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Effects of Xe Gas on Segmental Motion in a Polymer Blend As Studied by ^{13}C and ^{129}Xe High-Pressure MAS NMR

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ABSTRACT: ^{13}C and ^{129}Xe high-pressure (HP) magic-angle spinning (MAS) NMR was applied to a polystyrene/poly(vinyl methyl ether) (PS/PVME) = 50/50 blend under Xe pressure range of 0.0−4.0 MPa for investigating effects of the dissolved Xe atoms on the segmental motions of the individual component polymers. It is shown that the chemical shift of ^{129}Xe dissolved in the blend moves to the high-frequency side and the line becomes narrow with increasing Xe gas pressure. The ^{129}Xe higher-frequency shift is explained in terms of an increase of the Xe concentration in the blend. The line narrowing suggests that the Xe atomic diffusion is enhanced with increasing Xe concentration in the blend. On the other hand, the ^{13}C line widths under MAS and ^{1}H dipolar decoupling (DD) evidently show that the dissolved Xe atoms enhance the segmental motions of the individual component polymers (plasticization effect) at Xe gas pressures higher than 1.0 MPa. Furthermore, the observed pressure and temperature dependence of the line widths demonstrates that the motional frequency difference between PS and PVME at high pressures is less than that observed at high temperatures. It is concluded that the dissolved Xe atoms not only enhance the segmental motions of PS and PVME but also work to reduce the motional heterogeneity in the blend.

Introduction

Polymer materials have widely been used as membranes to permeate gas molecules selectively or as barrier of gas molecules in packaging. Because of its industrial importance as well as scientific interest, the dissolved gas effect on polymers has been examined by several experimental approaches such as permeation,[1] dilation,[2] sorption,[3] DSC,[4] dielectic,[5] and mechanical measurements.[6] It has been pointed out that the interchain distance is expanded due to the dissolved molecules with increasing gas pressure. This effect is referred to as plasticization effect and manifests itself most typically below 20 MPa[6] in many properties of polymers, for example, as the reduction of the glass transition temperature (T_g).[4−6]

Comparing to many experimental results on macroscopic properties of gas−polymer systems, only a few results are available on microscopic ones.[7−12] In most of these, NMR spectroscopy is applied to study relation between the polymer dynamics and the gas diffusion in a polymer.[8−12] Sefcik et al. showed that the ^{13}C spin−lattice relaxation time in the rotating frame ($T_{1\rho}$) in poly(vinyl chloride) decreases with increasing CO_2 gas pressure (0.0−0.1 MPa).[9] Smith et al. measured ^{2}H line shapes and ^{2}H spin−lattice relaxation times (T_1) of glassy polymers such as polystyrene (PS), poly(carbonate), and poly(methyl methacrylate) at CO_2 pressures of 0.0−4.0 MPa.[10] In these two investigations, it was shown that the local motions of polymers are enhanced, and also the diffusion rate of the dissolved CO_2 molecules increases as CO_2 gas pressure increases. Recently, we developed a simple method for high-pressure ^{13}C magic-angle spinning (HPMAS) NMR[11] and applied it to study molecular motions of the main and side chains of PS under CO_2 gas pressures of 0.0−7.0 MPa.[12] It was indicated that the CO_2 molecules dissolved in PS enhance the segmental motion homogeneously irrespective of local variation of density and conformation.

In this work, the ^{13}C HPMAS NMR experiment is applied to a polymer blend, and it is examined for the first time that how dissolved gas molecules affect the segmental motions of the individual component polymers. As a pressure medium, Xe gas is used, because ^{129}Xe as well as ^{13}C NMR can be used to examine the structural change of polymers under high gas pressures. So far, ^{129}Xe NMR has been applied to investigate free volume of polymers,[13,14] and phase structures[15−17] and domain sizes[18−21] in polymer blends and block copolymers under Xe gas pressures of 0.2−1.8 MPa. In these studies, the plasticization effect of the dissolved Xe atoms has been ignored. Hence, our aims are twofold, namely, (1) to investigate the effect of the dissolved Xe atoms on the segmental motions of the individual component polymers in a miscible blend and (2) to determine the pressure limit below which we can ignore the plasticization effect of the dissolved Xe atoms. A PS/poly(vinyl methyl ether) (PVME) blend is used, because PS and PVME form a miscible blend on a scale of 20−30 Å when they are cast from benzene and toluene solutions,[22−27]and the segmental motions of pure PS and pure PVME as well as PS and PVME in the blend have been well established in a wide temperature range.[28,29] It was pointed out that even though PS/PVME is thermodynamically homogeneous, there exists motional heterogeneity. Hence, it would be interesting to examine how the dissolved Xe atoms affect the motional heterogeneity in the blend.

Experimental Section

PS and PVME were purchased from Aldrich Chem. Co., whose molecular weight are M_w = 900 000 and M_w = 48 000, respectively. The PS/PVME (50/50 wt ratio) blend was prepared by mixing each benzene solution (1% (w/v)) at room temperature, and the solvent was evaporated on a glass plate

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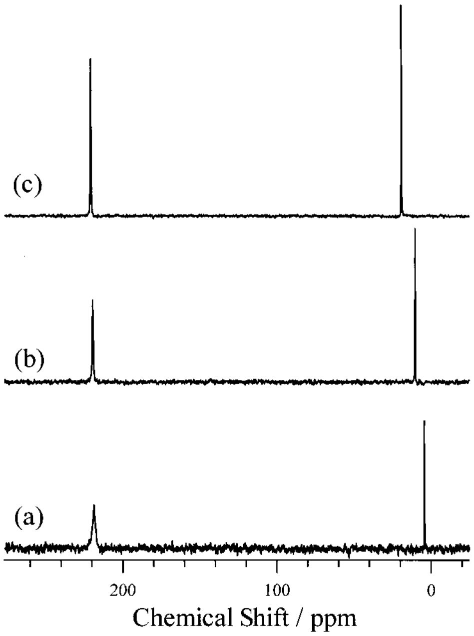

Figure 1. ^{129}Xe HPMAS NMR spectra of the PS/PVME blend with Xe gas pressures of (a) 0.8, (b) 2.0, and (c) 4.0 MPa. The MAS frequency is 4600 ± 10 Hz.

at room temperature for 1 week. The obtained film was further dried under a reduced pressure at 60 °C for 3 days. High-pressure magic-angle spinning (HPMAS)[11] up to a Xe gas pressure of 4.0 MPa was realized as follows: A Pyrex glass tube containing a sample, whose inside and outside diameters are 3.40 and 5.85 mm, respectively, was attached to a vacuum line and degassed. Then, Xe gas was transferred into the glass tube immersed into a liquid N_2 bath, and the tube was sealed off. The sealed glass tube was inserted into a Chemagnetics 7.5 mm MAS spinner with KBr powder. The spinning frequency of MAS was 4600 ± 10 Hz. The NMR experiments were performed using a Chemagnetics CMX-300 NMR spectrometer operating at 300.5 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 83.2 MHz for ^{129}Xe. For the ^{13}C−^{1}H double-resonance experiment, the radio-frequency (rf) field strength was 50 kHz for ^{1}H and ^{13}C. The contact time for cross-polarization (CP) was 0.5 ms with the repetition time of 4 s. The ^{13}C chemical shifts were calibrated by taking the methine carbon of adamantane (29.5 ppm) as an external reference. For ^{129}Xe NMR, the rf strength for ^{129}Xe was 50 kHz. ^{129}Xe NMR spectra were obtained in terms of a single 30° pulse with a repetition time of 1 s. The chemical shift of ^{129}Xe in the blend was calibrated with respect to that of free Xe gas extrapolated to 0.0 Pa as an external reference. Xe gas pressure was calibrated from the chemical shift of free ^{129}Xe gas in the sample.[30] It was shown that the line width of ^{129}Xe absorbed in NaA zeolite is reduced appreciably by applying MAS.[31] Therefore, we performed the ^{129}Xe NMR experiment under MAS.

Results and Discussion

Figure 1 shows ^{129}Xe MAS NMR spectra of the PS/PVME blend at some Xe gas pressures. The sharp peaks around 5−20 and 220 ppm are assigned to ^{129}Xe in free gas and ^{129}Xe in the blend, respectively. The ^{129}Xe dissolved in the blend shows a single peak whose chemical shift is an approximate average of those dissolved in pure PS and pure PVME,[21] indicating that Xe atoms dissolve in both the PS and PVME domains, and fast exchange between them occurs. The ^{129}Xe chemical shift in the blend moves to the high-frequency side with increasing Xe gas pressure (Figure 2a). It has been shown that an increase of the Xe−Xe collision times induces the high-frequency shift in free gas[30] and porous materials.[32] Hence, the observed high-frequency shift indicates that the ^{129}Xe concentration in the blend increases with increasing Xe gas pressure.

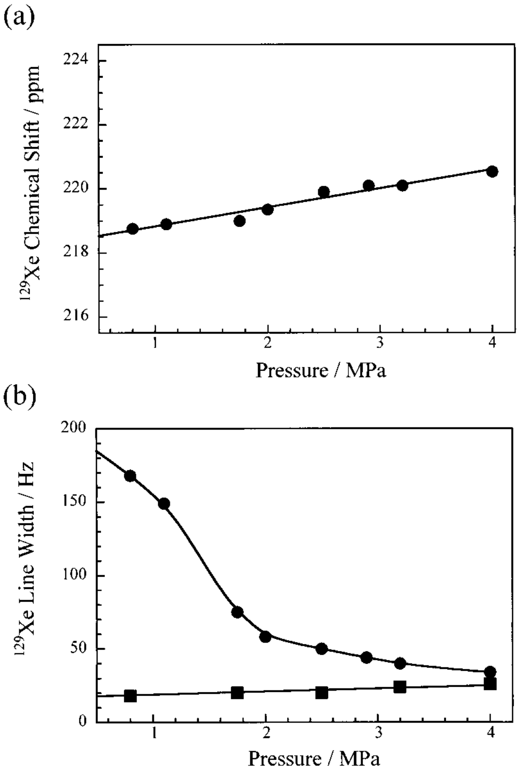

Figure 2. Pressure dependence of the obtained chemical shifts (a) and the line widths (b) of ^{129}Xe dissolved in the PS/PVME blend (●) and the free gas peak (■). The solid lines are only a guide for the eye.

The ^{129}Xe line width was obtained by fitting each single peak to a single Lorentzian line shape. It was found that the ^{129}Xe line width in free gas only slightly depends on pressure, while that in the blend markedly decreases with increasing Xe pressure above 1.0 MPa as shown in Figure 2b. At 4.0 MPa, the ^{129}Xe line width in the blend reaches 38 Hz, which is close to that of free gas (25 Hz). The reduced line width is due to an increase of the atomic diffusion among the various environments within the blend. It is, thus, suggested that the Xe atomic diffusion in the blend becomes fast as Xe gas pressure increases, and the diffusion rate at 4.0 MPa is almost similar to that in free gas.

The plasticization effect of the dissolved Xe atoms on the segmental motions of the component polymers is investigated through the resolved ^{13}C line widths under ^{1}H dipolar decoupling (DD) and MAS. The ^{13}C line broadening occurs when the motional frequency matches with a ^{1}H DD[33,34] field strength in hertz or a MAS frequency;[35] this phenomenon has been used to examine the segmental motion related to T_g in PS/PVME.[28,29] We made variable-temperature measurements to compare with the pressure dependence results. Figure 3a−c shows ^{13}C CPMAS spectra of the PS/PVME blend at some temperatures. The nonprotonated and protonated aromatic ^{13}C signals of PS are observed at 127 and 145 ppm, respectively. The methine and methoxy ^{13}C signals of PVME appear at 76 and 56 ppm, respectively. The peak at 40 ppm is a superposition of the methine and methylene ^{13}C signals of PS and the methylene one of PVME. With increasing temperature, the line widths of the PS signals broaden, while that of the methine

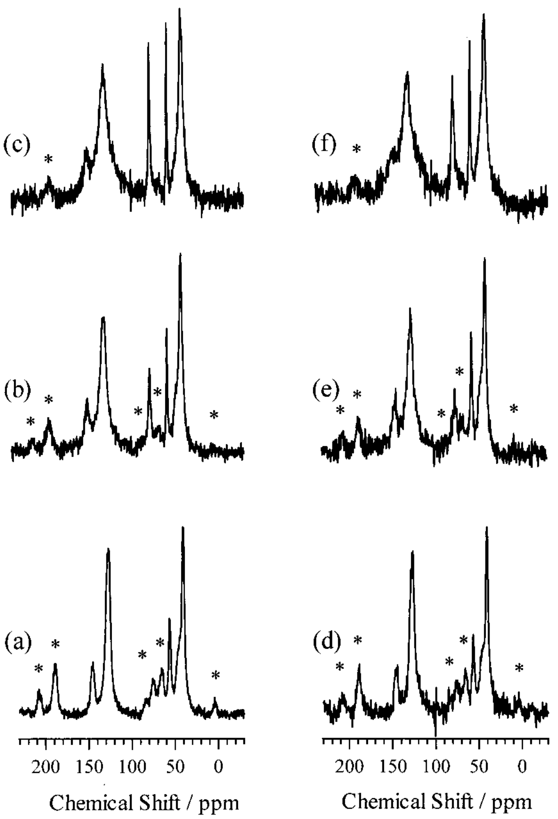

Figure 3. Temperature (a–c) and Xe gas pressure (d–f) dependence of ^{13}C CP and HPMAS NMR spectra of the PS/PVME blend under MAS frequency of 4.6 kHz: (a) 29, (b) 63, and (c) 91 °C; (d) 0.0, (e) 2.0, and (f) 4.0 MPa. The pressure dependence was obtained at 29 °C and temperature dependence at atmospheric pressure. The asterisks denote spinning sidebands.

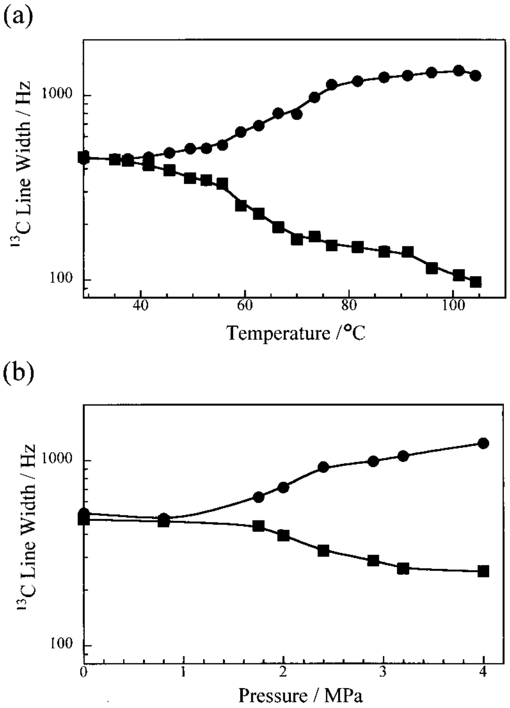

Figure 4. Temperature (a) and Xe gas pressure dependence (b) of the ^{13}C DDMAS line width. (●) and (■) represent the ^{13}C line width of the protonated aromatic carbon for PS and that of the methine carbon for PVME, respectively. The solid lines are only a guide for the eye.

signal of PVME becomes narrow. The apparent ^{13}C line width for the protonated aromatic carbons of PS and that of the methine carbon of PVME are plotted in Figure 4a. The observed line broadening of PS has been ascribed to the matching of the ^{1}H DD field strength in hertz and the segmental motion of PS.[28,29] On the other hand, since the motional frequency of PVME is much higher than the ^{1}H DD field strength in hertz and the MAS frequency, motional narrowing occurs at high temperatures above room temperature.[28,29]

Figure 3d–f shows ^{13}C HPMAS NMR spectra of the PS/PVME blend observed under some Xe gas pressures at room temperature. The overall line-shape change, which is brought about by the dissolved Xe atoms, is similar to those by increasing temperature, showing that the dissolved Xe atoms enhance both the segmental motions of PS and PVME (plasticization effect). The pressure dependence of the apparent ^{13}C line width for the protonated aromatic carbons of PS and that of the methine one of PVME are plotted in Figure 4b. There is no appreciable line-width change below 1.0 MPa, and, the line-width change is apparent above 1.0 MPa, indicating that the dissolved Xe atoms plasticize the component polymers in the blend above 1.0 MPa. The observed ^{129}Xe line width reduction above 1.0 MPa supports this. These results lead us to suggest that ^{129}Xe NMR should be applied at pressures less than 1.0 MPa to exclude the plasticization effect.

It is noted from Figure 4 that the amount of line broadening for the PS aromatic carbons under high gas pressures is similar to that observed under high temperatures, while the line narrowing for the PVME methine carbon at high pressures is much smaller than that observed at high temperatures. For example, the line widths of PS and PVME are 1250 and 140 Hz at 91 °C, respectively (Figure 3c), while those of PS and PVME are 1240 and 250 Hz at 4.0 MPa, respectively (Figure 3f). These results show that the segmental motion of PS is more effectively enhanced by the dissolved Xe atoms as compared to that of PVME. One possible explanation is a plasticization effect acting selectively to PS in the blend. This is, however, less likely since it requires that the Xe atoms preferably dissolve in the PS domain. As discussed above, the Xe atoms dissolve not only in the PS domain but also in the PVME domain, and the fast Xe atomic diffusion between them occurs. Furthermore, Tomaselli et al. showed that the solubility of the Xe atoms in the PS domain is similar to that in the PVME domain in an artificially laminated PS/PVME blend.[19] These results negate selective absorption of the Xe atoms in the PS domain. The observed difference between thermal and Xe pressure effects on the segmental motions of the component polymers indicates that motional frequency difference between PS and PVME becomes smaller at high Xe gas pressures than that at high temperatures. We postulate here that the Xe atomic diffusion between the PS and PVME domains works to reduce the motional heterogeneity of the component polymers. The Xe atoms dissolved in the blend act as media which translate mobility of component polymers with each other.

To conclude, we demonstrated that the dissolved Xe atoms have two effects on the component polymers in the miscible PS/PVME blend: the dissolved Xe atoms (1) enhance both the segmental motions of PS and PVME (plasticization effect) and (2) reduce the motional heterogeneity between the component polymers. Furthermore, it was found that ^{129}Xe NMR spectroscopy should be applied at pressures below 1.0 MPa to probe the microstructure of the solid polymers without plasticizing polymers.

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