NOTES

Two-Dimensional Exchange Deuteron NMR of Polystyrene and Poly(vinyl methylether) Blend

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The physical properties of polystyrene/poly(vinyl methylether) (PS/PVME) blend have attracted much interest and been studied by many methods. In previous papers we reported the results of deuteron quadrupole echo NMR of main-chain deuterated polystyrene (PS-*d*₃) in the blend.^{1,2}

Spiess *et al.* showed that two-dimensional (2D) exchange deuteron NMR spectroscopy is quite useful for detecting molecular motion in solid polymers.³ In this note we apply this technique to demonstrate molecular motion of polystyrene in blends.

PS-*d*₃ was synthesized by anionic polymerization of styrene-*d*₃, purchased from Cambridge Isotope Laboratories. The molecular weight determined by intrinsic viscosity is 260000. PVME was obtained from Aldrich Chemical Company, Inc. The molecular weight determined by the intrinsic viscosity is 44000.

The pure polystyrene and samples at a weight ratio of 1 : 1 were cast from benzene solution of a concentration of 3 g/100 ml on a glass plate at room temperature. The resulting films were dried under vacuum at 322 K for more than 6 days.

Deuteron NMR measurement was made using a modified JEOL JNM-GX270 spectrometer operating at 41.7 MHz. A fast (up to 20 MHz) A/D converter (AP501 Autonics) and a pulse programmer developed at Physics Department, University of British Columbia, were installed. The 90 degree pulse length was 2.2 μs. We used a pulse sequence of 2D exchange NMR reported by Spiess *et al.*³ The mixing time of 2D exchange NMR was 10 ms. The temperature of sample was controlled by gas flow from room temperature to 393 K.

Figures 1 and 2 show the 2D exchange NMR spectra of pure PS at 353 K and at 393 K, respectively. One-dimensional (1D) spectra are also depicted on the top of each spectrum. The 1D spectra show typical powder patterns which indicate that molecular motion is too slow to average out the quadrupole interaction.

The 2D spectrum at 353 K is localized on the diagonal without appreciable scatter. This means that the C–D bond of PS main chain does not undergo reorientational motion from one direction to another for a period of mixing time (10 ms), since the resonance position of deuteron is determined by the orientation of C–D

bond.

The spectrum at 393 K diffuses from the diagonal toward both axes and shows noticeable cross-peaks. The 1D spectrum is just the same as that at 353 K. The results indicate that PS molecules in the blend undergo reorientational motion fast enough to change the

Figure 1. Stacked plots (left) and contour plots (right) of the two-dimensional exchange deuteron NMR spectra of main-chain deuterated polystyrene at 353 K.

Figure 2. Stacked plots (left) and contour plots (right) of the two-dimensional exchange deuteron NMR spectra of main-chain deuterated polystyrene at 393 K.

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Figure 3. Stacked plots (left) and contour plots (right) of the two-dimensional exchange deuteron NMR spectra of a 1:1 blend of deuterated polystyrene and poly(vinyl methylether) at 393 K.

orientation in 10 ms but not so fast to average out the quadrupole interaction of an order of 100 kHz.

Figure 3 shows the spectrum of the blend at 333 K. The 1D spectrum shows a powder pattern due to quadrupole interaction. The 2D spectrum shows exchange cross-peaks. It is clear that PS molecules in the blend undergo reorientation at frequencies higher than 100 Hz and lower than 100 kHz at 333 K well below the glass transition temperature of pure PS.

It is well known that PS and PVME form compatible blend and mix together on a molecular scale. PS in the blend is embedded in a soft PVME matrix and is much more mobile than pure PS, as supported by present results.

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