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ORIGINAL ARTICLE

Characterization of the microvoids of a tetramethyl polycarbonate/polystyrene blend system using Xe sorption measurements and ^{129}Xe NMR spectroscopy

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Relationships among the ^{129}Xe NMR chemical shift, Xe sorption properties and density in the miscible tetramethyl bisphenol A polycarbonate (TMPC)/polystyrene (PS) polymer blend system were investigated to estimate the variation of microvoids resulting from blending. The Xe sorption properties of the TMPC/PS blend system indicated that blending reduced the amount of microvoids. The ^{129}Xe NMR chemical shift of the ^{129}Xe in the blend showed a nonlinear low-field shift with an increasing amount of total Xe sorbed for all the sample films. The estimation of microvoids in this polymer blend system using ^{129}Xe NMR spectroscopy has been coincident with the variation in the density and Xe sorption properties.

INTRODUCTION

The microvoids in glassy polymers are part of the interchain microspaces in the frozen segmental motions of the main chains.[1–3] The microvoids significantly affect the gas permeation, diffusion and sorption properties of glassy polymers.[4–6] In other words, the gas sorption property of a glassy polymer can provide information about the microvoids. Generally, the gas sorption isotherm of a glassy polymer can be interpreted using the dual-mode sorption model,[1–7] which is represented by the following equation,

$$C = C_D + C_H = k_D p + \frac{C_H' bp}{1 + bp} \quad (1)$$

where C is the equilibrium sorption amount at pressure p. The subscripts D (<u>D</u>issolved) and H (<u>H</u>ole) correspond to the Henry and Langmuir sites, respectively. C_D and C_H are concentrations due to Henry's law and the Langmuir mode contributions, respectively. k_D is Henry's law solubility coefficient, b is an affinity constant of the Langmuir site and C_H' is the hole saturation constant in the Langmuir sorption mode. The value of C_H' corresponds to the unrelaxed volume (so-called 'excess free volume') of a glassy polymer. This volume is defined as a gap between the specific and hypothetical equilibrium super-cooled liquid volumes. The unrelaxed volume increases with the increasing difference between the observation temperature and the glass-transition temperature and is related to the total amount of microvoids. Therefore, one can obtain essential information about the unrelaxed volume and microvoids from the C_H and C_H' parameters.

Recently, we demonstrated that ^{129}Xe NMR spectroscopy is a powerful technique for characterizing the higher-ordered structures of polymer solids.[8–15] As the Xe atom has a very large polarizability, the ^{129}Xe NMR signal is sensitive and easily influenced by its environment; specifically, the induced ^{129}Xe NMR chemical shift is strongly altered by the Xe electron density. The NMR chemical shifts for glassy polymers exhibited a nonlinear low-field shift with an increasing amount of Xe sorption because of the fast exchange of Xe between the Henry and Langmuir sites; therefore, we calculated the NMR chemical shifts for each site using the dual-mode sorption parameters. Consequently, we were able to evaluate the mean size of the microvoids in glassy polymers.[9] Our reported data for polystyrene (PS), bisphenol A polycarbonate (PC), tetramethyl bisphenol A PC (TMPC) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were similar to data from a related reported technique, positron annihilation lifetime spectroscopy, which suggests that ^{129}Xe NMR spectroscopy is a good method for characterizing microvoids in glassy polymers. Most recently, we have reported the Xe sorption properties and ^{129}Xe NMR spectra of PPO measured at various temperatures.[10] By analyzing the ^{129}Xe NMR chemical shift, it was observed that the mean diameter of the microvoids in PPO increases linearly with decreasing temperature, and the extrapolated value at the glass-transition temperature was close to 4.4 Å, which is the diameter of a Xe atom. Furthermore, the characteristic cavity in a crystalline region of poly(4-methyl-1-pentene) (PMP) was investigated using gas permeation and ^{129}Xe NMR measurements of PMP membranes with various degrees of crystallinity.[11] The measured size of the cavity in the PMP crystal was consistent with the results from not only

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crystallographic analysis but also gas permeation and Xe sorption measurements. The size of the molecular cavity in the crystalline syndiotactic PS has also been characterized using [129]Xe NMR spectroscopy.[12] In addition, the density of the side chain regions in a low-density liquid-crystalline polyester with n-alkyl side chains has been estimated.[13] We have also demonstrated that the line width of the [129]Xe NMR signal of the [129]Xe in this polyester corresponds to its diffusivity.

To establish the microvoid size determination using [129]Xe NMR spectroscopy, the accumulation of experimental data is important. Actually, for a miscible polymer blend system, PPO/PS blends, it has been successfully concluded that the contraction of microvoids occurs by blending, based on the Xe sorption properties and the [129]Xe NMR chemical shift analysis.[14,15] In this study, a miscible polymer blend system, TMPC/PS blends, was analyzed. The TMPC/ PS blend system is a well-known miscible blend, and many studies on this system have been reported elsewhere.[16–20] Using these blends, it becomes easy to control the contents of microvoids, as in the case of PPO/PS blends. However, because the glass-transition temperature of TMPC is lower than that of PPO, the unrelaxed volume and the total amount of microvoids in the TMPC/PS blends are smaller than those of the PPO/PS blends. If the results obtained are similar to those obtained with PPO/PS blends despite the relatively small size of the microvoids in TMPC/PS blends, this study will be a good indicator of the high reliability of microvoid size determination using [129]Xe NMR spectroscopy. Therefore, the relationship between variations of microvoids and Xe sorption properties for TMPC/PS blends were investigated using Xe sorption and [129]Xe NMR measurements.

EXPERIMENTAL PROCEDURE

Sample films (TMPC/PS ratio = 0/100, 20/80, 50/50, 80/20 and 100/0) were prepared using the solution-casting method with chloroform as a co-solvent for TMPC and PS. The film thickness was $\sim$50–100 μm. Each film was annealed above the glass-transition temperature (T_g) for 3 h and then cooled slowly. The film density was determined using the flotation method with a NaBr aqueous solution at 25 °C.

Xe sorption measurements were performed using a gravimetric sorption apparatus with an electromicrobalance (CAHN 2000, Cahn Instruments, Inc., Cerritos, CA, USA) at 25 °C. After the sorption apparatus containing the film was sufficiently evacuated, the desired pressure of Xe was introduced into the apparatus. The amount of Xe sorbed into the film was determined after correcting for the buoyancy. The T_g of the sample films were measured using a differential scanning calorimeter (DSC-7, Perkin-Elmer Co., Waltham, MA, USA) at a heating rate of 10 °C min^{-1}.

The cut and weighed film samples were packed into a 10-mmΦ Pyrex NMR sample tube with thick walls (type 513-7 JYH-7, Wilmad-LabGlass, Vineland, NJ, USA) and degassed in vacuo for at least 24 h. A desired amount of Xe (with a natural abundance of [129]Xe) was introduced into the NMR tube with the aid of liquid nitrogen, and then the tube was sealed with a Teflon valve. After a sufficient amount of time required to achieve an equilibrium sorption state under isothermal conditions (at 25 °C) had elapsed, the NMR experiment was performed. The internal pressure of this sealed NMR tube was determined by subtracting the amount of Xe sorbed into a sample from the total amount of Xe in the tube. The sorption amount at any pressure can be exactly predicted from the sorption isotherm data, and the total amount of Xe in the tube is easily obtained by weighing. The [129]Xe NMR spectrum was recorded on an INOVA400 NMR spectrometer (Agilent Technologies, Ltd., Santa Clara, CA, USA) at 110 MHz and 25 °C using the single pulse method with a 45° pulse. The repetition time was set to be 10 s, and the accumulation times were from 500 to 3000 to obtain a good signal to noise ratio. All of the [129]Xe NMR chemical shifts were referenced to an external standard of gaseous [129]Xe at zero pressure.

RESULTS AND DISCUSSION

The T_g and density values are summarized in Table 1. In the DSC thermograms from all of the blended sample films, only one heat flow

Table 1 Glass-transition temperature (T_g) and density of TMPC/PS blend system at 25 °C

TMPC/PS	T_g (°C)[a]	Density (g cm^{-3})[b]
0/100	108	1.047
20/80	118	1.058
50/50	132	1.072
80/20	165	1.081
100/0	196	1.086

[a]Determined by DSC.
[b]Determined by a flotation method with NaBr aqueous solution.
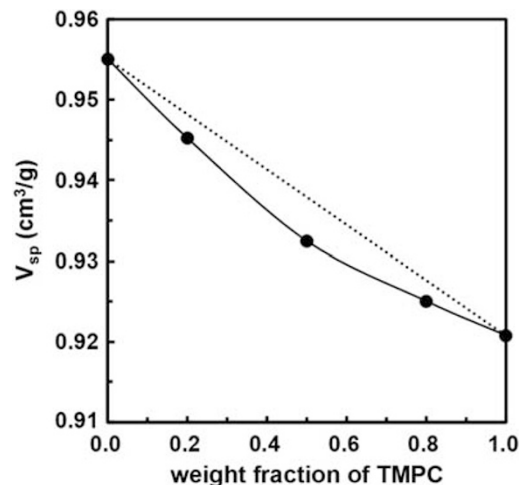
Figure 1 Specific volume (V_{sp}) plotted against the weight fraction of TMPC in the TMPC/PS blend system at 25 °C.

jump was observed. Therefore, all of the blended films prepared in this study are miscible, and the observed T_g values were similar compared with those reported in the literature.[17] It was also confirmed that all of the sample films were in a glassy state at 25 °C. Figure 1 shows the dependence of the specific volume (V_{sp}) on the composition of the films, which was determined from the density measurements. The V_{sp} of the blend is lower than that expected from the simple additive rule of the weight fraction of a pure polymer in a blend and the specific volumes of pure polymers, which is presented as a dotted straight line in Figure 1. Therefore, it can be said that volume contraction results from blending in the TMPC/PS blend system.

The Xe sorption isotherms are presented in Figure 2. It is clear that these isotherms are concaved toward the pressure axis. These isotherms could also be explained using the dual-mode sorption model (see equation (1)), and the results of curve fitting are presented in Figure 2 as solid lines. The dual-sorption parameters were determined using the nonlinear least-squares method, and are summarized in Table 2. The composition dependence of b was not confirmed because the b values of pure polymers are similar to each other. However, the k_D and C_H' values appeared to show a systematic variation with the polymer ratio. C_H' is a good indicator of microvoids in glassy polymers. Figure 3 shows the plot of C_H' against the volume fraction of TMPC in the blend system. It appears that the obtained C_H' value is smaller than that expected from the simple additive rule for each blend sample, whereas k_D generally follows the exponential additive rule. This fact indicates that blending has
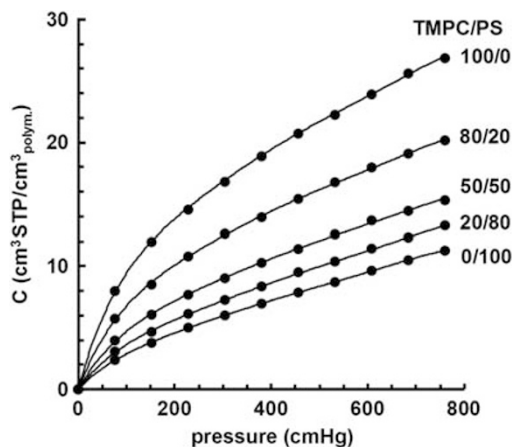
Figure 2 Sorption isotherms of Xe in the TMPC/PS blend system at 25 °C.

Table 2 Dual-mode sorption parameters of Xe of TMPC/PS blend system at 25 °C

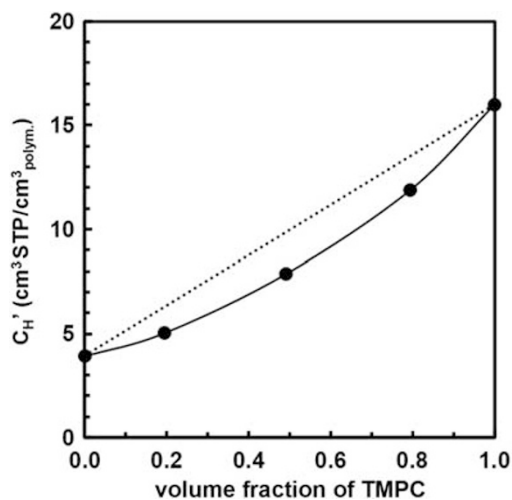| TMPC/PS	$k_D \times 10^2$ ($cm^3(STP)\,cm^{-3}_{polym}.cm\,Hg^{-1}$)	C_H' ($cm^3(STP)\,cm^{-3}_{polym}.$)	$b \times 10^3$ ($cm\,Hg^{-1}$)
0/100	1.04	3.93	8.83
20/80	1.16	5.04	9.57
50/50	1.14	7.87	8.23
80/20	1.31	11.88	8.40
100/0	1.71	15.99	9.25

Figure 3 Langmuir saturation constant (C_H') of Xe plotted against the volume fraction of TMPC in the TMPC/PS blend system at 25 °C.

induced a reduction in the amount of microvoids in the TMPC/PS blend system, whereas the solubility behavior was not remarkably changed by blending. These findings are consistent with the density measurement results.

As an example, Figure 4 shows the [129]Xe NMR spectra of [129]Xe in a TMPC/PS (= 80/20) blend film under various pressures of Xe at 25 °C. It is obvious that the NMR peak shifts to lower magnetic fields with increasing pressures of Xe, and the peak shape is almost
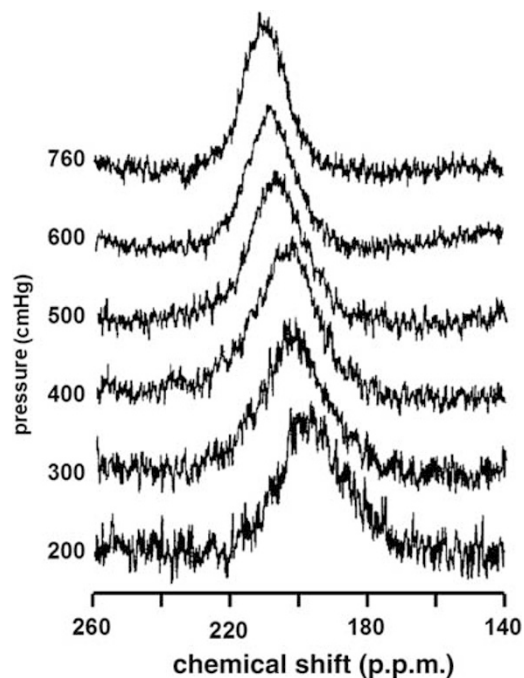

Figure 4 [129]Xe NMR spectra of the [129]Xe in a TMPC/PS (= 80/20) blend film under various pressures of Xe at 25 °C.

symmetric. Similar results were obtained for other samples. These downfield shifts are caused by increasing interactions among the Xe atoms.[21,22] Additionally, these symmetric peaks indicate that Xe atoms, which are dissolved in the samples, diffuse fast and then rapidly exchange between the Henry and Langmuir sorption sites on the NMR time scale.

Jameson *et al.*[23] reported that the [129]Xe NMR chemical shift of gaseous pure Xe linearly shifts to low field with increasing densities in amagat units (1 amagat is the density of a gas under STP conditions) in the low pressure region until ∼100 amagat. Furthermore, Fraissard and collegues[21,22] reported that the chemical shifts of [129]Xe in zeolites without strong charges also shift linearly with increasing amounts of Xe sorbed in them. The pressure dependence of the [129]Xe NMR chemical shift can be interpreted by the interactions between Xe atoms. The influence of this interaction is basically expressed by the time-averaged distance between them, and this distance can be replaced by frequencies of collisions among them. As a result, the chemical shift shows a linear relationship with the density of Xe, because the probability of three or more body collisions at considerably high densities is ignored. However, the observed [129]Xe NMR chemical shifts of all of the sample films prepared in this study exhibit a nonlinear low-field shift with increasing Xe density, that is, the total sorption amount, *C*. As the total sorption amount (*C*) for glassy polymers is composed of C_D and C_H (see equation (1)), it is necessary to individually evaluate the dependencies of C_D and C_H on the NMR chemical shift of [129]Xe. Assuming that there is a fast exchange of Xe atoms between the Henry and Langmuir sites, the observed NMR chemical shift (δ_{obs}) appears as a single peak at the resonant position described by

$$\delta_{obs} = \phi_D \delta_D + \phi_H \delta_H \qquad (2)$$

where ϕ_D and ϕ_H are the fractional concentrations of Xe for the Henry and Langmuir sites and δ_D and δ_H are the NMR chemical

shifts for the Henry and Langmuir sites, respectively. The definitions of ϕ_D and ϕ_H are:

$$\phi_D + \phi_H = \frac{C_D}{C} + \frac{C_H}{C} = 1 \tag{3}$$

These parameters are functions of pressure and can be calculated using the dual-mode sorption parameters (Table 2); therefore, ϕ_H is larger than ϕ_D in the low pressure region, whereas the opposite relationship is observed in the high pressure region. Under the assumption of a linear low-field shift of Xe sorption amount, δ_D and δ_H are individually defined by the following equations,

$$\delta_D = \delta(Xe)_D + \delta(S)_D = A_D C_D + \delta(S)_D \tag{4}$$

$$\delta_H = \delta(Xe)_H + \delta(S)_H = A_H C_H + \delta(S)_H \tag{5}$$

where $\delta(Xe)_i$ and $\delta(S)_i$ are the NMR chemical shifts due to the interactions between the Xe atom and the inner wall of the pore, namely, the polymer sample, and between Xe atoms, A_i is a constant proportional to the concentration of Xe and C_i is the amount of Xe sorbed in site i. Using equations (2)–(5), a set of δ_{obs} values at observed pressures were reproduced by substituting suitable values for four unknown parameters, A_D, $\delta(S)_D$, A_H and $\delta(S)_H$. These four parameters were determined when the sum of squares of deviation from the experimental data, $\Sigma[(\delta_{obs}^{calc} - \delta_{obs}^{exp})^2]$, reaches a minimum in the variation steps considered by experimental error, which is defined as a digital resolution of ~ 0.1 p.p.m. As an example, the results from the pure PS film are plotted against pressure in Figure 5. The relationships between δ_D–p and δ_H–p are linear and concave, respectively, which is in agreement with the results of the pressure dependences of C_D and C_H. However, the calculated values of the observed chemical shift, δ_{obs}^{calc}, exhibit good agreement with the corresponding experimental data, δ_{obs}^{exp}. From these results, the NMR chemical shift of ^{129}Xe sorbed in a glassy polymer apparently exhibits a nonlinear low-field shift with respect to the total sorption amount, C. Similar results were obtained for the other samples. The parameters in equations (4) and (5) are summarized in Table 3. This result proves that A_H is larger than A_D. This finding indicates that the dependence of the NMR chemical shift of ^{129}Xe on the Xe density in the Langmuir site is larger than that in the Henry site. In practice, for rubbery polymers that contain 'only' Henry sites, the NMR chemical shift of sorbed ^{129}Xe rarely presents a dependency on the Xe density (data not shown), which indicates the relatively large inhibition of the interaction between Xe atoms by the mobile polymer chains. In a similar manner, for a glassy polymer, it can be considered that the local molecular motions of the main chain and/or side chains may provide the Henry-mode sorption site and inhibit the Xe–Xe interaction. As there are no inhibitory factors in the Langmuir-mode sorption site, that is, microvoids, A_H becomes larger than A_D. In other words, the contribution of the Xe–polymer interaction (which is the frequencies of collision between Xe and polymer) to the ^{129}Xe NMR chemical shift at the Henry site is relatively larger than that at the Langmuir site. Therefore, the $\delta(S)_D$ values become larger than those of $\delta(S)_H$, and the polymer composition dependence of $\delta(S)_D$ is lower than that of $\delta(S)_H$.

It can be said that the NMR chemical shift extrapolated to $C_H = 0$ for the Langmuir site, that is, $\delta(S)_H$, reflects the mean size of the hole correlated with the microvoids in the glassy polymer. According to Fraissard and collegues[21,22], when the NMR chemical shift of ^{129}Xe in a micropore of dense materials, such as zeolites, is determined only by the interaction with the walls, the mean free path (λ) is linked to this chemical shift, $\delta(S)$. Therefore, $\delta(S)$ can be estimated by the mean size
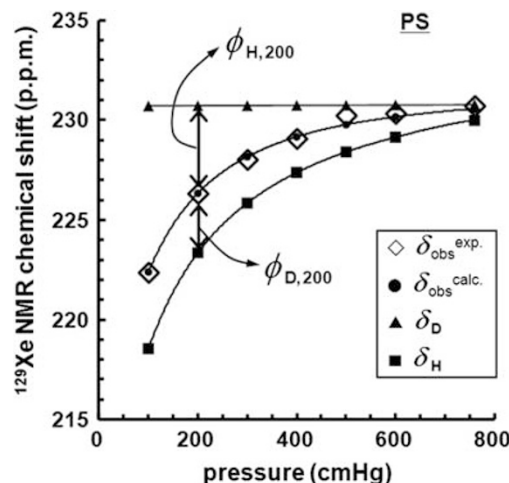

Figure 5 ^{129}Xe NMR chemical shifts of the ^{129}Xe in a PS film plotted against the pressure of Xe at 25 °C.

Table 3 Parameters of ^{129}Xe NMR chemical shifts and d_s of TMPC/PS blend system at 25 °C

|	Henry site		Langmuir site		
	A_D		A_H		
	(p.p.m. $cm^3_{polym.}$	$\delta(S)_D$	(p.p.m. $cm^3_{polym.}$	$\delta(S)_H$	d_s
TMPC/PS	cm^{-3} (STP))	(p.p.m.)	cm^{-3} (STP))	(p.p.m.)	(Å)
0/100	0.01	233.5	5.5	206.2	5.13
20/80	0.15	231.6	3.5	201.1	5.25
50/50	0.16	224.6	2.6	192.1	5.48
80/20	0.53	222.2	2.0	178.4	5.88
100/0	0.54	217.5	1.5	169.2	6.18

of the hole using the following relationship,

$$\delta(S) = 243 \times \frac{2.054}{2.054 + \lambda} \tag{6}$$

where λ is a function of both the shape and dimension of the hole. $\delta(S)$ can be experimentally obtained by linear extrapolating to the zero pressure of Xe using the pressure dependence data of chemical shifts. In the case of glassy polymers, the mean size of the microvoids can be estimated by $\delta(S)_H$ rather than $\delta(S)$. The individual shape of the microvoids is not a complete sphere, but the both shapes and directions of the microvoids are random even if the shape is anisotropic, such as an ellipsoidal hole. In addition, Xe atoms experience many microvoids for NMR observation because of their state in diffusion. Therefore, the statistically averaged shape of the considerable number of microvoids from viewpoints of both of space and time can be regarded as a sphere. When the shape of the hole is spherical, λ is derived by

$$\lambda = \frac{(d_s - d_{Xe})}{2} \tag{7}$$

where d_s is the diameter of the sphere and d_{Xe} is the van der Waals diameter of the Xe atom (4.4 Å). The calculated values of d_s are listed in Table 3. The order of the d_s value is consistent with those of T_g and C_H' (see Tables 1 and 2). Here, the mean volume of individual microvoids, v (cm^3), is calculated from d_s. Figure 6 shows the plot of v against the volume fraction of TMPC in the blend system. The v
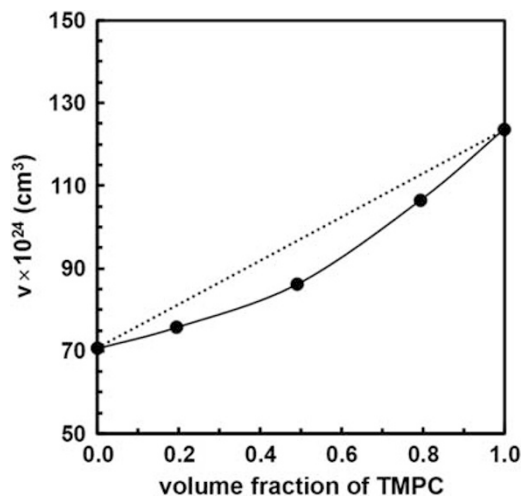
Figure 6 The mean volume of individual microvoids (v) plotted against the volume fraction of TMPC in the TMPC/PS blend system at 25 °C.

values for the blends are smaller than those predicted by a simple additive rule, which is also the case for the C_H' values (see Figure 3). This finding indicates that there is a decrease in the total amount of microvoids; in other words, C_H' is attributed to contraction of the volume of individual microvoids.

CONCLUSIONS

In this study, relationships between variations of microvoids and gas sorption properties for a miscible TMPC/PS blend system were investigated using Xe sorption and ^{129}Xe NMR measurements. The C_H' values for the blends were smaller than those expected from a simple additive rule because of the decrease in the total amount of microvoids resulting from blending. The ^{129}Xe NMR spectra of ^{129}Xe in the blends obtained at various pressures exhibited a nonlinear low-field shift because of a fast exchange of Xe between the Henry and Langmuir sites. This behavior is one of the characteristic features of glassy polymers compared to many cases of rubbery polymers and zeolites. From the analysis of $\delta(S)_H$, which is the NMR chemical shift that reflects the mean size of the microvoids, it was demonstrated that the mean volume of the individual microvoids varied nonlinearly from 71 Å^3 for PS to 124 Å^3 for TMPC with respect to the volume fraction of TMPC in the blend, which indicates a blending-induced contraction of the microvoids. For TMPC/PS blends, it is concluded that the contraction of microvoids occurs by blending and affects the gas sorption properties.

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