Diluent Motion in a Glassy Blend by Two-Dimensional Solid-State ^{31}P NMR

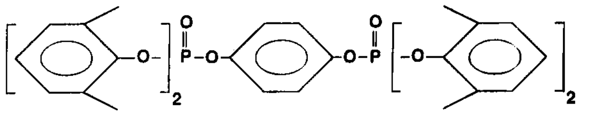
The modulus and glass transition temperature of polymeric materials can be controlled through the addition of low molecular weight diluents. This behavior is discussed in terms of plasticization and antiplasticization, with several molecular level factors contributing to the observed macroscopic properties.[1,2] These factors include the intrinsic mobility of the diluent, mechanical coupling of the diluent motion to the glassy matrix, molecular interactions between the matrix and the diluent, and internal flexibility of the diluent.

Traditionally sub glass transition motions of both the polymer and the diluent can be detected by dynamic mechanical and dielectric response though it is difficult to ascribe the observed relaxation behavior to a particular molecular level motion with these techniques. Solid-state NMR has been particularly successful at identifying the geometry and rate of local motions in glasses,[3,4] and these molecular level descriptions can be related to the bulk response of the polymer. Generally, the NMR experiment detects motion in the megahertz or kilohertz frequency regions, and a time-temperature shift is required to connect the bulk properties with the molecular observations.

A new two-dimensional experiment has been developed by Spiess and co-workers[5-7] to observe molecular dynamics on the time scale of milliseconds to seconds so that the NMR experiment and the dynamic mechanical experiment can now be performed on the same or nearly the same time scale. This reduces the amount of interpretation required to achieve a connection between molecular level motion and macroscopic properties. The two-dimensional NMR experiments developed to date have involved deuterium and carbon-13 NMR spectroscopy and have focused on the dynamics of the polymers at and below the glass transition.[5-7]

It is the purpose of this contribution to extend the technique to phosphorus-31 and to apply it to the case of a diluent in a glassy matrix. The system selected for study is a 50-50 blend of poly(phenylene oxide) (PXE) and polystyrene (PS) plus a phosphate ester diluent (tetraxylyl hydroquinone diphosphate) with the structure shown in Figure 1. This diluent is abbreviated as TXHQDP. The glass transition temperature of the pure diluent is 8 °C while the glass transition of the polymer blend is 150 °C. The glass transition temperature of the polymer blend plus 20 wt % diluent is 100 °C. This ternary system is apparently homogeneous, displaying both optical clarity and a single thermal glass transition temperature. The room-temperature modulus is slightly higher for the polymer blend plus diluent than it is for the polymer blend itself. The 1-Hz dynamic mechanical response of the system is presented in Figure 2. Note that a prominent mechanical loss appears starting at 20 °C below the DSC glass transition temperature.

The PXE-PS blend was compounded in a Werner-Pfleiderer twin-screw extruder from General Electric PXE resin powder with an intrinsic viscosity of 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 diluent blend with 20 wt % THXQDP was compounded on a twin-screw extruder under conditions that produced clear homogeneous extrudates. Viscoelastic characterization of the sample was performed at 1 Hz in rectangular torsion on a Rheometrics dynamic spectrometer.



TXHQDP

Figure 1. Structure of the diluent TXHQDP.

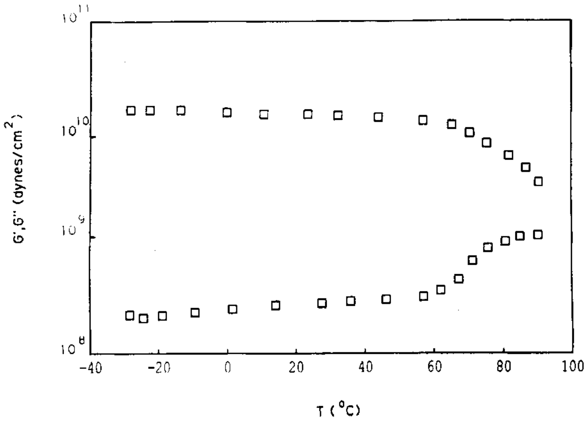


Figure 2. Shear modulus and loss versus temperature for 20 wt % TXHQDP in a 50-50 blend of polystyrene and poly(phenylene oxide).

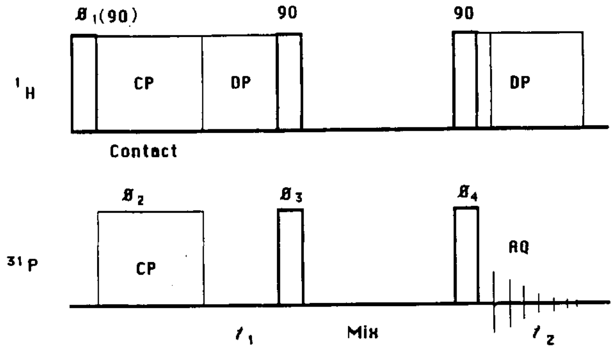


Figure 3. Two-dimensional pulse sequence.

The ^{31}P two-dimensional powder spectra were obtained on a Bruker MSL300 spectrometer at a frequency of 121 MHz using the pulse sequence depicted in Figure 3. The ^{31}P $\pi/2$ pulse was 3.5 μs and the receiver dead time estimated at 5 μs. A sweep width of 125 kHz with 64 data points in t_1 (evolution) and 128 in t_2 (detection) was employed. The mix time (τ_m) during which molecular reorientation is measured can be made identical with the time scale of the dynamic mechanical experiment. In order to avoid the phase twist problem and obtain a pure absorption-mode display, the method of RuSH[8] was used and the real (cosine) and imaginary (sine) parts of the transverse magnetization were collected in two separate experiments.

The first two-dimensional spectrum is shown in Figure 4a at a temperature of 71 °C and a mix time of 1 s. This temperature is below the region where a mechanical loss peak is observed, and the two-dimensional experiment shows only intensity along the diagonal corresponding to the axially symmetric chemical shift anisotropy line shape expected for a static phosphorus-31 nucleus. The absence of off-diagonal intensity also eliminates the presence of ^{31}P spin diffusion in this time scale.

For comparison, a second two-dimensional spectrum taken at 83 °C and a mix time of 1 s is shown as Figure 4e. At this temperature, the dynamic mechanical spectrum shows an increased loss, and the two-dimensional NMR

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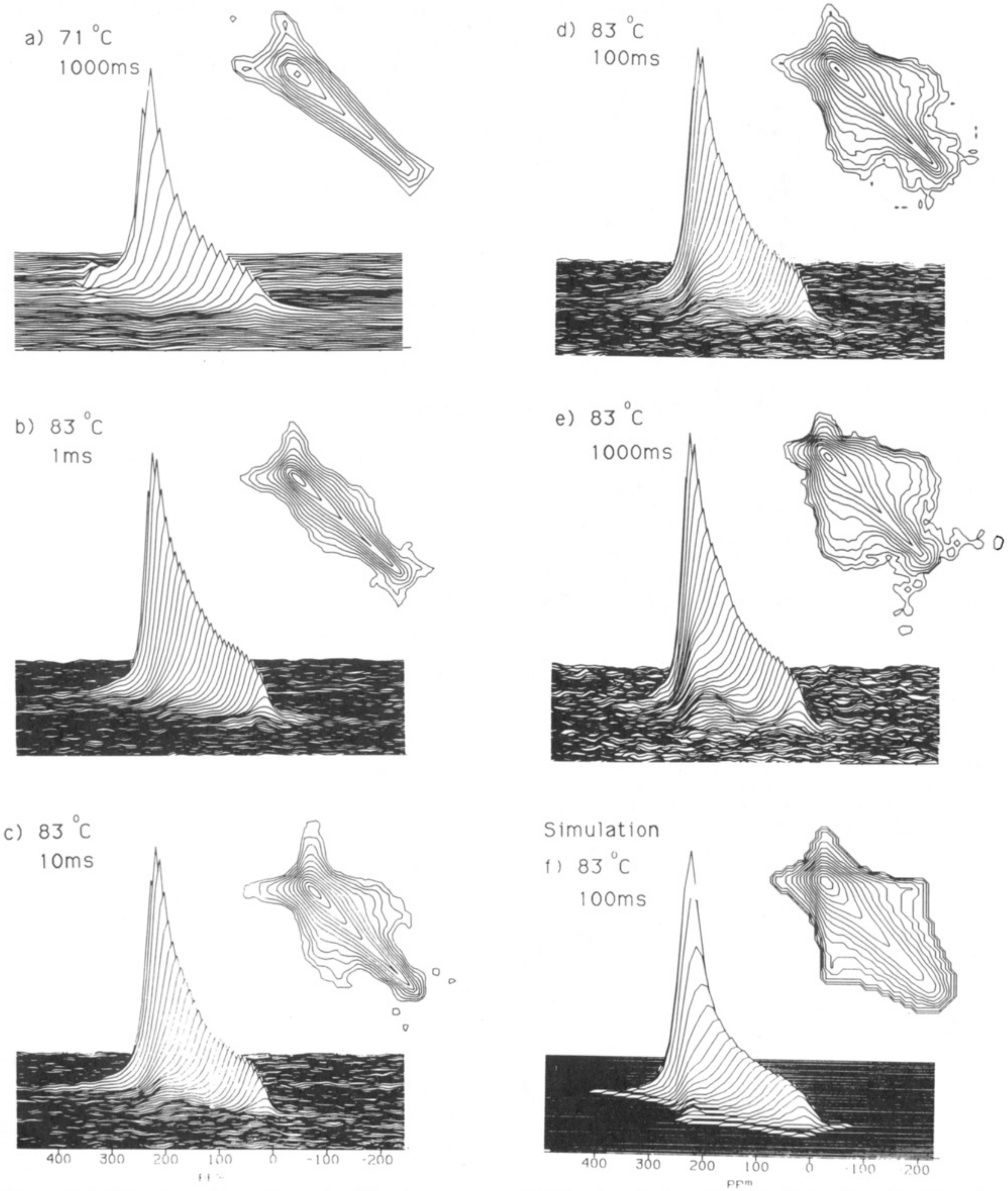

Figure 4. (a) Phosphorus-31 two-dimensional line-shape pattern at 71 °C and a mix time of 1 s. (b–e) Two-dimensional line-shape patterns at 83 °C and at mix times of 1, 10, 100, and 1000 ms. (f) Calculated two-dimensional line-shape pattern for comparison with the pattern obtained at 83 °C and a 100-ms mix time. The pattern is calculated by using two populations: one with a time scale of motion fast with respect to 100 ms and a second with a time scale of motion slow with respect to 100 ms.

spectrum shows significant off-diagonal intensity, which can only arise from molecular reorientation with a time constant less than or equal to the mix time of the pulse sequence. The rate and amplitude of the motion can be further characterized by acquiring two-dimensional patterns at several mix times. Such patterns are shown in Figure 4b–e at mix times of 1, 10, 100, and 1000 ms.

The two-dimensional line-shape pattern can be calculated for a variety of specific descriptions of motion.[6,7] For exchange of orientation by jumps between sites, elliptical ridge patterns are predicted and observed. No elliptical ridges are present in the two-dimensional spectra shown, but the off-diagonal intensity does indicate reorientation by rotational diffusion.[6,7] The rotational diffusion can further be characterized as Brownian diffusion since the two-dimensional patterns gradually spreads over the off-diagonal regions as mix time is lengthened[6,7] (see Figures 4b–e). The form of the off-diagonal intensity as revealed by the contour plots (e.g., Figure 4d–e) shows that all orientations are accessed by the motion of some of the TXHQDP molecules in the 100–1000-ms time window. The fact that the major intensity in the 2D pattern remains along the diagonal even for long mix times (1 s) signifies that only a portion of the TXHQDP molecules are undergoing motion on this time scale. The two-dimensional NMR spectrum at 100 ms can be simulated by assuming a fraction of the phosphate ester diluent molecules is undergoing rapid rotational diffusion during the mix time while a second fraction remains immobile. The resulting calculated spectrum shown in Figure 4f resembles the observed 83 °C and 100-ms experimental spectrum. In the calculated pattern the mobile fraction (approximately 10% of the TXHQDP) producing the off-diagonal intensity has sufficient angular mobility to access essentially all orientations between 0° and 90° during the 100-ms mix time. This mobile fraction is reorienting too slowly to lead to any appreciable collapse in the 1D spectrum at this frequency (121 MHz). The bimodal character of the simulation is reinforced by noting that off-diagonal intensity begins to appear in the 1-ms pattern, but even when the mix time is lengthened by a factor of 10^3 the predominant feature is still diagonal intensity associated with molecules remaining rigid on the time scale of the experiment.

In summary, the two-dimensional NMR experiment detects rotational diffusion of the phosphate ester on a time and temperature scale coincident with the appearance of a loss peak in the dynamic mechanical spectrum. At 71 °C, the 1-s two-dimensional pattern shows no motion and the 1-Hz dynamic mechanical loss peak is only beginning to rise. At 83 °C, the 1-s pattern shows considerable motion and the mechanical loss has risen significantly. The direct connection between the molecular level observation of motion by NMR and the bulk mechanical response without time–temperature shifts provides an excellent opportunity to link the fundamental information with the technological properties.

In the specific case at hand, the phosphate ester molecules observed to undergo rotational diffusion below the thermal glass transition temperature have been identified in a one-dimensional NMR study as the fraction of diluent that is in contact with other diluent molecules in a lattice model.[9,10] The diluent that is observed to be immobile is identified as the fraction that is completely surrounded by polymer units. The simple lattice picture and cluster calculations allow for a quantitative interpretation of the fraction of mobile and immobile diluent moieties, which will be compared in a later report with a quantitative interpretation of the two-dimensional exchange patterns.

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