Structure and Properties of Polyethylene Modified with Phosphonic Acid Side Groups. I. Mechanical and Thermal Studies

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ABSTRACT: A sample of low-density polyethylene containing 1.4 long chain branches per 100 carbon atoms was chemically modified by the inclusion of phosphonic acid side groups. Dynamic mechanical and differential scanning calorimetry (dsc) studies were carried out on the unmodified polyethylene and on samples containing 0.8, 1.8, 2.8, and 7.4 phosphonic acid side groups per 100 carbon atoms. The dsc results show that the weight per cent crystallinity is a decreasing function of the phosphonic acid concentration, no crystallinity being detectable by dsc in the material with highest phosphonic acid content. The effect is partly kinetic as illustrated by the fact that the weight per cent crystallinity may be considerably enhanced by prolonged annealing. However, no crystallinity was observable in the highest phosphonic acid content material under any thermal history investigated. The dynamic mechanical spectra exhibit four distinct dispersion regions. The unmodified polyethylene shows three loss peaks labeled α, β, and γ in order of decreasing temperature. The phosphonic acid containing polymers all have the β and γ dispersions in common with the polyethylene and those samples of appreciable degrees of crystallinity also have the polyethylene α relaxation. The sample containing 7.4 phosphonic acid side groups per 100 carbon atoms has a new relaxation, designated α' and occurring at 50° (110 Hz). It is postulated that the α' relaxation arises from motion occurring within domains formed from the clustering of hydrogen bonded phosphonic acid groups.

Recently there has been a great deal of interest in the phenomenon of microphase separation in solid polymers. Multiphase materials resulting from this phenomenon exhibit a wide variety of new physical properties. These properties obviously depend on the structure of the matrix, the size, structure, and distribution of the dispersed phase, and the nature of the interface between the matrix and the dispersed phase. For the purposes of this discussion we may define microphase separated materials as those in which the dispersed phase is too small to scatter visible light but large enough to affect significantly the mechanical properties of the material. This definition is far from quantitative inasmuch as the lower limit cannot be exactly determined, but operationally the size range of the dispersed phase can be regarded as extending from the order of tens of ångströms to the order of hundreds of ångströms. Examples of polymeric materials exhibiting the phenomenon of microphase separation are butadiene–styrene block copolymers,[2a] polyester and polyether urethan elastomers,[2b] and the salts of ethylene–methacrylic acid copolymers.[3,4] The latter two examples are perhaps the most analogous to the present system inasmuch as in the case of the polyurethans the domains are thought to consist of hydrogen-bonded urethan groups and in the case of the copolymer salts the domains are thought to consist of clusters of salt groups.[5,6] The analogy with these systems exists be-

cause if microphase separation occurs in the phosphonic acid modified polyethylenes the domains must be stabilized by hydrogen bonding as in the polyurethans and a phase-separated structure must result from a random copolymer as in the case of the ethylene–methacrylic acid copolymer salts. It should be pointed out that the presence of salt group domains in the ethylene–methacrylic acid copolymer salts is by no means universally accepted at present and that at least one alternative structural model has been put forward in which the salt groups are postulated to exist in the form of ionic cross-links uniformly dispersed throughout the amorphous polyethylene phase.[7] However, low-angle X-ray[6] and dielectric relaxation studies[5,8] are consistent with the domain model.

The investigations carried out on the ethylene–methacrylic acid copolymer systems led to much fruitful information. However, these copolymers are 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 methacrylic acid groups as a function of acid group concentration. Thus, characterization of a series of such copolymers with varying acid contents is difficult. Blyler and Haas[9] have characterized such a series after esterification to determine differences in molecular weight and branching by rheological measurements. The polyethylene–phosphonic acid system which is the subject of this series of papers 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

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(2) (a) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969); (b) S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 1361 (1967).

(3) R. Longworth and D. J. Vaughan, *Nature (London)*, **218**, 85 (1968).

(4) W. J. MacKnight, T. Kajiyama, and L. W. McKenna, *Polym. Eng. Sci.*, **8**, 267 (1968).

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

(6) B. W. Delf and W. J. MacKnight, *Macromolecules*, **2**, 309 (1969).

(7) E. P. Otocka and T. K. Kwei, *ibid.*, **1**, 401 (1968).

(8) P. J. Phillips and W. J. MacKnight, *J. Polym. Sci., Part A-2*, **8**, 727 (1970).

(9) L. L. Blyler and T. W. Haas, *J. Appl. Polym. Sci.*, **13**, 2721 (1969).

the basic polyethylene structure.[10] 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. In this and the following paper we present evidence based on mechanical and dielectric studies that microphase separation occurs in polyethylene modified by the inclusion of phosphonic acid side groups at high phosphonic acid concentrations. Subsequent publications will deal with the salts and esters of these polymers.

Experimental Section

Materials. The starting polyethylene was obtained through the courtesy of Mr. L. W. McKenna of the Monsanto Co. and had a number average molecular weight of 1.38×10^4, a weight average molecular weight of 1.72×10^5, a density of 0.926 and 1.4 long chain branches per 100 carbon atoms. It was precipitated twice from *p*-xylene and then dried. Four concentrations of phosphonic acid side groups were added by dissolving the starting material in PCl_3 at 60° and bubbling oxygen through the mixture for varying lengths of time. The $POCl_2$ groups thus formed were hydrolyzed to phosphonic acid groups by pouring the reaction mixture into cracked ice. The method has been described in detail previously.[11] The resulting structure may be schematically represented as

$$\begin{array}{c} H \\ | \\ (CH_2CH_2)_m(CH_2C-)_n \\ | \\ PO(OH)_2 \end{array}$$
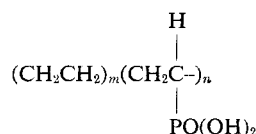
and may be regarded as a random copolymer of ethylene and vinyl phosphonic acid. The phosphonic acid content per 100 carbon atoms of the four samples was determined by chemical analysis and is A, 0.8; B, 1.8; C, 2.8; and D, 7.4.

Samples were prepared for subsequent measurements by compression molding between Teflon sheets at temperatures from 150 to 180° at 5000 psi. After 20 min the resulting films were rapidly quenched to room temperature.

Annealing was carried out in an oven at 10° below the observed melting points for 24 hr. Samples were then slowly cooled to room temperature during a period of 3-4 hr.

Measurements. Dsc studies were carried out on a Perkin-Elmer differential scanning calorimeter, Model D.S.C. 1B. All heating and cooling rates were 10°/min.

Dynamic mechanical spectra were obtained on a Vibron dynamic viscoelastometer, Model DDV II. The temperature range was from −165 to 110° and the frequencies employed were 3.5, 11, and 110 Hz.

Results

(a) Differential Scanning Calorimetry. The present studies confirm and amplify the preliminary conclusions of a previous note.[11] In Table I are presented the melting points, temperatures of recrystallization, and relative crystallinities of the samples studied. The melting points quoted correspond to the maximum excursion of the melting endotherms from the base line and the recrystallization temperatures to the onset of the recrystallization exotherm. Crystallinities are relative to an annealed sample of the parent poly-

(10) J. P. Schroeder and W. P. Sopchak, *J. Polym. Sci.*, **47**, 417 (1960).

(11) P. J. Phillips and W. J. MacKnight, *ibid.*, *Part B*, **8**, 87 (1970).

TABLE I

PO(OH)$_2$[a]	Sample	Mp, °C	T_c, °C	Relative crystallinity
	Polyethylene	121.5	105.0	100
	Q	111.7	91.9	85
0.8	A			
	A	131.1	95.4	83
	Q	106.0	80.7	63
1.8	B			
	A	110.4	84.7	73
	Q	93.7	63.3	46
2.8	C			
	A	98.3	6.52	60
7.4	D	A	No detectable crystallinity	

[a] Phosponic acid content per 100 carbon atoms.

ethylene and were derived from areas under the melting endotherms. It is to be noted that crystallinity was undetectable in sample D under any conditions. Presumably this is the ultimate effect to be expected from the phosphonic acid groups and is due to their inability to cocrystallize with ethylene segments and their restrictive effect on diffusional motion of chain segments arising from hydrogen bonding and/or clustering.

In the theory of Flory,[12] the dependence of the melting point on the concentration of crystallizable units in a random copolymer is given by

$$1/T_m - 1/T_m^0 = \frac{-R}{\Delta H_u} \ln N \tag{1}$$

where T_m is the melting point of the copolymer, T_m^0 that of the crystalline homopolymer, N is the mole fraction of crystallizable units in the copolymer, and ΔH_u the heat of fusion per mole of repeating homopolymer unit. Generally, the application of eq 1 to copolymer systems has resulted in predicted melting points considerably lower than those found experimentally.[13] A plot of $1/T_m$ against $-\log N$ for the present copolymer system is given in Figure 1. It is seen that a straight line results for the low phosphonic acid content materials and that the slope yields values
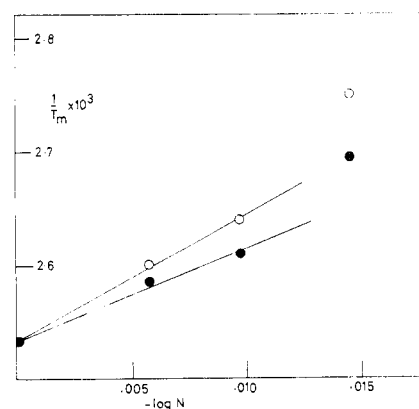

Figure 1. Reciprocal melting points *vs.* $-\log N$, the mole fraction of crystallizable units for quenched (●) and annealed (○) ethylene vinyl phosphonic acid copolymers.

(12) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).
(13) L. Mandelkern, *Rubber Chem. Technol.*, **32**, 1392 (1959).

of ΔH_u of 420 cal/mol of (–CH$_2$–) for the quenched samples and 580 cal/mol of (–CH$_2$–) for the annealed samples.

(b) Dynamic Mechanical Spectra. The temperature dependences of the storage moduli, E', and the loss moduli, E'', at 110 Hz, for the unmodified polyethylene and the four phosphonic acid containing materials are presented in Figures 2–4. Figure 2 compares copolymers A and B to the parent polyethylene and it is seen that the α, β, and γ relaxations of the parent polyethylene are discernible for these materials also although the magnitudes of the β and γ 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 3 reveals that the α relaxation has disappeared almost entirely and the major decrease in E' is associated with the β relaxation. Once again the temperatures of the γ and β 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 4 illustrates this difference, showing that in addition to the γ and β relaxations there appears a new relaxation in copolymer D at 50°, labeled α'. Inasmuch as copolymer D is totally amorphous, the α' relaxation cannot be identified with the α relaxation of polyethylene.

Discussion

Thermal Properties. Table I shows that as phosphonic acid content increases both the melting point and degree of crystallinity become strong functions of thermal history. This is a reflection of the effect of phosphonic acid side groups on the crystallization kinetics. Thus both the average size of the crystals
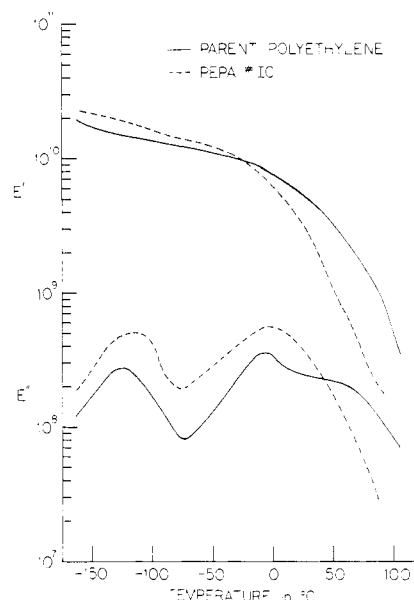

Figure 3. Temperature dependence of E' and E'' at 110 Hz for the parent polyethylene and sample C.

and the total concentration of crystalline material in the polymer can be varied over a considerable range by thermal treatment at high phosphonic acid levels. Extrapolation of a plot of relative crystallinity as a function of phosphonic acid groups per 100 carbon atoms from the data in Table I yields values for the total disappearance of crystallinity of 5.2 groups per 100 carbon atoms for the quenched samples and 6.9 groups per 100 carbon atoms for the annealed samples. Such an extrapolation is, of course, somewhat uncertain, but the results are consistent with the fact that no detectable crystallinity can be developed in sample D (7.4 groups/100 carbon atoms) under any of the conditions investigated. It is interesting to compare these results with other random ethylene copolymer systems in which the comonomer units are excluded from the
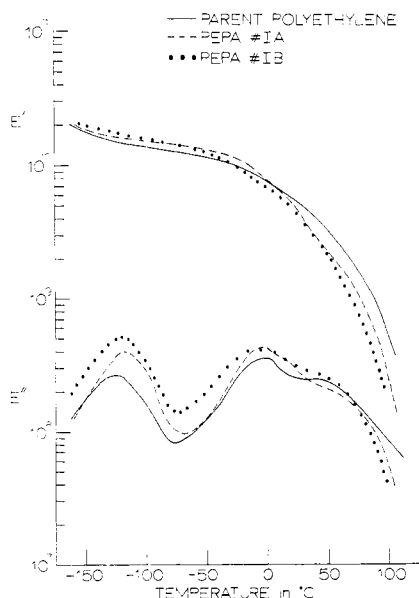

Figure 2. Temperature dependence of E' and E'' at 110 Hz for the parent polyethylene, sample A, and sample B.
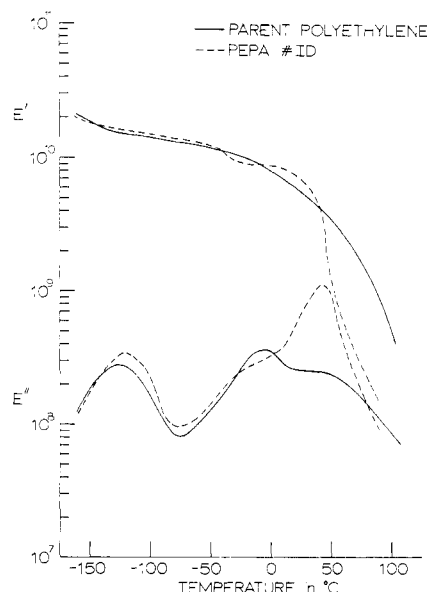

Figure 4. Temperature dependence of E' and E'' at 110 Hz for the parent polyethylene and sample D.

crystalline phase. Perhaps the most closely analogous study to the present work is that of Otocka and Kwei on ethylene–acrylic acid copolymers.[14] It is difficult to make direct comparisons because of differences in alkyl chain branching, but the effect of acrylic acid groups on the melting points and degrees of crystallinity of ethylene–acrylic acid copolymers seems roughly comparable to that of the phosphonic acid groups discussed above. The situation is far different, however, in the case of ethylene–vinyl acetate copolymers. Available data[15,16] indicate that the last trace of crystallinity in ethylene–vinyl acetate copolymers disappears at approximately 14 vinyl acetate groups per 100 carbon atoms. The most obvious explanation for the greater deleterious effect on crystallinity of both acrylic acid and phosphonic acid groups compared to vinyl acetate groups is the restrictions on chain mobility imposed by hydrogen bonding in the former cases, and the absence of this factor in the latter case. Whether this is the sole origin of the effect must await further experimental elucidation.

The results of the application of eq 1 to the phosphonic acid copolymer series have been presented above. It is to be noted that straight line plots passing through the melting point of the parent polyethylene are obtained only for samples A and B, sample C indicating a large deviation from linearity in both the annealed and quenched cases. The reasons for this deviation are not clear. One possibility is that restrictions on chain mobility caused by a tendency of the phosphonic acid groups to cluster at high phosphonic acid contents may be more severe than those imposed by the hydrogen bonded dimers and trimers probably present at low concentrations of phosphonic acid groups and hence lead to smaller crystals of lower melting point than predicted on the basis of eq 1. The values of ΔH_u of 420 cal/mol of (–CH$_2$–) for the quenched samples and 580 cal/mol of (–CH$_2$–) for the annealed samples differ considerably from the value of 755 cal/mol of (–CH$_2$–) obtained for the ethylene–acrylic copolymers.[14]

Mechanical Relaxations. Mechanical relaxations in polyethylene have been extensively studied, although the molecular origins of these relaxations remain a matter of some controversy.[17] It is widely accepted[18] that the α relaxation is a composite of chain motions occurring in the crystalline phase with one crystalline component perhaps consisting of a twisting motion of chains and the second component perhaps consisting of a twisting slip mechanism. The β relaxation is an amorphous phase motion occurring only in low-density polyethylene and is attributed to the microbrownian motion of chains associated with the glass transition. The γ relaxation is also a composite mechanism possibly arising from localized motions of a few repeat units in the amorphous phase and from localized motions
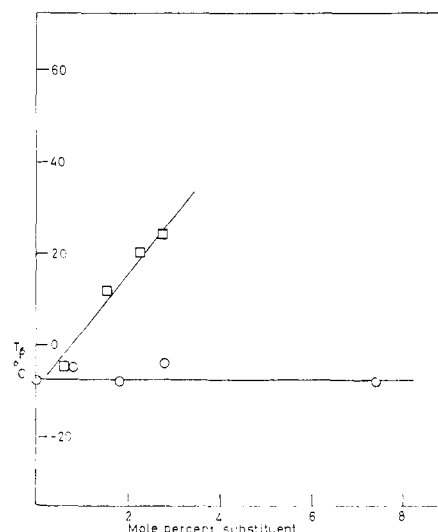

Figure 5. Temperature of the β relaxation at 110 Hz *vs.* acrylic acid groups per 100 carbon atoms ($\square$) and phosphonic acid groups per 100 carbon atoms (O).

around chain ends present as defects in the crystalline phase.[18] The results presented above for the phosphonic acid copolymers A, B, and C are generally consistent with these assignments. As crystallinity decreases, the α relaxation also decreases in magnitude, the β relaxation increases in magnitude, and the γ relaxation increases somewhat. It is interesting to compare the temperature locations of the β relaxations in the phosphonic acid copolymers to those of the ethylene–acrylic acid copolymers of Otacka and Kwei.[14] Such a comparison is only semiquantitative because of differences in branching between the two systems. Figure 5 is a plot of the temperatures of the β relaxation as a function of the number of substituent groups per 100 carbon atoms for the ethylene–acrylic acid copolymers and the ethylene–phosphonic acid copolymers of the present study. It is apparent that there is a large increase in the β relaxation temperatures with increasing acrylic acid content but that the β temperature is essentially independent of phosphonic acid content over the range studied. The effect of acrylic or methacrylic acid substituents was originally rationalized on the basis of the acrylic acid units being present in the form of hydrogen-bonded dimers acting as cross links.[14,19] It was further shown that the effect could not be explained on the basis of the copolymer composition alone.[14] It would thus appear that the phosphonic acid groups are not present as hydrogen bonded dimers to any appreciable extent. This may be so because of the inability of two phosphonic acid groups to form a symmetrical structure with all hydrogen bonding sites satisfied as is the case with the acrylic acid or methacrylic acid substituents.

The appearance of the new α' peak in the amorphous sample D is taken as evidence for microphase separation. The temperature behavior of E' (Figure 4) in sample D is also suggestive of the phenomenon. It

(14) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 244 (1968); E. P. Otocka, T. K. Kwei, and R. Salovey, *Makromol. Chem.*, **129**, 144 (1969).

(15) L. E. Nielsen, *J. Polym. Sci.*, **42**, 357 (1960).

(16) K. H. Illers, *Eur. Polym. J. Suppl.*, 133 (1969).

(17) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967, Chapter 10.

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

(19) W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1967).

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.

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.

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

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

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