

Notes

Chain Configuration of Polystyrene Arising from Freeze-Drying Dilute Solutions

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Introduction

Some time ago, an attempt was made by Chang and Morawetz to characterize the extent of polymer chain overlap in solutions of varying concentrations.¹ For this purpose solutions of polystyrene labeled with donor and acceptor fluorophores were rapidly frozen. After the frozen solvent was sublimed, the resulting powder was pressed into a pellet and its reflectance fluorescence was recorded. Although all these pellets had identical compositions, the emission spectra showed a strong increase of nonradiative energy transfer with an increasing concentration of the solution from which the sample was prepared. This was interpreted as an indication that during the rapid freezing the extent of chain interpenetration which had existed in solution had been preserved. In particular, it was concluded that, in samples freeze-dried from solutions well below the critical overlap concentration, very little chain entanglement existed.

In a related experiment, polystyrene doubly labeled with donor and acceptor was mixed in very dilute solution with a large excess of unlabeled polystyrene and freeze-dried.² Such a sample exhibited much more energy transfer than a sample in which the doubly labeled and unlabeled polymers were slowly dried to obtain random mixing. Moreover, when the freeze-dried sample was annealed above the glass transition temperature, the fluorescence spectrum gradually approached that of the slowly dried sample. This appeared to be a convincing demonstration of the gradual diffusion of the originally collapsed doubly labeled chains into the unlabeled matrix.

Melt viscosity measurements on polystyrene obtained via a similar freeze-drying process were interpreted in terms of an absence of chain entanglements, persisting from the original solution.^{3,4} However, small-angle neutron scattering measurements revealed that the chains had assumed their Θ condition size,⁵ consistent with a solid-state ¹³C NMR dipolar dephasing experiment indicating highly interspersed molecules.⁶

Obviously, the details of sample preparation may play a decisive role in the obtained extent of chain interpenetration. In particular, the rapidity of the solidification process may be crucial in governing the material's response during the transition from a dilute solution to a solvent-encapsulated glassy state. Conceivably, the seemingly contradictory results obtained by different investigators can be reconciled in terms of different sample preparations. To control this variable and thus become more confident in our understanding of this aspect of polymer behavior,

we employed a freeze-drying procedure identical to that used in the original fluorescence studies and examined the resulting polystyrene glass by a solid-state ¹³C NMR dipolar dephasing experiment. This technique provides an unambiguous measurement of the spatial separation of the nuclei averaged over the bulk sample; hence, the intimacy of mixing of the polymer chains can be assessed. Our results confirm substantial interpenetration of the chains in the polystyrene glass.

Experimental Section

The sample consisted of a mixture of hydrogenated polystyrene (Polysciences no. 00867) and deuterated polystyrene (Merck Isotopes no. MD-3330). The weight-average degrees of polymerization were 960 and 1040, respectively, with polydispersities less than 1.1. The intrinsic viscosity, $[\eta]$, in benzene at 25 °C equals 0.47 dL/g. Equal weights of the two components were dissolved in dioxane at a total concentration $c = 0.83$ g/dL. This is 4 times more dilute than the critical concentration, c^* , for overlap of the polystyrene chains at room temperature.⁷ Freeze-drying of the dilute solution was carried out by immersing the rotating flask in liquid nitrogen, followed by vacuum sublimation of the solvent at -5 to 0 °C at 10^{-3} Torr. Further details of the sample preparation can be found elsewhere and are identical to those used in the earlier fluorescence studies.^{1,2}

The extent of interpenetration of the deuterated and hydrogenous chains after freeze-drying was assessed using ¹³C solid-state nuclear magnetic resonance spectroscopy. A detailed description of the experimental procedure can be found elsewhere.⁶ Briefly, the Hartmann-Hahn technique of cross polarization⁸⁻¹⁰ is used to transfer nuclear magnetization from ¹H nuclei to ¹³C nuclei of the perdeuterated polystyrene chains. Since the efficiency of cross polarization has an r^{-6} dependence, where r represents the distance between specific hydrogen and carbon nuclei, efficient cross polarization only occurs over distances of ca. 1 nm.^{11,12} The deuterated polystyrene carbons can therefore undergo cross polarization from the hydrogenous component only if they are in intimate contact with the deuterated chains (i.e., mixed on a segmental level). A dipolar dephasing period immediately following cross polarization broadens the resonances of those carbons in proximity to protons (i.e., carbons from the hydrogenous polystyrene chains); any residual carbon intensity must arise from perdeuterated polystyrene which is intimately mixed with the hydrogenous polystyrene. The observation of carbon magnetization subsequent to a dipolar dephasing period of sufficient duration to broaden only carbons with directly bonded hydrogen provides unambiguous evidence of intimate contact between the isotopic components.

Results and Discussion

Figure 1 shows a plot of carbon intensity (aromatic carbon peak at 127.9 ppm) for pure hydrogenous polystyrene and the 1:1 blend obtained by freeze-drying the dioxane solution. The dipolar dephasing time is varied from 0 to 100 μ s using a fixed cross-polarization time of 6 ms (found empirically to maximize cross polarization of deuterated carbons in an annealed isotopic blend). The carbon intensity for the pure hydrogenous sample is observed to fall off rapidly, resulting in extreme resonance broadening after only 50 μ s of dipolar dephasing time. Qualitatively, this is the expected behavior since all carbons (except for one) in the hydrogenous component have directly bonded hydrogen nuclei, effecting strong dipolar

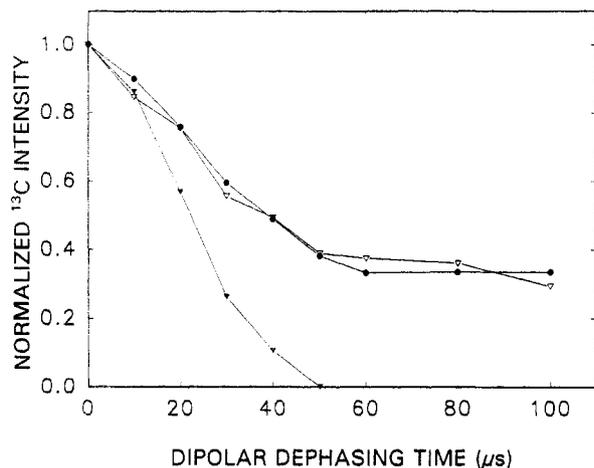


Figure 1. Dependence of the ^{13}C NMR spectral intensity (aromatic peak at 127.9 ppm) on dipolar dephasing time measured for a freeze-dried isotopic blend of polystyrene before (●) and after (▽) annealing at 120 °C for 16 h; pure hydrogenous polystyrene (▼). The cross-polarization time was fixed at 6 ms.

interaction. For the freeze-dried blend, a more gradual loss in carbon magnetization occurs with increasing dipolar dephasing times (Figure 1). In contrast to the results for the hydrogenous sample, approximately 30% of the carbon magnetization remains in the blend after a 50- μs dephasing time; very little additional magnetization is lost even after 100 μs of dipolar dephasing. The residual magnetization is ascribed to those deuterated chains sufficiently close to the hydrogenous component (less than ca. 1 nm) to be cross polarized but distant enough to be unperturbed by a 100- μs dipolar dephasing period. Such results demonstrate that significant interpenetration of the deuterated and hydrogenous components exists after freeze-drying of their dilute solutions.

A similar cross polarization/dipolar dephasing experiment was carried out on the freeze-dried sample after annealing for 16 h at 120 °C, conditions which effect complete chain interpenetration. The results of this experiment, as shown in Figure 1, are virtually indistinguishable from those on the unannealed freeze-dried sample and confirm that no measurable differences exist between the two preparations in terms of efficiency of cross polarization. When this NMR procedure was used on a physical blend of deuterated and hydrogenous polystyrene, prepared by grinding together in a mortar and pestle, complete broadening was observed after only 50 μs of dipolar dephasing.⁶ This result confirms the efficacy of the experimental procedure for detecting mixing on a segmental level in polystyrene isotopic blends.

Summary

The unambiguous conclusion drawn from these NMR experiments is that substantial interpenetration exists among polymer chains in a material obtained by quenching a solution for which $c^*/c \approx 4$ in liquid nitrogen and freeze-drying it. Since the quenching procedure used here was identical to that of the earlier work,^{1,2} we conclude that a highly interspersed state is in fact obtained by this method of processing, notwithstanding the fluorescence results.^{1,2} Evidently, an alternative explanation of the latter observation is required.

It must be emphasized that the spatial scale probed by the fluorescence and NMR techniques is different. The NMR experiment reflects interactions occurring over distances of 0.5–1.0 nm,^{11,12} while the donor–acceptor pairs allow nonradiative energy transfer to occur efficiently over

separations of at least 2 nm.¹³ Thus, the operational definition of chain mixing in the present NMR work is *more* stringent than that of the fluorescence experiments. Several possible explanations for the discrepancy between the conclusions reached from the NMR and fluorescence experiments can be envisioned. However, the operational distance over which intimate chain interactions is defined is *not* one of them.

There are some intrinsic physical differences between the fluorescence and NMR which should be kept in mind with regard to this work and to other possible investigations. Whereas the NMR technique reports a weighted average of *all* environments of chains throughout the sample, the fluorescence experiments, as conducted,^{1,2} probe only the polymer chains that are within $\sim 100 \mu\text{m}$ of the sample surface. It will always be the case that the fluorescence technique emphasizes probes near the surface, regardless of the nature of the polymer and the probe. In some cases this may be advantageous; in others, it may not be. One should keep this fact in mind in selecting which technique to employ. Also, the surface of the freeze-dried particles (in pellets) should differ from the surface of the cast films, with which their fluorescence intensity ratios were compared with respect to their ability to diffract and refract light.^{1,2} We mention these differences without a clear understanding of how they may contribute to the contradictory conclusions.¹⁴

Although it can be concluded that freeze-drying dilute polymer solutions yields highly interpenetrated chains, further experimentation is desirable to reconcile the curious contradictions between the NMR and fluorescence experiments.

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