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William MacKnight, *University of Massachusetts Amherst*

D. Rahrig

C. Azuma

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Dynamic Mechanical and Dielectric Properties of Phosphonylated Polypentenamers and their Hydrogenated Derivatives

D. RAHRIG, C. AZUMA, and W. J. MACKNIGHT, *Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

Dynamic mechanical and dielectric properties of substituted polypentenamers with phosphonate side groups and their hydrogenated derivatives have been studied. Methyl esters, acids, and salts were investigated at two concentrations, 6.5 and 11.1 mole percent. In the unhydrogenated derivatives, one principal relaxation, labeled β , is observed mechanically in the temperature range from -160 to 100°C . This β relaxation arises from micro-Brownian segmental motion accompanying the glass transition. Its temperature is substantially affected by the substituent concentration while its breadth is affected by the chemical nature of the substituent. An extended "rubbery plateau" region exists in the acid and salt derivatives. The dielectric results generally reinforce the mechanical assignments. In the hydrogenated derivatives, three relaxations labeled α , β , and γ in order of decreasing temperature occur mechanically in this temperature range. The temperatures at which the α and β relaxations occur depend greatly on the chemical nature of the substituents, the substituent concentration, and the thermal history of the sample; while the γ relaxation appears to be independent of these variables. Suggested assignments for the relaxations observed in these polymers, based on the dual glass transition theory of Boyer for semicrystalline polymers, have been proposed. The dielectric results are consistent with the proposed assignments.

INTRODUCTION

We have previously reported the phosphonylation of polypentenamer under reaction conditions which preclude modification of the chain backbone by scission or crosslinking.¹ The phosphonate groups can be obtained as esters, acids, or salts; while the residual double bonds in the polypentenamer can be hydrogenated to yield a crystallizable backbone. In this study we have employed dynamic mechanical and dielectric relaxation techniques to investigate two series of phosphonylated polypentenamers, one bearing a 6.5 mole percent concentration of pendant groups designated PP-PO(5); and the other bearing an 11.1 mole percent concentration, labeled PP-PO(10). Within each series the properties of the methyl ester, acid, and cesium salt are investigated for both the unsaturated polypentenamer and its fully hydrogenated derivative. In this manner the effects of the nature and concentration of pendant ionic groups can be examined for polymers having the identical chain backbone, and the contribution of backbone crystallinity to the relaxation behavior of these polymers can be studied.

The desired comparisons of this study are obscured somewhat by four factors. The first of these is the fact that quantitative conversion of the ester groups to the desired acid, and of the acid groups to salt was not possible. Second, owing

to the large content of *trans* double bonds in the starting polypentenamer, a low level of crystallinity is present even in the unhydrogenated materials. Third, in order to prepare films of the unsaturated materials suitable for dynamic mechanical testing, it was necessary to add a small amount of dicumyl peroxide as a crosslinking agent. A fourth factor is that the crystallizability of the hydrogenated backbone is greatly affected by the nature of the pendant groups, which results in less clear-cut distinctions between substrate and crystallinity effects with regard to relaxation behavior.

The dynamic mechanical results of this study are consistent with previous findings²⁻⁵ while also offering evidence of differences. For the unsaturated materials the concentration of the pendant groups considerably alters the temperature of the glass-rubber relaxation while the nature of the substituent influences the broadness of the relaxation. The extended pseudoplateau region which was observed with the acid and salt derivatives of the unsaturated thio-glycolate substituted polypentenamers² is also found in these samples, but the enhanced magnitude of the rubbery modulus of the salts is not observed. The saturated materials demonstrate the large impact of crystallinity on mechanical properties while displaying noticeable effects owing both to the nature of the pendant groups and thermal history on the relaxation behavior. The dielectric relaxation results are compatible with the dynamic mechanical findings for both the unsaturated and fully hydrogenated systems and aid greatly in the interpretation of the observed relaxations. The evidence from this study is not sufficient to support the proposed model suggesting microphase separation of the ionic groups into domains at the substituent concentration levels studied.^{2,4,6} However, there is sufficient evidence to verify the existence of some type of structures which act as temporary crosslinks for the acids and salts. Whether these structures take the form of aggregates or phase-separated domains is not clear.

EXPERIMENTAL

Materials

The starting polypentenamer (PP) was kindly provided by the Goodyear Tire and Rubber Company. It contains 82% *trans* and 17% *cis* double bonds with fewer than 1% vinyl side groups. The molecular weight averages are $\bar{M}_n = 94,000$ and $\bar{M}_w = 172,000$. Dimethyl phosphite (DMP) was added to the double bonds by a dibenzoyl peroxide (BPO) initiated free radical addition reaction described previously in detail.¹ Hydrogenation was achieved with *p*-toluenesulfonyl hydrazide (TSH).⁷ The methyl ester was converted to acid by treating with gaseous hydrogen chloride in various solvents. The cesium salts were obtained from the acid through reaction with a cesium hydroxide-methanol solution. These reactions are summarized as follows:

Characterization data for the samples investigated are in Table I. Molecular weight studies carried out by gel permeation chromatography (GPC) demonstrated no evidence for crosslinking or backbone degradation.

The hydrogenated samples were compression-molded into films suitable for measurement. For dynamic mechanical testing the films were prepared by preheating at 140–150°C for 5 min and then pressing at 140–150°C and 15,000 lbs for 7 min under nitrogen. The annealed samples were placed in a vacuum

TABLE I
Characterization Data for Substituted Polypentenamers

Sample	Combined DMP (mole %) ^a	Ionization (%) ^b	T _g ^{c,d} (°C)	T _m ^{c,d} (°C)
PP	0		-98	11
PP-PO(5)	6.5		-74	
PP-POH(5)	6.5		-72	
PP-POCs(5)	6.5	95	-70	
PP-PO(10)	11.1		-55	
PP-POH(10)	11.1		-54	
PP-POCs(10)	11.1	100	-53	
Hy-PP	0			131
HyPP-PO(5)	6.5			107
HyPP-POH(5)	6.5			108
HyPP-POCs(5)	6.5	95		103
HyPP-PO(10)	11.1			93
HyPP-POH(10)	11.1			94
HyPP-POCs(10)	11.1	90		95

^a Calculated from infrared (IR) analysis and carbon analysis.

^b Percent ionization to pendant content calculated from titration.

^c Determined by DSC.

^d All temperatures have error bounds of ±2°C.

oven at 80°C for three days, while the quenched samples were placed immediately in a dry ice-isopropanol bath. These samples were then stored under vacuum at room temperature until studied. The films for dielectric testing were prepared in identical manner, except they were preheated for 15 min and pressed for only 5 min. The unsaturated samples for use in dynamic mechanical testing were prepared by dissolving the polymer sample in tetrahydrofuran (THF) along with 0.05 wt % antioxidant (Santo White) and 0.5 wt % dicumyl peroxide, which acts as a crosslinking agent. This THF solution was then placed into a 2×3.5 cm² rectangular box fashioned from Teflon coated aluminum foil and the THF was removed under vacuum at room temperature. The residue was washed with water and acetone and then compression molded into a film by heating at 135°C for 1 hr at 3000 lbs. The film was then dried under vacuum for 12 hr. For dielectric study the unsaturated polymers were prepared as films by dissolving in THF containing 0.05 wt % of antioxidant relative to polymer and pouring this solution onto an aluminum plate within a vessel prepared from Teflon coated aluminum foil. The THF was evaporated at room temperature by putting the sample under a vacuum of 20 mm for 1–2 hr, followed by reduction of the pressure to 5–6 mm for 3–4 hr and finally further reduction to 0.1 mm for 4–5 hr. The residue was washed with water and acetone and then dried under vacuum for 12 hr. These aluminum supported films were then used for dielectric measurements.

Measurements

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer instrument, model DSC II. The scanning speed was 10°C/min in all cases, and cyclohexane and indium were used as standards. The temperature range scanned was –120 to 150°C. The peak temperature of the melting endotherm was taken to be the melting point of the polymers.

Dynamic mechanical measurements were carried out on a Vibron dynamic viscoelastometer, model DDV—II (Toyo Measuring Instruments Co.). The temperature range was from –160 to 100°C and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at 1–2°C/min under dry nitrogen.

Dielectric measurements were carried out using a General Radio capacitance measuring assembly of the transformer-ratio-arm bridge type (model 1620 A), in conjunction with a three-terminal cell (Balsbaugh type LD-3) having 53 mm diam electrodes. Capacitance and $\tan \delta$ measurements were carried out at 0.2, 0.5, 1, 2, and 10 kHz over the temperature range –160 to 100°C. Temperature variation was achieved by regulating the flow of dry nitrogen, chilled or heated as appropriate, through the cell. For temperatures above 30–40°C heating was accomplished by putting the cell inside two heating mantles. The temperature was increased at 1–2°C/min.

RESULTS

The dynamic mechanical analysis of the PP-PO derivatives reveals three relaxations. The largest of these is believed to result from the micro-Brownian segmental motion accompanying the glass transition and is labeled β . A sub- T_g relaxation, labeled γ , is observed for all of the derivatives while a higher-tem-

Fig. 1. Temperature dependence of E' and E'' at 110 Hz for (a) PP-PO(5), (b) PP-POH(5), and (c) PP-POCs(5).

perature relaxation, associated with melting, is discernible in a few of the derivatives. Figures 1(a)–1(c) show the temperature dependencies of E' and E'' for PP-PO(5), PP-POH(5), and PP-POCs(5) at 110 Hz with the three relaxation regions pointed out. Of particular note is the extended plateau region in both PP-POH(5) and PP-POCs(5). For the PP-PO(5) sample, E' continued to drop and could not be measured beyond the point displayed in Figure 1(a). This point was not reached with the PP-POH(5) sample until a temperature of 78°C, while for PP-POCs(5), no evidence for a drop in E' occurred experimentally; unfortunately this experiment was terminated prematurely at 50°C. In Figures 2(a)–2(c) the temperature dependencies of E' and E'' at 110 Hz for PP-PO(10), PP-POH(10), and PP-POCs(10) are shown. Here the high-temperature relaxation is no longer detectable, but the acid and salt again display the extended plateau. As was the case with PP-PO(5), the value of E' continued to drop for PP-PO(10), and could not be measured experimentally beyond 16°C. In Figure 3, the E' and E'' values versus temperature for a 2.5 mole percent concentration of the methyl ester of the phosphonylated polypentenamer, PP-PO(2.5), are

Fig. 2. Temperature dependence of E' and E'' at 110 Hz for (a) PP-PO(10), (b) PP-POH(10), and (c) PP-POCs(10).

shown. This figure displays the high-temperature relaxation and shows no indication of a rubbery plateau region. A summary of the dynamic mechanical relaxation data for the PP-PO derivatives is compiled in Table II. It is clear from these results that the γ transition is not affected by either the nature of the pendant groups or their concentration. For the T_g measured by DSC given in Table I and the β relaxation observed mechanically, it is seen that the concentration of pendant groups dramatically affects the temperature at which the glass-rubber relaxation process occurs. In addition, while the nature of the pendant group has little effect on T_g at lower pendant group concentrations, the broadening of the mechanical β relaxation and its occurrence at higher temperatures for the 10% acid and salt series indicates that at higher phosphonate concentrations, polar group interactions may be altering the glass-rubber relaxation mechanism.

Table III lists the weight percent crystallinities determined for the hydrogenated samples used in this study. These represent the ratio of $\Delta H_f/\Delta H_u$ where ΔH_f is the experimental enthalpy of fusion and ΔH_u is the enthalpy of fusion

Fig. 3. Temperature dependence of E' and E'' at 110 Hz for PP-PO(2.5).TABLE II
Temperatures^a of Transitions and Relaxations in Substituted PP's (°C at 110 Hz)

Sample	$\gamma(E'')$	$\beta(E'')$	Melting ^b	$\gamma(\tan \delta)$	$\beta(\tan \delta)$
PP	—	-85	10	—	-70
PP-PO(2.5)	-121	-80	-5	-117	-62
PP-PO(5)	-124	-46	-5	-123	-26
PP-PO(10)	-125	-20	—	-122	-2
PP-POH(5)	-120	-47	-5	-120	-20
PP-POH(10)	-120	-10	—	-120	16
PP-POCs(5)	-120	-52	-5	-120	-15
PP-POCs(10)	-123	-10	—	-125	20

^a All temperatures have error bounds of $\pm 3^\circ\text{C}$.^b Taken as the midpoint in the E' transition.TABLE III
Weight Percent Crystallinity of Hydrogenated Phosphonylated Polypentenamer Films for Rheovibron and Dielectric Study

Sample	Weight % crystallinity mechanical	Weight % crystallinity dielectric
HyPP-PO(5)A	42	52
HyPP-POH(5)A	37	45
HyPP-POCs(5)A	33	33
HyPP-PO(5)Q	36	52
HyPP-POH(5)Q	30	41
HyPP-POCs(5)Q	27	27
HyPP-PO(10)A	32	31
HyPP-POH(10)A	20	24
HyPP-POCs(10)A	16	14
HyPP-PO(10)Q	19	28
HyPP-POH(10)Q	14	20
HyPP-POCs(10)Q	12	12

of the hypothetical 100% crystalline polymer. Owing to the bulkiness of the phosphonate group it is reasonable to assume that these groups are completely excluded from the crystalline phase. As a result, the value of ΔH_u determined by the polymer-diluent technique for fully hydrogenated polypentenamer, evaluated as 59 cal/g,⁷ was used. While this value is appropriate for an unsubstituted, fully hydrogenated polypentenamer crystal of infinite thickness, it might

Fig. 4. Temperature dependence of E' and E'' at 11 Hz for (a) (x) HyPP-PO(5)A and (o) HyPP-PO(5)Q and (b) (x) HyPP-PO(10)A and (o) HyPP-PO(10)Q.

be reduced if the crystals are small. In addition, while the phosphonate groups may be excluded from the crystal lattice, their presence at the crystalline surface may distort the crystal lattice and thereby reduce ΔH_u further. These two factors may contribute to the low degrees of crystallinity determined for these samples.

The dynamic mechanical results for the HyPP-PO derivatives reveal the complex and important role that crystallinity plays in determining the mechanical properties of these polymers. Figure 4(a) displays the temperature dependence of the tensile loss modulus (E'') and tensile storage modulus (E') at 11 Hz for the quenched and annealed HyPP-PO(5) series samples, while Figure 4(b) displays the same information for the HyPP-PO(10) samples. Each of the samples displays three relaxation regions in its mechanical loss spectra. The relaxations are labeled α , β , and γ in order of decreasing temperature. It is significant that the temperature of the α relaxation increases about 5 $^{\circ}\text{C}$ in going from the 5% series to the 10% series, even though the crystalline content decreases; Table I shows a 14 $^{\circ}\text{C}$ decrease in T_m . The magnitude of the α relaxation is by far the largest as is apparent from the behavior of E' in this region. For the 5% series the β relaxation shows little effect owing to the additional crystallinity caused by annealing; however, for the 10% series, where the weight percent crystallinity difference between the annealed and quenched samples is seen from Table III to be quite large, the magnitude of this β relaxation increases significantly as the degree of crystallinity decreases. This would seem to indicate that

the β relaxation originates in the amorphous phase. The γ relaxation cannot be specifically assigned to either phase, though it does appear somewhat smaller for the 5% quenched case than for the 5% annealed sample. The position of this γ relaxation is independent of both pendant group concentration and crystallinity.

Table III shows that the difference in the weight percent crystallinity between the quenched and annealed HyPP-POH polymers is quite small. Nevertheless, the dynamic mechanical properties of these polymers show a dramatic dependence on thermal history, especially with regard to the positions of the relaxations. Figures 5(a) and 5(b) show the temperature dependences of E' and E'' for the four phosphonic acid samples. Each sample shows a high-temperature α and a low-temperature γ relaxation, but the behavior of this polymer series in the mid-temperature range is quite unusual. The magnitude of the high-temperature α relaxation appears to depend on the crystalline content in the 5% series, but this dependence is not as obvious for the 10% series. The α relaxation temperature, however, depends significantly on thermal history and pendant group concentration, as demonstrated by the fact that the α -transition temperature for the 10% annealed sample is about 20°C higher than that of any of the other HyPP-POH samples. The position of the β -transition peak varies greatly among these four polymers; occurring at ca. +5°C for the 5% annealed sample; -70°C for the 5% quenched case; at -30°C for the 10% annealed sample; and around +10°C for the 10% quenched species. The γ relaxation for all four

Fig. 5. Temperature dependence of E' and E'' at 11 Hz for (a) (x) HyPP-POH(5)A and (o) HyPP-POH(5)Q and (b) (x) HyPP-POH(10)A and (o) HyPP-POH(10)Q.

Fig. 6. Temperature dependence of E' and E'' at 11 Hz for (a) (x) HyPP-POCs(5)A and (o) HyPP-POCs(5)Q and (b) (x) HyPP-POCs(10)A and (o) HyPP-POCs(10)Q.

cases occurs around -120°C and shows little dependence on either pendant group concentration or crystallinity. The catastrophic decrease in the tensile storage modulus occurs in conjunction with the α relaxation, as was the case with the esters. Of particular note in the E' behavior of these polymers is the precipitous E' decrease for the 10% annealed sample, and the gradual but steady drop occurring in E' for the 5% quenched sample above the β -relaxation temperature.

The mechanical spectra for the phosphonate cesium salts demonstrate a much greater uniformity than is observed for the acids. In Figures 6(a) and 6(b) it is seen that all four of the salt samples display an α , β , and γ relaxation in order of decreasing temperature, while the 10% annealed cesium salt also displays a shoulder on the α relaxation at 70°C labeled α' . The temperature of the α relaxation increases slightly between the 5 and 10% series. Both the magnitude and position of the broad β -relaxation peak appear to be relatively independent of pendant cesium salt group concentration and crystallinity, while the γ relaxation also appears to be independent of these two variables. The E' versus temperature curves for these samples show the major decrease in storage modulus again occurring in conjunction with the α relaxation, except for HyPP-POCs(10)A, where the major decrease in E' starts with the α relaxation, falls moderately up to the temperature of the α' peak, and then falls off more rapidly.

A summary of the dynamic mechanical relaxation behavior for all of the HyPP-PO derivatives at 110 Hz is given in Table IV. The results demonstrate

TABLE IV
Temperatures^a of Mechanical Transitions and Relaxations in Hydrogenated Phosphonylated PP's (°C at 110 Hz)

Sample	$\gamma(E'')$	$\beta(E'')$	$\alpha(E'')$	$\alpha'(E'')$	$\gamma(\tan \delta)$	$\beta(\tan \delta)$	$\alpha(\tan \delta)$
HyPP	-115	-3	80	-	-112	10	100
HyPP-PO(5)A	-120	-50	42	-	-123	-60	60
HyPP-PO(5)Q	-120	-40	40	-	-122	-30	55
HyPP-PO(10)A	-120	-45	45	-	-122	-40	60
HyPP-PO(10)Q	-120	-45	42	-	-120	-35	60
HyPP-POH(5)A	-120	+15	50	-	-122	+25	76
HyPP-POH(5)Q	-118	-65	50	-	-110	-55	72
HyPP-POH(10)A	-120	-25	73	-	-120	-20	80
HyPP-POH(10)Q	-118	+20	61	-	-117	+30	75
HyPP-POCs(5)A	-118	-40	50	-	-115	-20	70
HyPP-POCs(5)Q	-118	-35	45	-	-120	-25	55
HyPP-POCs(10)A	-120	-25	52	72	-117	-18	70
HyPP-POCs(10)Q	-116	-25	50	-	-115	-17	70

^a All temperatures have error bounds of $\pm 3^\circ\text{C}$.

the large effect that hydrogenation of the polypentenamer backbone has on the mechanical properties of these materials. The ability of the hydrogenated backbone to crystallize and the complex interrelationship of crystallinity with pendant group nature and concentration are the dominant factors controlling the mechanical properties of these materials. Unlike the unhydrogenated materials, where the nature of the pendant group was of secondary importance relative to the pendant group concentration, the fully hydrogenated polymers show a major dependence on both the nature and concentration of the pendant groups, as well as a strong dependence on thermal history in some cases.

The dielectric results for the unhydrogenated polymers must be interpreted with caution because of the manner in which the films were prepared. Because of the rubbery nature of these materials, films of reasonably uniform thickness could only be obtained by solvent casting from THF. Despite the care taken in washing and drying these films, some of the results may be influenced by impurities which could be easily retained in the polymer films. The results are shown in Figure 7. Figure 7(a) displays plots of $\tan \delta_\epsilon$ versus temperature for the three PP-PO methyl esters. Two dielectric relaxations are displayed in these samples, both of which may be correlated with the mechanical results. The high-temperature relaxation, labeled β , increases in temperature as the phosphonate concentration increases. Such behavior was also displayed by the mechanical β transition, suggesting that these two observed relaxations may be of common origin.

The phosphonic acid substituted polypentenamers show the dielectric behavior displayed in Figure 7(b). The position of the high-temperature β relaxation and its dependence on pendant group concentration suggest that it is related to the mechanical β relaxation, as was suggested in the case of the esters above. The dielectric γ relaxation is very small.

The PP-POCs samples give the dielectric results shown in Figure 7(c). The huge increases in $\tan \delta_\epsilon$ displayed in these plots could result from a number of sources, including impurities in the THF used in solvent-casting these films and retained in these materials by the salt groups. Ionic conductivity measurements were not made on these samples; this too remains a possible explanation of the observed results.

Fig. 7. Temperature dependence of $\tan \delta_\epsilon$ at 0.2 kHz for (a) ($\square$) PP-PO(2.5), ($\circ$) PP-PO(5), and ($\times$) PP-PO(10); (b) ($\circ$) PP-POH(5) and ($\times$) PP-POH(10); and (c) ($\circ$) PP-POCs(5) and ($\times$) PP-POCs(10).

The dielectric results for the hydrogenated materials give an added perspective to the understanding of processes taking place in these samples. Figure 8 displays the temperature dependence of ϵ'' for each of the four HyPP-PO samples. These polymers display two well-resolved dielectric relaxations. The high-temperature relaxation, labeled α , increases slightly in temperature in going from the 5 to the 10% series, while its magnitude more than doubles. The fact that these phosphonate esters display a dielectrically active α relaxation is of interest, since the mechanical α relaxation is thought to originate in the crystalline phase. It is extremely unlikely that the phosphonate groups are incorporated into the crystal lattice, so the nature of both the dielectric and mechanical α relaxations could well be more complex than the mechanical spectra alone would seem to indicate. The low-temperature relaxation, which we will call γ , is very broad and spans the temperature range covered by both the β and γ relaxations observed mechanically. It is possible that this dielectric γ transition results from an overlap of the processes which lead to the mechanical β and γ relaxations. It is worthwhile to note that the dielectric γ transition also broadens further between the 5 and 10% series. Very little variation is evident in these samples between the quenched and annealed cases. Table III, however, illustrates the

Fig. 8. Temperature dependence of ϵ'' at 0.2 kHz for (×) HyPP-PO(5)A; (●) HyPP-PO(5)Q; (■) HyPP-PO(10)A, and (○) HyPP-PO(10)Q.

Fig. 9. Temperature dependence of ϵ'' at 0.2 kHz for (×) HyPP-POH(5)A; (●) HyPP-POH(5)Q; (■) HyPP-POH(10)A, and (○) HyPP-POH(10)Q.

fact that there is only a very slight change in the crystallinity of these dielectric samples between the quenched and annealed samples.

Fig. 10. Temperature dependence of ϵ'' at 0.2 kHz for (×) HyPP-POCs(5)A; (●) HyPP-POCs(5)Q; (■) HyPP-POCs(10)A, and (○) HyPP-POCs(10)Q.

Figure 9 demonstrates that for the HyPP-POH polymers, thermal history significantly affects the dielectric behavior of the 10% series while having little impact on the dielectric behavior of the 5% series. Two relaxations are observed in these polymers, a high-temperature α relaxation and a low-temperature γ relaxation. The position of the α relaxation shifts greatly upon annealing when the pendant phosphonic acid group concentration is around 10%, but it appears independent of annealing for the 5% series. The temperature of the γ relaxation is independent of both concentration and crystallinity. The magnitude of this relaxation is very small for all cases. The differences in the dielectric results for the acids relative to the esters seem to demonstrate that the hydrogen bonding which can occur in the former plays a major role in the properties of these materials.

The dielectric relaxation behavior of the cesium salts is summarized in Figure 10. In these HyPP-POCs samples three dielectrically active relaxations are evident. The temperature of the α relaxation increases both with increasing phosphonate concentration and with annealing. The β and γ relaxations are both quite broad and their positions show little change between the 5 and 10% series or between quenched and annealed samples. The affect of thermal history on the α and β relaxation magnitudes is unusual, in that it varies between the 5 and the 10% series. The magnitude of the γ relaxation, on the other hand, appears to be totally independent of thermal history. It appears that the dielectric results successfully illustrate significant differences in the behavior of these cesium salt materials relative to the methyl esters resulting from the ionic interactions among pendant groups.

A summary of all of the dielectric results is presented in Table V. These tabulated data demonstrate that among the hydrogenated samples, only the cesium salts possess a dielectrically distinct β relaxation. The absence of a dielectric α relaxation in the PP-PO derivatives is in keeping with what one would

TABLE V
Temperatures^a of Dielectric Transitions and Relaxations in Substituted PP's (°C at 0.2 KHz)

Sample	γ (°C)	β (°C)	α (°C)
PP-PO(2.5)	-	-59	-
PP-PO(5)	-85	-27	-
PP-PO(10)	-76	20	-
PP-POH(5)	-100	-5	-
PP-POH(10)	-97	26	-
PP-POCs(5)	-	-	-
PP-POCs(10)	-	-	-
HyPP-PO(5)A	-98	-	48
HyPP-PO(5)Q	-95	-	47
HyPP-PO(10)A	-80	-	55
HyPP-PO(10)Q	-70	-	55
HyPP-POH(5)A	-105	-	76
HyPP-POH(5)Q	-102	-	75
HyPP-POH(10)A	-100	-	>100
HyPP-POH(10)Q	-98	-	80
HyPP-POCs(5)A	-100	5	72
HyPP-POCs(5)Q	-97	15	60
HyPP-POCs(10)A	-85	10	>100
HyPP-POCs(10)Q	-85	25	85

^a All temperatures have error bounds of $\pm 3^\circ\text{C}$.

expect from the mechanical results. The fact that all of the hydrogenated samples display a dielectric α relaxation while the unsaturated samples do not would seem to indicate that while the dielectric α relaxation is probably not caused by phosphonate groups in the crystal lattice, it is definitely related to the existence of the crystalline phase.

DISCUSSION

Unsaturated Phosphonylated Polypentenamers

The study of the unsaturated phosphonylated polypentenamers has led to several significant results concerning the effects of the nature and concentration of pendant groups on the properties of such materials. The large increase in the temperature of the β relaxation with increasing phosphonate concentration regardless of the nature of the pendant group has major significance. In view of the fact that the methyl esters are free of hydrogen bonding or ionic effects, this demonstrates that the copolymer effect is the dominant factor affecting the β -relaxation temperature for all three types of phosphonate groups. Table II shows that the temperature of the β relaxation determined by E'' increases 65 degrees between the starting polypentamer and sample PP-PO(10), which contains just over two phosphonate groups per 100 backbone carbon atoms. For the PP-POH(10) and the PP-POCs(10) samples, the β relaxation determined by E'' is increased 75 degrees over that of the starting polypentamer, which is only 10 degrees greater than that determined for the corresponding methyl ester. It seems evident from these results that while hydrogen bonding on the part of the acids and ionic interactions on the part of the cesium salts play a significant role in the properties of these materials, the copolymer effect is the most crucial factor affecting the temperature of the β relaxation, which, as will be pointed out later in this discussion, is the glass transition in these materials.

Figures 1 and 2 illustrate the broadening that occurs in the E'' curves in the region of the β relaxation in going from ester to acid to salt. This broadening is much more prominent in the 10 than in the 5% series. It has been observed that increasing degrees of crosslinking result in broadened mechanical loss peaks,⁸ but the formation of phase-separated domains would also increase the breadth of the relaxation process.⁹⁻¹¹ In addition to the increased breadth of the β relaxation, the extended "rubbery plateau" regions in both the acid and salt derivatives indicate that these materials act like crosslinked rubbers, at least at short times. It must be recalled that a very small amount of dicumyl peroxide was added as a crosslinking agent to these samples in the preparation of the films used for mechanical testing. This was necessary to prepare stable films. However, while a crosslinking agent was added in the same concentration to all of the samples studied, only the acids and salts show the extended rubbery plateau. This, along with the broadening observed in the β relaxation, suggests that hydrogen bonds in the case of the acids and ionic interactions in the case of the cesium salts act as temporary crosslinks preventing flow of polymer chains past one another. From elementary rubber elasticity theory the equation for the equilibrium modulus is

$$E = 3\rho RT/M_c \quad (5)$$

where M_c is the molecular weight of a network chain, ρ is the polymer density,

TABLE VI
Experimentally Observed and Calculated Plateau Moduli for PP-POH and PP-POCs at 325°K

Sample	E' (expt) (dyn/cm ²)	E (calc) (dyn/cm ²)
PP-POH(5)	2.8×10^7	7.8×10^7
PP-POH(10)	4.4×10^7	1.3×10^8
PP-POCs(5)	4.4×10^7	7.8×10^7
PP-POCs(10)	7.9×10^7	1.3×10^8

and E is the plateau modulus. This relation may be used to gain some insight into the effectiveness of hydrogen bonding and ionic crosslinks. The applicability of this equation to the systems being studied is rendered only semiquantitative at best because the experimentally determined plateau moduli are not the equilibrium moduli, not all of the pendant groups have been converted to the respective acid or salt, and factors such as chain entanglements, network imperfections, and the dicumyl peroxide induced crosslinks cannot be taken into account. Nevertheless, this equation provides a point of departure for a relative comparison of the effectiveness of the various substituents in forming crosslinks. A summary of the observed and calculated plateau moduli is given in Table VI. In every case the calculated modulus is greater than that observed experimentally. Since a proper consideration of most of the limitations cited above would only further increase the calculated modulus, it becomes evident that even though salt linkages do appear to be somewhat more effective than those of the acid groups, neither of these substrates forms highly effective crosslinks. In addition, the reinforcing effect commonly observed in ionomers and interpreted as resulting from the microphase separation of ionic clusters^{2,6} is not demonstrated in this system. These results certainly do not preclude the existence of phase-separated domains in these materials, but they cannot be used to demonstrate their existence. The fact that the esters show flow behavior while the acids and salts behave like crosslinked rubbers, however, demonstrates that either crosslinks or clusters owing to hydrogen bonding in the case of the acids or ionic interactions in the case of the salts play a significant role in the properties of these materials.

All of the unhydrogenated, phosphonylated polypentenamer samples studied display a well-defined mechanical γ relaxation. It has long been known that three or more CH_2 units in sequence are necessary for the appearance of a γ relaxation,¹² and it has been proposed in previous studies that the local motions of the three methylene groups between the double bonds account for the γ process observed in the unsubstituted polypentenamers.^{3,13} It seems likely that this same mechanism explains the mechanical γ relaxation observed in the phosphonylated series. The position of this relaxation remains unaffected by either the nature or concentration of the pendant groups, while its magnitude is similarly independent of these variables. In addition, both thioglycolate and cyano-substituted polypentenamers exhibit identical behavior in this region,^{2,14} which further reinforces the proposal that the mechanism of the γ relaxation involves segments of the polymer apart from the pendant groups.

The behavior of the dielectric γ relaxation differs from that of the mechanical γ relaxation in that the concentration and nature of the pendant groups play a major role. Only the methyl esters display a dielectric γ relaxation of significant

magnitude. This could well be because hydrogen bonding in the acids and ionic interactions in the salts, severely alter the effective dipole moments of these pendant groups or seriously restrict their low-temperature mobility. The mechanism of the mechanical γ relaxation, on the other hand, probably involves short range reorientations of backbone methylene groups as well as motions including phosphonate side groups.

Dynamic mechanical and DSC results combine to demonstrate that the mechanical β relaxation is due to the micro-Brownian segmental motion accompanying the glass transition. The catastrophic decrease in the tensile storage modulus at the β relaxation is the primary evidence that this relaxation does correspond to the glass transition, but trends in the T_g determined by DSC and the dynamic mechanical β relaxation with phosphonate concentration reinforce this assignment. The dielectric β relaxations of the esters and acids correlate closely with these mechanical β relaxations, suggesting that they are the dielectric analog to the glass transition. The unusual dielectric results for the PP-POCs samples preclude any discussion of a dielectric β relaxation in these materials.

The mechanical α relaxation shown in the 5% materials is believed to be due to the melting of the low level of *trans* double-bond-containing crystals. Table II shows that for pure polypentenamer these crystals melt around 10°C. However, the incorporation of phosphonate groups in the polymer backbone decreases the crystallinity, resulting in a melting point depression to ca. -5°C. Perhaps the best evidence to support this assignment of the α transition comes from Figure 3, which shows E' and E'' versus temperature for PP-PO(2.5). It is evident that E' decreases between -90 and -55°C, increases between -55 and -40°C, and then decreases above -40°C. Since this material was stored at room temperature and quickly cooled at the start of the dynamic mechanical study, it is possible that *trans* double-bond-containing crystals formed during the rapid cooling. Then, during the dynamic mechanical study, once the experimental temperature was above the glass transition temperature, but still below the maximum melting temperature of *trans* double-bond-containing crystals, more crystallization could occur, existing crystals could grow, or small crystallites could melt and subsequently recrystallize into larger crystallites. Any or all of these factors could account for the decreasing-increasing-decreasing behavior of the storage modulus and would mean that the α relaxation results from the melting of these crystalline regions. Since no phosphonate groups would be incorporated into these crystals, no dielectrically active α relaxation is observed.

Hydrogenated Phosphonylated Polypentenamers

Complete hydrogenation of the unsaturated linkages in the phosphonylated polypentenamers leads to materials with a random distribution of phosphonate groups attached to a backbone resembling linear polyethylene. The dynamic mechanical results for the hydrogenated phosphonate esters [Figs. 4(a) and 4(b)], in many ways resemble those of linear polyethylene.¹² An α relaxation whose magnitude increases with increasing crystallinity is present in both, as is a β relaxation which increases as the amorphous concentration increases and a γ relaxation which appears to be composite in nature. Closer study of these relaxations, however, shows that they differ considerably from those in linear poly-

ethylene. The α relaxation temperature of the materials in this study increases in going from the 5 to 10% series. Crystallinity decreases in this direction, however, and the polyethylene α relaxation decreases in temperature as the crystallinity decreases. In addition, the crystalline α relaxation of polyethylene-based copolymers, where the polar comonomer is excluded from the crystalline region, is not found to be dielectrically active, but the hydrogenated phosphonate esters show a well-defined dielectric α relaxation. A third consideration involves the β relaxation. Previous studies on the dynamic mechanical properties of both high-*cis* and high-*trans* polypentenamers and their hydrogenated derivatives^{3,13} clearly demonstrate a large increase in the temperature of the β relaxation with increasing crystallinity. These β relaxations have been assigned to the micro-Brownian segmental motion in the amorphous phase accompanying the glass transition. For the unsaturated phosphonylated polypentenamers it is seen that the glass transition temperature increases greatly with increasing phosphonate content. Thus it seems logical to deduce that even higher glass transition temperatures should be observed for the phosphonylated derivatives as the double bonds are hydrogenated and segments of the polymer are incorporated into polyethylene-type crystals. If the β relaxation of the hydrogenated phosphate esters is assigned to the glass-rubber relaxation, however; it is seen that T_g decreases about 40 degrees in going from the unhydrogenated to the fully hydrogenated 10% ester. Thus it is apparent that polyethylene-type assignments for the relaxations observed in these materials are not satisfactory.

The only relaxation present in the dynamic mechanical spectrum of the hydrogenated phosphonate esters which occurs at a higher temperature than the β relaxation of the unsaturated phosphonate esters is the α relaxation. Assignment of this relaxation to the glass-rubber relaxation is supported by the facts that it correlates with the catastrophic decrease in the storage modulus (not a necessary condition for T_g in a semicrystalline polymer), its position increases in temperature with increasing phosphonate concentration, and it is dielectrically active. There are drawbacks to this assignment, however. The α relaxation obviously increases in magnitude with increasing crystalline content, which indicates that it cannot be a true amorphous-phase T_g ; it results in a T_g/T_m ratio which is much greater than 0.67; and it gives no explanation for the source of the β relaxation.

One approach which resolves the conflicts mentioned above and is consistent with the data is based on the double glass transition hypothesis of Boyer for semicrystalline polymers.^{15,16} This concept visualizes two different and distinct transitions arising from the presence of different types of amorphous material in semicrystalline polymers. The lower of these is labeled $T_g(L)$ and appears identical with the conventional T_g at zero crystallinity. The magnitude of the $T_g(L)$ relaxation continually decreases as crystallinity increases. The higher glass transition, designated $T_g(U)$, shifts to higher temperatures as the crystallinity increases. The magnitude of $T_g(U)$ is expected to increase gradually with increasing crystallinity up to a crystalline fraction of 0.5, and then gradually to decrease with further crystallinity. The nature of the different types of amorphous material leading to each of these transitions is not known for certain; though some concepts have been suggested. Nevertheless, this theory suggests the assignment of the α relaxation as $T_g(U)$ and the β relaxation as $T_g(L)$. While

such assignments are quite speculative, they are based on a theory with some experimental backing¹⁶ and they are both reasonable and consistent in view of the dynamic mechanical and dielectric results reported for the hydrogenated phosphonate esters.

The γ relaxation observed both mechanically and dielectrically for the hydrogenated phosphonate esters is assumed, as it was for the hydrogenated polypentenamers,^{3,13} to have both a crystalline component and an amorphous component. The amorphous contribution is envisioned as resulting from a "crankshaft" motion with three bonds between the stem bonds of the crankshaft, after the Boyd-Breitling mechanism;¹⁷ while the crystalline contribution is believed to result from motion around defects within the crystals.^{18,19}

For the hydrogenated phosphonic acid materials the already complex HyPP-PO system is further complicated by the prospect of hydrogen bond formation. While the hydrogen bonding mechanism for phosphonic acid groups is not well understood,²⁰ it is known that no free hydroxyl groups are present and that the groups do readily form hydrogen bonds. The dynamic mechanical and dielectric results for this series of polymers demonstrate an unusual dependence on phosphonate group concentration and thermal history. The mechanical γ relaxation can be assigned to the same processes mentioned above for the HyPP-PO series γ relaxation. The extremely small γ relaxation observed dielectrically correlates with the dielectric results obtained for the unsaturated phosphonic acid samples, and would seem to be explained by a similar hydrogen bonding type of argument. The α and β relaxations seen mechanically in this series and the dielectric α relaxation probably have the same origins as the corresponding relaxations for the hydrogenated phosphonate esters; however, there is a complex interrelation of thermal history and phosphonate concentration with crystallinity and hydrogen bonding which is superimposed on the behavior of these processes, thereby significantly altering the relaxation properties. For the 5% series the dielectric results show little impact of thermal history while the mechanical results display a significant difference between the behavior of the quenched and annealed samples. For the 10% series, both the dielectric and mechanical results display a marked dependence on thermal history. The experimental evidence collected for the samples in this series is not sufficient to support a detailed explanation of the interactions leading to the observed behavior. The evidence does indicate, however, that crystallinity, thermal history, phosphonate concentration, and hydrogen bonding interact in a complex manner to dramatically alter the dynamic mechanical and dielectric properties of the hydrogenated phosphonic acid polymers.

The dynamic mechanical behavior of the cesium salts shows some dependence on thermal history, but not as much as the acids showed. This is probably because the ionic aggregates formed in the salts maintain their integrity above the melting temperature while the hydrogen bonds in the acid do not. The behavior of the mechanical α , β , and γ relaxations as phosphonate concentration and thermal history vary for these salts is very similar to the behavior of the corresponding relaxations in the hydrogenated phosphonate ester series. This fact would seem to indicate that the assignments made for these relaxations in the case of the esters are also reasonable for the salts, with the added complication of ionic interactions taken into account. Unlike the esters, however, the 10% annealed salt sample displays a shoulder on the α relaxation at 70°C which we

have labeled α' . It has previously been shown in the study of ethylene-acrylic acid based ionomers²¹ that the intensity of the small-angle x-ray peak, attributed to microphase-separated domains, increases as the ionomer sample is annealed. Preliminary small-angle x-ray studies on these phosphonate cesium salts indicate the presence of ionic domains.²² In addition, it has been suggested that monovalent salts should display a relaxation in the temperature range 50–100°C, which reflects the motion in ionic clusters or domains.^{23,24} In view of these facts it seems reasonable to propose that the shoulder at 70°C, labeled α' , is due to the relaxations within ionic domains.

The dielectric behavior of these materials correlates well with the mechanical results. Both sets of data display well-defined α , β , and γ relaxations. The dielectric γ relaxation is assumed to be similar in origin to that observed for the phosphonate esters, but the ionic aggregates into which most of the salt groups are assembled probably result in either a reduced net dipole moment or greatly restricted mobility of these groups, thus diminishing the magnitude of the γ relaxation. The dielectric β reflects the behavior displayed mechanically in this region which we have speculated to be the result of the $T_g(L)$ process, after the theory of Boyer. The dielectric α relaxation would then be the result of the glass-rubber relaxation of $T_g(U)$ material if our assignments are correct. It is significant to note that the dielectric results for these salts show no clear-cut evidence to support the proposed phase-separated domain concept.

While they are in many ways consistent with the findings for low-density polyethylene modified with phosphonic acid groups^{4,25} and its dimethyl ester counterpart,⁵ the results of this study also offer substantial differences. The origin of these differences, however, probably lies both with the different polymer backbones and with the contrasting methods of polymer synthesis. For the HyPP-PO derivatives, the phosphonate group is first added to an unsaturated link in the polypentenamer backbone by a free-radical-induced reaction, and then the remaining unsaturation is removed by hydrogenation, yielding a linear polyethylene type of backbone. For the phosphonylated low-density polyethylenes, the phosphonate groups are added by a free-radical-induced substitution using PCl_3 and O_2 at 60°C. The nature of this reaction is such, however, that substitution would be expected to occur preferentially by removal of tertiary hydrogens at the various branch points followed by addition of the pendant phosphonate group. As a result, the polymers being studied could be represented schematically as follows

where R is simply a hydrogen atom for the polypentenamer reaction, but R is expected to be either an ethyl group, a butyl group, or a long side-chain for the low-density polyethylene (LDPE) samples. The presence of a branch group α to the phosphonate group would substantially affect the energy barrier to rotation at this junction and could therefore significantly alter the relaxation behavior.

CONCLUSIONS

1) In the unsaturated phosphonylated polypentenamers, the temperature of the glass transition is significantly increased with increasing phosphonate concentration. The nature of the pendant group, while it affects somewhat the temperature of the glass transition, appears to play only a minor role relative to the copolymer effect with regard to T_g at the phosphonate group concentrations studied.

2) Hydrogen bonds in acids and ionic interactions in salts form temporary crosslinks in the unsaturated materials which extend the rubbery plateau. However, elementary rubber elasticity theory demonstrates that these ionic crosslinks are not very efficient.

3) The mechanical relaxations for the hydrogenated phosphonylated polypentenamers cannot be satisfactorily explained by a modified polyethylene-type of relaxation behavior. The double glass transition theory of Boyer for semi-crystalline polymers can satisfactorily explain the observed relaxation behavior.

4) The nature of the pendant groups is seen to affect both the mechanical and dielectric behavior of the hydrogenated polymers in this study. In addition, the thermal history of the samples substantially affects the properties of the acids and moderately affects those of the salts in a manner which appears to be more than just the result of increased crystallinity.

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