

^{129}Xe n.m.r. study of free volume and phase separation of the polystyrene/poly(vinyl methyl ether) blend

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The polystyrene/poly(vinyl methyl ether) (PS/PVME) blend is studied by 1D and 2D ^{129}Xe n.m.r. The signal of ^{129}Xe dissolved in miscible PS/PVME blends exhibits a single peak, and the chemical shift shows non-linear dependence on the PVME content. The observed dependence is explained by the decrease of the total volume of the blend with the increasing PVME content. In the blend heated above the lower critical solution temperature, the single ^{129}Xe peak splits into two peaks, which can be ascribed to the PS-rich and PVME-rich phases. The observed chemical shifts of a phase-separated blend provide the component ratios of each separated phase at the initial stage. Further, 2D exchange ^{129}Xe n.m.r. measurements for the phase-separated blends heat-treated for various periods are performed to determine the average domain sizes of the PS-rich and PVME-rich phases. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The microstructure of polymer blends and copolymers is a research subject of both scientific and practical importance. So far, solid-state ^1H -, ^{13}C -, and ^2H n.m.r. methods have provided us with the various information about the polymer blend and copolymer structures¹.

Recently, ^{129}Xe n.m.r. spectroscopy has begun to be used as a new means to study their structures^{2–6}. The Xe atom is well suited to use as a probe of void spaces in porous materials^{7–9}. The Xe atom can easily get into the void space without causing the materials much disturbance, because it is small, nonpolar, and chemically inert. Of particular interest is that the ^{129}Xe chemical shift is sensitive to the size of the void spaces.

The following results of ^{129}Xe n.m.r. for the polymer blends and copolymers have been obtained: the chemical shift of ^{129}Xe dissolved in the poly(chloroprene)/epoxidized poly(isoprene) (PI) blend differs from those in the pure components²; the linewidth of ^{129}Xe dissolved in the polystyrene(PS)/PI copolymer is broader than those in the pure components³; ^{129}Xe in the phase-separated poly(butadiene)/PI blend⁴, and the poly(propylene)/ethylene-propylene (PP/PEP) copolymer and blend⁵ gives two resolved peaks; Xe atoms transfer between artificial two phases consisting of alternating 4–7 μm layers of PS/poly(vinyl methyl ether) (PVME) blends⁶. These results suggest that ^{129}Xe can be a good probe for examining the miscibility of polymer blends, differentiating the heterogeneous phases, and investigating the domain sizes of immiscible polymer blends and copolymers.

The present study is aimed at further developing potentialities of ^{129}Xe n.m.r. spectroscopy in structural

investigations of polymer blends and copolymers. Firstly, we study the free volume effects on the ^{129}Xe chemical shift in PS/PVME blends. Secondly, we apply one-dimensional (1D) ^{129}Xe n.m.r. to examine the initial stage of the phase-separation process of the PS/PVME blend. Finally, we use two dimensional (2D) ^{129}Xe exchange n.m.r. spectroscopy to determine the domain sizes of phase-separated blends at the late stage.

EXPERIMENTAL

Samples

PS and PVME were obtained from Aldrich, WI. The weight average molecular-weight of PS is 280 000 and the viscosity average molecular-weight of PVME is 44 000. Each polymer was separately dissolved in benzene by 5 wt%, and both were mixed at room temperature. The mixture was cast on a glass plate at room temperature, and dried for 1 week. The obtained transparent films were further dried at 60°C under high vacuum for 4 days. Several blends with different component-ratios were prepared by the same procedure.

The phase separation was achieved by heating the blend at 140°C for various periods in a glass tube immersed in an oil bath. After the heat-treatment, it was immediately cooled in icy water to freeze the phase-separated structure.

A polymer sample with a weight of 1 g was packed into a 10 mm n.m.r. tube with a wall thickness of 1.5 mm which is purchased from Wilmad, NJ. After the tube was thoroughly evacuated for 1 h through an attached vacuum line, enough Xe gas to give a final pressure of 8.5 atm at room temperature was transferred to the tube immersed in liquid nitrogen. After the tube was sealed

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off, it was left for 12 h at room temperature for Xe atoms to sufficiently dissolve into a polymer.

N.m.r. measurements

¹²⁹Xe n.m.r. spectra were measured on a JEOL-GSX 200 spectrometer with a ¹²⁹Xe resonance frequency of 55.26 MHz at room temperature. Chemical shifts were referenced to the resonance of a free ¹²⁹Xe gas which is extrapolated to zero pressure. 2D exchange n.m.r. spectra were measured using the conventional three pulse sequence¹⁰.

RESULTS AND DISCUSSION

Figure 1 shows spectra of ¹²⁹Xe dissolved into PVME, the 50/50 (wt/wt) PS/PVME blend, and PS. Every sample shows a single peak; the ¹²⁹Xe chemical shift values are 209.5 ppm for PVME, 219.9 ppm for the blend, and 225.6 ppm for PS. The appearance of a single peak for the blend is ascribed to the rapid exchange of Xe atoms in voids existing in PS and PVME domains, which are phase-separated in the order of 6–30 Å^{11–17}. The exchange rate *k* of the Xe atoms between the two domains should be higher than the chemical shift difference $\delta\omega$ in Hz. By assuming three-dimensional diffusion, the rate *k* is given by $6D/\langle L \rangle^2$ ¹⁸, where *D* is the diffusion constant and $\langle L \rangle$ is the average distance between the two domains. Using the diffusion constant of $1.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 25°C which was obtained for an artificially laminated PS/PVME blend⁶, $(6D/\delta\omega)^{1/2}$ is

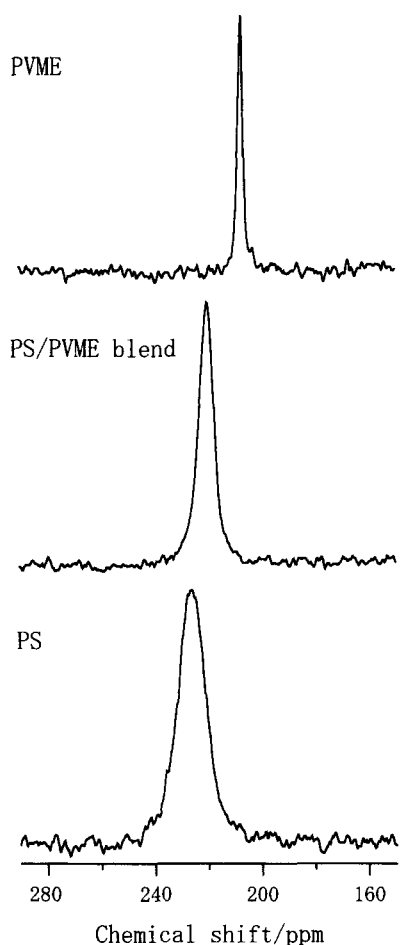


Figure 1 N.m.r. spectra of ¹²⁹Xe dissolved in pure PVME, the 50/50 (wt/wt) PS/PVME blend, and pure PS

calculated to be 90 nm. Therefore, the upper limit of the domain size to allow the observation of the fast exchange is calculated to be 90 nm. This threshold is larger than that (10–30 nm) achieved by ¹H spin diffusion studies^{11–17,19}. Therefore, ¹²⁹Xe 1D spectral measurements are useful to examine heterogeneous domain sizes larger than 10–30 nm.

The linewidth of ¹²⁹Xe should be interpreted in terms of the extent of the spatial distribution of void spaces and the exchange rate of the Xe atoms. Above *T_g*, the exchange rate of Xe atoms is affected by the segmental motion of polymers. Therefore, the observed narrow linewidth (100 Hz) for pure PVME shows that the broadening due to an inhomogeneous distribution of the PVME molecules is averaged by the molecular motion of PVME, the observation temperature being much higher than the glass transition temperature *T_g* = –37°C of PVME. In contrast, the ¹²⁹Xe linewidth for pure PS is broad (450 Hz). This result indicates that the exchange rate of Xe atoms in PS is slow, because the segmental motion of PS with a high *T_g* = 100°C is frozen at room temperature. For the blend, the line-width is about 250 Hz; the linewidth shows that PS becomes more mobile by blending with mobile PVME. Such effects of blending on molecular motion have also been found by ¹H-, ¹³C-, and ²H-n.m.r.^{16,20–23}.

Volume effect on ¹²⁹Xe chemical shift

In this section, we examine the chemical shifts of ¹²⁹Xe dissolved in the PS/PVME blends with various component ratios. Owing to the rapid exchange of Xe atoms, the volume effect on the ¹²⁹Xe chemical shift can be examined. The relation between the obtained ¹²⁹Xe chemical shift and the total volume are discussed, based on the free volume of the PS/PVME blend.

The chemical shift of ¹²⁹Xe dissolved in a material is expressed as the sum of the two contributions⁷: one is the shift due to the Xe–Xe interaction which is proportional to pressure, and the other is caused by the interaction between a Xe atom and the wall of the void space where the Xe atom is adsorbed. The second shift can be obtained by measuring pressure dependence of the Xe chemical shift and extrapolation to zero pressure. With increasing void space around the Xe atom, the ¹²⁹Xe chemical shift moves upfield. So far, the void spaces of several porous materials such as zeolites⁷, silicas⁸, and coals⁹ have been determined in this way.

By n.m.r. measurements of ¹²⁹Xe dissolved in the 50/50 PS/PVME blends at pressures lower than 8.5 atm, we found that the signal intensity increases with pressure, but the chemical shift remains constant. The same results were obtained in other polymers at pressures lower than 10 atm²⁴. These results indicate that the contribution of the Xe–Xe interaction to the chemical shift can be ignored at such low pressures. Therefore, the ¹²⁹Xe chemical shift can be a probe for the free volume of a PS/PVME blend. The chemical shift of ¹²⁹Xe in a polymer has been found to show linear dependence on temperature^{18–20} except for the presence of a change in the slope at *T_g*^{25,26}. The free volume in a polymer also shows the same behaviour²⁶. Therefore, we can assume that the observed ¹²⁹Xe chemical shift δ linearly depends on the free volume *V_f* of a polymer

$$\delta = A - BV_f \quad (1)$$

representing that δ shifts upfield with increasing V_f . Here, the free volume V_f ($\text{cm}^3 \text{g}^{-1}$) is defined by using the total volume V ($\text{cm}^3 \text{g}^{-1}$) and the core volume V^* ($\text{cm}^3 \text{g}^{-1}$) as

$$V_f = V - V^* \quad (2)$$

We can rewrite equation (1) as

$$\delta = C - BV \quad (3)$$

Assuming that the core volume is independent of the PVME-content, C is constant for the blends and the pure components. The total volume V of pure PS and PVME have already been measured at 25°C to be $0.9336 \text{ cm}^3 \text{ g}^{-1}$ ²⁷, and $0.9484 \text{ cm}^3 \text{ g}^{-1}$ ²⁸, respectively, by the float-and-sink method. From the ¹²⁹Xe chemical shifts in pure PS and pure PVME, and their total volumes, we can obtain C and B to be 1275 ppm and $1124 \text{ ppm g cm}^{-3}$, respectively. For the blends, the chemical shift δ_{blend} is also assumed to be represented by equation (3) using the values thus obtained for B and C . We define a weighted sum of the volumes of pure PS and pure PVME as

$$V_{\text{sum}} = w_{\text{PS}} V_{\text{PS}} + w_{\text{PVME}} V_{\text{PVME}} \quad (4)$$

where w_{PVME} and w_{PS} are the weight fractions of the individual polymers. If the total volume of a blend, V_{blend} , is given by V_{sum} , then the component-ratio dependence of the chemical shift can be obtained from equations (3) and (4).

In all the samples, dissolved ¹²⁹Xe showed a single resonance, reflecting that the PS/PVME blends are miscible¹¹⁻¹⁷. Figure 2 shows the PVME-content dependence of the observed chemical shift values. With increasing PVME content, the chemical shift moves upfield, the free volume becoming large. The V_{blend} vs. V_{sum} line roughly agrees with the experimental data as shown in Figure 2; however, the obvious discrepancy between the calculated and the observed values is seen in the middle range of the PVME content. This discrepancy arises presumably because the total volume of the PS/PVME blend is smaller than that calculated from equation (4). In fact, Shiomi *et al.*²⁷ measured the total volumes of the blends with PVME contents of 29.5, 30.5,

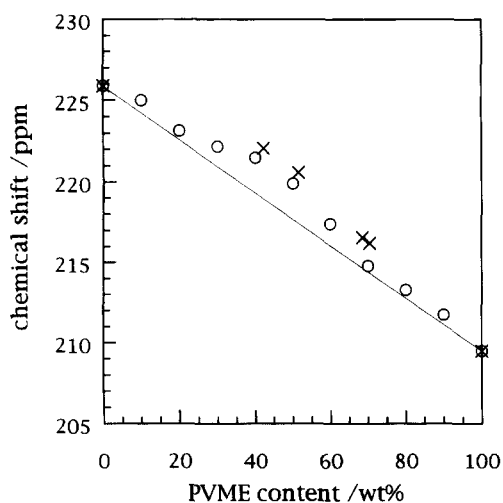


Figure 2 Component-ratio dependence of the ¹²⁹Xe chemical shift in the PS/PVME blends. Circles express the measured shifts. A solid line represents the calculated line (see text). Crosses are calculated using equation (3) and the literature f values

Table 1 Calculated total volume (V) of the miscible PS/PVME blends

PVME (wt%)	Chem. shift (ppm)	V ($\text{cm}^3 \text{ g}^{-1}$)
0	225.6	0.9336 ^a
10	225.0	0.9346
20	223.2	0.9363
30	222.2	0.9371
40	221.5	0.9377
50	219.9	0.9391
60	217.4	0.9414
70	214.8	0.9437
80	213.3	0.9450
90	211.8	0.9464
100	209.5	0.9484 ^b

^a Experimental value in ref. 21

^b Experimental value in ref. 22

49.5, and 58.8% at 50°C by the float-and-sink method, and found that the ratios $f = (V_{\text{blend}} - V_{\text{sum}})/V_{\text{sum}}$ are not 0 but -0.014 , -0.017 , -0.028 , and -0.027 , respectively. Assuming that the f values at room temperature are not different from those at 50°C, we can estimate the chemical shifts of ¹²⁹Xe in the blends using equations (3), (4), and the above f values, as shown in Figure 2. The agreement with the observed chemical shifts is very good, indicating that we can know the total volume of a blend from the measurement of the ¹²⁹Xe chemical shift. The obtained total volumes of the PS/PVME blends at room temperature are listed in Table 1 together with the observed ¹²⁹Xe chemical shift values.

The initial stage of the phase-separation

Since the PS/PVME blend exhibits a lower critical solution temperature (LCST) phase diagram, the blend undergoes phase separation when heated above the binodal point (100–120°C) at the component ratio of 50/50 (wt/wt)^{19,29-32}. The previous results also show that the phase-separation is initiated by spinodal-decomposition above 110–130°C^{19,30,31}. In this section, we examine whether and how the compositional change of the PS/PVME blend by spinodal decomposition is detected by analysing 1D ¹²⁹Xe n.m.r. spectra.

Figure 3 shows spectra of ¹²⁹Xe dissolved in the 50/50 (wt/wt) PS/PVME blends heat-treated at 140°C for 0–10 min. The almost symmetric lineshape for an unheated sample becomes gradually asymmetric with increasing heat-treatment time, and in the blend heat-treated for 10 min, two resolved peaks with different linewidths are clearly observed. The up-field and down-field peaks can be assigned to the signals of ¹²⁹Xe dissolved in the PVME-rich and PS-rich phases, respectively, by comparing with the ¹²⁹Xe chemical shifts for the pure component polymers. No appreciable change in spectra was observed for the blends heat-treated longer than 10 min.

At the initial stage of the spinodal decomposition, most compositional fluctuations increase in amplitude with time. The rate of increase depends upon the wavelength of the fluctuation, so that a characteristic fluctuation grows much more rapidly than others. Then, the characteristic wavelength (domain size) is expressed as³³

$$\lambda_m = 2\pi l \left[3 \left(\frac{T}{T_s} - 1 \right) \right]^{-1/2} \quad (5)$$

where T and T_s denote the heat-treatment temperature and the spinodal temperature, respectively, and l

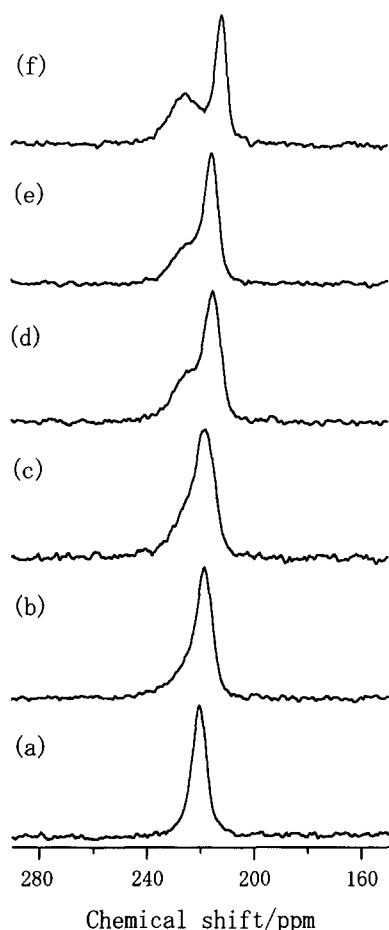


Figure 3 N.m.r. spectra of ¹²⁹Xe dissolved in the 50/50 PS/PVME blend heat-treated at 140°C for various periods; (a) no heating, (b) 1 min, (c) 2 min, (d) 3 min, (e) 5 min, and (f) 10 min

represents the Debye range of the intermolecular interaction³⁴. Nishi *et al.* obtained $l = 58$ nm and $T_s = 118^\circ\text{C}$ for the 50/50 (wt/wt) PS/PVME blend using microscopy¹⁹. When we adopt their results, the characteristic wavelength is calculated to be 900 nm at 140°C, being much larger than the threshold length of 90 nm for ¹²⁹Xe to discriminate two phases. Since the diffusion effect of Xe atoms between the two phases is ignored, at least two ¹²⁹Xe signals originating from the PS-rich and PVME-rich phases are expected. The chemical shift for each phase reflects the composition of each phase. At heat-treatment period less than 3 min, however, the component-ratio difference between PS-rich and PVME-rich phases is small. Thus, the two peaks are not resolved. After the heat treatment period of 3 min, the component-ratio difference becomes large enough to lead to the observation of the two peaks.

To deduce the two chemical shifts in both phases at various heat-treatment periods, we fitted a weighted sum of two Lorentzian lines to the observed lineshape. The obtained chemical shifts give the component ratios in the two phases via the observed chemical shift vs. PVME content relation listed in *Table 1*. The results are summarized in *Figure 4*, showing the compositional change in each phase at the initial stage. Since the chemical shift values for blends heat-treated shorter than 3 min could hardly be determined because of the low spectral resolution, we could not determine the component ratio in this region. Examining the compositional

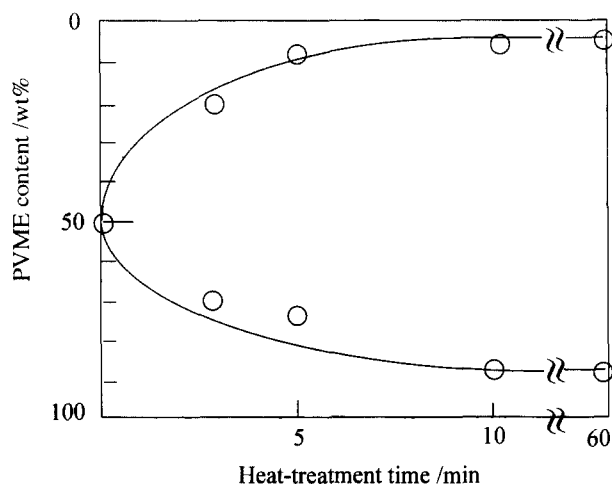


Figure 4 Compositional change in both the PS-rich phase and the PVME-rich phase of the 50/50 PS/PVME blend during the initial stage at 140°C. The solid lines are only for eye guide

change in the 50/50 (wt/wt) PS/PVME blend by ¹H $T_{1\rho}$ measurements, Asano *et al.*¹⁷ concluded that the component ratio of each phase reaches its equilibrium value within 2 min at 140°C. In our result, it takes about 10 min to reach the equilibrium value. This discrepancy may be attributed to the effects of the molecular weight of PS on the phase separation, which is different between the two studies³².

As mentioned in the previous section, the linewidths of ¹²⁹Xe in PVME, the 50/50 blend, and PS are narrow in this order. Similarly the linewidth of ¹²⁹Xe dissolved in the PVME-rich phase is narrower than that in the PS-rich phase. This result shows that the PVME-rich phase is more mobile than the PS-rich phase.

It is concluded that the ¹²⁹Xe chemical shifts are sensitive to the compositional change; therefore, ¹²⁹Xe n.m.r. spectra are useful to visualize the compositional change at the initial stage of the phase-separation process.

The late stage of the phase-separation

Even after the component ratio of each phase reaches its equilibrium value, the domain size becomes larger with increasing heat-treatment time. Although we cannot detect such growth of the domain size by 1D ¹²⁹Xe n.m.r. or ¹H spin-lattice relaxation measurements¹⁷, the domain size at the late stage can be estimated by the 2D ¹²⁹Xe exchange n.m.r. method as shown below.

Figure 5 shows the 2D exchange n.m.r. spectra of ¹²⁹Xe in the phase-separated blend, which were measured with a mixing time of 1 s. Apparent cross peaks between the peaks of ¹²⁹Xe in the PS-rich and PVME-rich phases are observed for the blend heat-treated for 30 min (*Figure 5a*). This shows that the diffusion of Xe atoms is fast enough to transfer between the two separated phases during 1 s. With increasing heat-treatment time, the cross peaks become weaker. The spectrum of a blend heated for 1200 min shows no appreciable cross peaks (*Figure 5b*); this result indicates that the domain size of each phase is too large for Xe atoms to diffuse into the other phase within 1 s.

Here, we assume that the Xe diffusion between the PS-rich and PVME-rich phases can be treated simply as two-site exchange. Then, the intensity ratio I_{AB}/I_{AA}

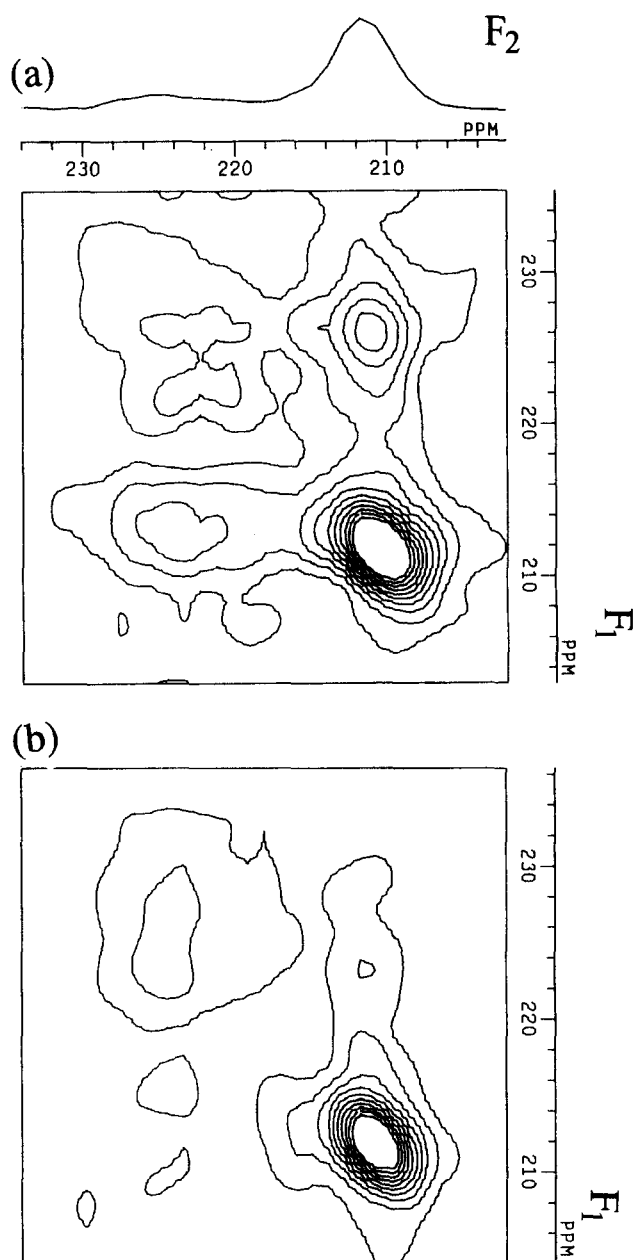


Figure 5 2D exchange spectra of ¹²⁹Xe dissolved in the phase-separated 50/50 PS/PVME blend with a mixing time of 1 s. The blends were heated at 140°C for 30 min (a) and 1200 min (b)

of the cross peak to the diagonal peak is expressed as¹⁰

$$\frac{I_{AB}}{I_{AA}}(\tau_m) = \frac{P_B k [1 - \exp(-2\epsilon\tau_m)]}{(\epsilon - \delta) + (\epsilon + \delta) \exp(-2\epsilon\tau_m)} \quad (6)$$

with

$$\epsilon = [\delta^2 + P_A P_B k^2]^{1/2} \quad (7)$$

and

$$\delta = \frac{1}{2} [k(P_A - P_B) + (R_{1A} - R_{1B})] \quad (8)$$

where A and B denote the PVME-rich and PS-rich phases, respectively, k is the exchange rate of Xe atoms between the two phases, P_x and R_{1x} represent the fractional population and the spin-lattice relaxation rate of ¹²⁹Xe, respectively, in the PVME-rich ($x = A$) or PS-rich ($x = B$) phases, and τ_m represents the mixing time.

The fractional populations for ¹²⁹Xe dissolved into the PVME-rich and PS-rich phases were obtained to be $P_A = 0.52$ and $P_B = 0.48$, respectively, from the 1D ¹²⁹Xe spectrum in Figure 3f, and we adopted the observed relaxation times of 10 and 13 s for R_{1A}^{-1} and R_{1B}^{-1} , respectively, which were obtained for the miscible 20/80 and 90/10 (wt/wt) PS/PVME blends, respectively. Using equations (6)–(8), and the above parameters, we obtained k of 1.8 s^{-1} for the blend heat-treated for 30 min. We assume that the diffusion constant of $1.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for an artificially laminated PS/PVME blend can be used for the phase-separated blend. Then, the average domain size of the separated phases is obtained to be $2.1 \mu\text{m}$ using $\langle L \rangle^2 = 6D/k$. Further, 2D exchange n.m.r. spectra were observed for the phase-separated PS/PVME blends for different heat-treatment periods, and the average domain sizes for the samples were similarly calculated. The obtained domain sizes are $3.0 \mu\text{m}$ for the blend heat-treated for 180 min, and $5.1 \mu\text{m}$ for that for 360 min. For the samples heat-treated for 30 min, 180 min, and 360 min, the 2D spectra were obtained with mixing times of 1 s, 1 s, and 5 s, respectively. In most polymers, dissolved ¹²⁹Xe shows the T_1 value of about 10 s. Therefore, 2D n.m.r. method allows one quantitatively to measure the domain size of the heterogeneous polymer blends below *ca.* $10 \mu\text{m}$.

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