

Notes

NMR Study of Chain Interactions in Freeze-Dried Polystyrene Solutions

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Introduction

The spatial configurations of flexible macromolecules exhibit two extremes corresponding to dilute solutions associated with excluded-volume effects and to high chain densities wherein long-range repulsive forces are negated.^{1,2} Some recent experiments have focused on the consequences of rapidly taking polymers from the dilute-solution regime to a concentrated state. Measurements of non-radiative energy transfer between fluorescent labels attached to polymers freeze-dried from dilute solutions suggest that the obtained neat polymer is comprised of nonoverlapping collapsed coils.^{3,4} This implies that the absence of chain entanglements in solution persists when the solution is freeze-dried.^{3,4} Since the rheology of polymer melts exhibits many manifestations of chain entanglements, the freeze-drying process might then be expected to produce a material with unusual rheological properties.^{5,6} However, no significant differences in melt viscosity were found between normal (e.g., melt-processed) polystyrene and polystyrene prepared by freeze-drying,⁶ a result that is incompatible with the notion that chain entanglements do not re-form over the course of freeze-drying. Moreover, recent small-angle neutron scattering measurements demonstrate that the coil dimensions in polystyrene prepared by freeze-drying are equal to those of the neat material.⁷

It is difficult to reconcile the equivalence of both the coil size and the rheological properties of normal and freeze-dried polystyrene with fluorescence measurements implying a collapsed molecular configuration in the latter. To clarify this issue, a solid-state ¹³C NMR dipolar-dephasing experiment^{8,9} was used to measure the intimacy of mixing of polystyrene coils after freeze-drying of dilute solutions. The dependence on the spatial separation of the nuclei of both the proton-¹³C cross-polarization intensity and the extent of dipolar dephasing enables an assessment of the degree of contact, and hence interpenetration, of the coils.

Experimental Section

The sample consisted of an equal weight 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 benzene at a total concentration, c , of 0.83 g/dL. This is a factor of 4 more dilute than the critical concentration, c^* , at which overlap of the polystyrene chains would commence.¹⁰ Freeze-drying of the solutions was carried out by quenching in liquid nitrogen, followed by sublimation of the solvent. The details of the sample preparation can be found

elsewhere.⁶ A physical mixture was also prepared by finely grinding in a mortar and pestle equal weights of the two polystyrene isotopes.

The interpenetration of the deuterated and hydrogenous chains after freeze-drying was probed using ¹³C solid-state nuclear magnetic resonance spectroscopy. By employing the Hartmann-Hahn technique of cross polarization,¹¹⁻¹³ nuclear magnetization from ¹H nuclei can be transferred to ¹³C nuclei which have a sufficiently strong magnetic dipolar interaction with the protons. 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 approximately a nanometer.^{14,15} The deuterated polystyrene carbons can therefore undergo cross polarization from the hydrogenous component only if the components are intimately in contact, i.e., mixed on a segmental level. A dipolar-dephasing period immediately following cross polarization broadens the resonances of those carbons in very close proximity to protons. This dipolar broadening is limited to carbons of the hydrogenous component, which have directly bonded protons. The more distant deuterated carbons, although sufficiently close to the hydrogenous component to undergo cross polarization, are essentially unperturbed by short dipolar-dephasing exposure. Therefore, intimate contact between the isotopic components is demonstrated by the observation of carbon magnetization subsequent to a dipolar-dephasing period of sufficient duration to broaden only carbons with directly bonded hydrogen.

Cross-polarization and dipolar-dephasing NMR spectra were obtained on a Bruker MSL 300 spectrometer in a static magnetic field of 7.0 T, using a double-tuned magic angle spinning (MAS) probe equipped for 7-mm-o.d. sample rotors. The proton and ¹³C Larmor frequencies were 300.1 and 75.5 MHz, respectively. The temperature was maintained at 295 K, which is ca. 80 K below the glass transition temperature, such that strong heteronuclear dipolar interactions are available for cross polarization. Proton and ¹³C radio-frequency fields of 62 kHz (4- μ s 90° pulse) were used, with a MAS frequency of 4.0 kHz \pm 5 Hz. All cross-polarization spectra were obtained under the matched Hartmann-Hahn technique.¹¹⁻¹³

Results and Discussion

Figure 1 shows the plot of the carbon intensity (aromatic carbon peak at 127.9 ppm) for pure hydrogenous polystyrene and the 1:1 blend obtained by freeze-drying the benzene solution. The dipolar-dephasing time is varied up to 100 μ s. A fixed cross-polarization time of 6 ms was employed. This value was determined to effect the maximum cross polarization of the samples. The intensity of other carbon peaks for the pure hydrogenous component is seen to fall off rapidly, resulting in complete broadening after a 50- μ s dipolar-dephasing time. This behavior is expected qualitatively since all carbons in the hydrogenous component have bound hydrogen nuclei, effecting strong dipolar interaction. For the blend obtained from the freeze-dried solution, a more gradual loss in carbon magnetization is observed with increasing dipolar-dephasing times (Figure 1). In contrast to the results for the hydrogenous sample, in the blend, even after a 50- μ s dephasing time, approximately half of the carbon magnetization remains; very little additional magnetization is lost after 100 μ s of dipolar dephasing. This 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

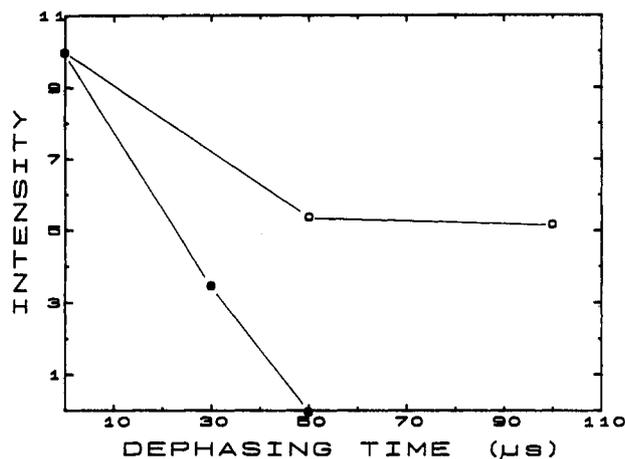


Figure 1. Dependence of the ¹³C spectral intensity (aromatic peak at 127.9 ppm) on the dipolar-dephasing time measured for pure hydrogenous polystyrene (●) and for a freeze-dried isotopic mixture (○). The cross-polarization time was fixed at 6 ms.

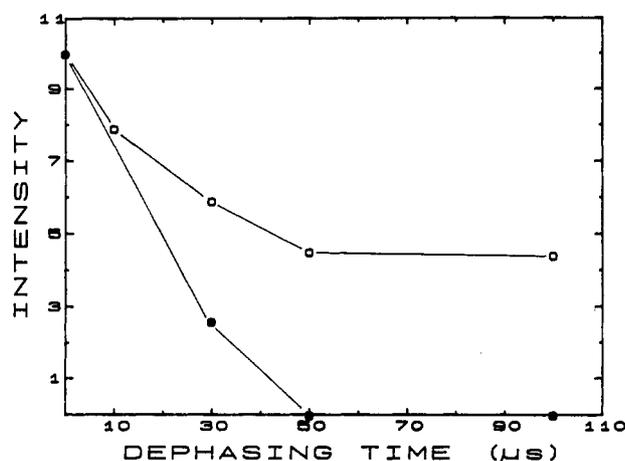


Figure 2. Effect of dipolar-dephasing time (contact time = 6 ms) on the ¹³C intensity of a physical mixture of the two polystyrene isotopes before (●) and after annealing for 25 h at 393 K (○).

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 solution.

A similar cross-polarization/dipolar-dephasing experiment was carried out on a physical mixture of the polystyrenes, prepared by grinding the two components together in a mortar and pestle. Spectra were recorded both as prepared and after subsequent annealing for 25 h at 393 K in order to effect segmental mixing. Figure 2 is a plot of the intensity of the aromatic ¹³C resonance as a function of dipolar-dephasing time. A complete loss of carbon intensity is observed in the unannealed sample after only 50 μs of dipolar dephasing. This is expected since segmental contact between the two components is absent, whereby the deuterated polystyrene can not be cross-polarized. After annealing of this physical blend, however, approximately half of the original intensity persists after 100 μs of dipolar dephasing. The deuterated carbons can be cross-polarized due to the segmental

mixing transpiring during annealing. This parallels the cross-polarization results of the freeze-dried mixture (Figure 1) in that approximately half of the carbon intensity is attributable to deuterated chains in segmental contact with a hydrogenous component. Since both samples were prepared using roughly equal quantities of the hydrogenous and deuterated components, it is concluded that a large fraction of the deuterated and hydrogenous components in the freeze-dried mixture are blended on a segmental level. These results affirm the efficacy of the present experimental technique for probing intimacy of contact between the isotopic components of a mixture.

Summary

The unambiguous conclusion drawn from the NMR experiments is that substantial interpenetration exists among polymer chains in a material obtained by freeze-drying a solution for which $c/c^* < 4$. Herein the product $c[\eta]$ equals 0.39, whereas the earlier fluorescence experiments suggest that interpenetration will be negligible when $c[\eta] < 1.4$. Although the details of the respective quenching procedures conceivably differ, the consistency of the present result with SANS experiments⁷ and rheological studies^{5,6} suggests that some alternative explanation of the fluorescence results on freeze-dried solutions may be required. There are indications that radiative energy transfer may occur in the fluorescence experiments, allowing interaction between donor and acceptor groups lying distant from one another.^{16,17} This could account for the discrepancy between the interpretation of the fluorescence experiments and both the present NMR results and the earlier studies.⁵⁻⁷

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