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Self-Diffusion of Hydrogenated Polybutadiene by Forward Recoil Spectroscopy

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We report here a brief experimental study of interdiffusion of a crystallizable polymer in the molten state by forward recoil spectrometry (FRES). This technique has been used to great advantage for observing diffusion at temperatures above T_g in amorphous or noncrystallizable systems.[1-3] Certain limitations are found, however, due to specimen preparation in the case of crystalline polymers.

The materials used for this work are hydrogenated polybutadiene (HPB) and its deuterated analogue (DPB). A linear polymer of molecular weight $M_w = 424\,000$ g/mol, $M_w/M_n = 1.05$, and a three-arm star of total molecular weight $M_w = 75{,}400$ g/mol, $M_w/M_n = 1.10$, were employed. Fractional deuterium contents are $y = 0.40$ and $y = 0.44$ for linear DPB and star DPB, respectively. Synthesis and characterization of HPB and DPB are described elsewhere.[4,5] Important for this work is that the HPB/DPB pair in each case was prepared from the same parent polybutadiene, and hence each pair component has identical chain length and chemical microstructure. Both linear and star molecules contain ~20 ethyl branches per 1000 C atoms which result from 1–2 (vinyl) additions of butadiene. These are thus model random copolymers of ethylene and butene-1, having a crystallinity of about 40% and a melting temperature of 105 °C.[6]

Specimens for FRES consisted of a relatively thick layer (ca. 5 μm) of HPB covered by a thin film (ca. 100 nm) of the analogous DPB. Thick HPB layers were solution cast on silicon wafers from hot (75 °C) cyclohexane solutions of 0.5–1.0% polymer concentration. It was found that directing an air flow over the solution minimized cracking as the film dried. The wafer was then heated to 125 °C for 5 min to complete the drying and to melt and recrystallize the HPB. The thin DPB films were formed by spinning solutions on a glass slide. Solvent, concentration, and temperature were the same as above. The DPB film was then floated off the glass in a distilled water bath and picked up on the HPB coated wafer. Completed bilayers were dried under ambient conditions for 1–2 h before the diffusion step.

Diffusion was initiated by heating the bilayer to 125 °C in a controlled-temperature air oven. Heating times were 180 s for the linear polymer and 1200 s for the three-arm star. Diffusion was terminated by an air quench. Interdiffusion time is this heating time minus 30 s, the interval required for the system to reach 125 °C.

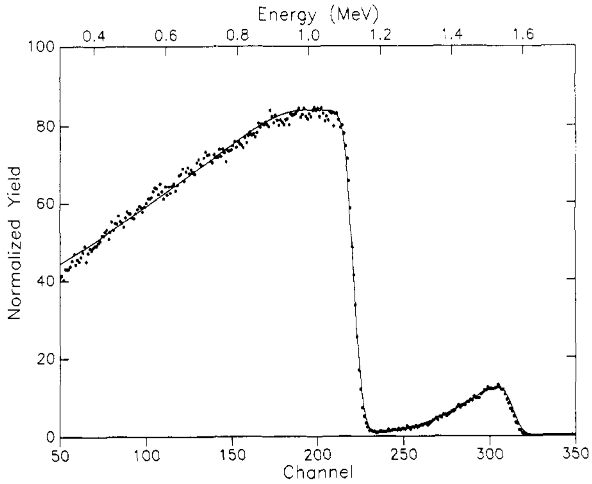

Figure 1. FRES data (●) and RUMP simulation (—) for three-arm star HPB/DPB interdiffused for 1170 s at 125 °C. Fitted parameters are $H = 110$ nm and $D = 2.4 \times 10^{-14}$ cm^2/s.

The concentration profile of DPB normal to the interface was determined by FRES with the apparatus described previously.[1] Experimental FRES data were fitted with the data analysis and simulation program "RUMP".[7] Concentration profiles are assumed to result from Fickian diffusion; thickness H of the undiffused DPB layer and the diffusion coefficient D are varied to produce the best fit of simulated to experimental data by a numerical optimization routine.[8] The scattering yields for H^+ and D^+ were calculated for atomic densities and cross-sections appropriate for HPB/DPB.

An example of an experimental FRES spectrum and the calculated FRES spectrum is shown in Figure 1 for the case of the three-arm star system that had interdiffused for 1170 s at 125 °C. Agreement is excellent, and the self-diffusion coefficient (interdiffusion of like chains mimics self-diffusion) is $D_s = 2.4 \times 10^{-14}$ cm^2/s, which is identical with the result obtained by small-angle neutron scattering (SANS) on the same HPB/DPB pair.[5] Similarly, $D_s = 1.1 \times 10^{-12}$ cm^2/s for the linear pair having $M_w = 424\,000$, very close to the value $D_s = 1.3 \times 10^{-14}$ cm^2/s obtained by extrapolating SANS results on linear HPB[4] to this molecular weight. It should be noted that fractional deuteration reduces the unfavorable thermodynamic interaction[9] between normal and labeled chains in the melt. For this linear DPB with $y = 0.40$ and a degree of polymerization $N = 7600$ (based on C_4H_8 repeats), the interaction term is calculated to be $\chi N = 1.3$, which will cause some "thermodynamic slowing down" at the earliest stages of interdiffusion. The modest difference between the present result with large linear chains and SANS studies on smaller chains is qualitatively consistent with enthalpic modification of the diffusion process, but the 20% effect is about the same size as the combined precision of the two techniques in question. It is not our purpose to pursue such effects here, beyond pointing out that the same experiment with a fully deuterated polymer ($y = 1$, $\chi \propto y^2$)[9] would have $\chi N = 8.7$, and the two components would have only limited miscibility.

Hence it is shown that FRES gives the same results as SANS for the interdiffusion of matched pairs of HPB and DPB. This enhances one's confidence in diffusion coefficients obtained by either method, but particularly the SANS technique. There it is *assumed* that concentration

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profiles evolve by Fickian diffusion; the present results (see Figure 1) show explicitly that such is the case for matched HPB/DPB pairs. Tracer diffusion coefficients have been measured by Klein et al.[11] at 176 °C for linear DPB (equivalent to that used here) in a matrix of polydisperse linear polyethylene. When appropriate adjustments are made for the temperature dependence of D, those tracer results are some 40% larger than self-difusion measured by SANS[4] and 60% larger than the present FRES result. While the reason for this apparent discrepancy is not known, it is possible that the tracer diffusion coefficient measured by Klein is affected by polydispersity of, and the absence of short chain branches in, the matrix polymer in those experiments.

Another consideration in these FRES studies is the thickness before diffusion of the DPB layer H, a quantity that is derived from the RUMP analysis of the FRES profile. For the spin-coating method used here, H = 60–170 nm for linear and star DPB's of different molecular weights. This thickness is appreciably larger than $H \approx 15$ nm, which can be achieved with amorphous polymers, a situation that is thought to derive from the semicrystalline microstructure of HPB (and DPB). The long period of semicrystalline HPB is about 15 nm,[12] a relatively coarse size scale, which makes formation of very thin films difficult or impossible. Since FRES measures interdiffusion over a length of about 700 nm,[1] a DPB layer thickness H of 100 nm means that appreciable volume fraction ϕ of the labeled chain is always present and the dilute tracer regime of $\phi < 0.1$ is not achieved. In the case of Figure 1, $\phi = 0.35$ at the maximum near channel number 300, the location of the original DPB surface.

Crystalline polymers thus lead to relatively thick overlayers which in turn prohibit the volume fraction of the "minority" species from achieving low values. This causes no problem in dynamically symmetric systems such as those reported here, but obvious difficulties are encountered if matrix-dependent tracer diffusion coefficients are desired. This idea was tested by experiments with the three-arm star DPB interdiffusing with linear HPB having molecular weights ranging from 49 000 to 424 000 g/mol. The apparent diffusion coefficient of the star was seen to increase as molecular weight of the linear "matrix" decreased, but the change was only by a factor of 10 rather than the factor of 1000 predicted by constraint release. H was in the range 60–100 nm and the maximum concentration of three-arm star DPB after interdiffusion was appreciable, on the order of 0.2 ± 0.1. The expected matrix effects are damped by the presence of an appreciable fraction of stars constituting the environment of any star DPB test chain.

In conclusion, FRES is shown to confirm quantitatively earlier SANS measurements of self-diffusion in matched HPB/DPB sets of linear and star-shaped macromolecules. The semicrystalline nature of these polymers leads to greater thickness of the DPB layer than is normally found with noncrystalline polymers. Even if thin uniform films cannot be prepared with crystalline polymers, tracer diffusion coefficients may be achieved with thicker FRES top films in which the deuterated polymer is diluted by the hydrogenated matrix polymer.

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