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Solid-state multipulse proton Nuclear Magnetic Resonance (NMR) characterization of self-assembling polymer films

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Abstract

Multipulse solid-state proton Nuclear Magnetic Resonance (NMR) has been used to study the domain structure in poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymers in clear and self-assembled polymer films. Films containing ordered arrays of microcavities (3–5 μm) were obtained by casting the polymer from carbon disulfide solution in a moist environment, while clear films were obtained by solvent evaporation under nitrogen. The domain sizes for the polystyrene and polyisoprene blocks were measured by proton spin diffusion using the dipolar filter pulse sequence. The domain sizes for the dispersed phase and the long period were measured to be in the range of 3–6 nm, depending on the polymer molecular weight, and no differences domain size were observed for the clear and the self-assembled polymer films. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Self-assembled polymer films are of current interest for a wide variety of technical applications. In favorable cases such materials can be prepared by trapping nonequilibrium structures during film preparation that are locked in as the film solidifies. In one dramatic example it was reported that films with nondisperse pores organized in hexagonal arrays could be produced from star-shaped polystyrene or block copolymers of polystyrene and paraphenylene by evaporating polymer solutions from carbon disulfide (CS_2) under a stream of moist gas [1]. With the proper choice of polymer and preparation conditions, it is possible to prepare films with pore sizes between 0.2–10 μm in films 10–30 μm thick. Such materials have many potential applications, including controlled drug release, optical devices, or as a scaffolding to induce other ordered morphologies in which the surface properties could be controlled and modified. More recently it has been observed that similar morphologies could be obtained in poly(styrene–isoprene–stryrene) triblock copolymers, raising the possibility that such structures could be formed in a variety of materials [2].

The honeycomb morphology noted above has been observed only for a few polymers cast under the proper conditions. Although the mechanism for the formation of such ordered arrays is not well understood, it is believed to arise from the trapping of nonequilibrium structures during film production, and the two factors that are believed to play a role are the

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gelation of polystyrene in CS_2 and dew formation. The concentration dependent gelation of polystyrene in CS_2 has long been known [3,4] and is expected to provide rigidity to the polymer matrix when the solvent concentration is reduced below some critical level. The hexagonal array of pores is reminiscent of the 'breath patterns' observed in dew formation [5,6]. The large enthalpy of vaporization of CS_2 leads to a surface cooling during evaporation that is expected to promote dew formation.

In these studies we investigate the domain structure in the phase separated poly(styrene–isoprene–stryrene) triblock copolymer films using proton spin diffusion and solid-state Nuclear Magnetic Resonance (NMR). Proton multipulse NMR [7] is used since much less material is required compared to that required for carbon NMR studies using magic angle spinning and cross polarization [8]. We have measured the domain sizes for the dispersed phase and the long period in clear and honeycomb films to evaluate the degree to which the nonequilibrium conditions required for the production of self-assembled films affects the molecular level structure of the triblock copolymer.

2. Methods and materials

The poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymers were obtained from Polysciences, and the poly(styrene–*b*-butadiene–*b*-styrene) was obtained from Scientific Polymer Products. The properties of the polymers are listed in Table 1.

Table 1
Table of polymer properties

Polymer	MW (kD)	%Styrene
poly(styrene–isoprene–styrene) I (SISI)	18.8	69.2
poly(styrene–isoprene–styrene) II (SISII)	32.4	49.4
poly(styrene–butadiene–styrene) (SBS)	100.	28

Samples for optical and NMR spectroscopy were obtained by casting films from 10 wt.% solutions in CS_2 on microscope slides. The honeycomb films were obtained by evaporation under a stream of moist air while the clear films were obtained by evaporation under nitrogen in a glove box. Samples for NMR spectroscopy were scraped from the microscope slides.

Solid-state proton NMR spectra were obtained on a Unity 400 Varian NMR spectrometer at 400 MHz using a 5 mm magic angle spinning probe from Doty Scientific. The spectra were obtained with combined rotation and multipulse spectroscopy [7,9] using the MREV-8 pulse sequence [10] with 1.5 μs 90° pulses and τ delay times of 4 μs with magic angle spinning at 2–3 kHz. Spin diffusion was measured with the dipolar filter pulse sequence [11] that uses a 12-pulse sequence to saturate the rigid phase, using 6–10 saturation pulse cycles with a delay time between pulses of 9 μs.

3. Results

Self-assembled polymer films of the poly(styrene–isoprene–styrene) triblock copolymers were obtained by casting films from CS_2 in a moist environment. Fig. 1 shows an optical micrograph of one such film containing arrays of hexonally packed holes. The size of the holes are on the order of 3–5 μm and 'grain boundaries' are observed between areas containing the regularly packed holes. Optically clear films without these regular features were obtained

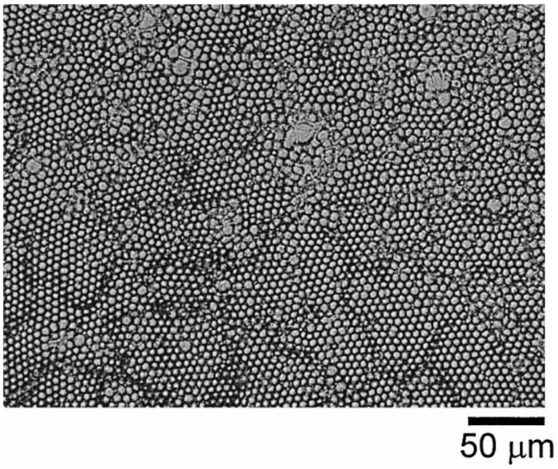


Fig. 1. The optical micrograph of the poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymer cast from CS_2 under a stream of moist air.

from solutions cast under nitrogen. Films of poly(styrene–butadiene–styrene) cast from CS_2 under a stream of moist air also gave white films, but did not show any evidence for the regularly packed array of holes observed for the poly(styrene–isoprene–styrene) triblock copolymers.

The structural organization of the styrene and isoprene domains in the poly(styrene–isoprene–styrene) copolymers was probed by solid-state proton spin diffusion measurements using combined rotation and multipulse (CRAMPS) NMR [7]. Using this method it is possible to obtain relatively high resolution solid-state NMR spectra in which signals from the styrene and isoprene blocks can be distinguished from each other. Fig. 2 shows the 400 MHz solid-state proton NMR spectrum of the poly(styrene–isoprene–styrene) triblock copolymer in which resonances can be observed in the aromatic and aliphatic regions. Two peaks are observed in the lowfield region that can be assigned to the double-bonded protons of polyisoprene near 5 ppm and a broad signal from the aromatic protons of polystyrene centered at 7 ppm. The difference in dynamics between the polystyrene and polyisoprene blocks is evidenced by the difference in line widths, where the sharper signals at 5 ppm are associated with the more mobile polyisoprene blocks. The higher field peak contains contributions from the polystyrene main chain signals and the methyl and methylene signals from polyisoprene.

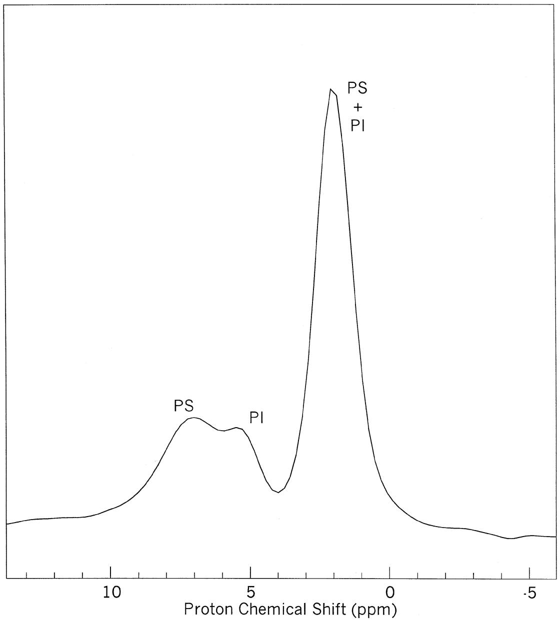


Fig. 2. The 400 MHz solid-state proton NMR spectrum of the poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymer. Some of the peak assignments are noted.

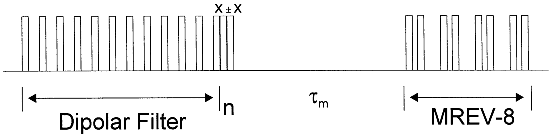


Fig. 3. The pulse sequence diagram for the dipolar filter pulse sequence with MREV-8 detection. The dipolar filter is repeated for several cycles to saturate the more rigid component. Following a pulse to compensate for T_1 relaxation during the mixing time a spin diffusion period is allowed, and the magnetization is observed using magic angle spinning and multipulse decoupling.

The domain sizes for the polystyrene and polyisoprene blocks in poly(styrene–isoprene–styrene) can be measured in the clear and honeycomb films by proton spin diffusion [12,13]. In such an experiment the signals from one of the blocks are saturated and magnetization transfer to the other is monitored. A variety of pulse sequences have been designed to measure proton spin diffusion, and we have investigated the structure of the poly(styrene–isoprene–styrene) block copolymers using the dipolar filter pulse sequence shown in Fig. 3 [11]. This experiment begins with a series of pulses that are designed to saturate the more rigid component (polystyrene) while leaving the magnetization from the more mobile component (polyisoprene) intact. Magnetization can be transferred between the blocks during the mixing time, and the rate of magnetization transfer depends on the morphology, the spin diffusion coefficients and the domain sizes [13].

Fig. 4 shows typical spin diffusion data obtained for the poly(styrene–isoprene–styrene) triblock copolymer in a self-assembled polymer film. At the shortest mixing time (50 μs) the polystyrene signal at 7 ppm has been saturated by the dipolar filter pulse sequence. The polystyrene aromatic peak is initially repolarized by intrachain spin diffusion from the methine and methylene protons, and then, on a millisecond time scale, by spin diffusion from the polyisoprene domains. No intensity or lineshape variations are observed at mixing times longer than

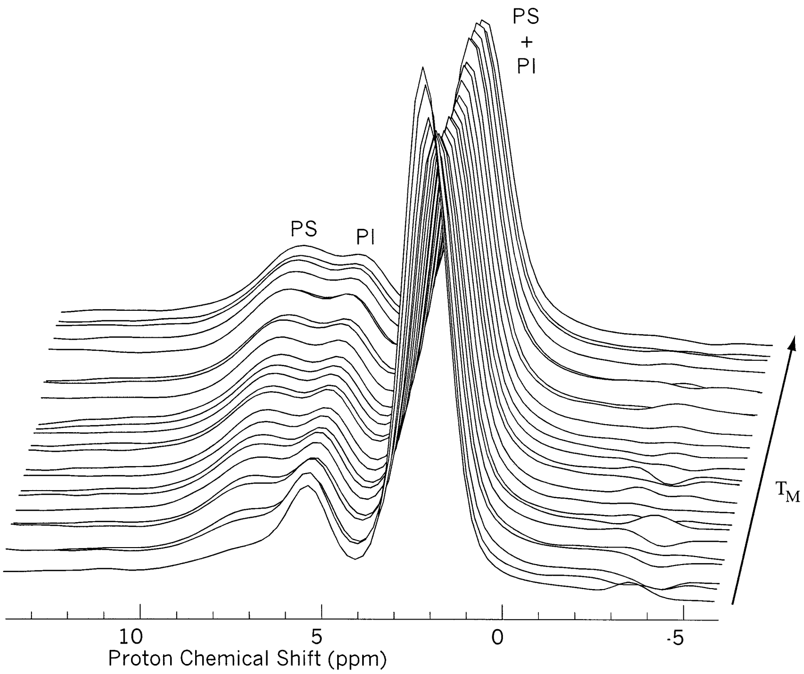


Fig. 4. The solid-state proton NMR spectra of the poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymer as a function of the delay time between the saturation pulse train and observation. The delay time τ_m varies between 50 μs and 50 ms.

50 ms, indicating that the spin system has achieved equilibrium.

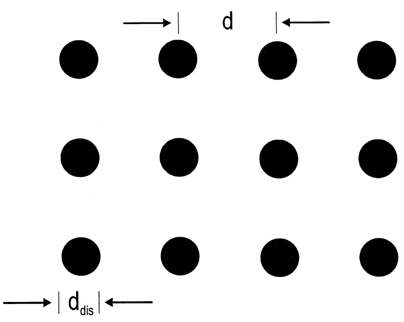
The domain sizes in phase separated materials can be calculated from the time course of magnetization transfer between the polystyrene and polyisoprene blocks of the poly(styrene–isoprene–styrene) triblock copolymer. A variety of morphological models, ranging from simple lamellar models [12] to those with interfaces with spin diffusion coefficients intermediate between those of the two phases, [11,14] have been used to model the spin diffusion recovery curves. More recently it has been shown that a good estimate for the size of the dispersed domain (d_{dis}) and the long period (d) (Scheme 1) can be obtained by extrapolation of the initial buildup rate to the plateau value in the spin diffusion recovery curves [13]. The size of the dispersed phase is given by

$$d_{dis} = \left(\frac{\rho_{HA}\varphi_A + \rho_{HB}\varphi_B}{\varphi_A \varphi_B} \right) \times \frac{4\varepsilon\varphi_{dis}\sqrt{D_A D_B}}{\sqrt{\pi}\left(\rho_{HA}\sqrt{D_A} + \rho_{HB}\sqrt{D_B}\right)} \sqrt{t_m *} \qquad (1)$$

where ρ_A and ρ_B are the proton densities, φ_A and φ_B are the volume fractions, φ_{dis} is the volume fraction of the dispersed phase, D_A and D_B are the spin diffusion coefficients, and ε is the dimensionality. The overall domain size d is given by

$$d = \frac{d_{dis}}{\sqrt[\varepsilon]{\varphi_{dis}}} \qquad (2)$$

Typical spin diffusion recovery curves for the clear and honeycomb films are shown in Fig. 5. Spin



Scheme 1.

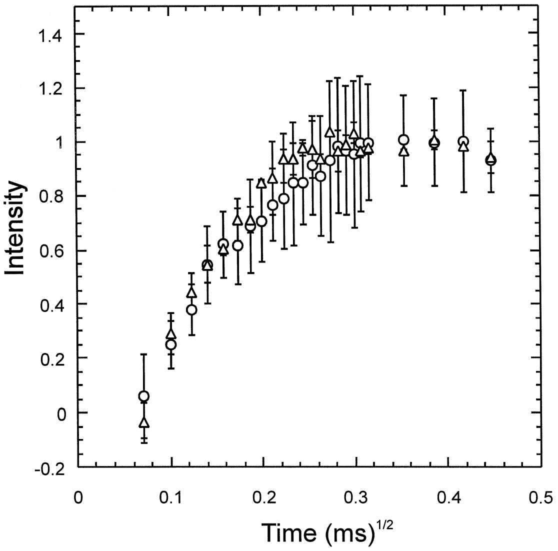


Fig. 5. A plot of magnetization recovery for the poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymer following the dipolar filter. The data are shown for the (Δ) clear and (○)honeycomb film.

diffusion in the clear and honeycombed films can be characterized by the characteristic spin diffusion time $\sqrt{t_m *}$ that is obtained by extrapolating the magnetization buildup to the plateau value. The domain sizes d and d_{dis} are calculated from Eqs. (1) and (2) using the homopolymer proton densities and the diffusion constants of 0.8×10^{-15} m^2/s for the polystyrene [13] and 0.05×10^{-15} m^2/s for polyisoprene [15] and a dimensionality of three. The dispersed domain size and the long periods are compiled in Table 2 for the clear and honeycomb films for the poly(styrene–*b*-isoprene–*b*-styrene) triblock copolymers and the poly(styrene–*b*-butadiene–*b*-styrene) triblocks prepared under identical conditions. As might be expected from the data shown in Fig. 5, no significant differences in the spin diffusion behavior between the clear and honeycomb films are observed. The domain sizes in the poly(styrene–*b*-isoprene–*b*-styrene) triblocks depend on the molecular weight and the fraction of styrene (Table 1) as expected.

Table 2
Domain sizes in clear and self-assembled polymer films measured by proton spin diffusion

Polymer	Film[a]	$\sqrt{t_m *}$ ($\mathrm{s}^{1/2}$)	d_{dis} (nm)	d (nm)
SISI	CF	0.140	3.57	5.06
	HF	0.134	3.42	4.83
SISII	CF	0.175	4.47	6.32
	HF	0.210	5.36	7.58
SBS	CF	0.142	2.83	5.35
	HF	0.152	3.03	5.72

[a] The clear and self-assembled films are denoted by CF and HF.

4. Discussion

Self-assembled polymer films can be prepared from phase separated styrene-containing block copolymers by solution casting from CS_2 solutions in a moist stream of gas. The honeycomb morphology has been reported for several diblock and triblock copolymers and the size of the pores can be controlled through the processing conditions [1]. There is considerable interest in these materials for the many possible applications.

In these studies we have used solid-state proton NMR to characterize the length scale of phase separation in the clear and honeycomb morphologies. Proton spin diffusion is sensitive to domain sizes in the range of 1–20 nm and can be used to study the length scale of phase separation in polymers. Proton NMR is particularly advantageous because of its high sensitivity, making it possible to obtain sufficient signal-to-noise to study thin film samples.

The combination of multipulse proton NMR and the dipolar filter experiments have been used to measure both the long period and the size of the disperse domains in the clear and honeycomb films. The domain sizes are extracted from an analysis of the initial slope of magnetization buildup following selective saturation of the more rigid polystyrene block. We used the approximate method [13] to measure the length scale of phase separation because of the difficulties in accurately characterizing spin diffusion at short mixing times, when the shape of the buildup is sensitive to the interface between the domains. The results show that there is little difference between the clear and self-assembled polymer films, demonstrating that the nonequilibrium structures trapped during film formation are not propagated to phase separation on the molecular level, suggesting that the unique honeycomb morphology is not due interactions between the polystyrene and polyisoprene blocks, but rather larger nonequilibrium structures that are trapped as the solvent is evaporated.

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