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THE PHYSICAL PROPERTIES OF POLAR DERIVATIVES OF POLYETHYLENE

A Dissertation Presented

By

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

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Polymer Science and Engineering
THE PHYSICAL PROPERTIES OF POLAR DERIVATIVES OF POLYETHYLENE

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CHAPTER I

OBJECTIVES AND BACKGROUND

Introduction

In recent years the need for polymers with specific mechanical and physical properties has increased in proportion to the number of applications of plastics, rubbers, and fibers. These needs can be filled by the choice of (1) tailor making polymers with specific properties, (2) modifying existing polymers to achieve the desired properties, or (3) synthesizing new polymers based on previous experiences of other workers. The properties of polymers are influenced by the architecture of the polymer chain and the interaction of individual polymer chains on an intermolecular basis. Polymer chains can interact in a number of ways,

1. Physical entanglements
2. Primary chemical bonds (crosslinking).
3. Secondary chemical bonds (van der Waal's, hydrogen bonding, ionic, etc.)

Physical entanglements of individual polymer molecules are associated with a characteristic molecular weight and for many polymers the critical molecular weight
is in the magnitude of 25,000. Above the critical molecular weight, the viscosity molecular weight relationship increases by about a power of two. To obtain useful engineering properties, a minimum molecular weight is necessary. Van der Waal's forces are short range interactions between molecules or polymer chains with a magnitude in the range of 1 Kcal/mole. They are an intrinsic interaction force of all molecular species.

To further enhance a polymer's mechanical and physical properties, primary and/or secondary chemical bonds can be incorporated into the polymer structure. Primary chemical bonds or crosslinks are indistinguishable from the polymer's backbone linkages, in most cases, and are very strong bonds with strengths in the order of 100 Kcal/mole. This type of linkage between polymer chains can account for a substantial change in physical properties. The crosslinks can be introduced by free radical mechanisms, chemical reactions between pendant groups, and by actual rearrangement of the polymer backbone as observed in the cases of polysulfides and polysiloxanes. Other secondary bonds that can be introduced into the polymer system or that may occur naturally are hydrogen bonds and ionic bonds, which have energies in the range of 10 Kcal/mole. This is the range of secondary forces that are of interest
in the present investigation.

The architecture of the polymer backbone is determined by the monomer(s) polymerized and the method of polymerization. The original architecture is permanent and can be changed only if the molecular structure in-the-large is changed. The chemical composition or the local structure can be altered by chemical means such as the hydrolysis of polyvinylacetate to polyvinyl alcohol. The polymer systems investigated in this work basically consist of low density polyethylene to which polar species have been introduced as pendant groups to change the chemical composition of the parent polymer. The two types of polar groups used in this study are (1) carboxylic acid and (2) phosphonic acid.

The investigations carried out on the ethylene-methacrylic acid and ethylene-acrylic acid copolymers led to much fruitful information. However, these copolymers were prepared by a high pressure free radical process and as a result it is difficult to maintain control over alkyl chain branching, molecular weight distribution, and the distribution of acid groups as a function of acid group concentration. Thus, characterization of a series of such copolymers with varying acid contents is difficult. The polyethylene-phosphonic acid system provides a means
for the elimination of many of these difficulties. The phosphonic acid side groups may be introduced randomly along a polyethylene chain without change in the basic polyethylene structure. Thus, a well characterized starting polyethylene results in a series of well characterized random copolymers whose properties may be meaningfully compared to those of the starting material.

Objective of Investigation

The objective of this research is two fold. The first objective is to investigate a series of ethylene-methacrylic acid and ethylene-acrylic acid copolymers and to determine structure-property correlations. Interpretations of the effects of secondary bonding on mechanical and physical properties will be made on a molecular scale from dynamic mechanical and dielectric relaxations, which will be supplemented by infrared data. The second objective is to change the chemical composition of commercial low density polyethylene so as to effect its intrinsic secondary bonding ability. The change in secondary bonding is studied by dynamic mechanical and dielectric techniques so as to determine structure-property correlations.
Studies of Ethylene-Methacrylic Acid and Ethylene-Acrylic Acid Copolymers

In an attempt to keep terminology consistent, the definitions for carboxylic acid containing copolymers used by Rees and Longworth and Vaughan will be summarized. It is generally agreed to use the term copolymer when speaking about polymers consisting of polyethylene and methacrylic acid or acrylic acid. This is the classical copolymer definition. The term ionomer refers to a copolymer of ethylene and methacrylic or acrylic acid which is partially or totally neutralized with a Group I or Group II cation.

The review of pertinent literature will be limited to that work which has relevance to infrared, mechanical, and dielectric properties of ethylene-methacrylic acid of ethylene-acrylic acid copolymers. An excellent review of the history and the future of ionomers and their corresponding copolymers has been reported by McKenna. Otocka has prepared a review of the physical properties of ionic polymers emphasizing materials derived from organic chemistry. MacKnight recently summarized the phenomena of microphase separation in organic polymers containing ions.

Infrared studies were carried out by Otocka and Kwei on acrylic acid copolymers. From their studies
they were able to determine association constants for the dimerized carboxylic acid group and show that the 1700 cm\(^{-1}\) and 940 cm\(^{-1}\) bands were dichroically active. They also observed that the dichroic ratios decreased with increasing acid content. MacKnight and coworkers worked with methacrylic acid copolymers and their sodium salts. They determined the dissociation constant for the methacrylic acid copolymer and reported an infrared technique to calculate the level of ionization for ionomers. From dichroism measurements on an ionomer they concluded that there is a significant amount of crystallinity, that the hydrogen bonds are intermolecular in nature, and the ionized carboxylate groups are oriented out of the plane of the polymer backbone. Read and Stein also performed infrared dichroism studies on an ionomer and concluded that the ionized carboxylate groups are oriented out of the plane of the backbone. Rees and Vaughan carried out early qualitative infrared work in 1965 on copolymers and ionomers.

Early reports of the mechanical properties of this class of polymers were made by Rees and Vaughan. Bonotto and Purcell reported physical and mechanical properties using the American Standard of Testing Materials (ASTM) testing procedure on copolymers and
and ionomers. MacKnight and coworkers studied the mechanical relaxations in methacrylic acid copolymers and their sodium salts. They observed four mechanical relaxations denoted alpha (α'), beta prime (β'), beta (β), and gamma (γ). Shortly after these initial works, a symposium on the effects of ions in the bulk properties of polymers was held by the American Chemical Society (ACS). At the symposium Longworth and Vaughan presented internal friction and dielectric results for a series of methacrylic acid copolymers and their salts having a range of 5-40% by weight methacrylic acid. MacKnight and coworkers presented work on the effects of different cations on the mechanical relaxation spectrum of a methacrylic acid copolymer.

Otocka and Kwei reported dealing with mechanical properties of acrylic acid copolymers and their corresponding ionomers. From their results on a series of acrylic acid copolymers they observed that the primary relaxation increased in temperature of appearance with increasing acid content. Bonotto and Bannek studied the effect of ion valency on the bulk physical properties of ionomers of acrylic acid copolymers. They concluded that it was the degree of ionization and not the type of ion that affected the physical properties. MacKnight and coworkers discussed the structure-mechanical property
relationships in methacrylic acid copolymers and their salts. McKenna and coworkers studied the mechanical relaxation in methacrylic acid copolymers and their salts and were able to separate the \( \gamma \) peak into two separate peaks.

The first dielectric experiments on ethylene-methacrylic acid copolymers and their corresponding salts were reported in 1968 by Longworth and Vaughan who made measurements using ASTM D-150 testing procedure. The next reported work in this area was performed by Read and coworkers and Phillips and Macknight in 1969 and 1970 respectively. They observed two major dielectric relaxations in a methacrylic acid copolymer and denoted these \( \beta' \) and \( \gamma \) in order of decreasing temperature. The assignment of a molecular specie(s) responsible for the observed dielectric relaxation spectrum was not conclusive from these investigations. It is the intent of this investigation to define structure-property correlations in light of secondary bonding and to elucidate the dipolar species responsible for the loss peaks observed in previous dielectric experiments.

Chlorophosphonated Polymers

Many workers have investigated the effect of incor-
poration of a comonomer containing a pendant carboxy-
ic acid group into homo-polymers, such as polybuta-
diene, polystyrene, and polyethylene. It has been
recognized that secondary bonding, specifically hydro-
gen bonding, affects the behavior of proteins, starch,
cellulose and commercially available polymers such as
nylons, polyurethanes, and polyvinylalcohol. It is a
continuous desire to understand and improve the sec-
dary bonding of these polymers so that widespread
applications can be achieved.

One method to improve secondary bonding is to
incorporate a pendant group different than the carboxy-
ic acid group into the polymer backbone which is capa-
ble of forming hydrogen bonds. The dissociation con-
stant \( K_d \) for a typical carboxylic acid (acetic acid) is
\( 10^{-5} \) and for phosphonic acid the first and second dis-
sociation constants \( K_{d1} \) and \( K_{d2} \) are \( 10^{-2} \) and \( 10^{-8} \) respectively.
Commercially available polyethylene was reacted in such
a way as to place pendant phosphonic acid groups ran-
domly on the polymer chain. The reaction used to do
this is called an oxidative chlorophosphonation reac-
tion. This review will be confined to the use of this
reaction on polymeric materials and the end uses of
properties of the resultant material.
Leonard and coworkers define a chlorophosphonated polymer as a polymer which has been reacted with a mixture of oxygen gas and phosphorous trichloride and subsequently hydrolyzed or esterified. The definition used here will consider phosphorous chlorides in general. In 1948 Clayton and Jensen reported chlorophosphonating low molecular weight hydrocarbons to form new alkane and cycloalkane phosphonyl chlorides. Yolles in 1958 was issued a patent for preparation of polyalkylene phosphonic acids for use as corrosion inhibitors. Yolles used PhPCl₂ in place of PCl₃ and solvent cast the hydrolyzed product from a mixture of trichloroethylene-ethanol (86/14, w/w) onto steel plates. After curing at 100°C for one half hour, the coating was not soluble in the casting solvent and had good corrosion resistance.

Hotten and Johnson followed shortly with a patent describing the application of a lithium salt of chlorophosphonated polyethylene as a high melting, work stable lubricating grease. These workers were the pioneers in this area.

The Spencer Chemical Company was issued a patent in 1960 for the preparation of chlorophosphonated polyethylene using air in place of oxygen gas, and in solvents, such as tetrachloroethylene, benzene, xylene, and ethylene.
at 300 lbs/in\(^2\). The resultant polymers had higher impact tensile strength and improved clarity. Schroeder and Leonard were awarded patents shortly after. They compounded high strength elastomers from a chlorophosphonated ethylene-propylene copolymer which had been terminated with 95% ethanol. A similar patent was issued to Leonard and Wheelwright in 1963. Schroeder and Leonard were also able to incorporate up to 16% by weight phosphorous into polyolefins. The chlorophosphonated polyolefins were tacky, elastic, brown rubbery resins which were insoluble in boiling xylene and burned reluctantly.

A chlorophosphonated low molecular weight polyethylene grease and low density polyethylene were reported by Schroeder and Sopchak. They studied various effects on the reaction, such as catalyst, \(O_2\) concentration, \(PCl_3\) concentration, and other variables. Their experiments argue for a free radical mechanism in the chlorophosphonation reaction. Mayo and coworkers deduced that the reaction was a free radical mechanism from analysis of the products of the reaction of cyclohexane. They proposed three overall reactions:

\[
R-H + 2PCl_3 + O_2 \rightarrow R-POCl_2 + POCl_3 + HCl
\]
Searching for a heat resistant elastomer, Leonard and coworkers compared an amorphous chlorophosphonated ethylene-propylene copolymer with neoprene, hypalon, and butyl elastomers. Leonard and fellow workers also studied the effects of copolymer composition, initial crystallinity, type of catalyst used in copolymer preparation, and copolymer molecular weight in the chlorophosphonation of ethylene-propylene copolymers.

Grishna and Sabirova reported the synthesis of alkylphosphonyl dichlorides from n-paraffins by oxidative chlorophosphonation. They reacted butane, pentane, hexane, heptane, octane, and dodecane and found that the products darkened rapidly upon exposure to air. Rafikov
and fellow workers synthesized oligomeric polyethylene phosphonic acids with up to 29% phosphorous introduced by chlorophosphonation. Those over 12% phosphorous content were reported to be water soluble. An unsaturated petroleum fraction was chlorophosphonated and found useful in the manufacture of floor tile because of its fire resistant properties. Rafikov and coworkers also synthesized and studied some mono- and di-valent salts of polymeric phosphonic acids having the composition \((\text{CH}_2)_n\text{-CH(PO}_3\text{H}_2)\) with \(n = 4, 9, 18, 27, 70\). They examined these salts by x-ray diffraction, infrared, and thermomechanical techniques. They found the salts to be generally heat resistant with a softening point around 200°C. The acids were found to be more thermally stable than polyethylene at 400°C, in respect to weight loss. They also concluded that the dielectric properties of these acids and salts were inferior to those of polyethylene.

Infrared absorption bands of phosphonyl containing compounds appearing in literature up to 1958 have been correlated and reviewed by Bellamy. Thomas and Chittenden correlated a massive amount of existing data and their own data on phosphorous compounds during the years 1964-1970. They concluded that it was surprisingly difficult to use published data for correlation.
purposes. This difficulty is partially due to the variety of samples, sample states, spectrometers, and absorption scales used by various authors. A review has also been published in Topics in Phosphorous Chemistry. Phillips and MacKnight reported infrared spectra of a chlorophosphonated polyethylene and the parent polyethylene. They observed several broad areas of absorption in the former polymer.

Bellus and coworkers prepared a number of chlorophosphonated polymers including atactic polypropylene. They found with increasing phosphorous content that the glass transition temperature increased, the polymers had greater hardness and were more flame resistant than their parent polymers. The chlorophosphonated polyethylene had been prepared by dissolving the polymer in carbon-tetrachloride, using aluminum trichloride or pyridine as catalyst, and phosphorous trichloride, dichloride, or monochloride. High pressure, medium pressure, and low pressure polyethylene, polypropylene, and ethylene-propylene copolymers have been chlorophosphonated in a mixture of PCl$_3$ and benzene or PCl$_3$ vapors. The products had increased resistance to oxidative thermal degradation as compared to the parent polymer and were dyeable with basic dyes. Polyvinyl acetate has also been
chlorophosphonated into its corresponding poly[vinyl (oxyacetoxy) phosphonic acid]. Buslaev and coworkers radiation grafted acrolein to cis-polybutadiene and then chlorophosphonated the grafted polymer. They found that the grafted polymer was easier to react and that its properties were different than those of a chlorophosphonated cis-polybutadiene.

With the increasing importance of ion exchange membranes, many workers have examined the possibility of chlorophosphonation. Nakanishi in 1962 received a patent for an ion-exchange resin incorporating phosphonic acid groups. A chlorophosphonated styrene-divinylbenzene copolymer was prepared using a Friedel-Crafts type reaction. Other workers have made studies in this area. For styrene-divinylbenzene copolymers phosphonated in tetrachloroethane it was found that the porosity of the polymer increased as the concentration of divinylbenzene segments increased and that the amount of phosphorous decreased. These copolymers were found to have good radiational, chemical, and mechanical stability. In polymers containing more than 10% divinylbenzene units, γ radiation had no effect on the membranes' ion exchange ability. Films of graft copolymers of polystyrene-51 polypropylene and polystyrene-polyethylene have
been chlorophosphonated to obtain ion exchange membranes also. Phosphonated spruce, pine, oak or beech sawdust has been used for uranium sorption from natural water. The sorption kinetics are in the range of 7 to 20 days and the phosphonated sawdust can be used for about 20 sorption cycles.  

Rafikov and coworkers synthesized and studied the properties of poly(alkylene phosphonic acids). They were able to incorporate up to 20% phosphorus into a chlorophosphonated low density polyethylene. The reaction rate increased with increasing oxygen gas flow and when PCl₃ was added in portions during the reaction. They also observed no conspicuous scission of the polymer chain. The polymer's solubility decreased with time after preparation and the crystallinity decreased with increasing phosphorus content. Alkaline solutions of the phosphonated polymer showed unusual viscometric behavior. Tensile strength increased and elongation decreased with increasing phosphorus content. The phosphonated polymer also exhibited lower weight loss than its parent polymer at 300°C. Phillips and MacKnight recently reported the mechanical and thermal properties of a chlorophosphonated low density polyethylene. They observed a lower melting point and a larger primary re-
laxation for the modified polyethylene. The investigation to be presented is a continuation of this work. Low density polyethylene of various degrees of chlorophosphonation will be investigated by mechanical, thermal, and dielectric techniques to determine the effects of the polar phosphonic acid group on its physical properties. The phosphonic acid copolymer will also be esterified or ionized and similar physical property measurements made.
CHAPTER II

EXPERIMENTAL

Sample Preparation

A series of ethylene-acrylic acid copolymers were obtained from Tennessee Eastman Company and two ethylene-methacrylic acid copolymers in the form of partially neutralized sodium salts (ionomers) were obtained from duPont Company. Both series of polymers were prepared by a free radical, high pressure copolymerization process. The partially neutralized copolymers were converted to the parent methacrylic acid copolymers by a technique to be described. The purified copolymers were further characterized as to branching, density, and crystallinity.

The parent low density polyethylene (LDPE) to be modified into ethylene-phosphonic acid copolymers was obtained from Monsanto Chemical Company. The starting polymer was purified and reacted by a technique to be described. The parent polymer had a density of 0.926 g/cc, a melt index of 2.9, a number average molecular weight of $1.38 \times 10^4$, a weight average molecular weight of $1.72 \times 10^5$, and 1.4 long chain branches per 100 carbon atoms.67
1. Purification of Ionomers. A variation of a technique reported previously was used to convert the methacrylic acid ionomers to the parent methacrylic acid copolymer. A mixture of 5% weight to volume (w/v) of methacrylic acid ionomer in a mixed solvent of 90% p-xylene and 10% tetrahydrofuran (THF) volume to volume (v/v) was heated to reflux in a three neck round bottom flask which was outfitted with a mechanical stirrer and a condenser. A two fold excess of concentrated hydrochloric acid (12M) was slowly added to the non-homogeneous mixture through a dropping funnel. The mixture changed to a homogeneous solution during the addition of the acid. The reaction mixture was allowed to reflux for one hour, and at the end of this time it was precipitated in a five fold volume of methyl alcohol. The collected polymer was washed three times in a methyl alcohol-water (90/10, v/v) wash and then dried in a vacuum oven. Completion of reaction was established by the disappearance of a band at about 1551 wave numbers (cm⁻¹) in the infrared spectrum which is attributed to the ionized carbonyl group of the methacrylic acid co-monomer. These samples are denoted 6M and 7M (Table 1).

2. Purification of Copolymers and Parent Low Density Polyethylene. The acrylic acid copolymers were dissolved in a mixed solvent of p-xylene and THF (90/10, v/v) and
precipitated in methyl alcohol to remove additives and impurities introduced during commercial processing. The parent low density polyethylene to be modified into a phosphonic acid copolymer was purified by the same technique. The precipitated polymers were collected and dried in a vacuum oven at room temperature to constant weight. The acrylic acid copolymers are denoted 1A - 5A and the parent low density polyethylene is denoted 8 (Table 1).

3. Preparation and Purification of Chlorophosphonated Low Density Polyethylene. The starting low density polyethylene was dissolved in phosphorous trichloride (PCl₃) at 70° at an optimum reaction ratio of 20 to 1 (PCl₃/LDPE, v/w) in a three neck round bottom flask which had been equipped with a magnetic stirrer, thermometer, and a modified cold finger type condenser. Purified oxygen gas (J.T. Baker) was bubbled into the mixture through a gas dispersion tube and the effluent gases from the reaction were bubbled into a basic solution (potassium hydroxide). The gases were taken off at the top of the modified cold finger type condenser. The chlorophosphonation reaction proceeds by a free radical mechanism and the overall reaction can be described by the equation

\[ \text{CH}_2\text{CH}_2^- + \text{PCl}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{CH}^- + \text{HCl} \]

\[ \text{POCl}_2 \]
The amount of phosphonyl dichloride attached to the backbone was controlled by varying the reaction times. Two series of phosphonated polymers were prepared. The first series had reaction times of 4, 6, 18, and 48 hours and are denoted samples A, B, C, and D respectively. The second series had reaction times of 6 hours and 12 hours and are denoted LD I and LD II in order of increasing reaction time. The phosphonic acid content of these co-polymers is shown in Table 2.

The phosphonyl dichloride containing polymer was hydrolyzed directly to the acid by carefully adding in small portions, all or half of the reaction mixture to crushed ice. The hydrolyzed polymer was broken into fine particle size and washed several times with distilled water until no further acid could be detected by pH paper in the water wash. The polymer was then dried in a vacuum oven at room temperature to constant weight.

4. Preparation and Purification of the Methyl Ester of Chlorophosphonated Low Density Polyethylene. The remaining portion of the reaction mixture was cooled to room temperature and then a major fraction (about 80%) of the unreacted PCl₃ and the by product, phosphorous oxychloride (POCl₃) was taken off under reduced pressure (300 mm Hg, 35 C). To the remaining jelly-like mass,
benzene was added (approximately 10% solids) and the mass broken up by stirring. Reagent methyl alcohol was added slowly to the mixture through a dropping funnel and the effluent gases were bubbled through a basic solution (potassium hydroxide). At the completion of the esterification reaction (18 hours) the mass was broken up and washed three times in methyl alcohol and then washed in a methyl alcohol-water solution (70/30, v/v) until pH paper detected no acid in the washing solution. The collected polymer was dried under the same conditions as described for phosphonic acid copolymers. These samples are denoted LD I Ester and LD II Ester and about 70% of the chloride groups have been esterified to the methyl ester.

5. Preparation and Purification of Ionized Derivatives of Chlorophosphonated Low Density Polyethylene. Two types of ionization procedures were used to prepare sodium and calcium salts of phosphonic acid copolymers. Copolymers having a low level of ionization were prepared by a method similar to that developed by Keresz and deKorosy and are denoted low calcium or low sodium salts of a given phosphonic acid copolymer. Five grams of polymer were dispersed in 200 ml of deionized water along with a 5-fold excess of sodium hydroxide or sodium acetate, and the mixture maintained at 75°C. At the end of one
week the mixture was washed five times with deionized water and then dried in a vacuum oven at room temperature. It was observed that the polymer had swollen slightly during the ionization reaction. Because of the swelling, it was thought that the ionization reaction had penetrated the polymer particles and ionized the interior of the polymer particles as well as the exterior. From cation analyses and infrared results, it appears that only partial ionization had taken place.

Reactions leading to a high level of ionization of the phosphonic acid copolymer were carried out in THF and p-xylene (20/80, v/v) using a five fold excess of either sodium hydroxide or calcium acetate solution. The ionization reactions were carried out near reflux conditions for one hour and at the end of that time the polymer was precipitated in cold methyl alcohol (0° C). The precipitated polymer was washed three times in 50/50 (v/v) methyl alcohol-water solution and then dried in a vacuum oven at room temperature. These samples are denoted as high salts of a given phosphonic acid copolymer. The ionization levels achieved by the two techniques are tabulated in Table 3.

Property Measurements

1. Preparation of Test Films. Samples for mecha-
nical relaxation and dielectric relaxation experiments were prepared by the method of compression molding. The methacrylic acid and acrylic acid copolymers were molded in a sandwich configuration consisting of polymer surrounded by a mold constructed of 15 mil brass shim stock and sandwiched between 5 mil virgin Teflon sheets and 1/8 inch chrome steel plates. Films were molded at 160°C and 10,000 psi in a Carver press. The samples were removed from the press and cooled quickly to room temperature. The phosphonic acid copolymers and the ester derivatives were compression molded in the same manner. The ionic derivatives of the phosphonic acid copolymers were molded at 180°C and 20,000 psi between layers of cellulose instead of Teflon in the sandwich configuration described previously. These samples were cooled to 75°C by a water cooling system before being removed from the press. Samples for infrared work were molded in the same manner except that a shim was not used. The high calcium salt of the LD II copolymer was impossible to mold into a film at 190°C and 37,000 psi. A similar condition was experienced by Otocka and Kwei in the magnesium salts of ethylene-acrylic acid copolymers containing more than 1.6 acid groups per 100 CH₂. The methacrylic acid and acrylic acid copolymers were annealed at 90°C for 12 hours and the
phosphonic acid copolymers and their derivatives were annealed at 85°C for 12 hours.

2. Infrared Measurements. Infrared measurements were made using a Perkin Elmer IR 257 spectrometer. Branching measurements were made on the copolymers utilizing the 1378 cm\(^{-1}\) band which is attributed to symmetric deformation of the methyl groups. Previously, the branching content of one of the methacrylic acid copolymers (sample 6M) had been accurately determined\(^7\) and this value was used to determine the branching content of the other copolymers which are listed in Table 1. Extinction coefficients were obtained by measuring three (or more) samples of different thicknesses. The extinction coefficients, denoted \(\varepsilon\) in cm\(^2\)/mole, were calculated from Beer's Law

\[
\frac{I_o}{I} = \log \frac{I}{I_o} = \varepsilon l C
\]

where \(A_{\text{max}}\) is the maximum absorbance of the peak, \(I_o\) is the value of the transmittance at the base line of the peak, \(I\) is the value of the transmittance at the maximum of the peak, \(l\) is the thickness of the sample and \(C\) is the concentration of the species in mole/cm\(^3\). A steady stream of nitrogen gas was blown on the sample during these measurements and subsequent crystallinity measurements to keep the sample at 30°C.\(^7\)
Crystallinity measurements on the methacrylic acid and acrylic acid copolymers were carried out using a method introduced by Read and Stein. Measurements were made on polymer films at least 25 mils thick. The volume fraction crystallinity \( X_c \) is given by the two formulas:\(^\text{10}\)

\[
X_c = \frac{e_{1894}}{6.4}
\]

\[
X_c = \frac{[e_{2016} - 2.1]}{6.0}
\]

where \( e_{1894} \) and \( e_{2016} \) are extinction coefficients of the 1894 cm\(^{-1}\) and 2016 cm\(^{-1}\) bands respectively. The 2016 cm\(^{-1}\) band is attributed to both a crystalline and an amorphous contribution whereas the 1894 cm\(^{-1}\) band is attributed strictly to a crystalline contribution. The base lines used for these determinations are shown in Figure 1 and the crystallinity results in Table 1. The 1894 cm\(^{-1}\) band appears to give better results for these systems, and a similar finding was reported by McKenna.

Hydrogen bonding of the carboxylic acid groups in the methacrylic acid and acrylic acid copolymers was studied as a function of temperature. Films were placed between polished salt plates and mounted in a specially constructed temperature chamber. The temperature chamber was continuously purged with nitrogen gas to eliminate water vapor
and any tendency for oxidation. Infrared spectra were taken approximately every 10° C. The temperature chamber was maintained at ± 0.5° C.

3. Density Measurements. Density measurements were made using a buoyancy technique. Baker Spectrograde methyl alcohol was added to deionized water until a small piece of polymer sample in the solution showed neither a tendency to rise to the surface or sink to the bottom of the vessel. The exact temperature and composition (weight fraction alcohol) of the solution were noted. From standard tables, the density of the solution was determined and this was assumed equal to the density of the sample. The densities were corrected to 20° C and are given in Table 1.

4. Dielectric Measurements. Dielectric measurements were made using a transformer ratio-arm bridge technique. A General Radio Capacitance Measuring Assembly (Type 1620-C) was used to measure capacitance and Tan δ or conductance at fixed frequencies of 50, 100, 200, 500, 1K, 2K, 5K, 10KHz. Measurements from room temperature to -160° C were made using a three-terminal cell supplied by Balsbaugh Laboratories (Type LD-3) with specially constructed 53 mm diameter electrodes. Temperature variation was achieved by blowing dry nitrogen gas through a
copper coil, which was immersed in liquid nitrogen, at
different flow rates. Temperature regulation of \( \pm 0.5^\circ C \)
was achieved. The temperature range from room tempera-
ture to elevated temperature was measured using a specially
constructed two-terminal stainless steel cell with 53 mm
diameter electrodes and Teflon insulation. The cell was
immersed in an oil bath regulated to \( \pm 0.1^\circ C \). Measure-
ments were not affected by the Teflon insulation. Alumi-
num electrodes of 50 mm diameter were attached to samples
when using the two-terminal cell. A thin layer of sili-
cone grease was applied to the surface between the alumi-
num electrode and the sample to improve surface contact.
The presence of the silicone grease had no effect on the
measurements.

A General Radio Megohmmeter (Type 1862-A) was used
to measure d.c. resistance in the range of \( 10^{12} - 10^6 \)
ohms. These readings were used to make d.c. conductance
corrections to the calculated results.

Values of the dielectric loss tangent, \( \tan \varepsilon' \), the
dielectric constant, \( \varepsilon' \), and the dielectric loss factor,
\( \varepsilon'' \), were calculated from the following equations:

\[
\varepsilon' = \frac{C_p}{C_0}
\]

\[
\varepsilon'' = \frac{J}{\omega C_0} = \frac{1}{R \omega C_0} = \frac{1}{2 \pi F C_0 R}
\]
\[ \tan \delta_\varepsilon = \frac{\varepsilon''}{\varepsilon'} = \frac{J}{\omega C_p} = \frac{1}{2\pi FRC_p} \]

where \( C_p \) is the capacitance of the cell containing a sample, \( C_o \) is the capacitance of the cell containing air, \( F \) is the frequency of measurement, \( J \) is the conductivity of the sample, and \( R \) is the resistance of the sample. Correction for the use of aluminum electrodes, an edge effect, high Tan \( \delta_\varepsilon \) readings (greater than 0.1) and d.c. conductivity were made in the calculations when necessary.

When aluminum electrodes were used, the ratio of the area of the electrode (\( A_e \)) of the test cell to the area of the aluminum electrode (\( A_{Al} \)) was the correction factor for \( \varepsilon' \) and \( \varepsilon'' \). The edge capacitance, \( C_o \), is subtracted from the observed capacitance of the sample (\( C_p \)) when the high temperature cell is employed. This correction was not necessary for the low temperature cell because of the third electrode. When Tan \( \delta_\varepsilon \) readings exceed a value of 0.1 the following equation was used to calculate \( \varepsilon' \):

\[ \varepsilon' = \frac{C_p}{C_o} \left( \frac{1}{1 + (\tan \delta_\varepsilon)^2} \right) \frac{A_e}{A_{Al}} \]

Conductivity measurements were corrected for a d.c. conductivity component when the d.c. resistance values were
less than $10^9$ ohms.

5. Dynamic Mechanical Measurements. Dynamic mechanical measurements were made on a Vibron Dynamic Viscoelastometer (Model DDV II, Toyo Measuring Instrument Co., Ltd.). A temperature range of $-165^\circ C$ to $+100^\circ C$ was covered using a single sample. Temperature variation was achieved by cooling the temperature chamber with liquid nitrogen to $-165^\circ C$ and then heating the chamber to elevated temperatures. The frequencies used in this experiment were 3.5, 11, and 110 Hz.

Values of the mechanical loss tangent, $\tan \delta$, were read directly from the apparatus, and values of the complex modulus, $E^*$, the real modulus, $E'$, and the imaginary modulus, $E''$, were calculated from the following equations:

$$E^* = \frac{L \cdot 2 \times 10^9}{T \cdot A \cdot DF}$$

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

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

where $A$ is the sample cross-sectional area in cm$^2$, $L$ is the strain of the sample, $DF$ is the dynamic force, and $A$ is a factor associated with the amplitude of the force.

6. Calorimetric Measurements*. Studies were car-

* The author is grateful to M.L. DeLucia for a portion of this work.
ried out using a Perkin-Elmer differential scanning calorimeter DSC 1B. Samples were cut from films and sealed inside aluminum pans supplied by Perkin-Elmer Corp. The samples were weighed on a micro-analytical balance and were in the range of 3-6 mg. Measurements were made at a heating and cooling rate of $10^0/\text{min}$.

The apparent heats of fusion ($\Delta H_f$) were derived from areas under the melting endotherms, using benzoic acid as a reference. The following equation was used to calculate percent crystallinity:

$$\%X_c = \frac{(W_T)(\Delta H_f^T)(A_S)(R_s)(100)}{(W_s)(\Delta H_f^{PE})(A_I)(R_I)}$$

where: $W$ is the weight of the sample in mg,

$A$ is the area under the melting curve,

$\Delta H_f$ is the heat of fusion in millicalories/mg,

$R$ is the recorder range,

$I$ refers to benzoic acid standard,

$S$ refers to the sample.

The $\Delta H_f^I$ of benzoic acid was taken as 33.89 mcals/mg and the $\Delta H_f^{PE}$ of 100% crystalline polyethylene was taken as 66 mcals/mg. The crystallinity values reported in Tables 2 and 3 are relative to an annealed sample of the parent polyethylene. The melting points quoted corres-
pond to the maximum excursion of the melting endotherms from the base line.
CHAPTER III

INFRARED STUDIES

Introduction

Infrared spectroscopy can be applied to organic compounds in a quantitative or qualitative manner. The technique covers the range of about 4000 cm\(^{-1}\) to 600 cm\(^{-1}\) in the electromagnetic spectrum and many molecular bonds can absorb energy in this range. Primarily, infrared spectroscopy is used as a qualitative tool in the determination of the existence of assorted molecular structures. Knowing the molecular bonding sequence and approximations for the force constants of the bonds, a spectrum-structure correlation approach can be made. Secondary forces, especially hydrogen bonding and ionic bonding, reduce the force constants of some molecular bonds and hence can be helpful in the determination of spectrum-structure correlations. Quantitative studies of the degree of hydrogen bonding can be made if the proportional factor (extinction coefficient) between the observed absorption peak and the known concentration of hydrogen bonded species can be established. Orientation of polymer chains can also be studied as a function of
elongation by infrared dichroism measurements. A technique has been formulated for crystallinity determination in polyethylene and some copolymers of polyethylene. Measurement of degree of branching and carbonyl concentration are other important properties of polymeric systems that can be measured quantitatively by infrared techniques.

The Infrared Spectrum

The role of secondary bonding, especially hydrogen bonding, on the mechanical-physical properties of polymers is enhanced due to the incorporation of acid side groups on polymer chains. Morawetz and coworkers concluded that the formation of hydrogen bonded dimers are primarily intramolecular from their studies of carboxylic acid containing copolymers in non-hydrogen bonding solvents. Otocka and Eirich working with mixtures of copolymers capable of having secondary bonding through hydrogen bonding or acid-base interaction made a similar conclusion. They concluded that the secondary bonding between carboxylic acid groups and pyridine(base) groups was intermolecular because the acid-base interaction raised the glass transition temperature beyond what could be gained by increasing the carboxylic acid content in its corresponding copolymer. Infrared dichroism
The number of dimers formed will be proportional to the total number of carboxylic acid groups and the equilibrium between the dimer and monomer structure will be a function of temperature.

An infrared technique has been used by Otocka and Kwei and MacKnight and coworkers to determine the association and dissociation constants respectively for the carboxylic acid dimer. The association constant is defined by the equation
\[ K_a = \frac{[\text{(COOH)}_2]^2}{[\text{COOH}]^2} \]

where \( K_a \) is the association constant in \( \text{cm}^3/\text{mole} \), \( [\text{(COOH)}_2] \) is the concentration of dimer species in \( \text{mole/cm}^3 \), and \( [\text{COOH}] \) is the concentration of monomer species in \( \text{mole/cm}^3 \). This determination makes use of the 935 cm\(^{-1}\) band which is attributed to out-of-plane bending of the \(-\text{OH}\) in the dimer form. This band has been used as an internal sample thickness band and has been shown to obey Beer's Law.

Figure 2 is a plot of maximum absorbance (\( A_{\text{max}} \)) of the 935 cm\(^{-1}\) band versus sample thickness for the samples under investigation. The extrapolation of \( A_{\text{max}} \) to zero thickness goes through the origin and Beer's Law is obeyed as has been shown previously. The \( A_{\text{max}} \) of the 935 cm\(^{-1}\) band is followed as a function of temperature and hence a function of the dimer concentration. Assuming complete dimerization at room temperature, the extinction coefficient for the 935 cm\(^{-1}\) band can be obtained by measuring the \( A_{\text{max}} \) of the 935 cm\(^{-1}\) band as a function of sample thickness. The extinction coefficients found by Otecka are listed in Table 4. The extinction coefficients are approximately constant. Table 4 lists the acid contents of the samples used in this work and the extinction coef-
The dissociation constant is defined as

\[ K_D = \frac{[\text{CCOH}]^2}{[\text{CCOH}]^2} \]

where \( K_D \) is the dissociation constant in mole/cm\(^3\). The technique used by MacKnight and coworkers to determine the dissociation constant depends upon the appearance, and the increase in intensity of the 3540 cm\(^{-1}\) band with increasing temperature. The 3540 cm\(^{-1}\) band is attributed to free \( \cdot \text{OH} \) and the 1750 cm\(^{-1}\) band is attributed to the carbonyl group in the free acid. This technique requires the 1750 cm\(^{-1}\) band to become distinct from the 1700 cm\(^{-1}\) band, which is very strong in intensity, at elevated temperatures. The 1700 cm\(^{-1}\) band is attributed to the carbonyl group in the dimer structure. The ratio between the 3540 cm\(^{-1}\) and 1750 cm\(^{-1}\) bands is determined at a temperature where a base line can be established for the 1750 cm\(^{-1}\) band. Using the assumption that this ratio is constant at other temperatures, the intensity of the 3540 cm\(^{-1}\) band at a given temperature can be used to determine the intensity of the 1750 cm\(^{-1}\) band at the same temperature. Hence, the amount of free acid, or indirectly the dissociation constant, is obtained by this method.
The extinction coefficient for the 1700 cm\(^{-1}\) band has been determined by McKenna for a methacrylic acid copolymer (sample 6M) and was found to be 9.14 x 10\(^5\) cm\(^2\) mole\(^{-1}\). This value is in good agreement with a value obtained by Chang who studied a system of pivalic acid in benzene. Chang also found that the extinction coefficient for the 1750 cm\(^{-1}\) band to be approximately one-half the value for the 1700 cm\(^{-1}\) band.

Both of these methods were applied to the copolymer systems used in this work. The association constant was calculated from information acquired by using the 935 cm\(^{-1}\) band. The dimer concentration was obtained directly from the intensity of the 935 cm\(^{-1}\) band through the use of Beer's Law. The monomer concentration was obtained from the difference between the total concentration and the dimer concentration. The dissociation constant is calculated from a formula derived by MacKnight and coworkers which is:

$$K_D = \frac{(A_{1\text{max}})^2}{4(A_{2\text{max}})^2}$$

where subscript 1 refers to the 1750 cm\(^{-1}\) band and subscript 2 refers to the 1700 cm\(^{-1}\) band. Essentially, the monomer concentration is measured directly and the dimer
concentration is found by the difference between the total concentration of acid groups and the concentration of monomer species.

The dissociation constants and association constants at a given temperature \((25^\circ)\) are listed in Table 6. Figures 3 and 4 are plots of \(\log K_a\) versus \(1/T\) and \(\log K_D\) versus \(1/T\). Table 6 lists the \(\Delta H^+\) for dimer formation deduced from the slopes of the lines in the previous plots.

Discussion

1. Hydrogen Bonding of the Carboxylic Acid Groups.

The extinction coefficients determined in this work decrease at higher acid contents, in contrast to the approximately constant values reported by Otocka. This discrepancy may be due to the use of acid contents greater than those used by Otocka or to the fact that a true dimer equilibrium was not initially established, through annealing, before measurements were made. Another proposal, which is favored, is that the dimerization is not complete at room temperature. If this is valid, then the concentration of dimers will be less than the total concentration of acid groups, and a correction factor for the true concentration of dimers must be used in the extinction coefficient calculation. One method to calculate this correction factor is to determine the concentra-
tion of "free" carboxylic acid groups at room temperature (which is defined as 25°C) from plots of log $K_a$ versus $1/T$. The concentration of "free" acid groups is listed in Table 5. The correction values are in the order of eight percent or less of the total acid concentration. It is also known that below the primary relaxation temperature, the glass transition temperature, the effect of bound groups decreases rapidly because they are frozen into position. This effect reflects the capture of an instantaneous equilibrium situation for the carboxylic acid species as the temperature approaches or exceeds the glass transition temperature.

The two independent methods of association and dissociation constant determination for the dimer species have pros and cons as to which is the most acceptable. Both the 3540 cm$^{-1}$ and the 935 cm$^{-1}$ bands are sufficiently sensitive to temperature that their intensities can be easily measured. Choosing a base line for the 3540 cm$^{-1}$ band is difficult at temperatures lower than 80°C due to a shifting intensity in this frequency region. The base line for the 935 cm$^{-1}$ band has no overlapping bands and is defined at all temperatures. For some samples the 1750 cm$^{-1}$ band never really separates well from the 1700 cm$^{-1}$ band, hence the base line used by Macknight and coworkers for the 1750 cm$^{-1}$ band cannot be defined. This may be due to
the sample size necessary to get sufficiently large intensities for the 3540 cm$^{-1}$ and the 935 cm$^{-1}$ bands to reduce error. Otocka and Eirich working with butadiene-methacrylic acid copolymers were unable to resolve the 1750 cm$^{-1}$ band. Morawetz and coworkers had separated the 1700 cm$^{-1}$ and 1750 cm$^{-1}$ bands successfully. Otocka and Kwei using a DuPont curve analyzer had found four absorptions occurring at 1750 cm$^{-1}$, 1735 cm$^{-1}$, 1705 cm$^{-1}$, and 1690 cm$^{-1}$ in ethylene-acrylic acid copolymers. The effect of the magnitude of the extinction coefficients also plays a role in these determinations.

The values of heat of dissociation and heat of association for the carboxylic acid dimer are in rough agreement with values previously determined in both polymeric and solvent mediums. The $\Delta H^\ddagger$'s determined from the $K_a$ plots are higher in value than most of the values available in literature and the $\Delta H^\ddagger$'s determined from the $K_D$ plots are scattered lower and higher than most literature values. These differences are attributed to measurement of infrared intensities from only the heating cycle of the hydrogen bonding experiments. Otocka and Kwei measured infrared intensities in both the heating and cooling cycles and found excellent agreement using the cooling cycle data.

From the table listing the values of $K_a$ and $K_D$ at a
given temperature, it is noted that the two infrared techniques are not complimentary; i.e., the $K_a$ and $K_D$ values are not reciprocals of each other. An explanation of this obvious discrepancy is lacking. The method used to determine the association constant is preferable, because the 935 cm$^{-1}$ band has no interfering bands, the extinction coefficient is in the order of $10^4$ cm$^2$/mole, and the band is sufficiently sensitive to temperature.

2. Qualitative Study of the Phosphonic Acid Copolymers. The infrared spectrum of a chlorophosphonated polyethylene reported by Phillips and MacKnight was composed of several broad areas of absorption. The presence of the phosphonyl group (P=O) and the hydroxyl group (P-O-H) results in the observed broad absorption due to the intense absorption of the P=O group and the hydrogen bonding of both groups. The P=O group has also been reported to give a doublet absorption the origin of which is not fully understood. The assignments suggested in this work are only tentative due to the complexity of the samples. The wavelength range of 1300 cm$^{-1}$ to 700 cm$^{-1}$ will be discussed. All samples used in the qualitative infrared analysis were compression molded into films of less than 2 mils thickness.

After surveying the available literature for a model
compound similar to the polymeric system with available data on the proper functionalities, the compound class of methylphosphonates was chosen. Sadtler spectrums number 21806 and 21787 were used for the methylphosphonic and monomethylester respectively. Corbridge and Lowe reported infrared spectra findings for some salts of phosphorous oxyacids. Among these compounds were salts of methylphosphonic acid from the following cations: sodium, magnesium, calcium, strontium, barium, silver, and lead. Table 7 lists the band positions in the range of 1300 cm\(^{-1}\) to 700 cm\(^{-1}\) from these references.

Using the concept of frequency shift in the infrared spectrum due to hydrogen and/or ionic bonding, a tentative spectra-structure correlation can be made for the absorptions listed in Table 7. It must be remembered that this correlation will be tentative because of the variation in spectrometers, sample states, workers, degree of hydration of the salts, and the discrepancies of structure-spectra correlations available in literature.

The suggested spectra-structure correlations are given in Table 7 and will be summarized here. Reduction of hydrogen bonding (from the acid to the ester) causes a shift in the 1120 cm\(^{-1}\) and 1160 cm\(^{-1}\) bands of the acid to 1140 cm\(^{-1}\) and 1190 cm\(^{-1}\) in the ester for the P=O group.
The doublet bands at 1016 cm\(^{-1}\) and 1102 cm\(^{-1}\), 1030 cm\(^{-1}\) and 1100 cm\(^{-1}\), 1035 cm\(^{-1}\) and 1062 cm\(^{-1}\) for the magnesium, calcium, and sodium salts respectively are assigned to the ionized P=O group. The bands appearing in the range of 955 cm\(^{-1}\) to 1055 cm\(^{-1}\) in the acid and ester are assigned to the P-O-H group and the band at 973 cm\(^{-1}\) to 985 cm\(^{-1}\) in the salts is attributed to the same group. The bands appearing from 757 cm\(^{-1}\) to 890 cm\(^{-1}\) for all samples are attributed to the P-C group, and the band at 730 cm\(^{-1}\) in the ester is assigned to the P-O-C group.

The chlorophosphonated polyethylene denoted LD I was investigated by infrared so as to confirm the existence of the proposed structures and to expand the available information in a difficult area. For the acid, ester, and low salt a band consisting of a doublet is present in the range of 1143 cm\(^{-1}\) to 1196 cm\(^{-1}\) and this is attributed to the P=O group. In the high salt, bands at 1138 cm\(^{-1}\) and 1070 cm\(^{-1}\) are attributed to the ionized P=O group. In the acid a band at 1003 cm\(^{-1}\) is assigned to the P-O-H group and a band at 1058 cm\(^{-1}\) in the ester is also assigned to this group. It is typical to observe shifts of 50 cm\(^{-1}\) due to the presence or absence of hydrogen bonding. Bands at 1048 cm\(^{-1}\) and 998 cm\(^{-1}\) in the low salt and a shoulder in the high salt at 936 cm\(^{-1}\) are also assigned to the P-O-H
group. A band appearing at about 930 cm$^{-1}$ for the acid, ester and low salt, and a band at 908 cm$^{-1}$ for the high salt are attributed to P-C linkages. The band at 798 cm$^{-1}$ in the ester is attributed to the P-O-C group. The tentative spectra-structure correlations are summarized in Table 8.
CHAPTER IV

DYNAMIC MECHANICAL STUDIES: ETHYLENE-METHACRYLIC
ACID AND ETHYLENE-ACRYLIC ACID COPOLYMERS

Introduction

The two different series of copolymers investigated in this work are similar in that the major portions of their backbones are polyethylene, similar to low density polyethylene. Mechanical relaxations in polyethylene have been extensively studied, although the molecular origins of these relaxations remain a matter of some controversy. 70,83,84

Low density polyethylene itself has three major mechanical relaxations denoted alpha, (\(\alpha\)), beta, (\(\beta\)) and gamma (\(\gamma\)), which appear at about 50\(^\circ\)C, -20\(^\circ\)C, and -120\(^\circ\)C respectively at low frequencies. It is widely accepted that the \(\alpha\) loss mechanism is a composite of chain motions occurring in the crystalline phase. Takayanagi has suggested that the molecular motion processes occur in crystal lamellae and are of two types: torsional motion about the chain axis, and translational motion along the chain axis. Other workers conclude that molecular motion in the amorphous region between crystal lamellae also contributes to the loss mechanism. The \(\beta\) relaxation is an amorphous phase motion occurring only in low den-
sity polyethylene and is attributed to the microbrownian motion of polymer chains involving branch points. These motions may also be cooperative segmental motions of side groups capable of undergoing hindered rotations independent of the chain backbone. The \( \beta \) relaxation is associated with the glass transition or the primary relaxation in low density polyethylene. The \( \gamma \) loss mechanism is also a composite mechanism and is thought to arise from localized motions of a few repeat units in the amorphous and/or crystalline phase. Schatzki has proposed a "crankshaft" motion of four linear methylene sequences between two colinear bonds. Because of the colinear restriction of the Schatzki model, the "crankshaft" motion cannot occur in the crystalline phase where the methylene sequences are in the trans conformation and consequently must occur in the amorphous phase. Recently Schatzki himself has cast great doubt on the validity of this model. Other workers relate the relaxation to defects in the crystalline phase.

Dynamic Mechanical Relaxation Spectra

The temperature dependence of the real modulus, \( E' \), and the imaginary modulus, \( E'' \), at 110 Hz for all the copolymers investigated and low density polyethylene are
shown in Figures 5 and 6. As the methacrylic acid or acrylic acid content of the copolymer is increased, the \( \beta \) peak changes in shape and position. Two overlapping peaks exist in samples 1A, 2A, and 3A and are attributed to the \( \alpha \) and \( \beta \) relaxations of low density polyethylene which exhibits only one relaxation in this region. The temperature position of the \( \beta \) peak maximum increases with increasing acid content of the copolymers.

The temperature maximum of the transition was established from expanded plots of \( E'' \) versus temperature. Using these temperature maximums, Arrhenius type plots of log frequency versus \( 1/T \) (Figure 7) were constructed. From the slopes of these lines an activation energy of the relaxation was calculated. Since only three frequencies, and hence only three points, were used to establish the Arrhenius plots, considerable error exists in the activation energy determination. The activation energies for the \( \beta \) and/or \( \beta' \) peak and the temperature maximum at 110 Hz for the samples used in this work are listed in Table 9.

The \( \gamma \) relaxation peaks for all the copolymers and low density polyethylene were observed to appear at the same temperature within experimental error. Activation energies were calculated in the same manner as described
for the \( \phi \) relaxation and Table 9 summarizes the temperature maximum at 110 Hz and activation energy data for the \( \gamma \) relaxation of all the samples.

Discussion

1. The \( \phi' \) and \( \phi \) Relaxation. Kline, Sauer and Woodward demonstrated that the magnitude of the \( \phi \) peak was proportional to the methyl content for polyethylene. The relation between magnitude of the \( \phi \) relaxation and methyl content is called the branching effect. It would predict that high density polyethylene would not exhibit a \( \phi \) transition, and this has been demonstrated by several workers.

Schneider and Wolf investigated the mechanical relaxations in chlorinated polyethylene as a function of chlorine content. They found that the \( \phi \) peak initially decreased in temperature maximum and then slowly increased up to about forty percent chlorine, and finally increased substantially above forty percent chlorine content. They attributed the change in the \( \phi \) peak temperature maximum to a combination of two effects resulting from the chlorine atom. At low chlorine content, the effect is the same as branching; i.e., to separate the polymer chains and hence
reduce the temperature maximum. At higher chlorine contents the dipolar effects induced by the chlorine atom become predominant and increase the temperature maximum of the relaxation. Nielsen observed a similar effect in the $\phi$ transition of ethylene-vinyl acetate copolymer. The temperature maximum remained constant as the volume percent acetate in the copolymers was increased up to 60%. At 60 volume percent acetate, the $\phi$ temperature maximum increases linearly with increasing acetate content. He concluded that almost any non-crystallizable groups incorporated in the polyethylene backbone will cause a relaxation in this temperature region.

Schneider and Wolf observed that the $\alpha$ peak decreases in intensity and temperature maximum with increasing chlorine content in chlorinated polyethylene. Kline, Sauer and Woodward observed the same phenomenon in their mechanical studies on polyethylenes of different degrees of branching; i.e., with increasing branching the $\alpha$ peak decreased in temperature maximum and magnitude. The $\alpha$ peak has been shifted due to the reduction in crystallinity by the chlorine atom or the branch point in polyethylene. These molecules interfere with the close packing ability of the polyethylene chain. Illers and Sinnott have shown that for linear polyethylene the
temperature maximum of the \( \alpha \) peak can be increased by annealing. Annealing increases the lamellae thickness which in turn increases the concentration of crystalline material in the bulk polymer. \[7,10,17\]

Several workers have demonstrated that the \( \beta \) transition in ethylene-carboxylic acid containing copolymers shifts to higher temperatures and increases in intensity as the carboxylic acid content is increased. This new peak is denoted \( \beta' \). These same workers have demonstrated by infrared, DSC, and x-ray diffraction techniques that the crystallinity of the carboxylic acid containing copolymer decreases with increasing acid content. \[16\]

MacKnight and coworkers demonstrated that the \( \beta' \) peak could be separated into two peaks, \( \beta' \) and \( \alpha \) by annealing. They observed that the \( \beta' \) peak did not shift from its position as determined in a quenched sample, and that the \( \alpha \) peak appeared at a higher temperature than the \( \beta' \) peak. They also found that the magnitude of the \( \beta' \) peak was proportional to the acid content.

The observed change from two peaks in the \( \beta' \) relaxation region for samples 1A, 2A, and 3A (Figure 5) to a single peak as the acid content of the copolymer is increased is interpreted in the following manner. The \( \beta \) peak is increasing in temperature maximum and magnitude at the
same time the $\alpha$ peak is decreasing in temperature maximum and magnitude, and both of these effects are due to the increasing concentration of carboxylic acid containing comonomer. This interpretation is supported by the previously discussed results of other workers, and the crystallinity results reported in Table 1 for these copolymers. The shift in the temperature maximum of the $\beta_{10}^1$ peak observed by Otocka and Kwei and in this work is summarized in Table 9. Otocka and Kwei using the equation of Gordon and Taylor concluded that the observed increase in the $\beta$ temperature maximum could not be accounted for by a copolymerization effect alone. Superimposed on the copolymerization effect is the general increase of cohesion of the material due to the increase in inter-molecular hydrogen bonding. Recently, Fujiki and fellow workers observed the $\beta$ peak temperature maximum of ethylene-vinyl acetate copolymer increased with increasing hydrolysis. They attributed the shift in temperature to the increase in hydrogen bonding. The pseudo-crosslinking due to carboxylic acid dimerization tends to stiffen the polymer matrix and hence increases the temperature at which the mechanical relaxation process occurs.

Fox and Loshaek derived a relationship between the density of crosslinks, $\rho$, and the change in glass tem-
perature, $\Delta \rho T_g$, which is:

$$T_g = \left( \frac{M_c \Delta \alpha_c T_g(c)}{\alpha_c - \beta_c - M_c \Delta \alpha_c \rho} \right) \left( 1 + \frac{\Delta V_o}{M_c \Delta \alpha_c T_g(c)} \right)$$

where

$$\Delta \rho T_g = T_g(\rho) - T_g(c)$$

$$\Delta \alpha_c = \alpha_c - \alpha$$

and

$T_g(c)$ and $\beta_c$ refer to the uncrosslinked copolymer composition $c$.

$T_g(\rho)$ refers to the corresponding copolymer of cross-link density $\rho$.

$M$ and $\alpha_i$ are the average molecular weight and the average volume-temperature coefficient of the comonomer mixture of composition $c$.

$\alpha_c$ refers to the corresponding uncrosslinked copolymer.

$\Delta V_o$ is the volume contraction at $0^\circ$K for the hydrogen bonding (crosslinking) of a mole of carboxylic acid groups.

At sufficiently low $\rho$ for a polymer of fixed composition the glass transition will increase linearly with
increasing $\rho$. If both composition and degree of cross-linking are varied simultaneously, the results may not be linear. Conversely, if the constants in the Fox-Iosshack equation are linear functions of composition, then the change in glass transition temperature and crosslink density will be linear. They have applied the relationship successfully to crosslinked polystyrene, polymethylmethacrylate, and polyglycoldimethacrylates.

The $\rho$ temperature maximum of low density polyethylene at 110 Hz (-20°C) is assumed to be the reference glass transition temperature, $T_g(c)$. Assuming all the acid groups are involved in intermolecular hydrogen bonding in the amorphous phase, the density of crosslinks in moles per gram of amorphous polymer can be calculated. The results are shown in Figure 8; data of Ctocka and Kwei are also included. For the data shown (Figure 8) no corrections for contribution due to changes in copolymer composition were taken into account. The linearity of the plots suggests the increase in glass transition temperature can be attributed to the crosslinking effect of hydrogen bonds by the theory of Fox and Iosheak.

In plots of $E''$ versus temperature, Figures 5 and 6, it is obvious for samples 1A, 2A, and 3A that two distinct temperature maximums are present and these have been assigned the $\alpha'$ and $\rho'$ peaks in order of decreasing temperature
as was discussed previously. For these samples an activation energy is not reported because it is difficult to justify an activation energy determination when more than one mechanism is involved in the relaxation. The copolymers with higher acid contents show a single peak in the $E''$ versus temperature plot and hence an activation energy was determined for these samples.

Woodward and Sauer in 1958 summarized the data of various workers for the $\phi$ transition in polyethylene. From this collection of data, which is quite scattered, they estimated the activation energy to be in the range of 20-100 Kcal/mole. Kabin reported a value of 16 Kcal/mole, Wada a value of 46 Kcal/mole and Sandiford and Willbourn a value of 38 Kcal/mole for the $\phi$ relaxation. It was found for the polyethylene used in this investigation that the activation energy is 124 Kcal/mole. As stated previously, considerable error exists in the present experimental determination of this quantity. Hoffman, Williams, and Passaglia refuse to discuss the $\phi$ relaxation because the origin of the relaxation is not settled in their opinion. The literature contains scattered data in this area, and studies of the $\phi$ relaxation as a function of branching and crystallinity in terms of activation energy analyses are non-
existent.

The activation energy for the $\rho'$ loss mechanism appears to be slightly higher than for the $\rho$ loss mechanism of low density polyethylene (when the value determined by Wada or by Sandiford and Wellbourn is used for low density polyethylene). The activation energy (Table 9) for the acrylic acid copolymer sample is about the same, but for the two methacrylic acid samples there is a significant difference. In general, the activation energy for the $\rho'$ relaxation is higher than the $\rho$ relaxation in low density polyethylene and appears to increase with increasing acid content. The higher and increasing values of the activation energy with acid content indicate that the molecular mechanism is more cooperative in nature than the mechanism in low density polyethylene.

2. The $\gamma$ Relaxation. Below the glass transition the effect of secondary bonding or bound groups on the bulk polymer decreases rapidly. McKenna and coworkers in 1969 reviewed previous work and interpretations of the $\gamma$ relaxation in polyethylene, and in similar copolymers. They also reported results for a study of the $\gamma$ relaxation in an ethylene-methacrylic acid copolymer in the acid and partially ionized form. The $\gamma$ mechanical relaxation peak for the samples studied in this work has its tempera-
ture maximum in the neighborhood of -125°C.

McKenna, working with a methacrylic acid copolymer (sample 6M) and ionomers based on the copolymer, demonstrated that the $\gamma$ peak could be resolved into two peaks denoted $\gamma_a$ and $\gamma_c$ having temperature maximums of -129°C and -163°C respectively. The $\gamma_a$ loss mechanism occurs in the amorphous phase whereas the $\gamma_c$ process occurs in the crystalline phase. No attempt was made in this investigation to resolve the $\gamma_c$ relaxation from the $\gamma_a$ relaxation. Due to the low crystallinities of these samples (Table 1) and the position of the temperature maximums, it is proposed that the relaxation occurs in the amorphous phase. The loss mechanism proposed by Schatzki is favored since this is an amorphous phase mechanism.

The activation energies deduced from plots of log frequency versus $1/T$ tend to be higher than reported by McKenna, but the values are in rough agreement with other workers, who report values in the range of 11 to 15 Kcals/mole. Woodward and Sauer have correlated the data of several workers for polyethylene and calculated an activation energy of 12 Kcal/mole over the frequency range of 1 Hz to 2 MegHz for the $\gamma$ process. The data in Table 9 implies that the range of carboxylic
acid containing copolymers studied has no significant
effect on the \( \gamma \) relaxation. There appears to be a ten-
dency for the temperature maximum to decrease at higher
acid content, but the experimental uncertainty is too large
to justify this statement.
CHAPTER V

DYNAMIC MECHANICAL STUDIES: ETHYLENE-PHOSPHONIC ACID COPOLYMERS AND THEIR SALT AND ESTER DERIVATIVES

Dynamic Mechanical Spectra

The results for the phosphonic acid copolymers and their derivatives are generally consistent with the assignments of the relaxation peaks of low density polyethylene described in Chapter 4. As crystallinity decreases, the \( \alpha \) relaxation also decreases in magnitude, the \( \phi \) relaxation increases in magnitude, and the \( \gamma \) relaxation increases somewhat.

The temperature dependence of the storage moduli, \( E' \), and the loss moduli, \( E'' \), at 110 Hz for the unmodified polyethylene and the phosphonic acid copolymers and the derivatives of the copolymer are presented in Figures 9-16. The composition of these samples is given in Tables 2 and 3. Figure 9 compares copolymers A and B to the parent polyethylene and it is seen that the \( \alpha \), \( \phi \), and \( \gamma \) relaxations of the parent polyethylene are discernible for these materials also, although the magnitudes of the \( \phi \) and \( \gamma \) mechanisms are enhanced in the copolymers. \( E' \) decreases more rapidly at high temperatures for both samples than for the parent polyethylene and this behavior
presumably arises from the lower crystallinity of the copolymers. The temperatures of the relaxations are little changed from those of the parent. In copolymer C, on the other hand, Figure 10 reveals that the \( \alpha \) relaxation has disappeared almost entirely and the major decrease in \( E' \) is associated with the \( \beta \) relaxation. Once again the temperatures of the \( \gamma \) and \( \beta \) relaxations show little change from the corresponding relaxations in the parent. The behavior of copolymer D, however, is qualitatively different from that of the parent as opposed to samples A, B, and C which show only quantitative differences from the parent. Figure 11 illustrates this difference showing that in addition to the \( \gamma \) and \( \beta \) relaxations there appears a new relaxation in copolymer D at 50°C labeled \( \alpha' \). Inasmuch as copolymer D is totally amorphous, the \( \alpha' \) relaxation cannot be identified with the \( \alpha \) relaxation of polyethylene. The \( \alpha' \) peak is associated with a phase separated structure; i.e., formation of domains. Copolymer D is the only sample to exhibit such a relaxation in this investigation. Some of the salts were not investigated in the \( \alpha' \) relaxation region because the relaxation occurs in excess of the maximum experimentally observable temperature.

Figures 12 and 13 compare the phosphonic acid and methyl ester derivs of copolymers LD I and LD II respectively. The acid and ester derivatives of LD I exhibit
similar relaxations to those observed for the parent polyethylene. The temperature of the \( \phi \) relaxation is about 10\(^\circ\)C higher than the parent polymer in both derivatives. This is not the case in the acid and ester derivatives of the LD II phosphonic acid copolymer. The \( \phi \) peak temperature maximum is shifted about 10\(^\circ\)C in the acid and about 30\(^\circ\)C in the ester higher than observed for the parent polymer. An \( \alpha \) relaxation is observed for the acid and ester derivatives of copolymer LD I and the parent polymer, but is essentially non-existent in the derivatives of the LD II copolymer.

Figures 14 and 15 compare the sodium and calcium salts derived from the LD I acid respectively. The \( \phi \) and \( \gamma \) relaxations for the two levels of ionization and the two cations are similar to their parent acid. The \( \alpha \) relaxation has been reduced in magnitude for the higher levels of ionization. In Figure 16 the sodium and calcium salts of the LD II acid are compared. The \( \beta \) and \( \gamma \) relaxations occur at about the same temperature as observed for the parent acid, but the magnitude of the \( \gamma \) peak increases and the magnitude of the \( \phi \) peak decreases in comparison. The magnitude of the \( \alpha \) peak has also been reduced, especially in the sodium salts. The values of \( E' \) in the temperature region between the \( \gamma \) and \( \phi \) relaxations
are slightly lower than the parent acid.

Discussion

1. The $\alpha'$ Relaxation. The appearance of the new $\alpha'$ peak in the amorphous sample D is taken as evidence for microphase separation. The temperature behavior of $E'$ in sample E is also suggestive of the phenomenon. It may be seen that there is a slight decrease in $E'$ at the temperature of the $\beta$ relaxation, but that the catastrophic decrease in $E'$ occurs in conjunction with the $\alpha'$ relaxation. It would thus appear that the glass transition of the hydrocarbon matrix occurs at the temperature of the $\beta$ relaxation while that of the phosphonic acid domains occurs at the temperature of the $\alpha'$ relaxation. The dielectric studies to be discussed in Chapter 7 serve to clarify and reinforce this interpretation. Final proof must await morphological studies in which the structure and dimensions of the phosphonic acid aggregates can be defined.

Work of Phillips and MacKnight and Read and co-workers on salts of ethylene-methacrylic acid copolymers suggests that a relaxation observed in their work in excess of 50°C can be assigned to motions within ionic domains formed by clustering of salt groups. As stated
previously, an $\alpha'$ peak was not observed for the salts of the LD I and LD II copolymer series. The concentration of phosphonic acid species and hence salt concentration was probably not high enough so that a phase separated structure could form. The necessary and sufficient conditions for clustering of groups to occur has not been defined for a matrix consisting of a hydrocarbon phase and an ionic phase.

2. The $\rho$ Relaxation. It is interesting to compare the temperature locations of the $\rho$ relaxations in the phosphonic acid copolymers to those of the ethylene-acrylic acid and ethylene-methacrylic acid copolymers. Such a comparison is only semi-quantitative because of differences in branching between the copolymer systems. Figure 17 is a plot of the temperatures of the $\rho$ relaxation as a function of the number of substituent groups per 100 carbon atoms for the acrylic acid, methacrylic acid and phosphonic acid copolymers investigated in this study. Also included is data of Stocker and Kwei on acrylic acid copolymers and the ester derivatives of LD I and LD II phosphonic acid copolymers. It is apparent that there is a large increase in the $\rho$ relaxation temperature with increasing acrylic acid or methacrylic acid content but that the $\rho$ relaxation temperature is essentially independent of phosphonic
acid content over the range studied. The ester derivatives of the phosphonic acids agree closely with the trend shown by the acrylic acid and methacrylic acid copolymers, in contrast to their parent phosphonic acids.

The increase of the $\beta$ temperature maximum for the methacrylic acid and acrylic acid copolymers was resolved into two effects in Chapter 4 which are, (1) copolymerization effect, and (2) increase in cohesion of the material. For the phosphonic acid copolymers an increase of 12°C in the $\beta$ temperature maximum over that for low density polyethylene was observed, but the temperature maximum is independent of phosphonic acid over the range studied. This occurrence is suggestive of the formation of clusters. The observed $\beta$ temperature maximum is that of the hydrocarbon matrix which has been slightly stiffened by the presence of clusters.

The previous argument is supported by the fact that the ester derivatives of the LD I and LD II phosphonic acid copolymers agree with the $\beta$ temperature maximum increase of the methacrylic acid and acrylic acid copolymers. The esterification reaction, on the average, esterifies about 1.5 phosphonyl chloride positions per pendant group. The remaining positions are hydrolyzed to the acid. The observed increase in the $\beta$ temperature maximum for the
esters is due mostly to the copolymerization effect and partially to the increased cohesion of the polymer through hydrogen bonding of the remaining phosphonic acid groups.

The ϕ temperature maximum observed for the sodium and calcium derivatives of the LD I and LD II copolymer series are similar to the parent phosphonic acid copolymers. The neutralized phosphonic acid copolymers are likely candidates for phase separation based on previous work with salts of methacrylic acid copolymers. The low calcium derivatives of the LD I and LD II copolymers tend to have higher ϕ temperature maximums than the other sodium or calcium derivatives. The calcium ion has the potential of being shared by two different phosphonic acid groups, and would appear to act as a pseudo-crosslink on this basis. The pseudo-crosslinking would increase the cohesion of the copolymer and hence explain the observed increase in the ϕ temperature maximum for the low calcium salts.

Activation energies were determined from the slope of plots of log frequency versus reciprocal temperature for the parent polymer, the phosphonic acid copolymers and their derivatives. The activation energies and the temperature maximums of the ϕ relaxation are given in Table 10. As pointed out in Chapter 4, considerable error exists in the
activation energy determination because of the use of only three frequencies. The activation energy for the ester derivatives of the phosphonic acid copolymers is substantially higher. This implies that the esters have a more cooperative molecular mechanism than the acids for micro-brownian segmental motion. The activation energies for the salts tend to be similar to their parent acids, except in the case of the calcium salts of the LD I phosphonic acid copolymer. The reason for this apparent increase is not obvious and has been suggested that the calcium ions are effectively shared by two different phosphonic acid groups and hence the amount of pseudo-crosslinks is increased. In general, the activation energies decrease with increasing ionization.

3. The \( \gamma \) Relaxation. The activation energies and the temperature maximums at 110 Hz for the parent polymer, the phosphonic acid copolymers, and the derivatives are listed in Table 10. The \( \gamma \) temperature maximum decreases with increasing acid content and the esters and salts tend to be higher than the parent acid. In general, the activation energies are the same magnitude as observed for low density polyethylene, and appear to be independent of phosphonic acid content. The relaxation is attributed to the \( \gamma \) mechanism associated within the amorphous
phase of polyethylene as described in Chapter 4.
CHAPTER VI

DIELECTRIC STUDIES: ETHYLENE-METHACRYLIC ACID AND ETHYLENE-ACRYLIC ACID COPOLYMERS

Introduction

The dielectric behavior of polymers in terms of molecular structure has been investigated by many workers. Dielectric activity is imparted by the presence of a permanent dipole moment in the polymer's backbone and/or as a pendant group on the polymer chain. The permanent dipole moment is used as an indicator or tracer to study molecular motions.

Polyethylene is considered a non-polar polymer because it has no permanent dipole moment and a $\tan \delta$ of the order of $10^{-4}$. A small concentration of carbonyl groups has been incorporated into the polyethylene chain to render the polymer dielectrically active by several workers. They introduced carbonyl groups into the polyethylene chain by oxidation and recently by copolymerization. Three dielectric relaxation peaks were observed with similar temperature positions as the $\alpha$, $\rho$, and $\gamma$ mechanical relaxation peaks. The dielectric and mechanical relaxation spectrums complement each other because the carbonyl groups are part of the polymer's backbone and con-
sequently relaxations arise from the same molecular motion.

The polar derivatives of polyethylene investigated possess a pendant group which has a permanent dipole moment. The pendant groups are either carboxylic acid or phosphonic acid and are capable of moving independently of the backbone by rotation. Superimposed on the expected dielectric relaxations of the polymer's backbone, as observed in the mechanical relaxation studies, will be relaxations associated only with the pendant group.

The Dielectric Relaxation Spectrum

The dielectric relaxation spectra of the ethylene-methacrylic acid and ethylene-acrylic acid copolymers are similar in shape and temperature position. The spectra are typical of amorphous polymers and not the actual semi-crystalline polymers as observed by the crystallinity measurements (Table 1). This observation implies that the dielectrically active species is excluded from the crystalline regions and must reside in the amorphous phase. A representative plot of $\varepsilon''$ versus temperature for 100 Hz, 1 KHz, and 10KHz is shown in Figure 16. Two major relaxations are present and are denoted $\gamma'$ and $\gamma$ in order of decreasing temperature. Table 11 summarizes
the relative magnitudes and temperature maximums for the
\( \rho^i \) and \( \gamma \) relaxations of the copolymers.

Temperature maximums were determined from plots of \( e'' \)
versus temperature at eight frequencies for the \( \rho^i \) and
\( \gamma \) relaxations of the copolymers. Activation energies
for these relaxations were determined from the slopes of
graphs of log frequency versus reciprocal absolute tempera-
ture and are tabulated in Table 11.

Discussion

1. The \( \beta^i \) Relaxation. Previous workers
have observed two major dielectric relaxations in meth-
acrylic acid copolymers. They worked with only one con-
centration of acid in the copolymer and consequently
were unable to specify the dipolar species responsible
for the observed dielectric relaxation. It has been pro-
posed that the dipolar species responsible for the re-
laxation may be residual carbonyl groups introduced
by thermal oxidation during processing or hydrogen bonded
species such as trimers and tetramers. The dimerized
carboxylic acid has no net dipole moment, because of its
symmetry, and does not contribute to the dielectric re-
laxation process. A more logical conclusion is that the
species are free carboxylic acid groups, but this
suggestion has been discounted by calculations made by Read and coworkers.

Phillips and Stein studied a series of ethylene-carbon monoxide copolymers and concluded that the presence of an α relaxation in their dielectric results implied the carbonyl group could fit into the polyethylene crystal lattice. The copolymers under investigation in this work did not show an α peak (Figure 10), and this is taken as evidence against the active dipolar species being assigned to the carbonyl group. The existence of only two relaxation peaks, which is typical for amorphous polymers, also implies that the active dipolar species is contained in the amorphous phase.

This leaves only the free carboxylic acid group to explain the observed dielectric behavior of the copolymers. From infrared results (Chapter 3) it was found that the concentration of "free" acid groups at room temperature was proportional to the total concentration of acid groups in the bulk. The number of free acid groups, \( N_f \), can be estimated by the following procedure. The association constant for the hydrogen bonded monomer-dimer equilibrium is given by the equation

\[
K_a = \frac{[(\text{COOH})_2]}{[\text{COOH}]^2}
\]
where $[\text{COOH}]$ is the concentration of monomeric acid groups in groups/cm$^3$ and $[(\text{COOH})_2]$ is the concentration of dimeric acid groups in groups/cm$^3$. The total concentration of groups/cm$^3$, $N_t$, is given by the mass balance equation:

$$N_t = 2[(\text{COOH})_2] + [\text{COOH}]$$

and, by substitution,

$$N_t = 2KaN_f^2 + N_f$$

Solving for $N_f$:

$$N_f = \frac{1}{4K_a} \left[ -1 \pm \sqrt{1 + 8KaN_t} \right]^{1/2}$$

with $KaN_t \gg 1.0$

then

$$N_f = \left( \frac{N_t}{2K_a} \right)^{1/2}$$

The experimentally observed dielectric relaxation can be related to a dipolar species by the following technique. The magnitude of a dielectric relaxation may be represented by the value $\varepsilon_R - \varepsilon_U'$. The quantity, $\varepsilon_R - \varepsilon_U'$, is the difference between the relaxed (low frequency) and the unrelaxed (high frequency) value of the $\varepsilon'$ (dielectric constant) over the relaxation region. Values
of $\xi_R - \xi_U$ can be estimated from the area under the curve of the $\varepsilon''$ (dielectric loss) versus the reciprocal of temperature by the following equation:

$$
(\frac{\varepsilon_R - \varepsilon_U}{T_{\text{max}}} = \frac{2\Delta H}{\pi R} \int_0^\infty \varepsilon'' d\left(\frac{1}{T}\right)
$$

where $\Delta H$ is the activation energy for the process, which will be discussed later, and $(\varepsilon_R - \varepsilon_U)_{T_{\text{max}}}$ is the value of $\varepsilon_R - \varepsilon_U$ at the temperature corresponding to the temperature maximum in a plot of $\varepsilon''$ versus $1/T$. A typical plot of $\varepsilon''$ versus $1/T$ and the base line used for the two relaxations investigated are shown in Figure 19.

Using the assumption that $\varepsilon' = (\varepsilon_R - \varepsilon_U)/2$ at the temperature maximum of $\varepsilon''$ versus $1/T$ and the estimated values of $\varepsilon_R - \varepsilon_U$, the values of $\varepsilon_R$ and $\varepsilon_U$ can be established. The values of $\varepsilon_R - \varepsilon_U$, $\varepsilon_R'$, and $\varepsilon_U'$ are summarized in Tables 12 and 13 for 100 Hz, 1 KHz, and 10 KHz for both the $\rho'$ and $\gamma$ relaxations.

Assuming the dipoles are placed randomly along the polymer chain so that they act independently of each other, then the Onsager equation can be used to estimate the magnitude of the relaxation due to dipole orientation. The Onsager equation is given by
\[ N \mu^2 = \frac{3kT}{4 \pi} \left( \frac{2 \varepsilon_R + \varepsilon_U}{3 \varepsilon_R} \right) \left( \frac{3}{\varepsilon_U + 2} \right) (\varepsilon_R - \varepsilon_U) \]

where \( N \) is the number of dipole species per \( \text{cm}^3 \), \( \mu \) is the dipole moment of each group in Debyes, \( k \) is Boltzmann’s constant, and \( T \) is the temperature maximum of the relaxation. Using the estimated values of \( \varepsilon_R - \varepsilon_U \), \( \varepsilon_R \), and \( \varepsilon_U \), the values of \( N \mu^2 \) can be calculated and these are listed in Tables 12 and 13.

The total number of dipoles can be calculated from the following equation:

\[ N = \frac{N_A \rho/M}{t} \]

where \( N_A \) is Avogadro’s number, \( \rho \) is the density of the polymer, and \( M \) is the molecular weight of the average copolymer repeat unit. This calculation assumes that all the carboxylic acid groups exist as free acid groups.

From dielectric studies on low molecular weight carboxylic acids, the dipole moment of the carboxylic acid group has been found to be 1.7 Debyes. Using this value for the dipole moment, values of \( N \mu^2 \) can be calculated and are listed in Table 12.

Examining the values of \( \varepsilon_R - \varepsilon_U \) and \( N \mu^2 \) for the relaxation (Table 12), it is observed that the values increase as the acid content increases and that for a given
acid content the values increase with increasing frequency. For a given copolymer the temperature maximum of the relaxation increases with increasing frequency also. Consequently the concentration of free acid groups is increased due to the shift in monomer-dimer equilibrium with temperature, and this is reflected in the values of $\varepsilon_R - \varepsilon_U$ and $N\mu^2$. This occurrence is taken as evidence that the active dipolar species is the free acid group.

Taking the ratio of $N_f\mu^2$ to $N\mu^2$ for the $\beta'$ peak (Table 12) will indicate what fraction of the observed relaxation magnitude can be attributed to the free acid groups. From the results of the ratio calculation, the free carboxylic acid groups account for about half of the observed relaxation. The agreement of experimental and predicted results is amazingly good when the approximations used to do the calculations are examined. The Onsager equation was derived for systems of rigid, non-associating molecules and has no correction factors for correlations of orientations of the dipole species. This equation has been applied successfully in the case of simple liquids. The estimated values of $\varepsilon_R - \varepsilon_U$ are functions of the activation energy of the relaxation process and the area under the curve of $\varepsilon''$ versus $1/T$. The very reasonable agreement of experiment and theory implies that the free acid groups act as independent dipolar species in a hydro-
carbon matrix and are the active dipolar species responsible for the observed $\phi'$ relaxation.

The activation energy of the $\phi'$ relaxation for the ethylene-acrylic acid copolymers (Table 11) is essentially a constant value of 38 Kcal/mole. Sandiford and Willbourn found the activation energy for the $\phi$ process in oxidized polyethylene to be 38 Kcal/mole. Phillips and Stein found for copolymers of ethylene and carbon monoxide (0.5% and 1.0% carbon monoxide) that the activation energy for the $\phi$ process was 35 Kcal/mole. The similarities of the activation energies for the $\phi$ relaxation process of these polymers is coincidental in that both active dipolar species contain a carbonyl group. The dielectric relaxation mechanism in each case is quite different, however. The relaxation mechanism for oxidized polyethylene involves microbrownian segmental motion of the polymer backbone whereas the mechanism for the acrylic acid copolymers involves side group rotation and/or microbrownian segmental motion of the polymer backbone.

For the two ethylene-methacrylic acid copolymers the activation energy increases with increasing acid content. Longworth and Vaughan studied a series of ethylene-methacrylic acid series in which the acid content varied from 5 to 40 weight %, and they found the activation energy
to be 65 Kcal/mole. Read and coworkers reported a value of 56 Kcal/mole for sample 6M, and a value of 54 Kcal/mole was found in this work for the same sample. The temperature maximum for the $\beta'$ peak for the acrylic acid copolymers is essentially constant whereas in the methacrylic acid copolymers there is a considerable increase in the temperature maximum with increasing acid content. The increase in the temperature maximum of the $\beta'$ relaxation in the methacrylic acid copolymers is reflected in the increase in activation energy. Higher activation energies are indicative of a more cooperative molecular relaxation mechanism.

Mechanical relaxation measurements (Chapter 4) established that the $\beta'$ temperature maximum increased in proportion to the copolymer's acid content. The $\beta'$ transition is considered the glass transition of the copolymer and is classically considered the onset of microbrownian segmental motion. In contrast, the $\beta'$ temperature maximum from dielectric relaxation experiments appears at about room temperature for all the copolymers except the highest methacrylic acid copolymer. Infrared results (Chapter 3) indicate about the same percentage of free acid groups at 25°C for all the copolymers. This suggests the $\beta'$ dielectric relaxation is associated with the existence of a minimum percentage of free acid groups. The $\beta'$ dielectric
relaxations occur above the observed mechanical glass transition temperature which is consistent with the assigned molecular motion.

2. The \( \gamma \) Relaxation. Values of \( N \mu^2 \) were estimated for the \( \gamma \) relaxation by the method described for the \( \beta' \) relaxation. These values are summarized in Table 13. The values of \( \varepsilon_R - \varepsilon_U \) and \( N \mu^2 \) tend to increase with increasing acid content and there is no specific trend for these quantities with increasing frequency for a single acid content. Assuming the free carboxylic acid groups are the dipolar species responsible for dielectric relaxations, the experimentally determined quantity, \( N \mu^2 \), is set equal to \( N_f \mu^2 \) and the number of free acid groups is calculated. This result is given in Table 13. The values of \( N_f \) determined are ten percent or less of the values calculated from infrared results at room temperature. If carbonyl groups are responsible for the relaxation, the concentration of carbonyl groups would be less than the free acid concentration, because the dipole moment for the carbonyl group is in the order of 2.7 Debye. Assuming the carbonyl group is the active dipole species, the concentration of carbonyl groups calculated from the experimental quantity, \( N \mu^2 \), is in the order of 0.0003 weight %. The magnitude of the relaxation, as measured by \( \varepsilon'' \) maximum, increases with increasing
acid content, which suggests the free acid group is involved in the \( \gamma \) peak.

The observed temperature maximum increases with increasing acid content of the copolymers. Phillips and Stein observed the same trend in ethylene-carbon monoxide copolymers. McKenna and coworkers were able to separate the mechanical \( \gamma \) peak for a methacrylic acid copolymer into two separate peaks denoted \( \gamma_a \) and \( \gamma_c \) in order of appearance with decreasing temperature as described in Chapter 4. The dielectric \( \gamma \) peak corresponds in temperature maximum to the \( \gamma_a \) peak observed mechanically. Consequently the dielectric \( \gamma \) peak is attributed to the amorphous phase of the copolymer on the basis of temperature maximum and the free acid groups being the dipolar species responsible for the observed relaxation.

The activation energies for the \( \gamma \) relaxation (Table 11) are approximately constant for the acrylic acid copolymers and are slightly lower for the methacrylic acid copolymers. Read and coworkers determined the activation energy for sample 6M to be 9 Kcal/mole using plots of \( \tan \delta_e \) for temperature maximums. Phillips and Stein report an activation energy of 14 Kcal/mole for ethylene-carbon monoxide copolymers, which is similar to the observed values for the carboxylic acid containing copolymers.
Summary

Through correlation of infrared, dynamic mechanical and dielectric experiments, the effect of pendant carboxylic acid groups on the physical properties of polyethylene has been ascertained. The primary mechanical relaxation, corresponding to a rapid decrease in the real moduli, is increased in temperature of appearance with increasing acid content. The increase in the glass transition temperature is attributed to the (1) copolymerization effect due to the carboxylic acid containing comonomer and (2) the formation of pseudo-crosslinks through intermolecular hydrogen bonding. Contrary to previous results, the dielectrically active species responsible for the observed dielectric relaxation spectrum has been attributed to the free carboxylic acid group.
Chapter VII

Dielectric Studies: Ethylene-Phosphonic Acid Copolymers and Their Salt and Ester Derivatives

Dielectric Relaxation Spectrum

The dynamic mechanical investigation in Chapter 5 added to the knowledge and understanding of the effects of phosphonic acid pendant groups and their derivatives on the properties of the parent polymer, polyethylene. The complementary dielectric experiments should reinforce the previous interpretations.

The temperature dependences of $\varepsilon'$ and $\varepsilon''$ for the ethylene-phosphonic acid copolymers A and LD I at various frequencies are displayed in Figures 20 and 25. The $\gamma$ relaxation appears at around -100°C and is very sharp unlike the broad dielectric $\gamma$ relaxations observed in most polymers. In addition, there is a very broad, low magnitude relaxation centered around room temperature. It is probable that this relaxation consists of two partially merged peaks inasmuch as the shift factors for frequency-temperature superposition are much greater at high temperatures ($80^0$C) than at low temperatures ($0^0$C). The difference in the shift factors could be explained on the basis of the presence of two low magnitude relaxation peaks with differing activation energies. It is thus possible that the
dielectric loss observed around room temperature in sample A and sample LD I acid corresponds to the $\beta$ and $\alpha$ mechanical loss regions with the peaks being merged. The $\alpha$ relaxation would be rendered dielectrically active by the presence of carbonyl groups in the crystal adventitiously introduced along the polyethylene chain by oxidation. This view is supported by the dielectric relaxation behavior of ethylene carbon monoxide copolymers and oxidized polyethylene which exhibit behavior similar to that observed in sample A and sample LD I acid in this temperature range.

The temperature dependences of $\varepsilon'$ and $\varepsilon''$ for sample B at various frequencies are shown in Figure 21. In this case three relaxation regions are observed. Starting from low temperatures, the $\gamma$ relaxation is of approximately the same magnitude as the corresponding relaxation in sample A and LD I acid, but occurs at a slightly lower temperature in sample B. The broad dispersion in the vicinity of room temperature which was tentatively assigned to the merged $\alpha$ and $\phi$ relaxations of polyethylene in the case of sample A and LD I acid is again present, but is much greater in magnitude. A new loss region of high magnitude occurs at temperatures in excess of $100^\circ C$. (i.e., well into the melt region, since sample B has a melting point of $105^\circ -110^\circ C$).
The peak maximum for this $\alpha'$ relaxation has not yet occurred at $180^\circ$C at the lowest measurement frequency (100 Hz). It should also be noted that no abrupt changes in either $\varepsilon'$ or $\varepsilon''$ occur in the melting range.

The temperature dependences of $\varepsilon'$ and $\varepsilon''$ for sample C given in Figure 22 again show three relaxation regions as in sample B. The $\gamma$ relaxation is of approximately the same magnitude as that of the corresponding relaxation in sample B as is the broad relaxation occurring around room temperature. The $\alpha'$ relaxation in sample C, however, has increased greatly in magnitude in comparison to that of sample B and has decreased in temperature by approximately 100°C. Once again, no abrupt changes in dielectric behavior are noted in passing through the melting point.

The temperature dependence of $\varepsilon'$ and $\varepsilon''$ of the amorphous sample D shown in Figure 23 is so dominated by the $\alpha'$ relaxation that the room temperature relaxation and the $\gamma$ relaxation appear only as small shoulders on the $\alpha'$ peak. The dielectric $\alpha'$ peak occurs at $40^\circ$C in sample D at 100 Hz which is identical to the temperature of the mechanical $\alpha'$ peak of sample D. The magnitude of the $\alpha'$ relaxation has again increased enormously compared to that of sample C. In sample C, $\varepsilon_{\text{max}}'$ is 18 while $\varepsilon_{\text{R}}'$ is about 35. In sample D, $\varepsilon''_{\text{max}}$ is 32 while $\varepsilon_{\text{R}}''$ is about 150. The temperature and frequency dependency of sample LD II acid (Figure 26) is
similar to that of sample D, except that no \( \alpha' \) peak is observed. The \( \alpha' \) peak would appear in excess of 100°C for the LD II acid based on the fact that the phosphonic acid concentration is similar to that of sample B.

It is not known why the copolymers LD II acid and D are similar in \( \varepsilon'' \) dependence on temperature but dissimilar in phosphonic acid content, melting point, and crystallinity (Table 2). The copolymer D may have undergone substantial side reactions (see mechanism outline in Chapter I) because of its long reaction time compared to the other copolymers, which would account for these observations.

In Figures 27-30 the temperature dependencies of \( \varepsilon'' \) for the salt and ester derivatives of the samples LD I acid and LD II acid at various frequencies are shown. The \( \gamma \) peak region for the esters and the high salts tend to be broad in shape and low in magnitude as observed in ethylene-carbon monoxide copolymers and oxidized polyethylene. This typical observed \( \gamma \) peak in the esters and high salts is in direct contrast to the results obtained on the parent acid copolymers, which were sharp in shape and large in magnitude. The temperature maximum of the relaxation has been shifted about 20°C lower than is observed in the parent acid. The \( \gamma \) peak for the low salts of the LD I acid has a shape and magnitude similar to the parent acid, however, the \( \gamma \) peak for the low salts derived from the LD II acid is
similar in shape and magnitude to the appropriate ester.

A broad peak is observed at around room temperature for all the derivatives investigated. For some of the samples $\varepsilon''$ was increasing at a rapid rate and resolution of the peak was not possible. The room temperature peak for the LD I acid and ester is similar to that observed for sample 3 in which the overlapping of two peaks is suggested. The LD II ester has a peak which occurs above room temperature and the shift factor for temperature-frequency superposition is about the same throughout the peak indicating that it is a single relaxation peak. Again, the low salts of the LD I series are similar to the parent acid. The high salts of the LD I series are different in respect to the peak in the region of room temperature or above. Both salts have a broad relaxation peak that appears to be a single peak from the consideration of shift factors, but the sodium salt has a higher temperature maximum than the calcium salt. It is obvious that the salts of the LD II series also have a peak in this area, but $\varepsilon''$ is increasing so rapidly due to d.c. conductivity that it is difficult to resolve the peak.

Discussion

1. The $\alpha_1$ Dispersion. The features of the $\alpha_1$ dispersion have been discussed in the results section. This
dispersion depends upon the presence of phosphonic acid groups increasing in magnitude with increasing phosphonic acid content and decreasing in temperature with increasing phosphonic acid content. Figure 24 is a plot of the temperature dependence of $\varepsilon'$ at 100 Hz for phosphonic copolymers A, B, C, and D in the temperature region of the $\alpha'$ relaxation. Values of $\varepsilon_R - \varepsilon_U$ representing the magnitude of the $\alpha'$ dispersion may be estimated from plots such as Figure 24. These are 33 for sample C and 146 for sample D. An estimate of the magnitude to be expected from a dipolar orientation mechanism involving the motion of phosphonic acid groups may be obtained on the basis of the Onsager equation\textsuperscript{111} (Chapter 6). Application of the Onsager equation to samples C and D using the value for of 2.6 D obtained for the dipole moment of phenyl phosphonic acid (Appendix I) leads to values of $\varepsilon_R - \varepsilon_U$ of 0.27 and 4.3 respectively. The Onsager equation is, of course, not strictly valid for a solid polymer inasmuch as intermolecular correlations are not taken into account among other things, but the disparity of greater than two orders of magnitude between values of $\varepsilon_R - \varepsilon_U$ calculated on the basis of the Onsager equation and those observed experimentally lead to the conclusion that the $\alpha'$ dispersion does not arise from dipole orientation. The fact that a
microphase separated structure is apparently present at least in the case of sample D (Chapter 5) provides for the possible assignment of the \( \alpha' \) dispersion to an interfacial polarization mechanism similar to the mechanism of Maxwell and Wagner.

A mechanical \( \alpha' \) relaxation was observed in sample D at the same temperature as the dielectric \( \alpha' \) dispersion in this polymer. The mechanical process involved in the \( \alpha' \) relaxation was apparently similar to a glass transition as evidenced by the catastrophic decrease by several orders of magnitude of the storage modulus, \( E' \), accompanying the relaxation. Thus the phosphonic acid domains apparently undergo a "softening" in the \( \alpha' \) relaxation region. Plots of \( \log \frac{f}{\text{max}} \) versus \( 1/T \) (Figure 31) for samples C and D show that the dielectric \( \alpha' \) processes in both polymers have identical activation energies (30 \( \pm \) 2 Kcal/mole) indicating similar origins, but that the activation energy for the mechanical \( \alpha' \) process in sample D is much higher. (76 \( \pm \) 2 Kcal/mole). Thus, in a sense, the mechanical \( \alpha' \) process and the activation energy results are consistent with the assignment of the \( \alpha' \) dielectric and mechanical processes to two different mechanisms.

The temperature dependence of the d.c. conductivity is presented in Figures 32 and 33 which are plots of \( \log \)
d.c. conductivity versus $1/T$. Activation energies from such plots are listed in Table 14. For the phosphonic acid copolymers, the activation energy increases with increasing acid content. Ionization of the acid group increases the activation energy and esterification reduces it. On the basis of results on urethane solutions, it would be expected that these activation energies are related to the activation energy for viscous flow. From Figures 32 and 33 and measured values of a.c. conductivity it emerges that the d.c. and a.c. conductivity are of similar orders of magnitude at the $\alpha'$ dispersion maximum. The nature of the conducting species has not been established.

Conductivity may arise from protons in the phosphonic acid copolymers and esters, from ionic species in the salts or from ionic impurities and water in all the samples. Protons are perhaps the best candidates for the effect inasmuch as the first and second dissociation constants for the phosphonic acid are $10^{-2}$ and $10^{-8}$. An assignment based on the values of the dissociation constants is far from conclusive, however, inasmuch as hydrogen bonding, (Chapter 5) and the presence of the acid groups in a nonpolar medium must also be taken into account. The conducting species in the salts, especially the high salts, must
be attributed to ionic species rather than protons. The phosphonic acid copolymers and the salts exhibit no increase in temperature maximum of the \( \beta \) mechanical relaxation peak with increasing concentration which implies that the hydrocarbon matrix is acting independently of another phase. The "other phase" is considered a cluster of phosphonic acid groups and/or salt groups as discussed in Chapter 5. The conducting species in the esters is most likely a mixture of protons, ionic impurities and water.

The \( \alpha' \) dispersion in the ethylene-phosphonic acid polymers cannot entirely consist of a Maxwell-Wagner \(^{113,114} \) mechanism of the type originally proposed, because in addition to the points raised above, such a mechanism requires both \( \varepsilon' \) and \( \varepsilon'' \) to increase without limit with increasing temperature, while in samples C and D the reaches a maximum value and the \( \varepsilon'' \) appears to approach a plateau value. Further, the Maxwell-Wagner mechanism postulates one phase of the two phase system to be entirely non-conducting and this does not seem physically reasonable for samples C and D.

Maxwell-Wagner interfacial polarization effects have \(^{116-118} \) been observed previously in polyamides, \(^{119} \) carbon black filled rubbers, \(^{120} \) and polyurethanes. In the case of the polyamides the effect was attributed to the
difference in conductivity between the amorphous and crystalline phases while in the rubber it was attributed to the carbon black filler. The most comparable system to the present is thus the polyurethanes where the effect was assigned to urethane domains stabilized by the hydrogen bonding of the urethane groups.

The above considerations lead to the postulate that a Maxwell-Wagner interfacial polarization mechanism occurs below the temperature at which large scale mobility occurs in the phosphonic acid domains. This mechanism increases in magnitude with increasing temperature due to increasing mobility in the phosphonic acid domains and/or the presence of an increased number of charge carrying species. When a temperature is reached at which large scale mobility of the phosphonic acid domains becomes possible (a temperature corresponding to the mechanical \( \alpha' \) relaxation) it becomes possible for phosphonic acid groups to be transferred or exchanged from one domain to another while still maintaining the two phase structure. Thus flow becomes possible above the mechanical \( \alpha' \) relaxation temperature. While the dielectric \( \alpha' \) dispersion cannot be a classical Maxwell-Wagner interfacial polarization process, the model proposed qualitatively accounts for the data.

2. The \( \rho \) Relaxation. The broad dispersion situated
around room temperature for all the polymers was tentatively assigned to the $\beta$ relaxation of low density polyethylene with perhaps some contribution from the polyethylene $\alpha$ relaxation in the polymers of high crystallinity.

Estimated values of $\varepsilon_R - \varepsilon_U$ for the $\beta$ relaxation in samples A, B, C, and D may be obtained from plots of $\varepsilon''$ versus $1/T$ and the relationship shown in Chapter 6. Areas were easily obtainable in the case of samples A and B, but for C and D, the $\beta$ relaxation appears as a shoulder on the large $\alpha''$ dispersion. As a consequence it was necessary to decompose the $\varepsilon''$ curves into two components, a somewhat arbitrary procedure. Thus the results for samples C and D can be considered only semi-quantitative at best. $\Delta H$ was taken to be 19 Kcal/mole which is the activation energy of the $\beta$ relaxation for copolymer B, the sample with the most clearly resolved relaxation peak. Values of $\varepsilon_R - \varepsilon_U$ obtained in this manner are collected in Table 15. Also given in Table 15 are values of $\varepsilon_R - \varepsilon_U$ calculated on the basis of the Onsager equation on the assumption that the phosphonic acid groups can be treated as isolated entities with a dipole moment identical to that of phenyl phosphonic acid. It is seen that order of magnitude agreement is achieved in all cases.
Such a calculation is, of course, a gross oversimplification in that, assuming the dielectric relaxation to involve the same type motions as the mechanical \( \phi \) relaxation, long range cooperative effects are certainly involved as well as the clustering of phosphonic acid groups. Returning to an examination of the effect of isolated phosphonic acid groups, we may reasonably expect this situation to apply to sample A because of the low concentration of phosphonic acid present. Such isolated groups may be schematically represented by

\[
\begin{array}{c}
\text{HO} \quad \text{P} \quad \text{HO} \\
\text{HO} \quad \text{P} \quad \text{HO}
\end{array}
\]

On the basis of available bond moment data and geometry (see Appendix I) it would be expected that the dipole moment of the group would be inclined at an angle of about 40° to the chain direction. Assuming free rotation about the C-P bond, only the perpendicular component of the dipole moment would contribute to the \( \phi \) relaxation and it would be reasonable to expect a value of \( \epsilon_R - \epsilon_U \) of about half the calculated value. It can be seen from Table 15 that this analysis leads to good agreement between observed and cal-
culated values of $\varepsilon_R - \varepsilon_U$ for sample A. Such agreement is not obtained for the other samples, probably for the reasons outlined above.

The ester derivatives of the LD I and LD II series tend to be similar to their parent phosphonic acid copolymers in position and magnitude in the $\beta$ relaxation region. The LD II acid samples show a large increase in $\varepsilon''$ starting at about room temperature, which is attributed to increasing d.c. conductivity. The ester derivative of LD II, in contrast to the parent acid, has a defined $\beta$ peak in this region. Estimates of $\varepsilon_R - \varepsilon_U$ were not made for these samples due to the difficulties described previously. Due to the low crystallinity of this sample (Table 3) it is reasonable to suggest that this relaxation occurs in the amorphous phase and is attributed to the perpendicular component of the dipole moment of the pendent group as described previously. The low salts of the LD I series are similar in behavior to the parent acid. The higher salts of the LD I series have $\varepsilon''$ magnitudes similar to the parent acid, but the temperature maximum at 100 Hz for the sodium salt is about $70^\circ C$ in contrast to about $30^\circ C$ for the calcium salt and the parent acid. Also by consideration of shift factors for temperature-frequency superposition and crystallinity it is concluded that the salts have a $\beta$ relaxation mechanism involving essentially one phase whereas the acid
is attributed to two phases. It is possible that these high salts can be involved in a Maxwell-Wagner situation. For salts derived from the LD II acid it is difficult to say anything about the $\theta$ peak region except that d.c. conductivity plays a major role above room temperature.

3. The $\gamma$ Relaxation. This low temperature dispersion is observed for all the phosphonic acid copolymers including the derivatives of the LD I and LD II copolymers. The peak moves to lower temperatures as the phosphonic acid content is increased and as the extent of ionization or esterification is increased for a given acid level. Plots of $\log f_{\text{max}}$ versus $1/T$ (Figures 34 and 35) for the $\gamma$ relaxation are linear yielding apparent activation energies which decrease with increasing phosphonic acid content, and decrease with ionization or esterification for a given acid content.

Comparison of temperature maximums and activation energies for the acids and their derivatives are given in Table 16. Also included are data for a random ethylene-carbon monoxide copolymer containing one weight percent carbon monoxide. In the case of sample D the $\gamma$ peak appears only as a shoulder and it was necessary to resolve it from the $\tilde{\phi}$ relaxation. As discussed in the case of the $\phi$ relaxation, this resolution leads to a certain amount of error.
In the case of the mechanical \( \gamma \) relaxation, the activation energies are essentially independent of phosphonic acid content and are low whereas the dielectric \( \gamma \) relaxation indicates high activation energies which approach the mechanical results only in the case of sample D. The esters and salts of the LD I and LD II series, except for the low salts of LD I also have activation energies that approach the mechanical results for the phosphonic acid copolymers. It should also be noted that the samples described in the previous sentence also have temperature maximums and activation energies very similar to the ethylene-carbon monoxide copolymer also listed in Table 16. The temperature maximum and the activation energy data indicates the \( \gamma \) process in sample D and the afore described samples is of the polyethylene type perhaps rendered dielectrically active by adventitious oxidation. This is supported by the similarities of the magnitude of the \( \gamma \) peak in the esters and high salts and ethylene-carbon monoxide copolymer. This is consistent with the phase separated structure believed to exist in sample D and which can possibly exist in the other samples.

The same arguments indicate that phosphonic acid groups must contribute to the \( \gamma \) relaxation in samples A, B, C, LD I acid, LD II acid, and the low salts of LD I acid. Assuming this contribution to arise from rotation of iso-
lated phosphonic acid groups about the D-P axis, we would expect only the perpendicular component of the dipole moment of the phosphonic acid group to be active (see discussion of the $\rho$ relaxation and Appendix ).

**Summary**

The model proposed to account for the experimental evidence is one in which, at low phosphonic acid or salt contents, we have essentially isolated randomly placed phosphonic acid groups throughout the polymer.

As the phosphonic acid or salt content is increased hydrogen and/or ionic bonding between groups occurs and increases with increasing phosphonic acid or salt content leading to dimers, trimers, etc.; and ultimately to a two phase structure in which we have large hydrogen-ionic-bonded aggregates embedded in a polyethylene matrix which still contains a few isolated phosphonic acid and salt groups.
SUGGESTIONS FOR FUTURE WORK

Equipment

With the present dielectric experimental apparatus a frequency range of 2.5 decades and temperature range of about 300 degrees C can be covered by the use of two separate temperature chambers and two test cells, one being a three terminal and the other a two terminal cell. Using two different test cells introduces some error into the final results of any experiment. It would be desirable to use one three terminal test cell for the entire frequency and temperature range studied. Bullock and coworkers have demonstrated for urethane solutions that the activation energy obtained from d.c. conductivity measurements is similar to the activation for viscous flow. The present d.c. resistance range is limited to $10^6 - 10^{12}$ ohms, therefore, it would also be desirable to extend the present range of d.c. resistance measurements. The Tinsley dielectric test set can cover a range of 5 decades, but only at room temperature. It would be advantageous to build an environmental chamber for the test cell so a temperature range could be studied.

Model Compound Study

Literature up to now is not abundantly endowed with
investigations of compounds that have been synthesized by chlorophosphonation. The dielectric properties of
\[ P(OC\textsubscript{2}H_{2n-1})_3 \] where \( n = 2, 3, 4, 8, 10 \) have been re-
ported by Freymann and Marvel and the synthesis and
study of polyalkylene phosphonates of type \( (CH_{2})_n-CH(PO_2H) \)
where \( n = 4, 9, 18, 27, 70 \) have been reported by Rafikov
and fellow workers. To aid future interpretations, it
would be desirable to perform studies on compounds of the
type \( CH_3(CH_2)_n P0_2H \) and \( CH_3(CH_2)_n-(P(R)O_2H) \). The model
compound study could also be extended to chlorophosphonated
normal paraffins. By using \( n \)-Paraffins the effects of
molecular weight and concentration of phosphonic acid groups
or derivatives could be investigated.

Extension of Present Study

40

It is known that a chlorophosphonated polymer can
be prepared by the use of phosphorous trichloride, di-
chloride, and monochloride. Using a known polymer back-
bone structure, preferably linear polyethylene, the
effects of randomly placed pendant phosphonyl containing
groups along the backbone could be studied by a reaction
involving the phosphorous monochloride. The effects of
the length of branch points on the mechanical and physical
properties of the parent polymer could also be studied by
esterification with a series of normal alcohols. By chlorophosphonating with a phosphorous dichloride, the effects of pendant groups containing a single acid function could be studied. The acid group could be ionized or esterified by procedures developed in this work. Working with pendant groups containing a single acid group would also aid the present interpretation.

Rheology

It would also be helpful in the interpretation of mechanical and physical properties in light of the nature of the polymer composition to perform rheology experiments. Using polymers derived from the same parent polymer having no acid groups, one acid group, and two acid groups per pendant group, the effects of the presence of a phosphoryl containing side group and with mono- or di- acid functionality on the rheological properties of the parent polymer could be investigated. It would be expected from work on carboxylic acid containing copolymers that the rheological properties would be very different from the parent polymer.

Extension of Theory

It was apparent in the discussion of the Maxwell-Wagner mechanism in Chapter 7, there is a need to improve
the theory if interpretations of recent data are to be accurate and complete. With the increasing importance of ionic containing polymers, the Maxwell-Wagner type mechanism could play an important role in a better understanding of these systems. In order to proceed further it would be necessary to modify the Maxwell-Wagner mechanism to account for the presence of two conducting phases with different temperature and conducting coefficients.

To further substantiate the applicability theory of Fox and Loshaek, as described in Chapter 4, the necessary corrections for the copolymer effect should be made. This would require the determination of various quantities as functions of copolymer composition and degree of crosslinking.
APPENDIX I

Dipole Moment of Phenyl Phosphonic Acid

Information on the bond angles and bond moments of phosphonic acids is not available in the literature, however, extensive data on carboxylic acids does exist. Therefore, in order to evaluate the significance of 2.6 D obtained experimentally bond moments and angles of acetic acid have been used. It is realized that large differences may occur between, say, the bond moment of the carboxyl group and that of the phosphonyl group, but in order to obtain anything meaningful such approximations are necessary.

It is further assumed that in a horizontal plane projection all O-P-O angles are equal to 120°.
The resultant dipole moment and the angle subtented by it to the C-P bond are both dependent on whether the OH bonds are taken to be cis or trans relative to the phosphonyl group.

In Table A are given the dipole moments and the angles $\theta$ for various configurations. The angle $\theta$ is defined as shown in the diagram

![Diagram](image)

Table A

<table>
<thead>
<tr>
<th>Situation</th>
<th>Dipole moment (Debyes)</th>
<th>$\theta$ (Degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Free rotation about P-O</td>
<td>2.14</td>
<td>29.5</td>
</tr>
<tr>
<td>b) OH bonds $\perp$ to PC=O plane</td>
<td>1.56</td>
<td>29.6</td>
</tr>
<tr>
<td>c) OH bonds in PC=O plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis to P=O</td>
<td>1.6</td>
<td>127.5</td>
</tr>
<tr>
<td>trans to P=O</td>
<td>4.7</td>
<td>47.5</td>
</tr>
<tr>
<td>one cis, one trans</td>
<td>2.04</td>
<td>57</td>
</tr>
</tbody>
</table>

The value of $\mu = 2.6$ D would appear to indicate that unlike in acetic where there is a definite bias toward the cis-form, the tendency is toward free orientation with some bias toward the trans-form. This would lead to a value of $\theta$ somewhere between 30° and 50°.
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65. C. Wooten, Tennessee Eastman Company, private communication.
67. L.W. McKenna, Monsanto Chemical Company, private communication.
69. Michael Yang, private communication.
University of Massachusetts, Amherst, Mass., June 1969.


### TABLE I

Physical Properties of Ethylene-Acrylic Acid and Ethylene-Methacrylic Acid Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt Viscosity&lt;sup&gt;a&lt;/sup&gt; c.p. at 190 °C</th>
<th>CH&lt;sub&gt;3&lt;/sub&gt; (100CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;4&lt;/sup&gt;</th>
<th>COOH (100CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;2&lt;/sup&gt;</th>
<th>P (g/cc)</th>
<th>2016 cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>1894 cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>%X&lt;sub&gt;0&lt;/sub&gt;</th>
<th>%X&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>10.5 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>4.1</td>
<td>1.28</td>
<td>0.923</td>
<td>24.2</td>
<td>26.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>12.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>4.4</td>
<td>1.71</td>
<td>0.926</td>
<td>21.8</td>
<td>24.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>30.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>4.7</td>
<td>2.12</td>
<td>0.930</td>
<td>21.7</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>18.0 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>3.1</td>
<td>2.84</td>
<td>0.936</td>
<td>0.0</td>
<td>14.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5A</td>
<td>2.8 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.5</td>
<td>5.07</td>
<td>0.952</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6M</td>
<td>------</td>
<td>2.6</td>
<td>3.61</td>
<td>0.934</td>
<td>2.8</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7M</td>
<td>------</td>
<td>2.8</td>
<td>6.30</td>
<td>0.953</td>
<td>0.0</td>
<td>8.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>------</td>
<td>1.4</td>
<td></td>
<td>0.926</td>
<td>43.7</td>
<td>44.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Samples 1A-5A are acrylic acid copolymers. Samples 6M and 7M are methacrylic acid copolymers. Sample 8 is low density polyethylene.
### TABLE II

Physical Properties of Ethylene-Phosphonic Acid Copolymers

<table>
<thead>
<tr>
<th>Sample&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PO(OH)&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Mp. °C</th>
<th>Relative Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>- - -</td>
<td>115.5</td>
<td>100</td>
</tr>
<tr>
<td>A</td>
<td>0.8</td>
<td>113.1</td>
<td>83</td>
</tr>
<tr>
<td>B</td>
<td>1.8</td>
<td>110.4</td>
<td>73</td>
</tr>
<tr>
<td>C</td>
<td>2.8</td>
<td>98.3</td>
<td>60</td>
</tr>
<tr>
<td>D</td>
<td>7.4</td>
<td>No detectable crystallinity</td>
<td></td>
</tr>
<tr>
<td>LD I</td>
<td>1.1</td>
<td>111.5</td>
<td>76</td>
</tr>
<tr>
<td>LD II</td>
<td>2.2</td>
<td>97.0</td>
<td>43</td>
</tr>
</tbody>
</table>

<sup>a</sup> Sample 8 is low density polyethylene. Samples A, B, C, D, LD I, and LD II are phosphonic acid copolymers.
TABLE III

Physical Properties of Derivatives of Ethylene-Phosphonic Acid Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Ionization</th>
<th>Temperature</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium</td>
<td>Calcium</td>
<td>Mp. C</td>
</tr>
<tr>
<td>LD I Ester</td>
<td>- - -</td>
<td>110.8</td>
<td>75</td>
</tr>
<tr>
<td>LD I Low Na</td>
<td>51</td>
<td>110.4</td>
<td>70</td>
</tr>
<tr>
<td>LD I High Na</td>
<td>69</td>
<td>107.7</td>
<td>55</td>
</tr>
<tr>
<td>LD I Low Ca</td>
<td>- - -</td>
<td>111.5</td>
<td>71</td>
</tr>
<tr>
<td>LD I High Ca</td>
<td>- - -</td>
<td>105.5</td>
<td>46</td>
</tr>
<tr>
<td>LD II Ester</td>
<td>- - -</td>
<td>98.4</td>
<td>35</td>
</tr>
<tr>
<td>LD II Low Na</td>
<td>35</td>
<td>91.3</td>
<td>74</td>
</tr>
<tr>
<td>LD II High Na</td>
<td>100</td>
<td>90.8</td>
<td>73</td>
</tr>
<tr>
<td>LD II Low Ca</td>
<td>- - -</td>
<td>93.0</td>
<td>17</td>
</tr>
<tr>
<td>LD II High Ca</td>
<td>- - -</td>
<td>91.6</td>
<td>0</td>
</tr>
<tr>
<td>Sample</td>
<td>Acid mole/cm³</td>
<td>Extinction cm²/mole</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>AA</td>
<td>$4.24 \times 10^{-4}$</td>
<td>$3.58 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>BB</td>
<td>$9.71 \times 10^{-4}$</td>
<td>$3.45 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>CC</td>
<td>$16.6 \times 10^{-4}$</td>
<td>$3.52 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>DD</td>
<td>$20.0 \times 10^{-4}$</td>
<td>$3.46 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>1A</td>
<td>$5.25 \times 10^{-4}$</td>
<td>$3.42 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>$7.07 \times 10^{-4}$</td>
<td>$3.73 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>$8.79 \times 10^{-4}$</td>
<td>$3.48 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>$11.8 \times 10^{-4}$</td>
<td>$3.10 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>5A</td>
<td>$21.6 \times 10^{-4}$</td>
<td>$2.90 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>6M</td>
<td>$12.6 \times 10^{-4}$</td>
<td>$3.23 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>7M</td>
<td>$23.9 \times 10^{-4}$</td>
<td>$2.24 \times 10^4$</td>
<td></td>
</tr>
</tbody>
</table>

a Samples AA, BB, CC, and DD are data of Otocka and Kwei (Reference 10).
TABLE V
Free Carboxylic Acid Concentration at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>FREE ACID (\text{mole/cm}^3)</th>
<th>% FREE ACID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>(2.93 \times 10^{-5})</td>
<td>5.6</td>
</tr>
<tr>
<td>2A</td>
<td>(5.28 \times 10^{-5})</td>
<td>7.5</td>
</tr>
<tr>
<td>3A</td>
<td>(6.56 \times 10^{-5})</td>
<td>7.4</td>
</tr>
<tr>
<td>4A</td>
<td>(8.10 \times 10^{-5})</td>
<td>6.9</td>
</tr>
<tr>
<td>5A</td>
<td>(17.8 \times 10^{-5})</td>
<td>8.3</td>
</tr>
<tr>
<td>6M</td>
<td>(8.56 \times 10^{-5})</td>
<td>6.8</td>
</tr>
<tr>
<td>7M</td>
<td>(13.3 \times 10^{-5})</td>
<td>5.6</td>
</tr>
</tbody>
</table>

TABLE VI
Characteristics of Carboxylic Acid Monomer-Dimer Equilibrium

<table>
<thead>
<tr>
<th>Sample</th>
<th>(K_a(25°C)) (\text{cm}^3/\text{mole})</th>
<th>(K_p(25°C)) (\text{mole/cm}^3)</th>
<th>(\bar{\text{pH}})</th>
<th>(K_D) (\text{Kcal/mole})</th>
<th>(K_a)</th>
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<td>1A</td>
<td>(61.0 \times 10^4)</td>
<td>(1.86 \times 10^{-8})</td>
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<td>(5.37 \times 10^{-8})</td>
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<td>(28.8 \times 10^{-8})</td>
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<td>CH PO(OH) (3)</td>
<td>CH PO(O Mg) (2)</td>
<td>CH PO(O Ca) (2)</td>
<td>CH PO(ONa) (2)</td>
<td>Species</td>
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<td>1190</td>
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<td>1310</td>
<td>1323</td>
<td>1310</td>
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<tr>
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<td>985</td>
<td>987</td>
<td>973</td>
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<td>885</td>
<td>877</td>
<td>831</td>
<td>P=CH(_3)</td>
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<td>815</td>
<td>770</td>
<td>768</td>
<td>757</td>
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<td>730</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P-O-C</td>
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- \(a\) Sadtler Standard Spectra #21787
- \(b\) Sadtler Standard Spectra #21806
- \(c\) Corbridge and Lowe
TABLE VIII

Tentative Spectra-Structure Correlations for Ethylene Phosphonic Acid Copolymers and Derivatives

<table>
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<tr>
<th>LD I Acid</th>
<th>LD I Ester</th>
<th>In cm(^{-1})</th>
<th>LD I Low Na</th>
<th>LD I High Na</th>
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<td>808</td>
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### TABLE IX

Characteristics of the $\beta'$ and $\gamma$ Mechanical Relaxation For Ethylene-Acrylic Acid and Ethylene-Methacrylic Acid Copolymers

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<th>Sample</th>
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<th>$\Delta H$ Kcal/mole</th>
<th>$T_0$ (°C)</th>
<th>$\Delta H$ Kcal/mole</th>
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<td>--</td>
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</tr>
<tr>
<td>CC</td>
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<td>--</td>
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<tr>
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<td>24</td>
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<td>-10</td>
<td>--</td>
<td>-128</td>
<td>18</td>
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<td>-1</td>
<td>--</td>
<td>-127</td>
<td>13</td>
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<td>3A</td>
<td>5</td>
<td>--</td>
<td>-128</td>
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<td>-20</td>
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<td>-126</td>
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TABLE X

Characteristics of the $\phi$ and $\gamma$ Mechanical Relaxations for Ethylene Phosphonic Acid Copolymers and Their Derivatives

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<th>$T$ (°C)</th>
<th>$\Delta H$ Kcal/mole</th>
<th>$T$ (°C)</th>
<th>$\Delta H$ Kcal/mole</th>
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<tbody>
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<td></td>
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<tr>
<td>B</td>
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<td></td>
<td>-117</td>
<td>10</td>
</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>D</td>
<td>-8</td>
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<td>-123</td>
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</tr>
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<td>-121</td>
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<td>-125</td>
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<td>53</td>
<td>-126</td>
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</tr>
<tr>
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<td>93</td>
<td>-123</td>
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<td>74</td>
<td>-123</td>
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<tr>
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TABLE XI

Characteristics of the \( \phi' \) and \( \gamma \) Dielectric Relaxation for Ethylene-Methacrylic Acid and Ethylene-Acrylic Acid Copolymers at 100 Hz

<table>
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<tr>
<th>Sample</th>
<th>Relative ( \varepsilon'' )</th>
<th>( T ) (°C)</th>
<th>( \Delta H^+ ) Kcal/mole</th>
<th>Relative ( \varepsilon'' )</th>
<th>( T ) (°C)</th>
<th>( \Delta H^+ ) Kcal/mole</th>
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<td>39</td>
<td>1.00</td>
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<td>70</td>
<td>2.58</td>
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**TABLE XII**

Calculated Values of $\varepsilon_R - \varepsilon_U$, $\varepsilon_R$, $\varepsilon_U$, $N\mu^2$, and $N_F\mu^2$ for the $\beta'$ Dielectric Relaxation of Ethylene-Methacrylic Acid and Ethylene-Acrylic Acid Copolymers

<table>
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<tr>
<th>Sample</th>
<th>$(H_3)$</th>
<th>$\varepsilon_R - \varepsilon_U$</th>
<th>$\varepsilon_R$</th>
<th>$\varepsilon_U$</th>
<th>$N\mu^2 \times 10^{16}$ (ergs)</th>
<th>$N_F\mu^2 \times 10^{17}$ (ergs)</th>
<th>$N_F\mu^2/N\mu^2 \times 100$</th>
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<td>(\varepsilon_U)</td>
<td>(N\mu^2) x10^18 (ergs)</td>
<td>(N\mu^2) x10^15 (ergs)</td>
<td>(N_{\eta}) moles/cm³ x10^-6</td>
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<td>28.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6M</td>
<td>10^4</td>
<td>.00235</td>
<td>1.8846</td>
<td>1.8822</td>
<td>8.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^3</td>
<td>.00216</td>
<td>1.8498</td>
<td>1.8476</td>
<td>6.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^2</td>
<td>.00187</td>
<td>1.8247</td>
<td>1.8229</td>
<td>5.82</td>
<td>2.20</td>
<td>3.35</td>
</tr>
<tr>
<td>7M</td>
<td>10^4</td>
<td>.0208</td>
<td>2.150</td>
<td>1.9942</td>
<td>7.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^3</td>
<td>.0200</td>
<td>1.9700</td>
<td>1.9500</td>
<td>6.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^2</td>
<td>.0172</td>
<td>1.9439</td>
<td>1.9267</td>
<td>5.35</td>
<td>4.03</td>
<td>30.8</td>
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</table>
### TABLE XIV

Activation Energies from d.c. Conductivity
Ethylene-Phosphonic Acid Copolymers and Derivatives

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H^\ddagger$ (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>28</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
</tr>
<tr>
<td>C</td>
<td>42</td>
</tr>
<tr>
<td>LD II Acid</td>
<td>38</td>
</tr>
<tr>
<td>LD II Ester</td>
<td>30</td>
</tr>
<tr>
<td>LD II Low Ca</td>
<td>30</td>
</tr>
<tr>
<td>LD II Low Na</td>
<td>33</td>
</tr>
<tr>
<td>LD II High Na</td>
<td>50</td>
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</table>

### TABLE XV

Magnitude of the $\phi$ Dielectric Relaxation of Ethylene-Phosphonic Acid Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_R - \varepsilon_U$ Observed</th>
<th>$\varepsilon_R - \varepsilon_U$ Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>.055</td>
<td>.09</td>
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<tr>
<td>B</td>
<td>.225</td>
<td>.21</td>
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<tr>
<td>C</td>
<td>.965</td>
<td>.27</td>
</tr>
<tr>
<td>D</td>
<td>1.46</td>
<td>.43</td>
</tr>
<tr>
<td>Sample</td>
<td>T&lt;sup&gt;max (°C)&lt;/sup&gt;</td>
<td>ΔH&lt;sup&gt;+&lt;/sup&gt; Kcal/mole</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>A</td>
<td>-93</td>
<td>40</td>
</tr>
<tr>
<td>B</td>
<td>-100</td>
<td>35</td>
</tr>
<tr>
<td>C</td>
<td>-104</td>
<td>27</td>
</tr>
<tr>
<td>D</td>
<td>-111</td>
<td>16</td>
</tr>
<tr>
<td>LD I Acid</td>
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<td>51</td>
</tr>
<tr>
<td>LD I Ester</td>
<td>-107</td>
<td>12</td>
</tr>
<tr>
<td>LD I Low Na</td>
<td>-88</td>
<td>40</td>
</tr>
<tr>
<td>LD I High Na</td>
<td>-108</td>
<td>13</td>
</tr>
<tr>
<td>LD I Low Ca</td>
<td>-88</td>
<td>34</td>
</tr>
<tr>
<td>LD I High Ca</td>
<td>-108</td>
<td>13</td>
</tr>
<tr>
<td>LD II Ester</td>
<td>-101</td>
<td>16</td>
</tr>
<tr>
<td>LD II Low Na</td>
<td>-102</td>
<td>15</td>
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<tr>
<td>LD II High Na</td>
<td>-103</td>
<td>15</td>
</tr>
<tr>
<td>ET-CC</td>
<td>-105</td>
<td>15</td>
</tr>
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</table>
CAPTIONS FOR FIGURES

Figure 1  Base lines used for crystallinity determinations from infrared spectra of samples 8 and 1A.

Figure 2  Maximum absorbance of the 940 cm⁻¹ band as a function of sample thickness for samples 1A - 5A, 6M and 7M.

Figure 3A  Log association constant as a function of reciprocal temperature for samples 1A - 5A.

Figure 3B  Log association constant as a function of reciprocal temperature for samples 6M and 7M.

Figure 4  Log dissociation constant as a function of reciprocal temperature for samples 1A - 5A and 6M.

Figure 5  Variation of E' and E'' for samples 1A - 3A and 8 as a function of temperature at 110 Hz.

Figure 6  Variation of E' and E'' for samples 4A, 5A, 6M, and 7M as a function of temperature at 110 Hz.
Figure 7 Arrhenius plots of the mechanical and/or relaxation.

Figure 8 Fox-Losheak plot of samples 1A - 5A, 6', 7M, and data of Stocka and Kwai.

Figure 9 Variation of $E'$ and $E''$ for the parent polyethylene, copolymer A and copolymer B as a function of temperature at 110 Hz.

Figure 10 Variation of $E'$ and $E''$ for copolymer C as a function of temperature at 110 Hz.

Figure 11 Variation of $E'$ and $E''$ for copolymer D as a function of temperature at 110 Hz.

Figure 12 Variation of $E'$ and $E''$ for copolymers LD I acid and LD I ester.

Figure 13 Variation of $E'$ and $E''$ for copolymers LD II acid and LD II ester.

Figure 14 Variation of $E'$ and $E''$ for LD I low Na and LD I high Na.

Figure 15 Variation of $E'$ and $E''$ for copolymers LD I low Ca and LD I high Ca.

Figure 16 Variation of $E'$ and $E''$ for copolymers LD II low Na, LD II high Na, and LD II low Ca.

Figure 17 Temperature variation of the $\phi$ relaxation temperature as a function of mole percent substituent.
Figure 18  Variation of $\varepsilon''$ as a function of temperature at various frequencies: $\bigcirc$ 10 KHz, $\bigtriangleup$ 1 KHz, $\times$ 100 Hz.

Figure 19  Baselines used for determination of the magnitude of the $\beta$ and $\gamma$ dielectric relaxations.

Figure 20  Variation of $\varepsilon'$ and $\varepsilon''$ for copolymer A as a function of temperature at various frequencies: $\bigcirc$ 10 KHz, $\bigtriangleup$ 1 KHz, $\times$ 100 Hz.

Figure 21  Variation of $\varepsilon'$ and $\varepsilon''$ for copolymer B as a function of temperature at various frequencies: $\bigcirc$ 10 KHz, $\bigtriangleup$ 1 KHz, $\times$ 100 Hz.

Figure 22  Variation of $\varepsilon'$ and $\varepsilon''$ for copolymer C as a function of temperature at various frequencies: $\bigcirc$ 10 KHz, $\bigtriangleup$ 1 KHz, $\times$ 100 Hz.

Figure 23  Variation of $\varepsilon'$ and $\varepsilon''$ for copolymer D as a function of temperature at various frequencies: $\bigcirc$ 10 KHz, $\bigtriangleup$ 1 KHz, $\times$ 100 Hz.

Figure 24  Variation of $\varepsilon'$ with frequency at room temperature for copolymer A-D.

Figure 25  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymers LD I ester (upper) and LD I acid (lower).
Figure 26  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymer LD II acid.

Figure 27  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymers LD I high Ca (upper) and LD I low Ca (lower).

Figure 28  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymers LD I high Na (upper) and LD I low Na (lower).

Figure 29  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymers LD II low Ca (upper) and LD II ester (lower).

Figure 30  Variation of $\varepsilon''$ as a function of temperature at various frequencies for copolymers LD II high Na (upper) and LD II low Na (lower).

Figure 31  Arrhenius plots of the mechanical and dielectric $\alpha'$ relaxations.

Figure 32  Temperature dependence of d.c. conductivity present in copolymers B, C, and D.
Figure 33  Temperature dependence of d.c. conductivity present in copolymers LD II acid, LD II ester, LD II low Na, LD II high Na, and LD II low Ca.

Figure 34  Arrhenius plots of the dielectric $\gamma$ relaxation.

Figure 35  Arrhenius plots of the dielectric $\gamma$ relaxation.
\[ \rho \left( \frac{\text{mole}}{g \text{ of amorphous polymer}} \right) \times 10^3 \]
Fig. 2

- PARENT POLYETHYLENE
- PEPA #IA
- PEPA #IB

TEMPERATURE in °C

E'

E''

-log_{10} (E') vs. TEMPERATURE in °C
Fig. 3
Fig. 4
Fig. 1

Temperature in °C

$\varepsilon'$

$\varepsilon''$
Fig. 7