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Glass Transition and Dynamics of Phosphate Esters Dissolved in Two Glassy Polymer Matrices

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ABSTRACT: Three phosphate ester diluents were added to 50:50 blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide), also known trivially as poly(xylylene ether) (PXE). One of the three diluents was also added to BPA polycarbonate (BPA-PC). The diluents were trioctyl phosphate (TOP), triphenyl phosphate (TPP), and tetraxylyl hydroquinone diphosphate (TXHQDP). The dynamics of these single-phase systems vs temperature were monitored by dynamic mechanical relaxation and phosphorus-31 NMR. Dynamic mechanical characterization revealed the rise of a new low-temperature relaxation when TOP or TPP was added to the PXE-PS blend. The addition of TOP to BPA-PC partially suppressed the well-known polycarbonate low-temperature relaxation. The ^{31}P chemical shift anisotropy line shape was used to detect the rotational mobility of the phosphate esters. In all four blend systems studied, a substantial fraction of the diluent was found to undergo rapid overall Brownian rotation at temperatures well below the DSC glass transition temperature. This behavior was exhibited in the spectra as a narrow line on top of a broader line. The fraction of mobile diluent associated with the narrow component of the line was estimated from a lattice model in which the portion of diluent molecules in contact with other diluent molecules in microclusters was calculated. A random distribution of repeat units and diluent molecules among the lattice sites was assumed with no phase separation. The ^{31}P line shapes were simulated as a function of temperature by assuming the presence of two populations of diluent molecules with different rotational rates. Apparent activation energies for the rates increased from TOP to TPP to TXHQDP, reflecting increasing rigidity of the diluent. The rate of rotation of TOP in polycarbonate is about 3 times slower than in the PXE-PS blend. This difference in rate is attributed to a stronger interaction between the diluent and the more polar polycarbonate matrix. In all the polymer-diluent systems studied, the more mobile fraction of diluent molecules has achieved a degree of rotational mobility characteristic of a liquid at temperatures below the DSC glass transition temperature. In some sense such systems could be regarded as having two glass transitions: one for the mobile diluent and one for the less mobile diluent and polymer repeat units.

Introduction

The dynamic properties of phosphate ester diluents in a matrix of glassy polymer can be observed by phosphorus-31 nuclear magnetic resonance spectroscopy.[1] The rotational motion of such diluents is reflected in the ^{31}P chemical shift anisotropy (CSA) line shape, and such line shapes can yield information on the energetics, heterogeneity, and rate and/or amplitude of this motion.[2,3] The addition of such diluents affects the mechanical and thermal properties of the glassy matrix in a complex manner depending on the mobility of the polymer, the mobility of the diluent, and interactions between the polymer and the diluent.[1,4,5] This report focuses on a detailed analysis of the motion of the diluents based on the NMR line shape.

The three phosphate diluents chosen for study here vary in size and internal flexibility though they might be expected to interact with the polymer matrix in a similar fashion reflecting the common presence of the phosphate ester group in all three.

Two different polymer matrices were chosen for a comparative study of one of the diluents. All three phosphate esters were added to a 50:50 blend of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide), or poly(xylylene ether) (PXE). One of the diluents was also added to BPA polycarbonate (BPA-PC). Both the PXE-PS blend and the BPA-PC have similar glass transition temperatures (T_g) of ca. 150 °C. However, the BPA-PC has a pronounced low-temperature loss peak,[6] while the PXE-PS blend has no distinct sub-glass transition loss peak.[7] Dynamic mechanical spectroscopy frequently shows suppression of low-temperature loss peaks upon addition of a diluent, i.e., so-called antiplasticization.[8-11] This phenomenon occurs with BPA-PC but no comparable effect is observable when the diluents are added to the PXE-PS blend. In vivid contrast, a new sub-glass transition mechanical loss peak appears when a phosphate ester is added to the blend. In both cases, ^{31}P NMR allows for a quantitative assessment of diluent behavior in the temperature regions where the mechanical changes are seen.

In an earlier report, the ^{31}P CSA line shapes of trioctyl phosphate (TOP) in PXE-PS were observed to be at least superficially bimodal.[1] That is, the line shape appeared to be composed of broad, less mobile component and a narrow more mobile component. In this report, an interpretation in terms of a slowly rotating population of diluent molecules plus a rapidly rotating population of diluent molecules is formulated. The motional parameters are assessed as a function of temperature for each of the three diluents in the PXE-PS blend, allowing for comparisons based on the differing structures of the three species. This form of interpretation is also used to compare differences in behavior of one of the diluents in the blend and in BPA-PC.

Bimodal chain dynamics in a glassy polymer-diluent blend have been observed by NMR and interpreted with a lattice model to calculate local polymer-diluent envi-

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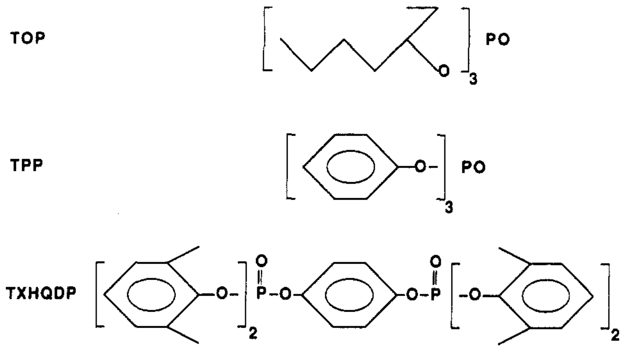

Figure 1. Structures and abbreviations of the three diluent molecules.

ronments by counting polymer–diluent contacts.[12] This same model can be applied to the apparently bimodal line shape data obtained here for the diluent.

Based on the bimodal line shape appearance and the quantitative interpretations developed here, it is necessary to reconsider the nature of the glass transition in these systems. Extruded pellets of the polymer are clear and show no signs of phase separation for the concentrations reported here (15–20 wt % diluent). Thermal studies of these polymer–diluent combinations show only a single glass transition.[4,5] However, from the standpoint of molecular dynamics, the onset of the glass transition as temperature is raised is associated with essentially complete rotational freedom of the constituents though the extent of cooperativity or range of motion is an important question. For the polymer, the molecular mobility associated with the glass transition is the onset of nearly isotropic segmental motion. For a low molecular weight species, it is the onset of simple isotropic rotation. In the polymer–diluent systems under consideration here, some fraction of the diluent has attained nearly complete rotational freedom below the glass transition temperature as determined by thermal analysis. Is it appropriate to consider this fraction of diluent to have a lower glass transition temperature distinct from that perceived by thermal analysis? This point can be considered in terms of the rates of motion determined in the bimodal fitting of the line shapes and in terms of the lattice model used to interpret the bimodal character of a polymer–diluent system.

Experimental Section

The PXE–PS blend was compounded in a Werner-Pfleiderer twin-screw extruder from General Electric PXE resin powder with intrinsic viscosity 0.50 dL/g with M_n = 17 000 and M_w = 34 000 and Shell Chemical Co. general-purpose polystyrene 203 with M_n = 84 000 and M_w = 250 000. The polycarbonate was General Electric Lexan 141 resin with M_n = 10 700 and M_w = 25 600.

The three diuents were tris(2-ethylhexyl) phosphate (TOP), triphenyl phosphate (TPP), and tetraxylyl hydroquinone diphosphate (TXHQPD). The structures of the three diluents are shown in Figure 1.

The polymer–diluent blends were compounded on a twin-screw extruder under conditions that produced clear homogeneous extrudates. Thermal and mechanical properties of these materials have been presented in other reports.[4,5] Concentrations of the diluents and the DSC glass transition temperatures of the blends are listed in Table I.

Viscoelastic characterization of the samples from −150 to +25 °C was performed at 1 Hz in rectangular torsion on a Rheometrics dynamic spectrometer.

The ^{31}P NMR spectra were taken on a Bruker WM 250 at a frequency of 101 MHz and a sweep width of 100 kHz. No proton decoupling was employed. It should be emphasized that the spectra are taken under very simple conditions: free induction decays are acquired following a single pulse. A 30° pulse (10 μs) was used with delay times between 10 and 60 s. Temperature was maintained within 2 °C, and probe temperature was calibrated with the usual chemical standards.

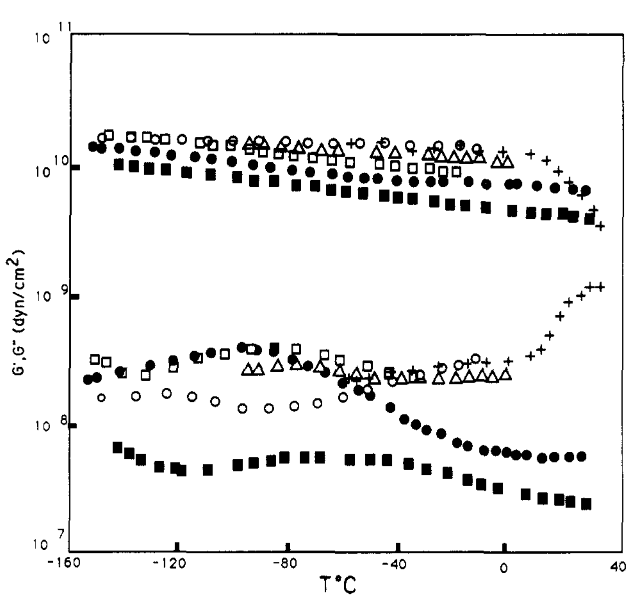

Figure 2. Storage and loss shear moduli versus temperature: (○) 50:50 blend of PXE and PS; (□) 20% TOP in PXE–PS; (△) 20% TPP in PXE–PS; (+) 20% TXHQDP in PXE–PS; (●) pure polycarbonate; (■) 15% TOP in polycarbonate.

Table I
Glass Transition Temperatures

		T_g, °C	
system	% diluent	diluent pure	system
PXE–PS (50:50)	0.0		150.0
TXHQDP in PPO–PS	21.4	+8.0	100.0
TPP in PXE–PS	20.0	−60.0	72.0
TOP in PXE–PS	20.0	−134.0	74.0
BPA-PC (100%)	0.0		160.0
TOP in BPA-PC	15.0	−134.0	73.5

Results

Storage and loss shear moduli are presented in Figure 2 for the PXE–PS blend, pure BPA-PC, and four polymer–diluent compositions. The four polymer–diluent systems will be abbreviated as PXE–PS–TOP, PXE–PS–TPP, PXE–PS–TXHQDP, and BPA-PC–TOP.

The ^{31}P chemical shift line shape spectra for each of the four diluent systems are shown in Figures 3–6 as a function of temperature (K).

Interpretation

PXE–PS 50:50 blend has no distinct sub-glass transition loss peak though this material is somewhat lossy in general.[7] Pure BPA-PC has a well-known,[6] pronounced low-temperature loss peak centered at ca. −100 °C. The addition of 20 wt % TOP to PXE–PS introduces a noticeable loss peak centered at −60 °C, and a less distinct loss peak appears at a slightly higher temperature from when TPP is added. No loss peak is discerned by eye for the case of TXHQDP added to PXE–PS. The addition of TOP to BPA-PC reduces the sub-glass transition loss at −100 °C though a very broad flat-topped peak remains.

These dynamic mechanical data can be compared to the ^{31}P line shape data in an attempt to establish the role of diluent motion in the changes of the mechanical response of these glasses. This has been qualitatively pursued in

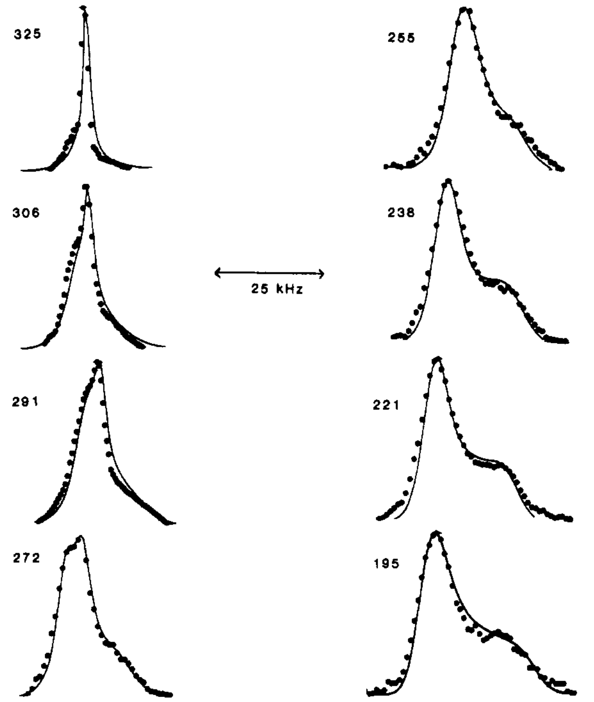

Figure 3. ^{31}P spectra of 20% TOP in PXE–PS at various temperatures. The points are experimental data, and the lines are simulations described in the text.

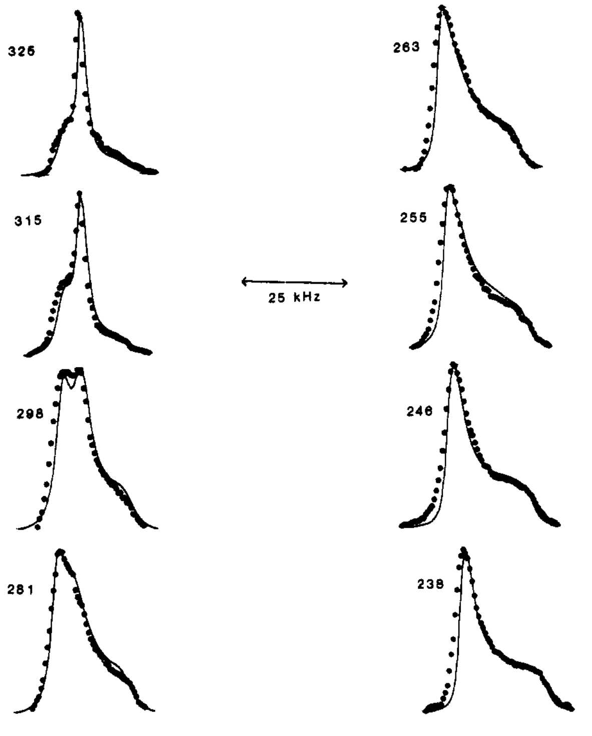

Figure 4. Same as Figure 3 except for 20% TPP in PXE–PS.

the PXE–PS–TOP case in an earlier report, and both qualitative and quantitative comparisons can now be made for all four systems.

First, the low-temperature line shape can be fit to the equations of Bloembergen and Rowland for chemical shift anisotropy.[13] These fits are included in Figures 3–6, and the parameters, particularly the principle values of the shielding tensors, are listed in Table II relative to phosphoric acid. It is necessary to fold the CSA line shape equations of Bloembergen and Rowland with a Gaussian line shape to include the effects of dipolar broadening from nonbonded protons. The line shapes are found to be axially symmetric at low temperatures with anisotropies of the order of 200 ppm (20 000 Hz at the field strength employed) broaded by a Gaussian with a width of ca. 5000 Hz. The choice of a temperature that is "low" is somewhat arbitrary since at least limited librational motion is likely to be present in these polymeric matrices at the temper-

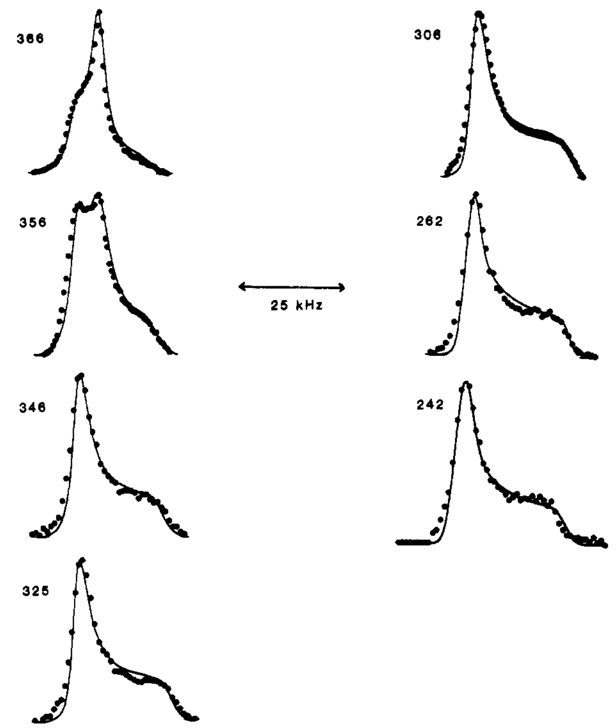

Figure 5. Same as Figure 3 except for 20% TXHQDP in PXE–PS.

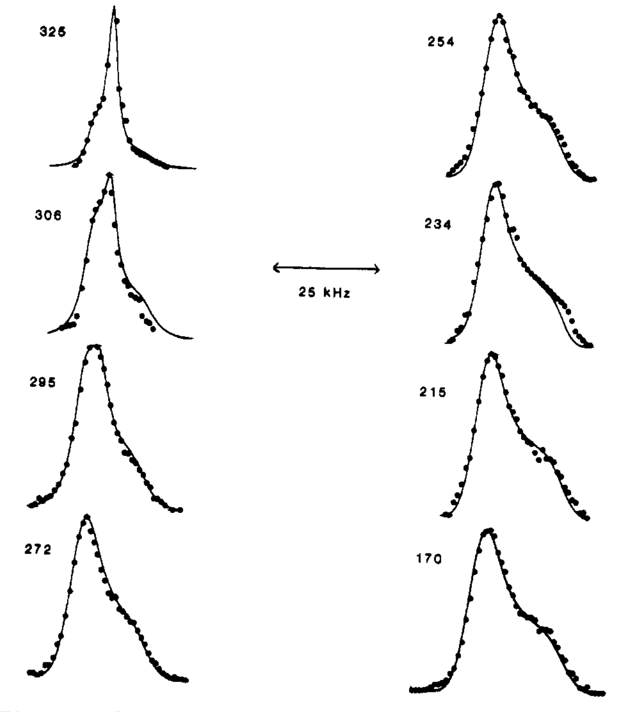

Figure 6. Same as Figure 3 except for 15% TOP in BPA-PC.

Table II

polymer in diluent	T, K	σ_1	σ_2	σ_3
TOP in PXE-PS	195	66	66	-162
TOP in BPA-PC	170	60	60	-125
TPP in PXE-PS	178	57	57	-145
TXHQDP in PXE-PS	244	67	67	-160

atures employed as "low". However, since the change in narrowing between the "low" temperature for each system and the highest temperatures is very large (nearly the whole anisotropy is averaged), the chemical shift anisotropy line shape changes contain good information on the motional dynamics relative to the defined "low"-temperature line shapes.

The limiting high-temperature spectra are usually analyzed to ascertain the amplitude and/or geometry of the motion.[14] In one sense, this is relatively easy in these systems since the high-temperature spectra are all dominated by a sharp line at the average shielding position. Such a line is associated with isotropic motion of the diluent, which is significant in itself since all spectra were acquired below the calorimetric glass transition temperature. Thus the simplest assumption that could be employed to analyze spectra at intermediate temperatures is that these line shapes are partially collapsed by the occurrence of isotropic motion at a rate less than the shielding anisotropy expressed in frequency.

This may be the simplest assumption, but there are several complicating factors. First, the bimodal character of the line shape precludes quantitative analysis on the basis of a single rate for rotational diffusion. While the high-temperature spectra are dominated visually by the sharp line, there is always a broad component underneath the sharp component that has a significant area. The bimodal line shape can be produced either by a broad continuous distribution of rates[2,3] or by two rates, a fast and a slow rate. In glassy polymers, broad continuous distributions of rates have frequently been used to analyze line shape collapse. However, a recent study of the motion of a polymer in a glass containing diluent has shown the polymer motion to be bimodal through the presence of two $T_{1\rho}$ minima in the dependence of $T_{1\rho}$ on temperature.[12] Such $T_{1\rho}$ behavior cannot be the result of a single bell-shaped distribution of rates. This behavior was interpreted by attributing the more mobile polymer component to those polymer segments that were in contact with more than one diluent molecule. A simple lattice model and random statistics were used to estimate the fraction of polymer that would have increased mobility because of contact with several diluent molecules. If polymer segments in contact with more than one diluent molecule have increased mobility, it is reasonable to assume that diluent molecules in contact with other diluent molecules will also have greater mobility, which could lead to the sharp component observed in the ^{31}P chemical shift anisotropy line shapes.

Following this assumption, the line shapes will be interpreted by using two rates and two populations. This approach is suitable for comparing the relative motional freedom of one diluent versus another or for comparing the motion of the same diluent in the two different polymeric matrices.

To simulate line shapes when the frequency of molecular motion is comparable to the spectral width, the exchange model of Sillescu[15] for Brownian rotation and jump diffusion will be used. In NMR, the line shape $I(\omega)$ is the real part of $g(\omega)$.[16,17]

$$I(\omega) = \mathrm{Re}\, g(\omega) \tag{1}$$

The quantity $g(\omega)$ can be calculated from

$$g(\omega) = \mathbf{1}\cdot\mathbf{A}(\omega)^{-1}\cdot\mathbf{W} \tag{2}$$

where the matrix $\mathbf{A}(\omega)$ can be written in terms of the rate matrix π and the matrix ω.

$$\mathbf{A} = i(\omega\mathbf{1} - \omega) - \pi \tag{3}$$

The matrix ω is composed of elements $\omega_j + (i/T_{2j})$ on the diagonal and zeroes elsewhere. In the general case, ω_j is given by

$$\omega_j = \sigma_{\mathrm{iso}} + (\sigma_{33} - \sigma_{\mathrm{iso}})[P_2(\cos\theta) + (3/4)\sin 2\theta \sin 2\beta \times \cos[2(\phi + \gamma)] - 3\sin\theta\cos\theta\sin\beta\cos\beta\cos(\phi + \gamma)] \tag{4}$$

where P_2 is the Legendre polynomial. The Euler angles of the rotation axis with respect to the principal axis of the shielding tensor are (α, β, γ), and the Euler angles of the magnetic field with respect to the molecular axis of motion are (θ, ϕ). For an isotropic powder sample, one has to average over all tensor orientations in terms of the solid angle Ω.

$$I(\omega) = \int \mathrm{d}\Omega\, P(\Omega) I(\omega,\Omega) \tag{5}$$

For Brownian diffusion the rate matrix elements can be written as

$$\Pi(\theta_m,\theta_{m\pm1}) = \frac{D}{\Delta^2}\frac{\sin(\theta_{\mathrm{m}} \pm \Delta/2)}{\sin\theta_{\mathrm{m}}}$$

$$\Pi(\theta_m,\theta_m) = -(D/\Delta^2)(\Pi(\theta_m,\theta_{m-1}) + \Pi(\theta_m,\theta_{m+1}))$$

$$\Delta = \theta_{m+1} - \theta_m = \pi/2N$$

$$0 < \theta_m = (m - 1/2)\Delta < \pi/2$$

$$W(\theta_m) = \sin\theta_m / \sum_{n=1}^{N} \sin\theta_n \tag{6}$$

The number of sites over a $\pi/2$ range is N and is typically set at 40 or 50. For the case of jump diffusion

$$\Pi(\theta_m,\theta_n) = \frac{1}{\tau}[W(\theta_n) - \delta_{\mathrm{mn}}]$$

$$\tau = 1/6D \tag{7}$$

with $W(\theta_n)$ the same as for Brownian rotation.

At intermediate stages of line shape collapse, Brownian diffusion and jump diffusion produce noticeably different line shapes.[15] Brownian diffusion leads to line shapes with the characteristic CSA pattern even at the stage of partial collapse, while jump diffusion at the same stage yields only an asymmetric line shape. The ^{31}P spectra reported here are better simulated with Brownian diffusion, and the rest of the analysis will be based on this model.

In Figures 3–6, the simulations based on a bimodal description, two populations and two rates, and Brownian rotation are shown as solid lines, while the experimental spectrum is given by the points. Fairly good simulations of the spectra of all four systems at the various temperatures can be obtained with this approach.

The parameters of the simulation are shown in Table III and Figure 7. The fractional population of the slow component as a function of temperature is shown in Table III. The τ values as Arrhenius treatments of the correlation times for the two components for each of the four systems, the apparent activation energies, E_a's, determined from the slopes, and the prefactors, τ_∞'s, from the intercepts at infinite temperature are contained in Table IV.

Discussion

The ^{31}P CSA line shapes are well simulated by using a bimodal description as described. With this assumption

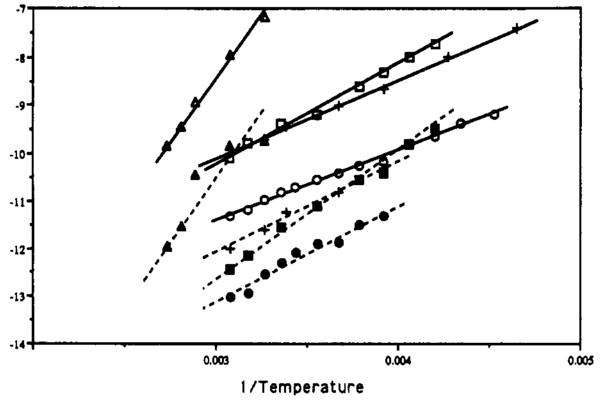

Figure 7. Correlation time versus inverse temperature. The correlation times for the broad or slow component of the line shape and the fast or narrow component are plotted versus inverse temperature for each of the four polymer–diluent systems: (○, ●) TOP in PXE–PS; (□, ■) TPP in PXE–PS; (△, ▲) TXHQDP in PXE–PS; (+) TOP in BPA-PC. The solid lines refer to the slow component and the dashed lines to the fast component.

Table III
Fractional Population of Slow Component

T, K	TOP in PXE–PS	TXHQDP in PXE–PS	TPP in PXE–PS	TOP in BPA-PC
366		0.41		
356	↑	0.56	↑	↑
346	above T_g	0.70	above T_g	above T_g
325	0.40	0.70	0.45	0.35
315	0.70		0.45	
306	0.70	0.70		0.65
298	0.70	rigid	0.60	
291	0.70	↓		
281	0.70		0.60	
272	0.70			0.70
264	0.70		0.60	
255	0.70		0.60	0.70
238	0.70		0.60	
230	1.00		rigid	1.00
221	1.00		↓	1.00
195	rigid			
170	↓			rigid

Table IV

	τ_∞, ns		E_a, kJ/mol	
diluent in polymer	slow	fast	slow	fast
TOP in PXE–PS	150.0	4.0	12	17
TOP in BPA-PC	380.0	15.0	13	16
TPP in PXE–PS	87.0	1.0	17	21
TXHQDP in PXE–PS	0.0615	0.082	42	35

of a distribution described in terms of two populations or components distinguished on the basis of their motional freedom we can make a number of comparisons and qualified conclusions with respect to the diluents in terms of both dynamics and resulting properties.

The correlation times for the broad component, which will also be referred to as the slow component, have values in the range of 10^{-5} s at the highest temperatures studied. Rate constants in this range produce only limited collapse with the Brownian diffusion description and the 200 ppm anisotropy present in these phosphate esters. Since full collapse is not observed for the slow component below the glass transition, the assumption of isotropic motion at a slow rate for this component may only be an approximation. Another possibility is rotation over a limited range described by the area on the surface of a sphere subtended by a cone of angle α. Motion over this range could be assumed to be rapid at all temperatures, and the angle α could increase with temperature. This approach could lead to the type of partially collapsed spectra we are associating with the slow component. At this time we do not wish to rule out this motional model, and indeed it is not clear that line shape analysis alone could distinguish between slow rotation over a full angular range and rapid rotation over a limited range.[18] The interpretation developed here for the slow component should be suitable for some comparative purposes among the diluents, though the prospect of other models should be kept in mind.

Some of the same ideas may be applicable to the fast-moving, narrow component as well. However, in this case motion is about an order of magnitude faster, and the high-temperature limit of full rotation at a fast rate is achieved. Full rotation at a fast rate could have been achieved by expansion of the angle α with a fast rate at all temperatures instead of a changing rate at full amplitude. Again such distinctions are difficult to establish on the basis of line shape analysis alone.

The activation energies for the slow and fast components are very close to being equal given the experimental error of ca. 4 kJ. From a simplistic viewpoint, a higher activation energy might be expected for the slower component but this is not observed. The actual values of the activation energies may not be particularly accurate. An analysis of relaxation in polymers based on a single relaxation time frequently leads to a low estimate of the activation energy, and the approach followed here may suffer from that deficiency.[2,19]

Some physically sensible comparisons among the interpretations for the diluents can be made even though the absolute values of the activation energies may be in error. First, the activation energies increase with the rigidity and, to a certain extent, the size of the diluent molecule. The largest diluent that has little internal flexibility is TXHQDP, and this diluent has the highest activation energy. Collapse of the spectra associated with this diluent in PXE–PS is compressed to a narrow temperature range just below the glass transition of the ternary mixture as can be seen in Figure 5. The collapse of the spectra associated with the other two diluents is spread out over a much wider range centered at lower temperatures, thus associated with a lower activation energy.

If we now compare the diluents TOP and TPP, the diluent TPP has a higher activation energy and moves more slowly at the same temperature. TOP is the larger diluent molecule based on molecular weight but TPP is the less flexible. It would appear that the flexibility of TOP more than compensates for the larger size in contributing to mobility.

The correlation time for the fit of the narrow component at the highest temperature studied for each of the diluent–polymer systems fulfills the condition $(\Delta\omega)\tau < 1$. The freuency $\Delta\omega$ is estimated from the 200 ppm anisotropy and the Larmor frequency of 101 MHz as 1.27×10^5, which corresponds to a correlation time of 7.9×10^{-6} s. Thus the narrow component is in the rapid-motion regime, while the broad component in all cases remains in the $(\Delta\omega)\tau > 1$ regime. The fraction of diluent associated with the broad component is found to be 40 ± 5% for all three diluent–polymer systems just below the DSC T_g. From the standpoint of NMR, this is the fraction of diluent that has the rotational mobility of a glass.

This value for the fraction of immobile diluent compares well with that calculated from a simple lattice model previously introduced to account for the fraction of polymer repeat units that were found to be more mobile in a glassy polymer–diluent system.[12] The model classifies either polymer repeat units or diluent molecules based on the number of contacts with diluent molecules in a manner related to percolation theory.[20] A random distribution of diluent molecules is assumed on the lattice but "microclusters" of diluent are associated with increased mobility. For the problem at hand, the fraction of diluent molecules that are more mobile (i.e., the "microclusters") and lead to the narrow component of the line shape are considered to be those that are in contact with other diluent molecules. Conversely, the slower moving diluent molecules are assumed to be those that are completely surrounded by polymer repeat units. The details of the lattice model relevant to this case are presented in the Appendix.

For the various diluent–polymer compositions studied, ca. 60% of the diluent molecules are in the rapid-motion limit ($\Delta\omega\tau < 1$) below the DSC T_g. From the standpoint of the NMR line shape, this component has become a liquid. The other 40% of the diluent molecules and the polymer matrix have not passed through any transition either according to DSC or from the standpoint of the NMR line shape. The new mechanical relaxation appears far below the depressed resin T_g when TOP or TPP is added to PXE–PS. We would identify the appearance of the loss peak with the rapid rotation of the diluent molecules. If this association is correct, then dynamic mechanical spectroscopy senses the mobility transition as does NMR spectroscopy. DSC does not detect the mobility transition of some of the diluent, and this may simply reflect the breadth of the transition, which extends over a considerable temperature range in the dynamic mechanical spectrum, and the fact that only 60% of the diluent that is present at a level of 20% undergoes the transition. It is also not clear how much of a change in heat capacity (ΔC_p) should be associated with the onset of rotation of a fraction of the diluent in a glassy matrix. Perhaps ΔC_p is too small to be readily detected. The mobility transition that is observed by NMR and dynamic mechanical spectroscopy could be of limited spatial range and therefore fundamentally different from a glass transition which involves a macroscopic sample. The presence of highly mobile regions surely alters some characteristics of the material, and the prospect of deviations from traditional glassy behavior should be considered.

Any difference would most likely be present between the temperature of the onset of rotation of a substantial portion of the diluent and the onset of general rotation of the rest of the system. Since the majority of the system does not have significant rotational freedom, most bulk characteristics would probably remain glassy. However, a careful examination of bulk properties in light of the bimodal behavior might reveal other interesting aspects. In another recent NMR line shape study of a purely amorphous polymeric glass, the glass transition was observed to commence through the onset of a high degree of mobility of a small fraction of the polymer matrix that was considerably more mobile than the remainder of the matrix.[21] It should be emphasized that no diluent was present in this study and the more mobile component was associated with microscopic regions of low density and high free energy present in the disordered glass. A measurement of the size of these regions through a spin diffusion experiment showed them to be only 30 Å or so 40 or 50 °C above the glass transition.[22] The temperature dependence is such that these more mobile regions may only contain one or two repeat units at the DSC glass transition temperature. Thus the glass transition might be viewed as starting in some highly mobile regions that could be viewed as defects.

The mobile component of the diluent in the plasticized glasses can be considered a highly mobile defect itself. This defect is not created by the disorder of the glass but is introduced by adding a component that has considerably greater intrinsic mobility. In fact it appears to be the internal mobility of the diluent itself which controls the temperature at which rotational motion of some of the diluent in the polymer matrix commences.[5] Thus the larger, more rigid diluents do not commence rotation until quite near the temperature at which the matrix as a whole undergoes the glass transition. The more flexible, smaller diluents experience rotational mobility at temperatures well below the glass transition of the matrix. Thus through choice of diluent structure, the nature of the glass transition process can be modified and controlled.

For the diluent TOP in BPA-PC, there is an additional factor to be considered relative to the diluents in PXE–PS. As mentioned TOP suppresses (i.e., broadens) the low-temperature mechanical relaxation present in pure BPA-PC. Another organic ester has been shown to have a structurally specific spatial disposition relative to the BPA-PC repeat unit, indicating local intermolecular structure caused by local interactions.[12,23] In the same system, π flips of the phenylene groups, which are associated with the low-temperature loss peak,[12,24] are suppressed. It is reasonable to assume that TOP exhibits generally analogous behavior since it too suppresses the low-temperature loss peak. The motion of TOP in BPA-PC can be compared with its motion in PXE–PS. There is no low-temperature loss peak to suppress in PXE–PS blends and there are not likely to be as strong local intermolecular interactions between the diluent and the polymer matrix in the less polar PXE–PS. According to the bimodal rate analysis, TOP is moving about 3 times slower in BPA-PC relative to PXE–PS at the same temperature. The glass transition of the two diluent–polymer systems are about the same. This lower rate of diluent motion in BPA-PC may reflect the same relatively strong interaction with the polymer segments that also causes their slowing. In short, the specific interaction may cause both the diluent and the chain segments to slow down.

There would be offsetting mechanical effects between the suppression of polymer motion by the TOP–BPA-PC segment interaction and the onset of motion of TOP in microclusters. The first effect would raise the modulus, and the second would lower the modulus. These factors together appear to control the shape of the broad low-temperature mechanical relaxation. Such a competition between plasticization and antiplasticization effects would also be expected to depend upon the temperature and diluent concentration. The changes in mobility of the various components can be monitored with a series of NMR experiments, and the lattice model allows for at least a semiquantitative framework for discussion. The interpretation is not sufficient for us to quantitatively connect the NMR correlation times with the position and breadth of the low-temperature mechanical loss peaks though this is a desirable goal for the future.

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Appendix: The Lattice Model

To quantitatively apply this model, first consider a system where the polymer repeat unit and the diluent molecule are the same size and therefore each occupies one lattice site. The lattice is assumed to be such that each site has six nearest neighbors. For a polymer repeat unit two of the nearest neighbors must be other polymer units because of chain connectivity. The remaining four units could be occupied either by polymer repeat units or by diluent molecules. If one focuses on the diluent molecule there is no constraint comparable to chain connectivity as long as the diluent occupies one lattice site. Using random statistics, we can calculate the probability of a given diluent molecule having zero, one, two, three, four, five, and six nearest-neighbor diluent molecules as a function of concentration of diluent. To do this we define occupancy probabilities; in particular

p = fraction of sites occupied by polymer repeat units

d = fraction of sites occupied by diluent molecules

We can then calculate the fraction of diluent molecules with zero, one, two, three, four, five, and six diluent moieties as neighbors, although for the interpretation here we only need the fraction of isolated diluents, G_1, and the fraction of diluent molecules in contact with other diluent molecules, $1 - G_1$.

$$G_1 = p^6 \tag{A1}$$

Note that the quantity g_i is not the population of clusters of size i as is considered in percolation theory but only a count of nearest-neighbor groupings.[20] Actually, G_1 and G_2 are also clusters of size one and two, respectively, in the percolation theory context, and the quantity $(1 - G_1)$ is the sum of all clusters larger than size one in that same context.

Unfortunately, the diluent molecules selected for study are significantly larger than the polymer repeat units. The repeat unit weight for PS is 104, and the repeat unit weight of PXE is 120. For the diluent TOP, the repeat unit weight is 434 so one diluent occupies about four lattice sites. TOP has a more spherical shape in contrast to the linear polymer chain and one might consider placing it on the lattice in a square block composed of four lattice sites. If this configuration is employed, then each of the four lattice sites containing part of the TOP molecule has two adjacent lattice sites that are occupied by the same TOP molecule and four nearest-neighbor sites that should be filled according to the random statistics of the lattice occupancy in general. This correction is quite analogous to the calculation of nearest-neighbor occupancy for chain repeat units which is affected by chain connectivity. If this procedure is implemented quantitatively, the fractional population of diluent nearest-neighbor groupings becomes

$$G_1 = p^4 \tag{A2}$$

Now we can calculate the fraction of diluent molecules, G_1, that are isolated from other diluent molecules and are completely surrounded by polymer units. At a concentration of diluent of 20 wt % used here $G_1 = 0.41$, which is close to the experimentally observed value for the slower moving TOP molecules in PXE–PS.

Corrections to the calculation could be made such as using volumes instead of weight fractions but at this stage such refinements are unlikely to significantly change the estimate of G_1. The other diluent molecules have different molecular weights and might require some other lattice configuration than the block of four squares used for TOP. The molecular weight of TPP is 326 so it would occupy about three lattice sites, and the molecular weight of TX-HQDP is 676 so it would occupy about six lattice sites. However, if some arrangement of lattice sites is chosen so that two nearest-neighbor sites are occupied by subunits of the same diluent molecule, then the equations just used would be applicable. Actually, some deviation of the "connectivity" correction for the diluent from two is easily imagined but two is also a reasonable approximation. Such deviations in volume and the connectivity corrections might account for some of the scatter in the estimate of the population of the slow component, which ranges from 35 to 45%. However, the experimental accuracy of the determination is about the same as the range so a more complex analysis seems to be of limited utility at the moment.

For TOP in BPA-PC, a reconsideration of the size of lattice sites is called for since a repeat unit of BPA-PC is about twice as large as units in the PXE–PS blend. Perhaps TOP should be considered to occupy two adjacent units in this case so that G_1 becomes p_5. However, the concentration of TOP in BPA-PC was 15 wt %, which compensates and yields a value of G_1 of 0.38. Again, the value comes out about the same as the other examples and about the same as the experimental results showing the relative insensitivity to specific choices concerning the correction for connectivity and diluent volume.

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