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# Properties of Polyethylene Modified with Phosphonate Side Groups. II. Dynamic Mechanical Behavior

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## Synopsis

The viscoelastic behavior of phosphonate derivatives of phosphonylated low-density polyethylene (LDPE) was studied by dynamic mechanical techniques. The polymers investigated contained from 0.2 to 9.1 phosphonate groups per 100 carbon atoms and included the dimethyl phosphonate derivative and two derivatives for which the phosphonate ester group was an oligomer of poly(ethylene oxide) (PEO). The temperature dependences of the storage and loss moduli of the dimethyl phosphonate derivatives were qualitatively similar to those of LDPE. At low phosphonate concentrations, the  $\alpha$ ,  $\beta$ , and  $\gamma$  dispersion regions characteristic of PE were observed, while at concentrations greater than 0.5 pendent groups per 100 carbons atoms, only the  $\beta$  and  $\gamma$  relaxations could be discerned. At low degrees of substitution, the temperature of the  $\beta$  relaxation  $T_\beta$  decreased from that of PE, but above a degree of substitution of 0.1,  $T_\beta$  increased. This behavior was attributed to the competing influences of steric effects which tend to decrease  $T_\beta$  and dipolar interactions between the phosphonate groups which increase  $T_\beta$ . For the phosphonates containing PEO, a new dispersion region designated as the  $\beta'$  relaxation was observed as a low-temperature shoulder of the  $\beta$  relaxation. The temperature of the  $\beta'$  loss was consistent with  $T_g(U)$  of the PEO oligomers as determined by differential scanning calorimetry, and it is suggested that the  $\beta'$ -loss process results from the relaxation of PEO domains which constitute a discrete phase within the PE matrix.

## INTRODUCTION

In a recent paper<sup>1</sup> we described the modification of a commercial low-density polyethylene (LDPE) by the inclusion of phosphonate pendent groups,  $-\text{P}(\text{O})(\text{OR})_2$ , attached to the polymer backbone through a C—P bond. We reported that, in general, introduction of the phosphonate group resulted in reductions of the polymer crystallinity, melting point, and tensile modulus. The thermal and mechanical behaviors of several different phosphonates were predictable from random copolymer theory; that is, they were dependent only on the extent of the polymer modification. The molecular weight and the chemical structure of the phosphonate ester group did not appear to have a significant effect on the polymer properties.

We noted, however, that for the polymers having the highest degree of substitution (9.1 phosphonate groups per 100 carbon atoms) and for which the phosphonate ester group was an oligomer of poly(ethylene oxide) (PEO) ( $\text{R} = -(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_3$ ), the melting points deviated from those predicted by random copolymer theory. These polymers melted approximately 10°C higher than their low-molecular-weight analog, the dimethyl phosphonate ( $\text{R} = -\text{CH}_3$ ), indicating that the polymeric phosphonate ester has less of a disruptive effect on the ability of the PE backbone to crystallize than does the lower-molecular-

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weight ester. It was suggested that the polymeric phosphonates form a distinct phase within the PE matrix, and in doing so, have a lesser influence on the crystallization behavior of the PE.

The purpose of the present paper is to discuss the phenomenon of microphase separation in phosphonated PE. We present some dynamic mechanical data which demonstrate that PEO chains relax independently of the PE backbone. In addition, some recent thermal data that are consistent with our interpretation of the dynamic mechanical results are also discussed.

## EXPERIMENTAL

### Materials

The phosphonates of LDPE were prepared by an oxidative chlorophosphorylation technique that was described in an earlier paper.<sup>1</sup> The LDPE was supplied by Cities Service Research and Development Company and had a density of 0.923 g/cm<sup>3</sup>, a number-average molecular weight of 20,000, and a weight-average molecular weight of 80,000. The polymers studied included the dimethyl phosphonate and two different phosphonates for which the ester group was a PEO oligomer with a number-average molecular weight of either 350 or 750. These materials are described in Tables I-III.

Samples for dynamic mechanical analysis and for differential scanning calorimetry (DSC) were compression molded between Teflon sheets for 20 min at

TABLE I  
Dynamic Mechanical Results for Phosphonates, —P(O)(OR)<sub>2</sub>, of LDPE (R = CH<sub>3</sub>)

Sample	D.S. <sup>b</sup>	α Relaxation <sup>a</sup>			β Relaxation <sup>a</sup>				γ Relaxation <sup>a</sup>			
		T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	ΔH	T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	ΔH
LDPE	0	40	33	30	2	-2	-5	70	-119	-123	-125	25
A1	0.09	30	20	15	-10	-14	-16	71	-120	-124	-126	29
A2	0.35	30	19	17	-1	-4	-6	68	-110	-115	-117	25
A3	0.44	28	19	14	-2	-6	-8	72	-120	-125	-128	20
A4	2.7	-	-	-	4	-2	-4	55	-122	-126	-128	23
A5	4.5	-	-	-	34	26	21	45	-105	-110	-112	26
A6	5.8	-	-	-	8	4	1	70	-114	-122	-126	13
A7	9.1	-	-	-	42	34	29	46	-120	-127	-130	15

<sup>a</sup> Temperatures in °C correspond to  $E_{max}^*$ ; activation energies are given in kcal/mole; temperature subscript denotes frequency in Hz.

<sup>b</sup> Degree of substitution = number of phosphonate groups per 100 carbon atoms.

TABLE II  
Dynamic Mechanical Results for Phosphonates, —P(O)(OR)<sub>2</sub>, of LDPE (R = PEO(350))<sup>a</sup>

Sample	D.S.	α Relaxation			β Relaxation				γ Relaxation			
		T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	ΔH	T <sub>110</sub>	T <sub>11</sub>	T <sub>3.5</sub>	ΔH
LDPE	0	40	33	30	2	-2	-5	70	-119	-123	-125	25
B2	0.35	15	9	7	6	3	2	109	-105	-115	-120	12
B5	4.5	-	-	-	17	10	8	63	-114	-122	-126	13
B6	5.8	-	-	-	1	-2	-4	109	-122	-131	-134	9
B7	9.1	-	-	-	26	18	14	48	-115	-121	-124	17

<sup>a</sup> See footnotes to Table I.

TABLE III  
Dynamic Mechanical Results for Phosphonates,  $-\text{P}(\text{O})(\text{OR})_2$ , of LDPE (R = PEO(750))<sup>a</sup>

Sample	D.S.	$\alpha$ Relaxation			$\beta$ Relaxation				$\gamma$ Relaxation			
		$T_{110}$	$T_{11}$	$T_{3.5}$	$T_{110}$	$T_{11}$	$T_{3.5}$	$\Delta H$	$T_{110}$	$T_{11}$	$T_{3.5}$	$\Delta H$
LDPE	0	40	33	30	2	-2	-5	70	-119	-123	-125	25
C1	0.09	18	10	8	-1	-6	-8	76	-113	-120	-124	15
C5	4.5	-	-	-	17	14	12	109	-113	-122	-126	12
C6	5.8	-	-	-	2	-1	-3	92	-118	-125	-128	17
C7	9.1	-	-	-	37	34	32	109	-111	-119	-123	15

<sup>a</sup> See footnotes to Table I.

180°C. The molded films were quenched in water to room temperature and were dried at 25°C under vacuum for 48 hr. Annealed samples were prepared by heating the polymer films for 24 hr at 20°C below the melting point. DSC measurements of the PEO oligomers were made on the material as received from Polysciences, Inc.

### Measurement

Dynamic mechanical measurements were made with a Toyo Vibron Viscoelastometer, model DDV-II (Rheovibron), using annealed rectangular films, 0.2–0.6 mm thick, 2–5 mm wide, and 5–20 mm long. The temperature range covered was from -160 to 100°C and measurements were made at three frequencies: 3.5, 11, and 110 Hz. Values of the mechanical loss tangent,  $\tan \delta$ , were recorded directly from the Rheovibron and were used to calculate the storage modulus  $E'$  and the loss modulus  $E''$  as a function of temperature and frequency. The details of these calculations are given elsewhere.<sup>2</sup> Thermal measurements were made between -120 and 150°C with a Perkin-Elmer DSC-2 using a heating rate of 20°C/min.

## RESULTS AND DISCUSSION

### LDPE

The temperature dependence of the dynamic mechanical storage and loss moduli of the Cities Service LDPE are shown in Figure 1 for a frequency of 110 Hz. The loss modulus exhibits three major maxima, at 40, 2, and -119°C, which are consistent with previous reports of the  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxations of LDPE.<sup>3</sup>

Although a comprehensive discussion of the origins of these relaxations is beyond the scope of this study (an excellent review of this subject is given in ref. 3), some explanation is necessary in order to better understand the dynamic mechanical data of phosphonated PE.

Numerous interpretations of the  $\alpha$ -loss mechanism in PE have been advanced; however, it is generally accepted that this relaxation results from chain motion in the crystalline regions of the polymer. Rempel and co-workers<sup>4</sup> were the first to suggest that the  $\alpha$  relaxation arises from vibrational motion within the crystals. Sinnott<sup>5</sup> proposed that the molecular motion was caused by the reorientation of the folds at the surface of the lamellas. Upon annealing, the polymer crystals irreversibly thicken and the number of folds decrease and at the same time the

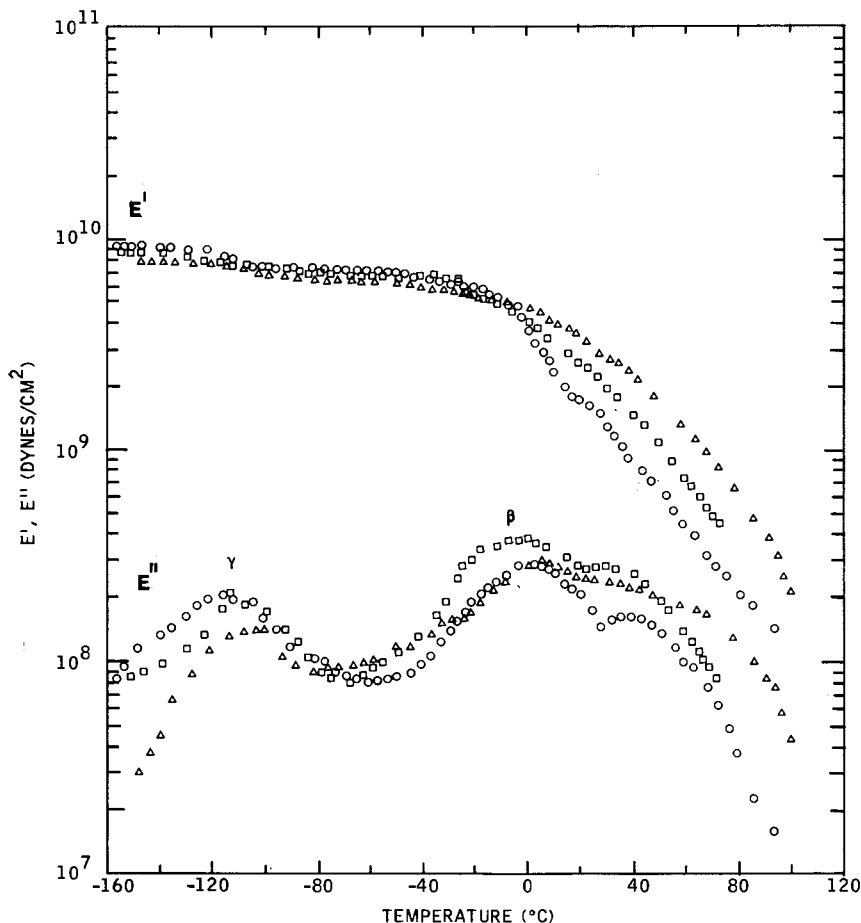


Fig. 1. Temperature dependence of  $E'$  and  $E''$  at 110 Hz for the Cities Service LDPE (O), sample A2 ( $\square$ ), and sample B2 ( $\Delta$ ).

magnitude of the  $\alpha$  relaxation decreases. Hoffman et al.<sup>6</sup> suggested that the  $\alpha$ -relaxation process consisted of two overlapping mechanisms—motion of the chain folds and translation of chains in the interior of the lamellas. This was consistent with the interpretation of Takayanagi<sup>7</sup> that the molecular motion was due to a combination of torsional motion about the chain axis and reorientational motion parallel to the chain.

The  $\beta$  relaxation of branched PE is believed to involve micro-Brownian segmental motion of the portion of the molecule containing the branch point.<sup>8-12</sup> For low branching concentrations, the  $\beta$  relaxation is unaffected by the size and chemical nature of the branch group.<sup>12</sup> The amount of branching, however, affects the  $\beta$  relaxation; an increase in the magnitude of the  $\beta$  loss and a decrease in the temperature of the loss maximum are seen with an increasing number of side branches.<sup>8</sup> The strong dependence of this relaxation on chain branching has led many authors to designate this loss process as the primary glass transition of branched PE,<sup>3</sup> an assignment that is, however, not universally accepted.

The  $\gamma$  relaxation has also been designated as the glass transition of PE,<sup>13</sup> although, as with the assignment of the  $\beta$  relaxation, this assignment is contro-

versial. It is generally accepted, however, that the  $\gamma$  relaxation results from localized motion of the methylene units of the PE chain. The most popular mechanism for this relaxation was proposed in two papers by Schatzki,<sup>14,15</sup> in which he described a "crankshaft" model involving the unhindered rotation of a chain section of at least four methylene units around two collinear bonds. Recently, it was demonstrated that a "crankshaft" motion is prohibited in a glassy matrix, and instead, it was proposed that the mechanism of the  $\gamma$  relaxation involves a "flip-flop" motion of two *gauche* bonds of opposite sense separated by a *trans* bond.<sup>16</sup>

### PEO

The viscoelastic behavior of PEO is discussed in detail by McCrum et al.<sup>17</sup> High-molecular-weight PEO ( $M_w > 10^5$ ) exhibits three mechanical loss maxima below its melting point: 1) the  $\alpha$  loss between  $-10$  and  $0^\circ\text{C}$  caused by motion in the crystalline polymer, 2) the  $\beta$  loss between  $-60$  and  $-30^\circ\text{C}$  caused by micro-Brownian motion in the amorphous polymer, and 3) the  $\gamma$  loss near  $-130^\circ\text{C}$  which has been attributed to the local twisting of the main chains in the noncrystalline regions.<sup>18</sup> Read<sup>19</sup> has suggested that the  $\beta$  relaxation is the glass transition of PEO and he found it to be strongly dependent upon the polymer crystallinity and molecular weight. As molecular weight decreases from  $M_w \sim 10^7$ , the temperature of the  $\beta$ -loss maximum increases from  $-59^\circ\text{C}$  to a maximum of about  $-24^\circ\text{C}$  for  $M_w \sim 10^4$ . Below  $M_w \sim 10^4$ , the temperature of the  $\beta$ -loss maximum decreases.

Dynamic mechanical data for low-molecular-weight PEO are scarce (PEO exists as a grease or a liquid below  $M_w \sim 10^3$ ), although it has been reported that below  $M_w \sim 10^5$ , PEO exhibits only one loss dispersion.<sup>17</sup> This occurs between  $-30$  and  $-10^\circ\text{C}$  at low frequencies, but it is not clear whether this is related to either the  $\alpha$  or the  $\beta$  loss of high-molecular-weight PEO. Connor et al.<sup>19</sup> suggested that this relaxation may be due to overlapping mechanisms attributable to both the amorphous and the crystalline polymer. Recently, Lang et al.<sup>20</sup> studied the solid-state relaxations of a PEO sample having a molecular weight of  $10^4$  by DSC. They argue for two glass transition temperatures, a  $T_g(L)$  at  $190$ – $200^\circ\text{K}$  and a  $T_g(U)$  above  $233^\circ\text{K}$  which increases upon annealing.

The DSC thermographs of the PEO oligomers used in our investigation are given in Figure 2. Each sample exhibits two transitions below its crystalline melting point: at  $188$  and  $230^\circ\text{K}$  for the lower-molecular-weight oligomer and at  $193$  and  $254^\circ\text{K}$  for the higher-molecular-weight oligomer. These transitions are consistent with the assignments of Lang et al.<sup>20</sup> for  $T_g(L)$  and  $T_g(U)$ . The melting points of the two polymers, defined by the maximum in the DSC endotherm, were  $264$  and  $307^\circ\text{K}$  for molecular weights of  $350$  and  $750$ , respectively. The exotherm observed for the lower-molecular-weight oligomer above  $200^\circ\text{K}$  was reproducible and probably indicates some crystallization taking place above  $T_g(L)$ . This occurs because this sample was "shock cooled" from above its melting point to below  $T_g(L)$ . Above  $T_g(L)$ , some chain motion is allowed and crystallization can take place.

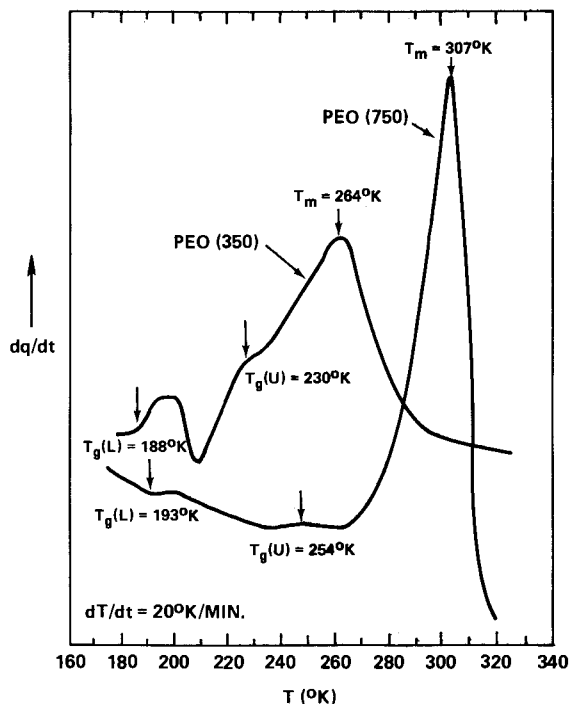


Fig. 2. DSC thermographs of PEO oligomers.

### Phosphonylated PE

The temperature dependence of the dynamic mechanical storage and loss moduli for a frequency of 110 Hz are shown in Figures 1, 3, and 4 for several phosphonate derivatives of phosphonylated LDPE. The temperatures of the loss moduli maxima  $E''_{\max}$ , corresponding to the  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxations of PE are given in Tables I-III for all the polymers studied.

#### Series A—Dimethyl Phosphonates

The behaviors of the dynamic mechanical moduli for the polymers containing dimethyl phosphonate pendent groups were qualitatively similar to that for the unmodified LDPE. At low degrees of substitution (D.S. is defined as the number of phosphonate groups per 100 backbone carbon atoms), the polymers exhibited the three characteristic loss regions described earlier for PE. The temperatures of these relaxations were, however, perturbed from that of the unmodified polymer. Above a degree of substitution of 0.5, the  $\alpha$  relaxation could no longer be distinguished from the large  $\beta$  loss. Two factors contributed to this result. First, the magnitude of  $E''_{\max,\beta}$  increased owing to an increasing number of chain branch points, while at the same time the magnitude of  $E''_{\max,\alpha}$  decreased because of the decrease in the polymer crystallinity. Similarly, the temperature of the  $\beta$  maximum of the loss modulus  $T_\beta$  increased, while  $T_\alpha$  decreased. The net result of these effects is that the  $\alpha$  relaxation at high degrees of substitution probably occurs as a shoulder of the  $\beta$  relaxation and is, therefore, difficult to detect. Although, resolution of multiple relaxations is possible by mathematical techniques, this procedure was not attempted here.

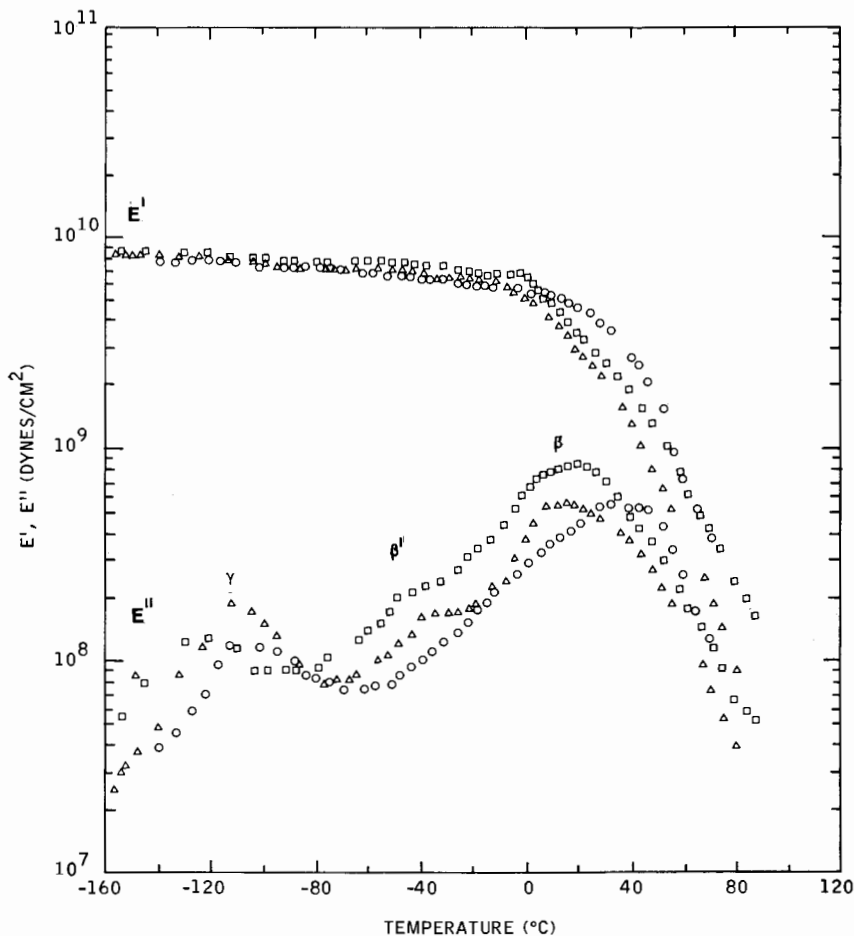


Fig. 3. Temperature dependence of  $E'$  and  $E''$  at 110 Hz for sample A5 (O), sample B5 (□), and sample C5 (Δ).

The dependence on the extent of phosphonation of the temperature of the  $\beta$ -loss maximum is shown in Figure 5. Initially, phosphonation results in a decrease in  $T_\beta$ , however, above D.S. = 0.1,  $T_\beta$  increases with increasing phosphonation. This result is similar to the observations of Schmeider and Wolf<sup>21</sup> for the mechanical  $\beta$  relaxation of chlorinated PE. They found that as the chlorine substitution increases, the  $\beta$ -loss maximum initially decreases in temperature, but above a concentration of 10% chlorine (ca. 4.4 chlorine groups per 100 carbon atoms), the trend reverses and  $T_\beta$  increases with increasing chlorination.

Schmeider and Wolf attributed this behavior to a twofold effect of the chlorine pendent group on the relaxation process. First, there is a steric effect similar to that of chain branching which increases the polymer free volume, and, as a consequence, results in a lowering of  $T_\beta$ . There also exists, however, a dipolar interaction between the C—Cl dipoles which stiffens the branch groups, and, therefore, acts to increase the temperature of the  $\beta$  relaxation. At low levels of chlorine substitution, the steric effect dominates and  $T_\beta$  is lowered; while at higher chlorine concentrations, the dipolar interaction becomes more important and  $T_\beta$  increases.



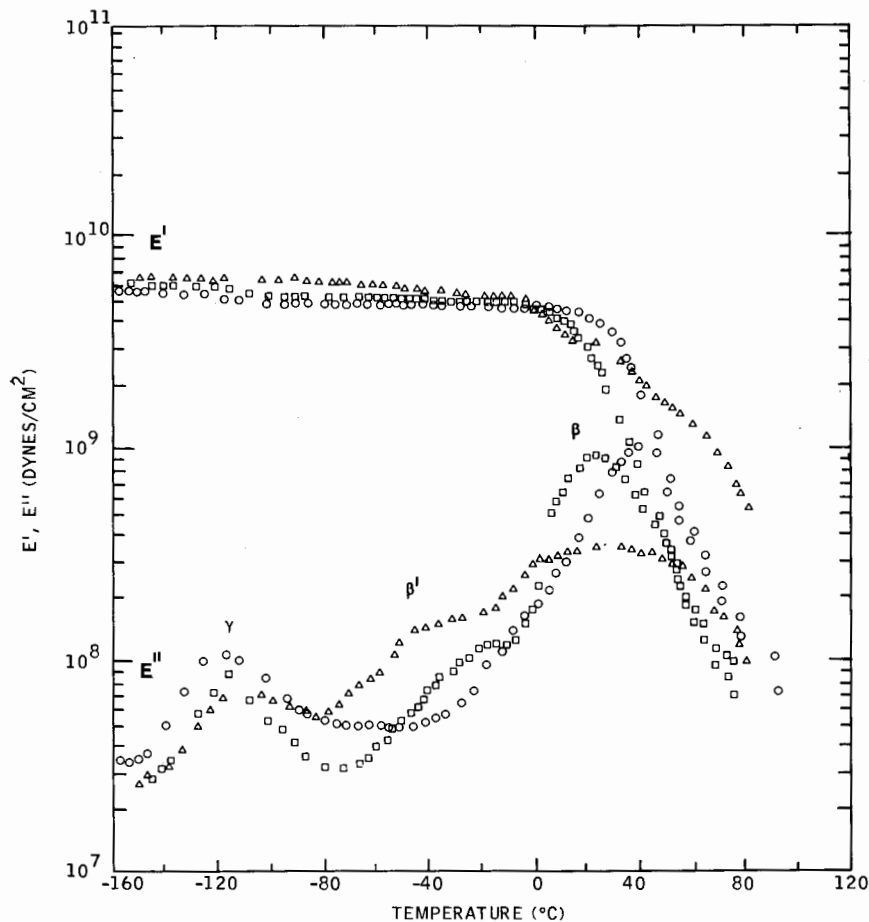


Fig. 4. Temperature dependence of  $E'$  and  $E''$  at 110 Hz for sample A7 (O), sample B7 ( $\square$ ), and sample C7 ( $\Delta$ ).

The identical argument can be advanced to explain the dependence of  $T_\beta$  on phosphonate substitution. At low phosphonate concentrations, the steric influence of the bulky pendent group results in a decrease in  $T_\beta$ , while at higher degrees of substitution the interaction between the C—P(O)(OCH<sub>3</sub>)<sub>2</sub> dipoles becomes the dominant factor and  $T_\beta$  increases.

The effect of phosphonation on the melting temperature of these polymers led to the conclusion that these materials behave as random copolymers,<sup>1</sup> and the influence of dimethyl phosphonate on the temperature of the  $\beta$  relaxation supports this result. For the phosphonic acid derivatives of LDPE, Emerson<sup>22</sup> observed that  $T_\beta$  was independent of pendent group concentration, and a new relaxation was observed near 50°C for polymers with high phosphonic acid contents. He suggested that the phosphonic acid groups segregated into microscopic domains and relaxed independently of the continuous PE phase. Since  $T_\beta$  for the dimethyl phosphonates of PE exhibits a very strong temperature dependence (Fig. 5), it appears that microphase separation does not occur in these systems, or at least it is not obvious from the dynamic mechanical results.

Activation energies were calculated for the  $\beta$ -loss process using Arrhenius plots of log frequency versus the reciprocal of  $T_\beta$  and these values are reported in Table

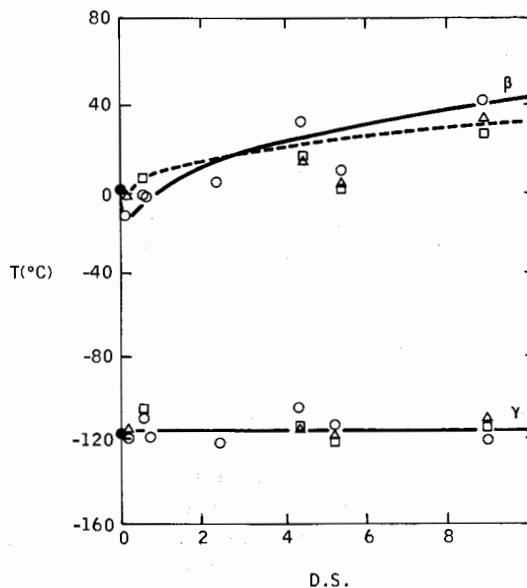


Fig. 5. Effect of phosphonate concentration on  $T_{\beta}$  and  $T_{\gamma}$  for the series A (O), series B ( $\square$ ), and series C ( $\Delta$ ) phosphonates;  $f = 110$  Hz.

I. The activation energy of the unmodified LDPE was calculated to be 70 kcal/mole, which is consistent with the range of values of  $\Delta H_{\beta}$  reported in the literature.<sup>23</sup> Within the error expected from calculating activation energies from only three frequency-temperature measurements, the activation energies of the  $\beta$  relaxation for the dimethyl phosphonates agree with  $\Delta H_{\beta}$  for LDPE.

The temperature of the  $\gamma$ -loss maximum  $T_{\gamma}$  for the dimethyl phosphonate derivatives is also plotted against phosphonate concentration in Figure 5. There is a considerable amount of scatter in these data, which can probably be attributed to difficulties in maintaining equilibrium of the sample at very low temperatures. Temperature was varied in these experiments by first cooling the sample to  $-160^{\circ}\text{C}$  with liquid nitrogen and then allowing the sample to warm up to  $0^{\circ}\text{C}$  by convection. Over most of the temperature range the temperature increased at  $1\text{--}2^{\circ}\text{C}/\text{min}$ , which should have been slow enough to maintain equilibrium conditions. At very low temperatures, however, the heating rate was often times as great as  $5^{\circ}\text{C}/\text{min}$ , which suggests that the actual sample temperature may have been different from that of the temperature measuring thermocouple. Given this fact, the scatter in Figure 5 for  $T_{\gamma}$  is most likely not significant, and we can conclude that phosphonation does not affect the  $\gamma$  relaxation. We should point out, however, that no such difficulties with controlling temperature were experienced in the neighborhood of the  $\beta$  and the  $\alpha$  relaxations and, in fact, the values for  $T_{\beta}$  and  $T_{\alpha}$  given in Tables I-III were reproducible within  $2\text{--}3^{\circ}\text{C}$ .

The activation energies for the  $\gamma$  relaxations of the LDPE and for the phosphonated polymers were calculated by the Arrhenius method and are reported in Table I. Literature values for  $\Delta H_{\gamma}$  for PE range from 11 to 15 kcal/mole<sup>6,23</sup> and the activation energies for the phosphonated polymers ranged between 9 and 29 kcal/mole, with no significant trend in the data. The large scatter of the data was most likely a result of the errors associated with the calculation of the

activation energies from only three frequencies and with the measurement of  $T_\gamma$  as outlined above. The results suggest, however, that the effect of phosphonation on the  $\gamma$  relaxation was not significant.

#### Series B and C—Polymeric Phosphonates

The temperature dependences of the dynamic mechanical moduli for the phosphonates containing PEO ester groups were significantly different from that for the dimethyl phosphonate. The major difference was the appearance of a new dispersion region, which we have designated  $\beta'$ , as a low-temperature shoulder of the  $\beta$ -loss process (cf. Figs. 1, 3, 4). Resolution of the  $\beta'$ -loss maximum was not possible owing to the interaction of this process with the  $\beta$  loss; however, the temperatures over which the  $\beta'$  loss was observed are summarized in Table IV for a frequency of 110 Hz. In general, the  $\beta'$  loss appeared between 210–270°K, a range consistent both with literature references for the mechanical  $\beta$  loss of low-molecular-weight PEO (see the earlier discussion on the dynamic mechanical behavior of PEO) and with the DSC results discussed above for the PEO oligomers used in this investigation. It is also conceivable that the  $\beta'$ -loss dispersion may extend to higher temperatures and include the melting transition of crystalline PEO. This, however, is difficult to ascertain because of the interference of the  $\beta$  relaxation of these polymers at the upper end of the temperature ranges reported in Table IV.

These results suggest that the  $\beta'$ -loss mechanism can be attributed to PEO. The fact that the magnitude of the  $\beta'$  loss was dependent on the concentration of PEO in these polymers (i.e., the degree of substitution) further supports this assignment. The implication here is that the polymeric phosphonates containing PEO exhibit microphase separation—that is, the phosphonate groups form a discrete phase which relaxes independently of the PE backbone. Further evidence for this assignment can be found by comparing the behavior of the  $\beta$  relaxation for these polymers to that of the series A polymers containing dimethyl phosphonate.

In Tables II and III the temperatures of the loss moduli maxima corresponding to the  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxations are given for the phosphonates containing PEO. We showed earlier that the  $\beta$  relaxation was affected by phosphonation in two

TABLE IV  
Temperature Range of the  $\beta'$  Loss for the Series B and C Phosphonates

Sample	D.S. <sup>a</sup>	$T_{E'}$ (°K) <sup>b</sup>
PEO mol wt = 350		
B2	0.35	233–268
B5	4.5	218–263
B6	5.8	211–253
B7	9.1	211–263
PEO mol wt = 750		
C1	0.09	233–269
C5	4.5	217–253
C6	5.8	211–250
C7	9.1	203–255

<sup>a</sup> Degree of substitution = number of phosphonate groups per 100 carbon atoms.

<sup>b</sup> Frequency = 110 Hz.

ways: a steric effect which depresses  $T_{\beta}$  and a dipolar interaction which raises  $T_{\beta}$ . If phase separation of the phosphonate groups occurs, we would expect the two effects to be diluted. At low levels of phosphonation the steric effect should dominate and, as with the dimethyl phosphonates, we would expect  $T_{\beta}$  to decline. Association of the phosphonate groups such as would occur if the PEO formed a discrete phase should, however, reduce the free volume effect, resulting in a smaller decrease of  $T_{\beta}$ . On the other hand, at higher degrees of phosphonate substitution where dipolar interactions are important, phase separation should reduce the influence of the dipoles. Therefore, we would not expect  $T_{\beta}$  to increase to the same extent as it does in the case of the lower-molecular-weight phosphonates. In Figure 5, the dependence of  $T_{\beta}$  on phosphonate substitution is shown for the series A-C polymers, and it can be seen that the effect of the polymeric phosphonate is consistent with the above discussion.

We alluded earlier to the fact that for a degree of substitution of 9.1 phosphonate groups per 100 carbon atoms, the polymeric phosphonates melted about 10°C higher than the dimethyl phosphonate. We believe that this result is a consequence of microphase separation of the PEO groups which reduces steric hindrance and, therefore, allows the PE chains to more efficiently crystallize. In our earlier thermal analyses of these polymers,<sup>1</sup> we did not observe any evidence of PEO domains. In order to further justify our conclusion that microphase separation occurs in these systems, we have again investigated their thermal behavior, with a special emphasis on the region in which we observed the dynamic mechanical  $\beta'$  relaxation (i.e., 210–270°K).

The DSC heating scans for the most highly substituted polymeric phosphonates are given for annealed series B samples in Figure 6 and quenched series C samples in Figure 7. Included for comparison is the scan of the unmodified PE. The behavior of the series A polymers, the dimethyl phosphonates, was similar to that of PE. The polymeric phosphonates exhibit a broad exotherm between 230–280°K, and it is significant that this transition was not observed

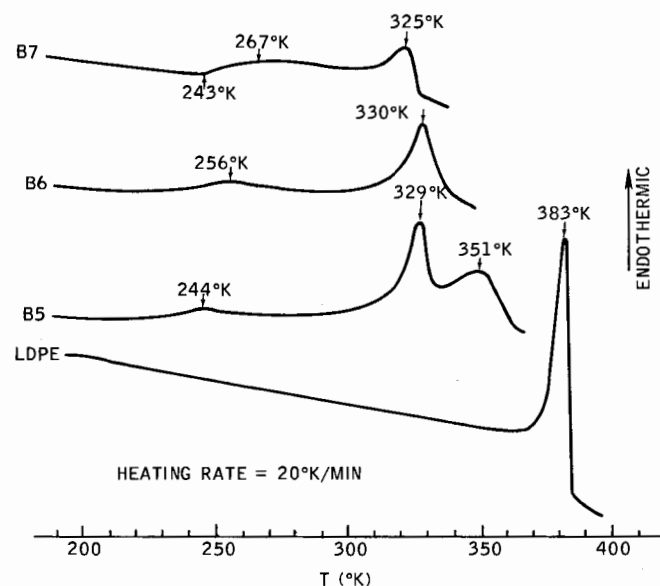


Fig. 6. DSC thermographs of quenched LDPE and series B phosphonates.

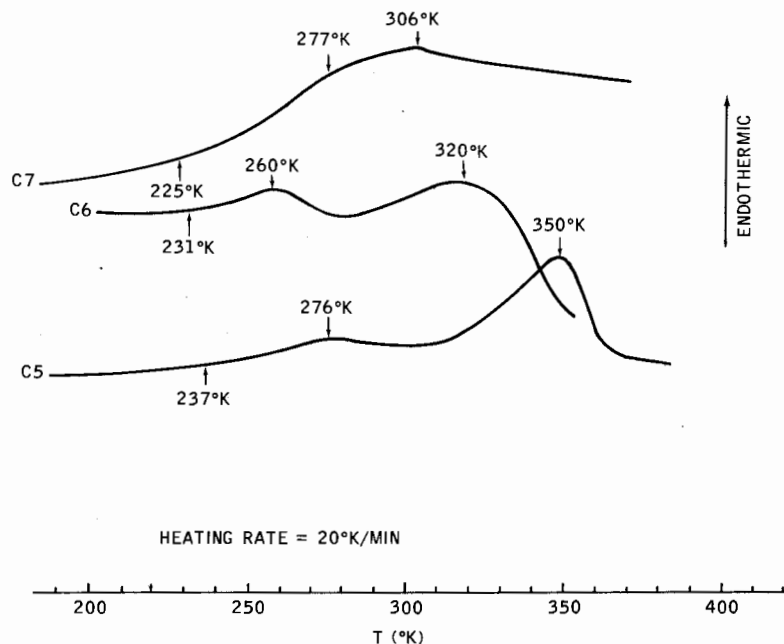


Fig. 7. DSC thermographs of annealed series C phosphonates.

in the scan for PE or in the scans for the series A polymers. The temperature of this transition is consistent with the temperatures observed for the mechanical  $\beta'$ -loss maximum for these polymers, and it is apparent that it results from the presence of PEO. Furthermore, a thermal transition between 230–280°C is consistent with  $T_g(U)$  of the starting PEO oligomers, indicating the presence of PEO as a distinct phase. Another indication that microphase separation occurs in these polymers is the exotherm at 306°K in the thermograph of sample C7 in Figure 7. This transition is consistent with the melting point of the starting PEO oligomer ( $T_m = 307^\circ\text{K}$ ) which suggests that the PEO domains may be crystalline. This endotherm was not apparent in the other samples, but this may be due to the higher PE crystallinity of these materials, which might obscure the PEO melting endotherm.

### CONCLUSIONS

The dynamic mechanical behavior of the dimethyl phosphonate substituted PEs are qualitatively similar to that of LDPE. The major effect of phosphonation is to shift the temperature of the  $\beta$  relaxation. Below a degree of substitution of 0.1 phosphonate groups per 100 carbon atoms,  $T_\beta$  decreases; while at higher levels of phosphonation, it increases. This behavior can be attributed to the competing influences of increasing steric interference, which tends to lower  $T_\beta$ , and increasing dipolar interactions, which stiffen the side groups, and, therefore, act to increase  $T_\beta$ .

A dispersion region due to PEO the  $\beta'$  relaxation, is observed in the dynamic mechanical response of substituted PE containing a polymeric phosphonate, i.e., grafted PEO. The temperature of the  $\beta'$  loss is consistent with references in the literature for the mechanical  $\beta$  relaxation of low-molecular-weight PEO,

243–263°K. Furthermore, a thermal transition is observed between 230–280°K in the DSC thermographs of the polymers containing PEO; this transition is absent for unmodified PE and for the polymers containing the dimethyl phosphonate pendent group. This temperature range is consistent with the DSC value of  $T_g(U)$  of the PEO oligomers used in this investigation.

The dynamic mechanical and the thermal data presented here for the polymeric phosphonates are consistent with the occurrence of microphase separation in these systems. Consequently, these polymers can be thought of as composites containing: 1) a crystalline PE phase, 2) an amorphous phase of PE and, perhaps, some PEO, and 3) a dispersed phase of PEO domains. Furthermore, the thermal data suggest that the PEO domains may be crystalline.

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### References

1. R. A. Weiss, R. W. Lenz, and W. J. MacKnight, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1409 (1977).
2. *Instruction Manual, Rheovibron Model DDV-II*, Toyo Measuring Instruments Co., Ltd., Tokyo, Japan.
3. N. G. McCrum, B. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, Chap. 10.
4. R. C. Rempel, H. E. Weaver, and R. H. Sands, *J. Appl. Phys.*, **28**, 1082 (1957).
5. K. Sinnott, *J. Polym. Sci. C*, **14**, 141 (1966).
6. J. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci. C*, **14**, 173 (1966).
7. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 1 (1963).
8. D. Kline, J. Sauer, and A. Woodward, *J. Polym. Sci.*, **22**, 455 (1956).
9. W. Oakes and D. Robinson, *J. Polym. Sci.*, **14**, 505 (1954).
10. L. Nielsen, *J. Polym. Sci.*, **42**, 357 (1960).
11. S. Matsuoka, *Polym. Eng. Sci.*, **5**, 142 (1956).
12. A. Wilbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).
13. L. Mandelkern and F. C. Stehling, *Macromolecules*, **3**, 242 (1970).
14. T. F. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962).
15. T. F. Schatzki, *Polym. Prepr.*, **6**, 646 (1965).
16. R. H. Boyd and S. M. Breitling, *Macromolecules*, **7**, 855 (1974).
17. N. G. McCrum, B. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, Chap. 14.
18. B. Read, *Polymer*, **3**, 529 (1962).
19. T. Connor, B. Read, and G. Williams, *J. Appl. Chem.*, **14**, 74 (1964).
20. M. C. Lang, C. Noel, and A. P. Legrand, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1319 (1977).
21. K. Schneider and K. Wolf, *Kolloid Z.*, **134**, 149 (1953).
22. F. Emerson, Jr., Ph.D. dissertation, University of Massachusetts, Amherst, 1972.
23. A. E. Woodward and J. A. Sauer, *Adv. Polym. Sci.*, **1**, 115 (1958).

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