Figure 4 shows the change of the peak shape as a function of cross-polarization time. All the spectra were normalized for the comparison of shape. Compared to the CP–T_1 experiment, the shape change is not so obvious. This is reasonable because there are no large differences in T_2 in the glassy state. However, the situation might be different near the glass transition point. There is a slight narrowing of line width with increasing contact time. From ^{13}C NMR measurements in solution, the fraction of each triad stereosequence in our atactic PMMA sample has been estimated as 5% mm, 43% mr (rm), and 52% rr. The α-methyl resonance in the solid-state CP/MAS spectra appears to contain much more than 5% mm component[4] because of efficient cross-polarization dynamics. On the other hand, the rr component must be inefficiently cross polarized, judging from the reduced intensity observed for this triad stereosequence. For a more quantitative discussion, we need to be able to decompose the broad α-methyl resonance into individual stereosequence components. Generally, if there is some difference in τ_{CH}, there should be a change of shape until max(τ_{CH}(i)). For τ_{CH} more than max(τ_{CH}(i)), there is no shape change because the $T_{1\rho}$ for these individual peaks should be similar due to spin diffusion in the homogeneous homopolymer. Actually, we observe no shape change for contact times of more than 2 ms.

We have demonstrated the possibility of decomposing the broad α-methyl resonance observed in the CPMAS spectrum of atactic PMMA into its individual stereoisomeric peaks. This separation is made possible by the different rates of rotation, as reflected by different T_1's, for the α-methyl groups in each stereosequence. Comparison of the α-methyl T_1's measured here for the mm, mr (rm), and rr stereosequences in atactic PMMA to those observed in stereoregular isotactic and syndiotactic PMMA may indicate a sensitivity to interchain packing which is different between the crystalline stereoregular PMMA's and the amorphous atactic sample.

We are now studying the temperature dependence of T_1 for each stereosequence to make clear the origin of the large difference in T_1 values between stereosequences and the effect of motion on the averaged values of chemical shift anisotropy tensors. The detailed results will be published elsewhere.

Registry No. PMMA, 9011-14-7.

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Spectroscopic Studies of Diluent Motion in Glassy Plasticized Blends

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ABSTRACT: No subglass transition mechanical loss peaks are observed in 50–50 blends of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene. However, if trioctyl phosphate is added to the blend the modulus lowers and a broad low-temperature loss peak appears. Nonspinning phosphorous line shapes were observed to determine if the diluent itself was moving in the glassy matrix, which is clearly the case. At low temperatures a typical axially symmetric line shape is observed which evolves to a narrow line just below the glass transition of the three-component system. The pattern of the collapse appears to take the form of a shift in population from nearly immobile diluent to fairly mobile diluent. This pattern of collapse can be associated with a broad distribution of correlation times. The geometric character of the motion of the mobile diluent is apparently isotropic rotation.

The mechanical properties of bulk amorphous polymers depend on the local chain motions present and in turn the local motions reflect the chemical structure of the repeat unit of the polymer chain. The motions are also influenced strongly by intermolecular interactions between chains so that in the glassy state the apparent activation energy of a given motion may be much higher than that expected for the same motion in an isolated polymer chain.[1] Two general strategies can be followed to control properties of amorphous polymers without changing the morphology. First, the local motions present can be changed by modifications of the chemical structure of the repeat unit; and second, intermolecular interactions can be modified by the addition of a second type of molecule to the bulk polymer. In the latter case, the second component could be either a small molecule diluent or another polymer. The addition of a second type of polymer not only modifies the intermolecular interactions but also introduces a new repeat unit structure which may have its own set of local motions distinct from the host polymer.

A recent survey[2] of the mechanical properties of a set of plasticized blends has revealed a strong dependence of

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these properties on the T_g of the diluent, independent of its effect on the polymer T_g. In this paper we report the mechanical data for a particular diluent and a nuclear magnetic resonance study of the microscopic mobility of the diluent in the blend.

The general behavior of low molecular weight diluents in glassy polymers is often categorized as either plasticization or antiplasticization.[3-6] Plasticizers are diluents which lower the glass transition and lower the modulus. Antiplasticizers also lower the glass transition but not necessarily the modulus. One mechanism for antiplasticization is suppression of local motions and by contrast a mechanism for plasticization would be by increase in either the rate or the amplitude of local chain motion. An increase in the rate or amplitude of motion could be produced through a reduction in intermolecular interactions. That is, the diluent molecule may act as a lubricant, reducing interchain interactions and allowing for more chain motion.[7] The results presented below indicate that the behavior of diluents is more complex and includes possibilities not contained in this brief summary.

The polymer system reported here is a combination of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE) where each component is present in equal amounts by weight. These two polymers are miscible over the whole composition range[8] though only the one composition mentioned will be used as the basic polymeric component. Moreover, neither resin exhibits substantial secondary motions at low temperatures.[9] The diluent blended with the two polymers is trioctyl phosphate which is particularly convenient for NMR studies since the phosphorous chemical shift anisotropy line shape can be used to monitor the motion of the diluent. No magic angle spinning or isotopic labeling is required to follow the motion of the diluent since it is the only component containing phosphorous. Furthermore phosphorous 31 is a 100% spin one-half isotope which simplifies data acquisition and interpretation. The NMR data are used to supplement determinations of shear dynamic mechanical response, compressive yield stress, Young's modulus, and the glass transition temperature. The combination of traditional materials science techniques with NMR spectroscopy provides new insights into the action of diluents in polymer blends.

The PPE used was General Electric PPO resin powder with intrinsic viscosity of 0.05 dL/g with M_n = 17 000 and M_w = 34 000. The polystyrene (PS) was Shell Chemical Co. general purpose polystyrene 203 with M_n = 84 000 and M_w = 250 000. The diluent is a tris(2-ethylhexyl)phosphate (TOP). By differential scanning calorimetry its T_g was found to be −134 °C.

The PPO/PS/TOP blend was compounded on a twin screw extruder under conditions that produced clear homogeneous extrudates. Compression molded sheets approximately 2.3 mm thick were formed from chopped extrudates under time–temperature conditions designed to minimize molecular orientation. Cylinders about 1 cm in diameter and 2.5 cm in length were compression molded from these blends.

The elastic modulus of the blend was determined on specimens cut from sheets compression molded one month before testing. Measurements were made at 0.02 in./min in an Instron servohydraulic tester using an extensometer. Modulus was calculated from the slope of the force–strain curve between 0.02% and 0.4% strain. Viscoelastic characterization of selected blends from −150 to 25 °C was effected at 1 Hz in rectangular torsion in a Rheometrics dynamic spectrometer. Yield stress was determined under compressive loading at a crosshead rate of 0.002 in./min on an Instron Universal tester. Glass transition temperatures, T_g, of all blends were determined with a Perkin-Elmer DSC II differential scanning calorimeter at a heating rate of 20 deg/min.

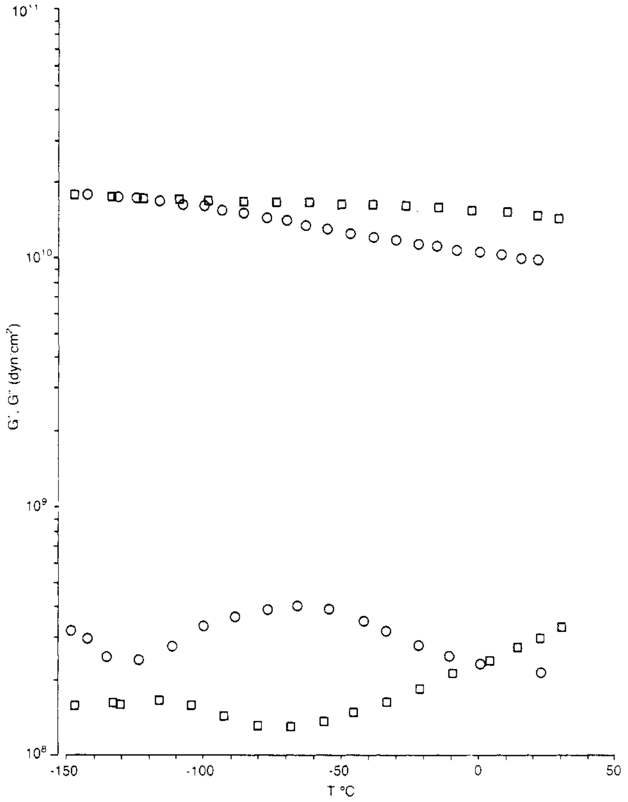

Figure 1. Temperature dependence of storage and loss shear moduli G' and G'' for the neat blend (PPO and PS, 50:50) (squares) and a blend containing 20% trioctyl phosphate (circles).

Table I
Mechanical and Thermal Properties

wt % TOP	tensile E, MN/m^2	compressive yield stress, MN/m^2	T_g, °C
0	3006	107.5	150
5	2980	99.3	112
10	2888	92.4	104
15	2520	84.8	96
20	2580	64.8	72
25	2020	51.0	60

Mechanical and thermal data are summarized in Table I and dynamic mechanical data are presented in Figure 1.

For observation of the ^{31}P line shape, pellets of the ternary system were sealed in a 10-mm NMR tube under vacuum. The spectra were taken on a Bruker WM-250 at a frequency of 101 MHz and a sweep width of 100 kHz. Temperature was maintained within two degrees and the probe temperature was calibrated with the usual chemical standards. The resulting spectra are shown in Figure 2.

Young's modulus and the glass transition temperature drop continuously as the TOP concentration is raised, indicative of plasticization behavior. More interestingly, a distinct though broad loss peak appears in the shear dynamic mechanical response and is centered near −60 °C at a frequency of 1 Hz. There is no comparable subglass transition loss peak in the polymer blend without the diluent present.

A well-defined loss peak is usually associated with the presence of a motion which can be characterized in terms

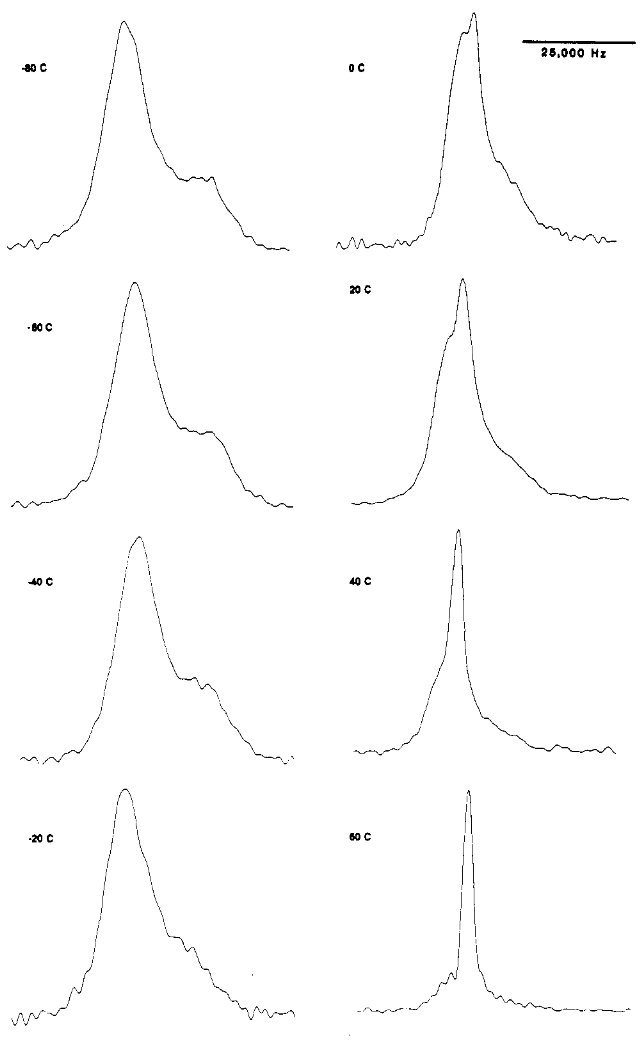

Figure 2. ^{31}P line shapes of the three-component system PPO/PS/TOP as a function of temperature.

of some aspect of the chemical structure of the polymeric glass. Since the polymeric blend without diluent shows no loss peak, it is particularly intriguing to attempt to identify molecular motions present in this system. Some earlier spectroscopy (mechanical, dielectric, and NMR) studies have pointed to motion of the diluent as a cause of relaxations below the polymer T_g.[10-13] The possibility of rotational motion of the diluent can be explored through the ^{31}P spectra as a function of temperature. The solid-state ^{31}P line shape of trioctyl phosphate is dominated by chemical shift anisotropy which arises from the magnetic shielding of the electronic environment surrounding the phosphorous nucleus. The lowest temperature spectra shown in Figure 2 are classic examples of the "polycrystalline" line shape expected for an axially symmetric chemical shift anisotropy which is consistent with the local electronic environment of a phosphorous nucleus in a trialkyl phosphate. The term "polycrystalline" refers to the presence of a sum over all orientations in the sample and an absence of molecular motion. Both of these characteristics are reasonable for a low-temperature spectrum of an amorphous glass.

As temperature is raised, the ^{31}P line shape narrows which is conclusive evidence for motion of the TOP. The nature of the line-shape collapse allows for the identification of several important features of the motion. The geometry of the motion can be determined from the line-shape pattern which appears at the higher temperatures. All spectra displayed in Figure 2 are below the glass transition but the 60 °C spectrum is largely composed of a single sharp line. This result indicates that the TOP is rotating isotropically with a correlation time shorter than tenths of milliseconds at the highest temperature observed.

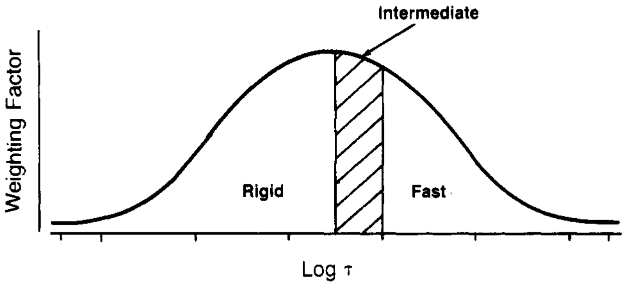

Figure 3. Weighting factor for a given correlation time as a function of correlation time for a typical distribution of correlation times. Rigid, intermediate, and fast refer to characteristics of the NMR line shape.

A second feature of the motion of the TOP can be determined by a consideration of the intermediate spectra which are only partially collapsed. The line shape at −80 °C is indicative of no motion on the NMR time scale which is of the order of milliseconds for these phosphorous line shapes. The line shape at 60 °C is indicative of nearly isotropic motion on a time scale which is fast relative to the NMR time scale. The intermediate spectra, especially those at 0, 20, and 40 °C can be approximated as a superposition of the low-temperature spectrum and the high-temperature spectrum with an increasing proportion of the high-temperature spectrum as temperature is raised.

This superficially bimodal character of the intermediate spectra is evidence for heterogeneous motion which is a characteristic of local motion in glassy polymers demonstrated in earlier line-shape studies.[14-16] Previous line-shape studies have focused on the local motion of the polymer chain and the result obtained here shows that heterogeneity of motion is a general feature of glassy dynamics which is not a chain property. Rather it is to be identified as a property of a glass which is structurally heterogeneous on the size scale of chemical groups. Local motions on this same size scale show the heterogeneity dynamically because the local intermolecular environment differs at various spatial distributions in the glass. Intermolecular interactions are the major source of the apparent activation energies so that it is easy to imagine a distribution of intermolecular interactions leading to a distribution of barrier heights and thus a distribution of rates of motion.

The superficially bimodal appearance of the line shapes can be explained through examination of Figure 3. For numerical discussions of NMR line-shape collapse, the correlation time, τ, is used which is the inverse of the rate constant for collapse. If the motion is heterogeneous there is a broad distribution of rates and this situation is depicted in Figure 3. As explained there are three general rates of motion which can be classified relative to line-shape collapse. Those labeled rigid in Figure 3 are two slow to produce collapse, those labeled intermediate produce partial collapse, and those labeled fast are so fast collapse has already occurred and little further line-shape narrowing is produced by faster rates. If the distribution of rates or times is broad, the rigid and fast parts of the distribution account for the majority of rates and lead to the superficially bimodal spectra. The intermediate rates which yield intermediate stages of collapse are a smaller fraction of the observed line and therefore less obvious. Although the motion is identified as isotropic and heterogeneous, further details remain to be considered. The rotation can occur by jump diffusion or Brownian diffusion and a distribution of amplitudes may be present. The ability to distinguish these subtle differences from the NMR data is uncertain.

NMR spectroscopy has clearly identified the diluent as a mobile species in the ternary system of interest. It is our proposal that the mechanical loss peak arises from the liquidlike motion of the diluent, a conclusion that reinforces the results of a survey of mechanical properties of a large number of plasticized PPE/PS blends.[2] Further quantitative work will be carried out to link the collapse of the NMR line shape to the breadth and temperature of the mechanical loss peak as has been done in an earlier study[1] of polymer motion in glasses.

With this proposal in mind, two distinct mechanisms of plasticization can be imagined. First, a diluent may expedite a local motion of the polymer and thereby lower the modulus of the glass. Second, the diluent itself may undergo local motion, changing the modulus of the glass. Of course both or neither of these mechanisms may be operative when a diluent is added to a glassy polymer. In addition we have not yet introduced modes for antiplasticization behavior. However, a focus on identifying local motions via solid-state NMR and relating these motions to bulk mechanical behavior is a powerful approach for understanding plasticization and antiplasticization.

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Heterogeneous Microscopic Mobility near the Glass Transition from NMR Line Shapes

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ABSTRACT: At or below the glass transition, a Pake doublet is observed for polycarbonates containing only phenylene protons. The Pake doublet arises from the dipole–dipole interaction between adjacent protons on the phenylene ring, and this interaction is essentially unaveraged by sub-glass transition motions since it is parallel to the virtual bonds of the chain backbone. As the glass transition is traversed, the line shape becomes bimodal with the Pake doublet still present plus a Lorentzian line superimposed in the middle of the doublet. The Lorentzian line is approximately 10 times narrower than the Pake component just above T_g, indicative of much more mobile phenylene groups. The fraction of narrow component grows from 2% just above T_g to 17% at 50 °C above T_g. The population of the narrow component can be modeled on the basis of free volume theory or defect concentration. An alternative view is provided by considering the glass transition to be highly spatially heterogeneous with a correspondingly broad distribution of correlation times.

In amorphous polymers just above the glass transition, there is a considerable range in the amplitude of motion at the level of the repeat unit.[1-7] To a first approximation, the mobility just above the glass transition can be divided into two classes: more mobile and less mobile. This categorization has been based on observations of NMR line shapes where commonly a narrow component is seen to be superimposed on a broad component. Both the narrow and broad components arise from amorphous material, although crystalline material can contribute to the latter if the polymer is semicrystalline. The less mobile amorphous line shape is typical of that seen in a fairly rigid solid and is much like the line shape observed below the glass transition. As the temperature is raised above the

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