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 directly bonded hydrogen provides unambiguous evidence of intimate contact between the isotopic components.8

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 period is varied from 0 to 100 µs 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 µs 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

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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. 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 C4/D4 = 4 in liquid nitrogen and freeze-drying it. Since the quenching procedure used here was identical to that of the earlier work,12 we conclude that a highly interpenetrated 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 ~100 μm 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.1,12 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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References and Notes

(14) Radiative energy transfer, a process potentially competitive with nonradiative energy transfer and which also decreases the donor/acceptor fluorescence intensity ratios,16 should be of comparable importance in the freeze-dried pellets and the films and, therefore, cannot explain their very different ratios.