallinity. Work discussed previously has shown large changes in the amorphous phase behavior, particularly in the \( \beta \) transition region, caused by change in ionization level, cation type and thermal treatment. Thus, the independence of the \( \gamma_c \) area with these variables leads
to the conclusion that this is a relaxation occurring exclusively in the polyethylene crystalline region. That the crystalline regions are composed only of the polyethylene segments of the chain is supported by the findings of Otocka on poly(ethylene-co-acrylic acid) systems and by the results of Bodily and Wunderlich using polyethylene copolymers containing vinyl acetate groups. Both conclude that the comonomer is excluded from the crystalline regions.

The $\gamma_a$ peak area is plotted in Figure 28 as a function of $1-X$. Again, there is a linear relation between the strength of the absorption and the amount of amorphous material, with some apparent dependency on the chemical nature of the groups in the amorphous areas. The $\gamma_a$ relaxation is therefore assigned to the amorphous regions of the polymer.

Although specific mechanisms cannot be assigned to these processes, several features should be pointed out. The DSC examinations showed that the nature of the crystalline morphology is complex and is significantly different depending on whether the samples are quenched or annealed. Furthermore, the X-ray and electron microscopy studies of others (cited earlier) on similar systems show drastic
changes in the crystalline morphology on ionization. Since
the $\gamma_c$ relaxation is unaffected by thermal treatment or
degree of ionization per sé, this mechanism must involve
motions in the crystal phase.

Our data contains one disturbing but highly interesting aspect with regard to the $\gamma_c$ transition: the failure
of the line in Figure 27 to extrapolate to zero area at $\chi = 0$. It is possible that this is a result of some systematic
error in area and crystallinity measurements. However, the
area measurements have a high degree of reproducibility;
correction of the possible errors involved in the X-ray
measurements would certainly make the extrapolation to zero
more difficult, not better. Sinnott, in his examination of
polyethylene single crystals$^{134}$ plotted the area of the $\gamma$
peak against the NMR mobile fraction and found a similar
failure to extrapolate to zero area. He suggested this may
be due to an unresolved lower temperature relaxation. No
evidence for a lower temperature peak in the neighborhood
of the $\gamma$ relaxation was found in this work.

It is believed more likely that the data shown in
Figure 27 is a demonstration of the origin of the $\gamma_c$ relax-
ation in more than one kind of crystal defect. In the dis-
discussion that follows, it is proposed that the $\gamma_c$ relaxation occurs both in the interior of the crystal lattice and in the side surfaces. Hoffmann has suggested that the $\gamma_c$ mechanism in poly(chlorotrifluoro ethylene) may involve twisting of chain segments adjacent to row defects in the crystal. This model is appealing since it explains the observed increase in $\gamma_c$ with annealing by showing that the additional insertion of chain ends drawn into the crystal during annealing increases the row vacancy defect concentration. These defects result in an unsymmetrical potential field around the chain segments adjacent to the vacancy. The $\gamma_c$ relaxation is a result of these local chain segments twisting or flip-flopping in and out of the vacancy. Adding to this concept, the present work suggests that there will also be a similar unsymmetrical potential field for chains on the side surfaces of the crystallites as a result of vacancies at the crystal-amorphous boundary plane. These vacancies may exist as imperfections on the growth faces of the crystal where many chains are entering and leaving the ordered lattice structure. Alternatively, there may be vacancies in the amorphous areas adjacent to the crystal face which provide sites for twist motions of
segments of crystallized chains. This model would be especially applicable to the ionomer system, where the crystallite sizes are very small at low degrees of crystallinity and therefore likely to have imperfect surfaces. The important consequence of this postulated model is that the contribution of surface defect motion to the total $\gamma_c$ relaxation strength should be large at small crystal volumes where the ratio of surface area to volume is large. However, as the crystal size increases due to lateral growth, the contributions of surface defect motions will become proportionately smaller and eventually interior defect motions will swamp the effects of surface defects. When this occurs, the relaxation strength is then a linear function of crystal volume.

The form of the contributions of each of these motions can be represented in a qualitative way by the following relationship:

$$\Psi (E") = f \text{ (internal defect motion) } + g \text{ (side surface defect motions)}$$

where, $\Psi (E")$ is some function of the total relaxation strength of the $\gamma_c$ region in a plot of the loss modulus versus reciprocal temperature.
The functions $f$ and $g$ should involve both the specific strength of the relaxation modes and the concentration of defects of each type. It becomes apparent, then, that $f$ is proportional to the volume of the crystal, while $g$ is proportional to the side surface area. Thus,

$$\Psi(E'') = f \text{ (crystal volume)} + g \text{ (side surface area)}$$

To examine the forms of each of these contributions, a box is postulated as a simple model of the crystal. The volume, $V$, and the side surface area, $A$, are given by ($l = \text{height and } a = \text{width and depth}$):

$$V = la^2$$

$$A = 4la$$

The equation for $\Psi(E'')$ is now rewritten in terms of crystal volume or size:

$$\Psi(E'') = f \text{ (V)} + g \left( V^{\frac{1}{3}} \right)$$

To apply this equation to the data shown in Figure 27, the $V$ terms are identified with degree of crystallinity, $\chi$. Although this is a tenuous identification, it may be justified by the fact that all samples were prepared from the melt in exactly the same way and, therefore, should have approximately the same number of crystal nuclei. Thus, the differences in degree of crystallinity can be identified
with differences in crystal size. When this is done, \( \Psi(E'') \) can then be rewritten as:

\[
\Psi(E'') = f(X) + g(X^2)
\]

The data in Figure 27 is replotted in Figure 29 along with a curve representing this equation. Values for the functions \( f \) and \( g \) were selected to fit the curve to the data points. Inspection of Figure 29 shows that the treatment described above is a way of accommodating both the data observed and the fact that at zero crystallinity the \( Y_c \) relaxation strength should also vanish. Techniques for preparing samples of lower X-ray crystallinity to experimentally check the curvilinear portion of the curve were tried but were unsuccessful.

The \( \gamma_a \) mechanism appears to arise only from short range local motions of polyethylene segments in the amorphous phase. The specific relaxation strength, calculated as the \( \gamma_a \) area per unit volume of amorphous material, is plotted against degree of ionization in Figure 30. It is seen that there is no dependency on either the ionization level or the chemical nature of the comonomer groups. This is in dramatic contrast to the behavior of the \( \beta \) region
where the longer range motions of amorphous phase polyethylene segments are controlled by ionization and comonomer structure. It is interesting to note that the \( \gamma_a \) mechanism occurs at a higher temperature than the \( \gamma_c \) motions, \( T_{\text{max}}(\gamma_a) = -129^\circ C; T_{\text{max}}(\gamma_c) = -163^\circ C. \). The same result was also observed for PCTFE.\(^{116} \) This must indicate that the \( \gamma_a \) motion is more restricted, possibly because the size of the vacancies in the amorphous regions are somewhat smaller than those in the crystal.

While the foregoing arguments show that the specific relaxation strength of the \( \gamma_a \) peak does not change with ionization level, cation or thermal history, the activation energy of the \( \gamma_a \) process does appear to vary with ionization level. Activation energy, \( \Delta H_* \), was calculated for a series of samples by observing the shift of the peak maximum on the temperature scale at various test frequencies, \( (3.5, 11 \text{ and } 110 \text{ Hz}) \). The slope of a plot of log frequency versus reciprocal temperature is related to activation energy by the equation:

\[
\Delta H^* = -(2.303) (R) \frac{d \log f}{d(1/T)}
\]
The values thus obtained are listed in Table VIII. The values range from a low of about 8.5 kcal./mole (acids) to a high of about 11.5 (highly ionized salts). These values are in fair agreement with those of Sandiford and Wilbourn, and of Hoffmann et al. for polyethylene, which range from 11 to 15 kcals./mole, depending on the method of measurement. Since \( \Delta H^* \) tends to increase with ionization level, but is little affected by the other variables (thermal history, cation), it is tempting to suggest that even partial phase segregation places sufficient strain on the amorphous chains to increase the potential energy barrier for the \( \gamma_a \) relaxation. At high levels of crystallinity, the crystalline regions in polyethylene ought to have much the same effect on chains in the amorphous phase. Thus, that part of the \( \gamma \) relaxation in polyethylene due to amorphous phase motions should show a change in activation energy with crystallinity. This has not been done yet, due to the difficulty of separating the \( \gamma_a \) and \( \gamma_c \) peaks in polyethylene.
SUMMARY

The dynamic mechanical properties and crystallization behavior of a poly(ethylene-co-methacrylic acid) copolymer were studied using a variety of characterization techniques. The relatively small amount of carboxylic acid in the chain significantly modifies the polyethylene-like character of the polymer; ionization of the acid groups results in unique changes in the mechanical relaxations and crystallization behavior. A model of the system which is consistent with these observations invokes the concept of segregation of the ionic groups into domains. The extent of this phase segregation is increased with ionization and annealing. The nature of the crystalline regions is also affected by ionization; the ionic phase segregation influences both the development of crystallinity and the lamellar structure. Thus, the model of the ionized copolymer consists of three phases: a polyethylene-like amorphous matrix in which is dispersed ionic domains and ill-developed crystalline regions.
SUGGESTIONS FOR FUTURE WORK

Studies on the Relaxations

1. The $\alpha$ relaxation. The nature of this relaxation is still controversial and needs to be examined further. An understanding of the $\alpha$ relaxation in the ionomers may also be useful for interpreting the exact nature of a similar peak in polyethylene. Of crucial importance is the question: Is the $\alpha$ relaxation in ionomers due to motions of ions or, rather, motions of polymer chain segments under some constraint by the ions? An approach to providing some answers might be made by blending alkyl carboxylate salts (e.g. sodium stearate) into polyethylene and studying the resultant changes in dynamic mechanical and dielectric behavior. In this case, the polymer chains will not be connected directly to the ionic regions. Possible relaxations in the ionic regions could be detected by dielectric measurements and compared with the dynamic mechanical results. In addition, similar work comparing the effect of "plasticizers" specific for the ionic phase and amorphous polyethylene region might yield profitable results.

2. The $\beta'$ and $\beta$ relaxations. The polymer motions re-
sponsible for these peaks are fairly clear. Additional evidence may be obtained, however, by interrupting the acid dimerization by a method other than ionization. Two approaches are: deuteration by exchange of the acid proton with D₂O and formation of the ester by reaction with diazomethane.

Each of these relaxations could be investigated with polymers modified by the procedures discussed in the next section.

Studies on the Domain Formation

The ionic phase behavior and its effect on properties may be examined by experiments in which the domains are modified. For example, ionization with various alkyl ammonium hydroxides or organic amines should yield polymers with "looser" domain structures. Alternatively, ionization might be done at a low temperature where chain motion necessary for phase segregation of ionic groups is inhibited. Thin films of the acid copolymer with varying thermal histories could be exposed to ammonia vapors at temperatures below the β transition and then tested directly without prior melting. The domain structure should be quite
primitive for an ionomer prepared in this manner.

A comparison of polymers with equal acid contents but grossly different distributions of the acid groups may help to further elaborate the nature of the phase segregation due to ionization. For example, graft copolymers, because of their "blocky" architecture, may form ionic phases and crystalline regions to a different extent than a random copolymer. Preferably, such a study should compare the two different types of copolymers against a polyethylene homopolymer of otherwise similar characteristics. A series of polymers could be prepared by selecting a suitable polyethylene homopolymer and chemically modifying it to produce the two copolymers as follows:

a. graft copolymer - free radical graft polymerization of acrylic acid on the polyethylene backbone;

b. random copolymer - free radical grafting of a non-homopolymerizable carboxylic acid monomer, e.g., crotonic acid.

Study on the Crystallinity

The crystallization kinetics and the nature of the crystalline phase should be examined in more detail. Much
longer annealing times may allow quantitative treatment of the kinetics. Comparison of samples annealed from the melt with those annealed at the same temperature but after quenching from the melt may produce interesting results.

The differences in the observed degrees of crystallinity as measured by DSC and IR on the one hand, and X-ray on the other, must be explained. Possible errors in the analysis of the X-ray diagrams which may lead to high estimates of crystallinity have already been discussed. It should be pointed out, however, that the DSC work could give low values of crystallinity if the true $\Delta H_f$ for the crystals in this system is lower than 66 cals./gram. This is a very real possibility when considering the work of Knox. He suggests that the $\Delta H_f$ of crystals in branched polyethylene is severely reduced, presumably because of the inclusion of methyl branches in the crystal lattice. In addition, the fold surface free energy may be higher than that for ordinary branched polyethylene if the comonomer groups are included in the folds. Both of these effects may require corrections to the DSC treatment which would result in an increase in the estimate of crystallinity.

The crystalline phase, and possibly the ionic phase,
may be an interesting subject for dynamic rheo-optical
studies. Since neutralization affects long range crystal-
linity (e.g., spherulitic structure development), the sizes
of the crystalline regions are obviously altered and, thus,
should show significant changes in a dynamic IR or X-ray
experiment. These studies may help to better define the
effects of the ionic groups and the morphological nature of
the copolymer.

Finally, it should be recalled that a maximum limit
on per cent neutralization of the acid groups was found in
this work. It is possible that this could be due, at
least in part, to electrostatic effects, as found for homo-
polymers containing acid groups.\textsuperscript{151} This would mean that
some of the acid groups in the ionomer occur as nearest
neighbors and could be evidence for a small amount of
"blockiness".
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TABLE I

EFFECT OF IONIZATION ON THE ABSORBANCE AT 1700 cm.$^{-1}$

<table>
<thead>
<tr>
<th>Integrated Absorbance of 1700 cm.$^{-1}$ peak/cm. Sample Thickness cm.$^{-2}$ x 10$^{-3}$</th>
<th>% Ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.32</td>
<td>0</td>
</tr>
<tr>
<td>14.71</td>
<td>19.7</td>
</tr>
<tr>
<td>7.26</td>
<td>60.4</td>
</tr>
<tr>
<td>4.10</td>
<td>77.6</td>
</tr>
</tbody>
</table>

TABLE II

CALORIMETRIC EVENT TEMPERATURES, QUENCHED SAMPLES

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionization %</th>
<th>Crystalinity %</th>
<th>Temperatures, °C.</th>
<th>Estimated Melting Range, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>15.9</td>
<td>$T_m$: 96, $T_i$: 63(+2), $T_f$: 106</td>
<td>43</td>
</tr>
<tr>
<td>Na</td>
<td>21</td>
<td>15.4</td>
<td>$T_m$: 96, $T_i$: 77(+2), $T_f$: 106</td>
<td>29</td>
</tr>
<tr>
<td>Na</td>
<td>76</td>
<td>15.0</td>
<td>$T_m$: 95, $T_i$: 77(+3), $T_f$: 106</td>
<td>29</td>
</tr>
<tr>
<td>Ca</td>
<td>21</td>
<td>11.0</td>
<td>$T_m$: 93, $T_i$: 75(+4), $T_f$: 103</td>
<td>28</td>
</tr>
</tbody>
</table>
### TABLE III

**CALORIMETRIC EVENT TEMPERATURES, ANNEALED SAMPLES**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionization</th>
<th>Crystalinity</th>
<th>Temperatures, °C.</th>
<th>Estimated Melting Range, °C.</th>
<th>Endotherm Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>16.2</td>
<td>98</td>
<td>85 (+2) 104</td>
<td>19 B</td>
</tr>
<tr>
<td>Na</td>
<td>21</td>
<td>14.0</td>
<td>99</td>
<td>92 (+2) 105</td>
<td>13 A</td>
</tr>
<tr>
<td>Na</td>
<td>76</td>
<td>13.2</td>
<td>97</td>
<td>85 (+2) 107</td>
<td>22 A</td>
</tr>
<tr>
<td>Ca</td>
<td>21</td>
<td>10.0</td>
<td>98</td>
<td>87 (+2) 103</td>
<td>16 B</td>
</tr>
</tbody>
</table>

### TABLE IV

**EFFECT OF ANNEALING TEMPERATURE ON T_m**

<table>
<thead>
<tr>
<th>Cation</th>
<th>% Ionization</th>
<th>Annealing Temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>Acid</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>Na</td>
<td>21</td>
<td>96</td>
</tr>
<tr>
<td>Na</td>
<td>76</td>
<td>97</td>
</tr>
<tr>
<td>Ca</td>
<td>21</td>
<td>96</td>
</tr>
</tbody>
</table>

*New peak at 102°C.*
TABLE V

RECRYSTALLIZATION TEMPERATURE, $T_c$

<table>
<thead>
<tr>
<th>Cation</th>
<th>% Ionization</th>
<th>$T_c$, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>77.0</td>
</tr>
<tr>
<td>Na</td>
<td>21</td>
<td>80.5</td>
</tr>
<tr>
<td>Na</td>
<td>56</td>
<td>60.0</td>
</tr>
<tr>
<td>Na</td>
<td>76</td>
<td>55.5</td>
</tr>
<tr>
<td>Ca</td>
<td>21</td>
<td>45.0</td>
</tr>
<tr>
<td>Ca</td>
<td>56</td>
<td>&lt;25.0</td>
</tr>
</tbody>
</table>

TABLE VI

DETERMINATION OF CRYSSTALLINITY VIA INFRARED MEASUREMENTS

<table>
<thead>
<tr>
<th>Cation</th>
<th>% Ionization</th>
<th>Thermal History</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>Quenched</td>
<td>15.9 14.0 18.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75°C./1 hr.</td>
<td>9.5   3.2 11.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75°C./23 hr.</td>
<td>13.0  12.5 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75°C./70 hr.</td>
<td>15.0  11.1 18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85°C./44 hr.</td>
<td>12.0  9.8 13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95°C./48 hr.</td>
<td>10.2  10.0 11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110°C./5 hr.</td>
<td>14.2  6.5  9.9</td>
</tr>
<tr>
<td>Sodium</td>
<td>76</td>
<td>Quenched</td>
<td>15.0  -  ~0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85°C./21 hr.</td>
<td>12.3  -  9.7</td>
</tr>
<tr>
<td>Calcium</td>
<td>21</td>
<td>Quenched</td>
<td>11.0  -  ~0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85°C./18 hr.</td>
<td>8.1   -  7.9</td>
</tr>
</tbody>
</table>
TABLE VII

DETERMINATION OF CRYSTALLINITY VIA X-RAY MEASUREMENTS

<table>
<thead>
<tr>
<th>Cation</th>
<th>% Ionization</th>
<th>Thermal History</th>
<th>% Crystallinity (±5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>Quenched</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>Annealed</td>
<td>42.4</td>
</tr>
<tr>
<td>Lithium</td>
<td>21</td>
<td>Quenched</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>Annealed</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>Quenched</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>Annealed</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>Quenched</td>
<td>24.3</td>
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<td></td>
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<td>Annealed</td>
<td>44.3</td>
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<td>Quenched</td>
<td>19.1</td>
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<td>72</td>
<td>Annealed</td>
<td>47.7</td>
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<td>Sodium</td>
<td>20</td>
<td>Quenched</td>
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<td>20</td>
<td>Annealed</td>
<td>44.0</td>
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<tr>
<td></td>
<td>60</td>
<td>Quenched</td>
<td>26.6</td>
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<td>60</td>
<td>Annealed</td>
<td>42.8</td>
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<td></td>
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<td>Quenched</td>
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<td></td>
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<td>Annealed</td>
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<td>Quenched</td>
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<td></td>
<td>21</td>
<td>Annealed</td>
<td>40.0</td>
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<tr>
<td></td>
<td>46</td>
<td>Quenched</td>
<td>20.8</td>
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<td></td>
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<td>Annealed</td>
<td>42.8</td>
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<tr>
<td></td>
<td>80</td>
<td>Quenched</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Annealed</td>
<td>46.5</td>
</tr>
</tbody>
</table>
## Table VIII

**Activation Energies of the $\gamma_a$ Process**

<table>
<thead>
<tr>
<th>Cation</th>
<th>% Ionization</th>
<th>Thermal History</th>
<th>$\Delta H_{\gamma}^*$, (kcal./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0</td>
<td>Quenched</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>Annealed</td>
<td>8.7</td>
</tr>
<tr>
<td>Lithium</td>
<td>20</td>
<td>Quenched</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Annealed</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>Quenched</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>Annealed</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>Quenched</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>Annealed</td>
<td>11.7</td>
</tr>
<tr>
<td>Sodium</td>
<td>78</td>
<td>Quenched</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>Annealed</td>
<td>10.0</td>
</tr>
</tbody>
</table>
1. Infrared spectra of ethylene-methacrylic acid copolymer films ionized to different extents with sodium. (Thickness: 0%, $1.2 \times 10^{-3}$ cm.; 20%, $2.5 \times 10^{-3}$ cm.; 60%, $6.1 \times 10^{-3}$ cm.; 78% $9.4 \times 10^{-3}$ cm.).

2. Diagram of the torsion pendulum.

3. Temperature dependence of the infrared spectrum of the unionized ethylene-methacrylic acid copolymer. The dotten line on the 1750 cm.$^{-1}$ band at 99°C. was used to determine the baseline for the peak absorbency measurement of the band.

4. Temperature dependence of the peak absorbency per cm. of the 3540 cm.$^{-1}$ free hydroxyl stretching band.

5. van't Hoff plot ($\log_{10} K$ versus $1/T$) of the dissociation constant for the acid monomer-dimer equilibrium. The open circles are the experimental points. The cross (X) is the literature value for low molecular weight carboxylic acids in non-polar solvents.

6. Polarized infrared spectra for the 70% ionized copolymer.

7. Dichroic ratio versus per cent extension for three bands of the 70% ionized copolymer.
8. Types of melting endotherms and the exotherm curves.


10. Melting curves for the acid copolymer (annealed at 85°C. for the times indicated).

11. Melting curves for the 76% sodium copolymer (annealed at 85°C. for the times indicated).

12. Degree of crystallinity versus annealing time at 85°C.

13. Temperature dependence of $G'$ for quenched ethylene-methacrylic acid copolymers at various degrees of ionization. Each curve is displaced by one decade above the preceding curve.

14. Temperature dependence of $G'$ for annealed ethylene-methacrylic acid copolymers at various degrees of ionization. Each curve is displaced by one decade above the preceding curve.

15. Temperature dependence of the logarithmic decrement for quenched ethylene-methacrylic acid copolymers at various degrees of ionization.

16. Temperature dependence of the logarithmic decrement for annealed ethylene-methacrylic acid copolymers at various degrees of ionization.

17. Temperature dependence of $G''$ for quenched ethylene-
methacrylic acid copolymers at various degrees of ionization.

18. Temperature dependence of $G''$ for annealed ethylene-methacrylic acid copolymers at various degrees of ionization.

19. Temperature dependence of tan $\delta$ for the quenched copolymers ionized with lithium.

20. Temperature dependence of tan $\delta$ for the annealed copolymers ionized with lithium.

21. Temperature dependence of tan $\delta$ for the quenched copolymers ionized with calcium.

22. Temperature dependence of tan $\delta$ for the annealed copolymers ionized with calcium.

23. Temperature dependence of $E''$ in the $\beta$ relaxation region for quenched sodium, lithium and calcium salts of the copolymer.

24. Temperature dependence of $E''$ in the $\beta$ relaxation region for annealed sodium, lithium and calcium salts of the copolymer.

25. a. Temperature dependence of $E''$ for the quenched and annealed acid copolymer in the $\gamma$ relaxation region.
b. Temperature dependence of $E''$ for the quenched and annealed sodium ionized copolymer in the $\gamma$ relaxation region.

26. Method of $\gamma$ peak decomposition (acid copolymer).

27. Area of the $\gamma_c$ peak versus degree of crystallinity for the acid copolymer and its sodium, lithium and calcium salts.

28. Area of the $\gamma_a$ peak versus amorphous fraction for the acid copolymer and its sodium, lithium and calcium salts.

29. Data points from Figure 27 replotted with a calculated curve representing $\Psi(E'') = f(\chi) + g(\chi^2)$.

30. Specific relaxation strength of the $\gamma_a$ peak versus per cent ionization for the acid copolymer and its sodium, lithium and calcium salts.

31. Per cent crystallinity (X-ray) versus per cent ionization for the quenched and annealed copolymers.
FIGURE 2

Counterbalance

Torsion Disc

Temperature Chamber

Sample

Transducer (LVDT)

Low Friction Bearing
Figure 4

3540 cm$^{-1}$

FREE OH STRETCH

ABSORBANCE / cm

TEMPERATURE (°C)
\[
(-\text{COOH})_2^K \rightleftharpoons 2(-\text{COOH})
\]

\[\Delta H = 11.6 \text{ KCALS/ MOLE}\]
FIGURE 8

TYPE A

$T_i \rightarrow T_m \rightarrow T_f$

TYPE B

$T_m$

TYPE C

$T_m$

RECRYSTALLIZATION

$T_c$
FIGURE 9

Anneal Temp

150°C

Liq. N₂

Annealing Time

0

T
FIGURE 14

ANNEALED

G^1 DYNES CM^-2

0%

20%

60%

78%

-100  0  100

TEMPERATURE (°C)
FIGURE 19

LITHIUM QUENCHED

TEMP. °C

0%  γ

21%  β

52%  γ

72%  β

TEMP. °C
**FIGURE 23**

\( \beta \text{ REGION ABSORPTION (QUENCHED)} \)

FREQ. = 110 Hz.

<table>
<thead>
<tr>
<th>CATION</th>
<th>% IONIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>SODIUM</td>
<td>78</td>
</tr>
<tr>
<td>LITHIUM</td>
<td>72</td>
</tr>
<tr>
<td>CALCIUM</td>
<td>80</td>
</tr>
</tbody>
</table>

\( E'' \times 10^{-7} \) Dynes/cm²

TEMP. °C
\( \beta \) REGION ABSORPTION (ANNEALED)

FREQ. = 110 Hz.

<table>
<thead>
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</tr>
<tr>
<td>CALCIUM</td>
<td>80</td>
</tr>
</tbody>
</table>

\( E' \times 10^{-7} \) Dynes/cm\(^2\) vs. TEMP. °C
FIGURE 2.5b

$E'' \times 10^{-8}$

$1/T \times 10^3 \, ^\circ\text{K}$

$T \, ^\circ\text{C}$

78% Na

○ Quenched

● Annealed
○ UN-IONIZED ACID
○ SODIUM SALTS
□ LITHIUM SALTS
△ CALCIUM SALTS

AREA

DEGREE OF CRYSTALLINITY, \( x \)

FIGURE 27
FIGURE 31

Crystallinity (X-Ray):

Dependence on Ionization Level and Cation Type

% Crystallinity

% Ionization

Annealed
Na
Li
Ca
Quenched