may be seen that there is a slight decrease in E' at the temperature of the β relaxation but that the catastrophic decrease in E' occurs in conjunction with the α' relaxation. It would thus appear that the glass transition of the hydrocarbon matrix occurs at the temperature of the β relaxation while that of the phosphonic acid domains occurs at the temperature of the α' relaxation. The dielectric studies to be discussed in the companion paper[20] 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. It would be expected that the phosphonic acid domains contain considerable quantities of nonpolar hydrocarbon segments.

(20) P. J. Phillips, F. A. Emerson, and W. J. MacKnight, *Macromolecules*, 3, 771 (1970).

Conclusion

The mechanical and thermal properties of a series of low-density polyethylenes modified by the inclusion of phosphonic acid side groups strongly suggest the occurrence of microphase separation at high phosphonic acid contents. The exact concentration of phosphonic acid necessary for the formation of a mechanically distinct phase of phosphonic acid domains has not been precisely defined but a sample containing 7.4 phosphonic acid groups per 100 main chain carbon atoms clearly exhibits phase separation.

Acknowledgments. The authors are grateful to the National Science Foundation for partial support of this research under Grant GP 8581 and to the Petroleum Research Fund of the American Chemical Society for partial support of this research under Grant 2914 A5.

Structure and Properties of Polyethylene Modified with Phosphonic Acid Side Groups. II. Dielectric Properties

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ABSTRACT: Dielectric relaxation studies have been carried out on the polyethylene modified by the inclusion of phosphonic acid side groups discussed in part I. The temperature range investigated was from −180 to +200° and the frequency range was from 100 to 10^8 Hz. Two dielectric relaxation regions are observed for all the polymers and these correspond to the β and γ mechanical relaxations. High phosphonic acid content polymers show an additional dielectric dispersion labeled α'. Available evidence indicates that the α' dispersion arises from an interfacial polarization mechanism of the Maxwell–Wagner type. The values of the dielectric constants for the high phosphonic acid content polymers are greatly in excess of those predicted on the basis of conventional theories involving dipole orientation. These results are taken to be a direct consequence of the microphase separated structures of the polymers.

The dynamic mechanical and thermal investigations described in part I[2] led to the conclusion that phosphonic acid side groups present in polyethylene have a tendency to cluster together and that microphase separation occurs, at least in the sample containing 7.4 phosphonic acid groups per 100 carbon atoms. This polymer has a structure consisting of an amorphous hydrocarbon matrix with domains of phosphonic acid clusters dispersed throughout. The mechanical and thermal results do not so far allow the establishment of the detailed structure of the phosphonic acid domains nor do they fix the exact size of these domains.

In the present paper we extend the studies on ethylene–vinyl phosphonic acid copolymers to include dielectric relaxation. The results are similar in many respects to those obtained by the dynamic mechanical technique. However, the presence of a dielectric relaxation region which all available evidence indicates to arise from an interfacial polarization mechanism provides strong support for the presence of a two-phase structure in the copolymers investigated.

Experimental Section

Materials. Details of the addition of phosphonic acid side groups to low-density polyethylene have been given in the previous paper.[2] Samples were identical with those of the previous paper and contained the following phosphonic acid concentrations per 100 carbon atoms: A, 0.8; B, 1.8; C, 2.8; and D, 7.4. Samples were compression molded into circular disks measuring about 5 cm in diameter and approximately 0.07 cm in thickness. Prior to the dielectric measurements the samples were dried by pumping under vacuum to a constant weight. All measurements were carried out on annealed samples. Details of the annealing process are described in the preceding paper.[2] Commercially obtained phenylphosphonic acid was dissolved in dioxane for dipole moment measurements.

Dielectric Measurements. Measurements in the frequency range 50–10^4 Hz were made using a General Radio capacitance measuring assembly (Type 1620 A). This device is a transformer ratio-arm bridge.[3] The temperature range from −130 to 20° was investigated using a three-terminal cell (Balsbaugh Type LD-3), the interior of which was cooled with dry nitrogen which had been passed through a copper coil immersed in boiling liquid nitrogen. Temperature

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(1) (a) Queen Mary College, University of London; (b) to whom correspondence should be addressed.

(2) P. J. Phillips, F. A. Emerson, and W. J. MacKnight, *Macromolecules*, 3, 767 (1970).

(3) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967.

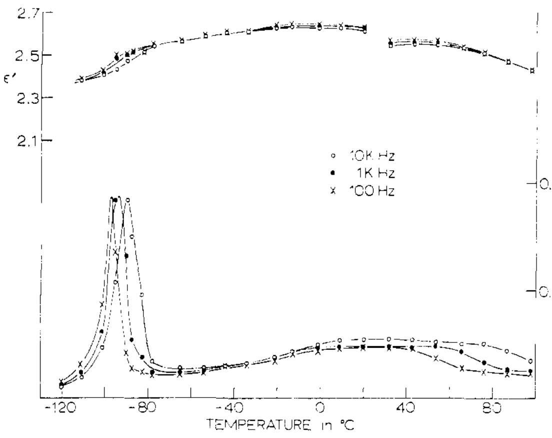

Figure 1. Variation of ϵ' and ϵ'' for copolymer A as a function of temperature at various frequencies: ○, 10 KHz; ●, 1 KHz; ×, 100 Hz.

control was achieved to within 1° by varying the rate of flow of the nitrogen gas. The resulting scatter in the $\tan \delta$ measurements was usually much less than 10% and the scatter in ϵ' was less than 0.2%.

Measurements in the temperature range from 20 to 200° were made using a specially constructed stainless steel two-terminal cell with Teflon insulation. The sealed dielectric cell was immersed in an oil bath thermostated to ±0.1°. Measurements made without a sample in the cell showed that the Teflon insulation made no significant contribution to the dielectric relaxation in this temperature range.

A Tinsley dielectric test set (Type 4206 F) was used over the frequency range 10^4–10^8 Hz. Measurements were made at room temperature only. This device operates on the resonance circuit method and is of the Hartshorn–Ward type.[4]

To ensure good contact between the sample surface and the electrodes, metal foil was attached to the specimen with a thin film of silicone grease.

It was previously found in the case of ethylene-methacrylic acid polymers and their salts[5] that it was necessary to maintain a dry atmosphere in the temperature range from 10 to $-20°$ in order to obtain reproducible results. Such conditions are maintained in the present measurements due to the dry nitrogen flushed through the cell and good reproducibility was obtained.

Dc resistance measurements were made using a General Radio megohmmeter, Type 1862A.

The dipole moment of phenylphosphonic acid was determined by the method of Guggenheim[6a] and Smith.[6b] This method involves measurements of the dielectric constant and refractive index of solutions of decreasing concentration of the compound under investigation in a nonpolar solvent (dioxane).

Dielectric constants were determined at 50 MHz using the Tinsley dielectric test set and refractive indices were measured on an Abbé refractometer.

Results

In the following, all the ϵ'' values are corrected for contributions due to dc conductivity.

The temperature dependences of ϵ' and ϵ'' for sample A at various frequencies are displayed in Figure 1.

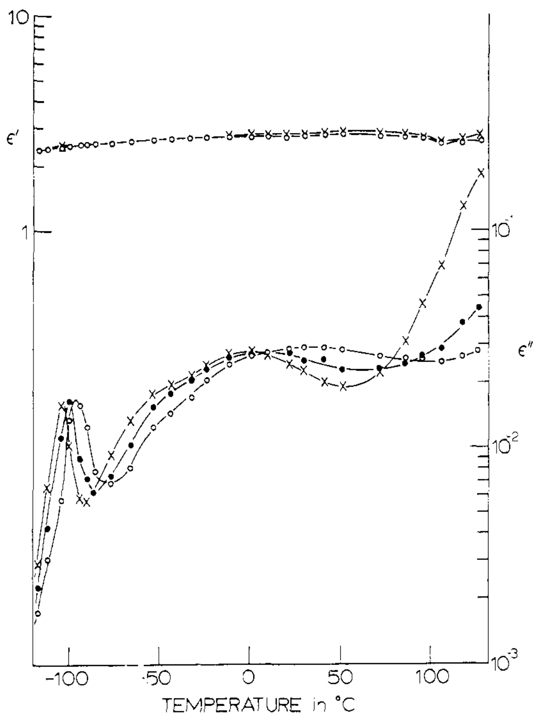

Figure 2. Variation of ϵ' and ϵ'' for copolymer B as a function of temperature at various frequencies: ○, 10 KHz; ●, 1 KHz; ×, 100 Hz.

The γ relaxation appears at around $-100°$ and is very sharp unlike the broad dielectric γ relaxations observed in most polymers.[7] 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°) than at low temperatures (0°). 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 corresponds to the β and α mechanical loss regions with the peaks being merged. This α 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[8] and oxidized polyethylene[9] which exhibit similar behavior to that observed in sample A in this temperature range.

The temperature dependences of ϵ' and ϵ'' for sample B at various frequencies are shown in Figure 2. In this case three relaxation regions are observed. Starting from low temperatures, the γ relaxation is of approximately the same magnitude as the corresponding relaxation in sample A, but occurs at a slightly lower temperature in sample B. The broad dispersion in the vicinity of room temperature which was tentatively as-

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(4) L. Hartshorn and W. H. Ward, *J. Inst. Elec. Eng.*, **79**, 597 (1936).

(5) B. E. Read, E. A. Carter, T. M. Connor, and W. J. MacKnight, *Brit. Polym. J.*, **1**, 123 (1969).

(6) (a) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); (b) J. W. Smith, *ibid.*, **46**, 394 (1950).

(7) J. D. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **14**, 173 (1966).

(8) P. J. Phillips, G. L. Wilkes, and R. S. Stein, to be published.

(9) G. P. Mikhailov, S. P. Kabin, and T. A. Krylova, *Sov. Phys. Tech. Phys.*, **2**, 1899 (1957).

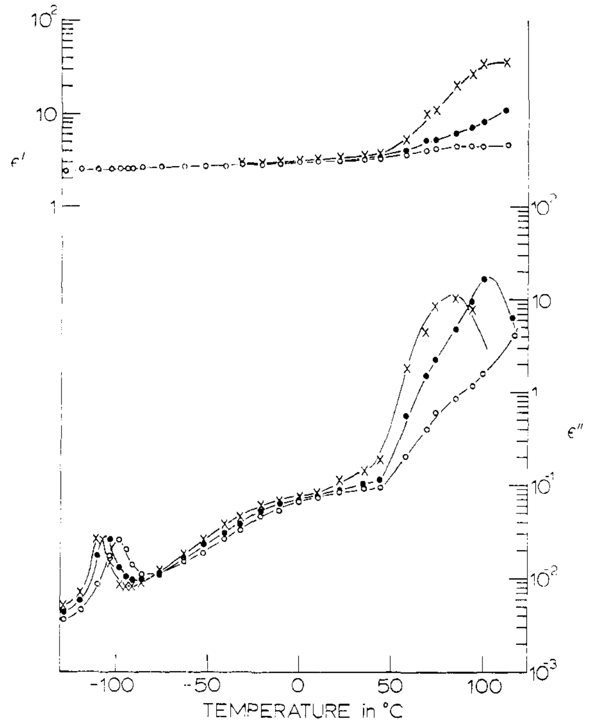

Figure 3. Variation of ϵ' and ϵ'' for copolymer C as a function of temperature at various frequencies: ○, 10 KHz; ●, 1 KHz; ×, 100 Hz.

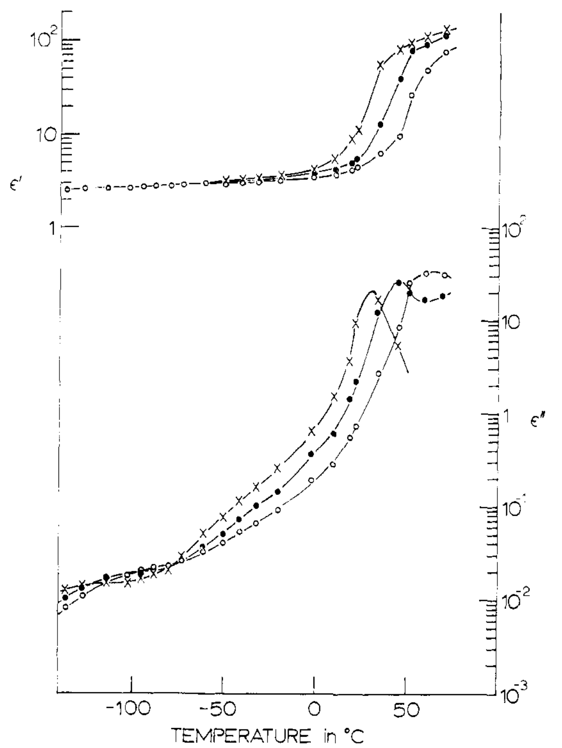

Figure 4. Variation of ϵ' and ϵ'' for copolymer D as a function of temperature at various frequencies: ○, 10 KHz; ●, 1 KHz; ×, 100 Hz.

signed to the merged α and β relaxations of polyethylene in the case of sample A is again present but is much greater in magnitude than is the case in sample A. A new loss region of high magnitude occurs at temperatures in excess of 100° (*i.e.*, well into the melt region, since sample B has a melting point of 106–110°). The peak maximum for this α' relaxation has not yet occurred at 180° at the lowest measurement frequency (100 Hz). It should also be noted that no abrupt changes in either ϵ' or ϵ'' occur in the melting range.

The temperature dependences of ϵ' and ϵ'' for sample C given in Figure 3 again show three relaxation regions as in sample B. The γ 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 α' 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°. Once again, no abrupt changes in dielectric behavior are noted in passing through the melting point.

The temperature dependence of ϵ' and ϵ'' of the amorphous sample D shown in Figure 4 is so dominated by the α' relaxation that the room temperature relaxation and the γ relaxation appear only as small shoulders on the α' peak. The dielectric α' peak occurs at 40° in sample D at 100 Hz which is identical with the temperature of the mechanical α' peak of sample D. The magnitude of the α' relaxation has again increased enormously compared to that of sample C. In sample C, $\epsilon_{\max}''$ is 18 while ϵ_0' is about 35. In sample D, $\epsilon_{\max}''$ is 32 while ϵ_0' is about 150.

The frequency dependence of ϵ' for samples A–D is shown in Figure 5 at room temperature. Corresponding plots of ϵ'' at room temperature show no relaxation peaks up to 10^5 Hz.

Discussion

The α' Dispersion. The features of the α' 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 6 is a plot of the temperature dependence of ϵ' at 100 Hz for all the polymers in the temperature region of the α' relaxation. Values of $\epsilon_0 - \epsilon_\infty = \Delta\epsilon'$, where ϵ_0 and ϵ_∞ are the relaxed (low frequency or high temperature) and unrelaxed (high frequency or low temperature) values of ϵ' representing the magnitude of the α' dispersion, may be estimated from plots such as Figure 6. 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[10]

$$\mu^2 = \frac{9kT(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{4\pi S\epsilon_0(\epsilon_\infty + 2)^2} \tag{1}$$

where μ is the dipole moment of the relaxing species, T is the absolute temperature, k is Boltzmann's constant, and S is the number of dipolar groups/cm³. S is calculated from

$$S = \frac{N_0 \rho W}{M} \tag{2}$$

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(10) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

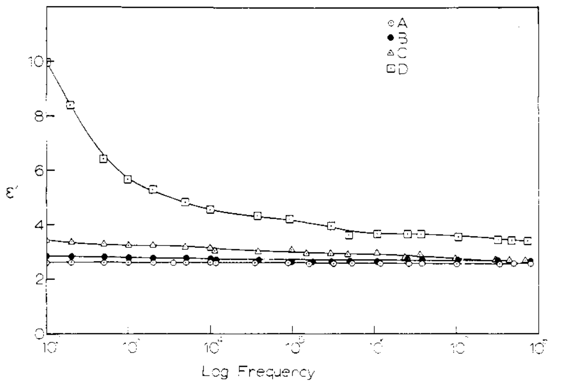

Figure 5. Variation of ϵ' with frequency at room temperature for all samples.

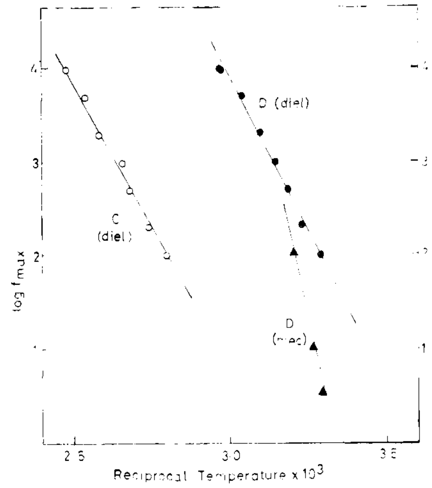

Figure 7. Arrhenius plots of the mechanical and dielectric α' dispersions.

where N_0 is Avogadro's number, ρ is the density of the polymer, W is the weight fraction of phosphonic acid-groups, and M is the molecular weight of a phosphonic acid group. Application of eq 1 to samples C and D using the value for μ of 2.6 D obtained for the dipole moment of phenylphosphonic acid lead to values of $\Delta\epsilon'$ of 0.27 and 0.43, respectively. Equation 1 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 $\Delta\epsilon'$'s calculated on the basis of eq 1 and those observed experimentally lead to the conclusion that the α' 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[2] provides for the possible assignment of the α' dispersion to an interfacial polarization mechanism similar to the mechanism of Maxwell and Wagner.[11,12]

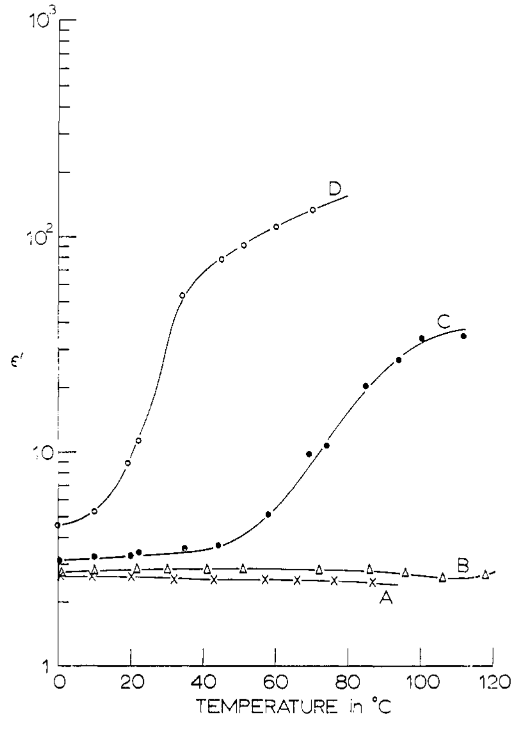

Figure 6. Temperature dependence of ϵ' at 100 Hz for all polymers.

A mechanical α' relaxation was observed in sample D at the same temperature as the dielectric α' dispersion in this polymer.[2] The mechanical process involved in the α' 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 α' relaxation region. Plots of log f_{max} *vs.* $1/T$ (Figure 7) for samples C and D show that the dielectric α' processes in both polymers have identical activation energies (30 ± 2 kcal/mol) indicating similar origins, but that the activation energy for the mechanical α' process in sample D is much higher (76 ± 2 kcal/mol). Thus, in a sense, the mechanical α' process seems to be more cooperative in character than the dielectric α' process and the activation energy results are consistent with the assignment of the α' dielectric and mechanical processes to two different mechanisms.

Cole–Cole plots for sample D at various temperatures are depicted in Figure 8.[13] From these plots may be derived values of $\Delta\epsilon'$ and the parameter $(1 - \alpha)$ characterizing the distribution of relaxation times. These results are collected in Table I for sample D and it may be seen that both the magnitude of the α' dispersion and the breadth of the distribution of relaxation times increase markedly with increasing temperature.

The temperature dependence of the dc conductivity

Table I
Data Derived from Cole–Cole Plots for α' Relaxation (Copolymer D)

	T, °C			
	34	45	51	60
$1 - \alpha$	0.876	0.80	0.745	0.57
$\Delta\epsilon'$	57	71	85	103

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(11) K. W. Wagner, *Arch. Elektrotech. (Berlin)*, **2**, 371 (1914).

(12) J. S. Dryden and R. J. Meakins, *Rev. Pure Appl. Chem.*, **7**, 15 (1957).

(13) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1942).

is presented in Figure 9 which is a plot of log conductivity *vs.* $1/T$. Activation energies from such plots are 28 kcal/mol for B, 40 kcal/mol for C, and 42 kcal/mol for D. The latter two values are identical within experimental error. On the basis of results on urethan solutions,[14] it would be expected that these activation energies are related to the activation energy for viscous flow. From Figure 9 and measured values of ac conductivity it emerges that the dc and ac conductivity are of similar orders of magnitude at the α' dispersion maximum. The nature of the conducting species has not been established. Conductivity may arise from ionic impurities, water, or protons. 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[15] and the presence of the acid groups in a nonpolar medium must also be taken into account.

The α' dispersion in the ethylene–phosphonic acid polymers cannot entirely consist of a Maxwell–Wagner mechanism of the type originally proposed,[11,12] because in addition to the points raised above, such a mechanism requires both ϵ' and ϵ'' to increase without limit with increasing temperature while in samples C and D the ϵ'' reaches a maximum value and the ϵ' appears to approach a plateau value. Further, the Maxwell–Wagner mechanism postulates one phase of the two phase system to be entirely nonconducting and this does not seem physically reasonable for samples C and D.

Maxwell–Wagner interfacial polarization effects have been observed previously in polyamides,[16–18] carbon black filled rubbers,[19] and polyurethans.[20] 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 polyurethans where the effect was assigned to urethan domains stabilized by the hydrogen bonding of the urethan 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 α' 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 α' relaxation temperature. While the dielectric α' dispersion cannot be a classical Maxwell–Wagner interfacial polarization process, the model proposed qualitatively accounts for the data. 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 differing temperature coefficients. Such calculations are presently being initiated.

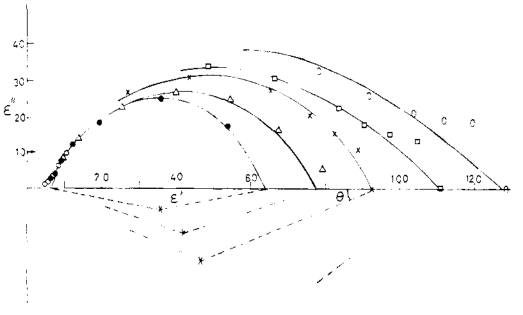

Figure 8. Cole–Cole plots of the α' dispersion data for copolymer D at various temperatures: ○, 22°; ●, 34°; △, 45°; ×, 51°; □, 60°; ○, 71°.

The β Relaxation. The broad dispersion situated around room temperature for all the polymers was tentatively assigned to the β relaxation of low-density polyethylene with perhaps some contribution from the polyethylene α relaxation in the polymers of high crystallinity (samples A and B).

Estimates of $\Delta\epsilon'$ for the β relaxation may be obtained from plots of ϵ'' *vs.* $1/T$ and the relationship[21]

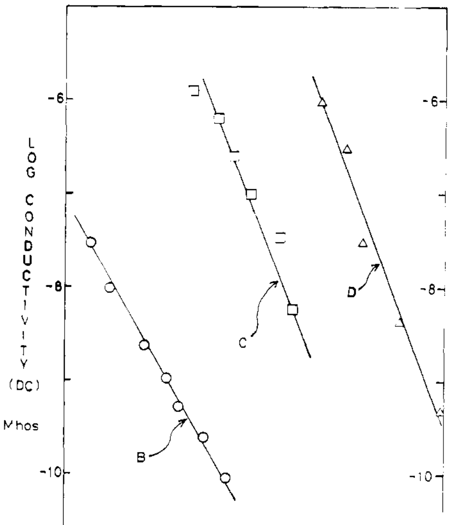

Figure 9. Temperature dependence of dc conductivity present in copolymers B, C, and D.

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(14) A. T. Bullock, A. M. North, and J. S. Shortall, *Eur. Polym. J.*, **4**, 587 (1968).

(15) P. J. Phillips and W. J. MacKnight, *J. Polym. Sci., Part B*, **8**, 87 (1970).

(16) W. O. Baker and W. A. Yager, *J. Amer. Chem. Soc.*, **64**, 2171 (1942).

(17) R. A. Boyd, *J. Chem. Phys.*, **30**, 1276 (1959).

(18) D. W. McCall and E. W. Anderson, *ibid.*, **32**, 237 (1960).

(19) W. C. Carter, M. Maget, W. C. Schneider, and C. P. Smyth, *Trans. Faraday Soc.*, **42A**, 213 (1946).

(20) A. M. North, J. C. Reid, and J. B. Shortall, *Eur. Polym. J.*, **5**, 437 (1969).

(21) B. E. Read and G. Williams, *Trans. Faraday Soc.*, **57**, 1974 (1961).

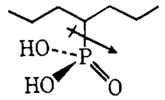
TABLE II
MAGNITUDE OF THE β RELAXATION

	Copolymer A	B	C	D
$\Delta\epsilon'$ (obsd)	0.055	0.225	0.965	1.46
$\Delta\epsilon'$ (calcd)	0.09	0.21	0.27	0.43

$$(\Delta\epsilon')T_{\max} = \frac{2\Delta H}{\pi R}\int_0^\infty \epsilon''(\mathrm{d}\ 1/T) \qquad (3)$$

where ΔH is the activation energy for the process. Areas were easily obtainable in the case of samples A and B, but for C and D, the β relaxation appears as a shoulder on the large α' dispersion. As a consequence it was necessary to decompose the ϵ'' curves into two components, a somewhat arbitrary procedure. Thus the results for samples C and D can be considered only semiquantitative at best. ΔH was taken to be 19 kcal/mol which is the activation energy of the β relaxation for copolymer B, the sample with the most clearly resolved β relaxation peak. Values of $\Delta\epsilon'$ obtained in this manner are collected in Table II. Also given in Table II are values of $\Delta\epsilon'$ 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 with that of phenylphosphonic 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 β 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



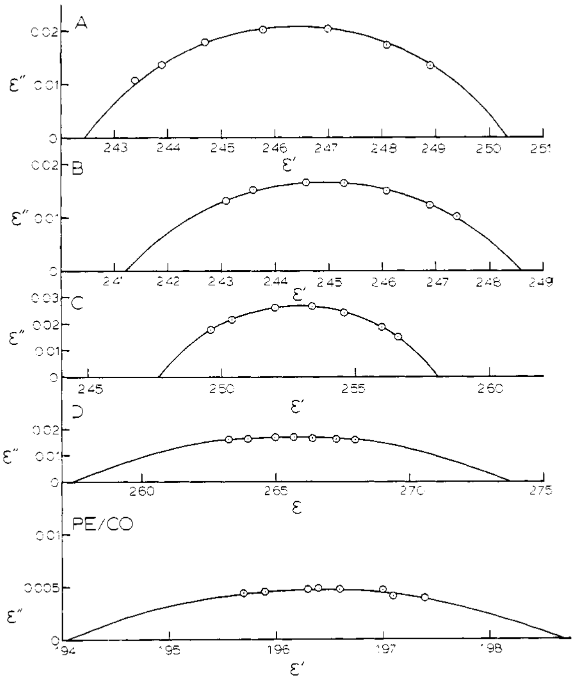


Figure 10. Cole–Cole plots of the γ relaxation data for all copolymers and a copolymer of ethylene with carbon monoxide.

TABLE III
THE γ RELAXATION. ARRHENIUS DATA

	Dielectric		Mechanical	
Copolymers	E_A, kcal/mol	1 KHz max, °C	E_A, kcal/mol	110 Hz max, °C
A	40	−93	10	−114
B	34.8	−100	10	−117
C	26.7	−103.5	8.5	−118
D	16.2	−111	9	−123
ET–CO	14.3	−105	9	−125

Values for the bond angles and bond moments of phosphonic acids are not available. Thus, in order to obtain an estimate of the angle between the dipole moment of the phosphonic acid group and the main chain, literature values for the bond moments and angles of acetic acid have been used.[22] Assuming the phosphonic acid group to possess a dipole moment of 2.6 D, the results of this procedure indicate that the dipole moment of the phosphonic acid group is 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 β relaxation and it would be reasonable to expect a value of $\Delta\epsilon'$ of about half the calculated value. It can be seen from Table II that this analysis leads to good agreement between observed and calculated $(\Delta\epsilon')$s for sample A. Such agreement is not obtained for the other samples, probably for the reasons outlined above.

The γ Relaxation. This low-temperature dispersion is observed for all the copolymers and moves to lower temperatures as the phosphonic acid content is increased. Plots of log $f_{\max}$ *vs.* $1/T$ for the γ relaxation are linear yielding apparent activation energies which decrease with increasing phosphonic acid content.

Comparisons in temperature and activation energy between the dielectric and mechanical relaxations are given in Table III. Also included are data for a random ethylene–carbon monoxide copolymer containing 1 wt % carbon monoxide. In the case of sample D the γ peak appears only as a shoulder and it was necessary to resolve it from the β relaxation. As discussed in the case of the β relaxation, this resolution leads to a certain amount of error.

In the case of the mechanical γ relaxation, the activation energies are essentially independent of phosphonic acid content and are low whereas the dielectric γ relaxation indicates high activation energies which approach the mechanical results only in the case of sample D. Figure 10 shows Cole–Cole plots for the dielectric γ relaxation for all the copolymers as well as the ethylene–carbon monoxide copolymer for compari-

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(22) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955.

TABLE IV
THE γ RELAXATION. COLE–COLE PLOT DATA

Copolymer	$(1 - \alpha)$	$(\Delta\epsilon')$ (area)	$(\Delta\epsilon')$ (Cole–Cole)	$(\Delta\epsilon'_{\max})$ (theory)
A	0.62	0.097	0.078	0.05
B	0.45	0.106	0.085	0.11
C	0.61	0.206	0.105	0.13
D	0.27	0.206	0.121	0.21
ET–CO	0.30			

son purposes. It is seen that the shape of the Cole–Cole plots for sample D and the ethylene–carbon monoxide polymer are quite similar but that samples A, B, and C show quite different behavior. Table IV collects the parameters derivable from the Cole–Cole plots for the γ relaxation as well as values of $\Delta\epsilon'$ estimated from eq 3. It is seen that the breadth of the relaxation time distribution as evidenced by the parameter $(1 - \alpha)$ is considerably greater for sample D than for A, B, and C, and is in fact comparable to the value obtained for the ethylene–carbon monoxide copolymer. This and the activation energy data would indicate that the γ process in sample D is of the polyethylene type perhaps rendered dielectrically active by adventitious oxidation. This is consistent with the phase separated structure believed to exist in sample D.

The same arguments indicate that phosphonic acid groups must contribute to the γ relaxation in samples A, B, and C. Assuming this contribution to arise from rotation of isolated phosphonic acid groups about the CP axis, we would expect only the perpendicular component of the dipole moment of the phosphonic acid group to be active. Using this simple model and calculating $\Delta\epsilon'$ on the basis of the Onsager equation, fairly good agreement results for A, B, and C as shown in Table IV. In general the agreement is better for values of $\Delta\epsilon'$ derived from Cole–Cole plots than from areas of plots of ϵ'' *vs.* $1/T$.

Summary

The model proposed to account for the experimental evidence is one in which, at low phosphonic acid contents (*e.g.*, copolymer A) we have essentially isolated randomly placed phosphonic acid groups throughout the polymer.

As the phosphonic acid content is increased hydrogen bonding between acid groups occurs and increases with increasing phosphonic acid content leading to dimers, trimers, etc., and ultimately (*e.g.*, copolymer D) to a two-phase structure in which we have large hydrogen-bonded aggregates embedded in a polyethylene matrix which still contains a few isolated phosphonic acid groups and oligomers.

The situation here is quite different from that reported for ethylene–carboxylic acid systems in which carboxylic acid dimers prevail due to the unusual symmetry of that dimer. There is, however, reason to believe that a similar situation to the one reported here may exist for ethylene–carboxylic acid copolymers of very high carboxylic acid content.[23]

Acknowledgments. The authors are grateful to the National Science Foundation for partial support of this research under Grant GP 8581 and to the Petroleum Research Fund of the American Chemical Society for partial support of this research under Grant 2914 A5.

(23) R. Longworth, private communication.

Thermodynamic and Hydrodynamic Properties of Linear Polymer Solutions. I. Light Scattering of Monodisperse Poly(α-methylstyrene)

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ABSTRACT: Second virial coefficients and expansion factors of monodisperse poly(α-methylstyrenes) covering a wide range of molecular weight are determined by light scattering measurement in Θ and non-Θ solvents and are compared with current theories of these solution properties. It is concluded that the Flory theory of α^5-type is valid when the molecular weight is high enough to permit reliable determination of the radius of gyration.

There are, roughly speaking, two groups of theories on the expansion factor of linear polymers as a function of molecular weight, temperature, solvent species, etc. One is represented by the theory of Flory (eq 1) which is usually called an equation of the α^5-type,[1-4] while the other is represented by the theory of Stockmayer and Fixman (eq 2) which is called an equation of the α^3-type.[5-8] The expansion factor α is defined by $\alpha_s^2 = \langle S^2\rangle/\langle S^2\rangle_0$, where $\langle S^2\rangle_0^{1/2}$ and $\langle S^2\rangle^{1/2}$ are the radii of gyration at the Θ and non-Θ temperatures, respectively

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