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ORIGINAL ARTICLE

Temperature dependence of the mean size of polyphenyleneoxide microvoids, as studied by Xe sorption and ^{129}Xe NMR chemical shift analyses

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Both the Xe sorption isotherms and ^{129}Xe NMR spectra of poly(2,6-dimethyl-1,4-phenylene oxide), PPO, were obtained across a temperature range of –55 °C to +80 °C to investigate the temperature dependence of the gas sorption and the unrelaxed volume of PPO. All of the obtained sorption isotherms were analyzed based on the dual-mode sorption model, and the Langmuir saturation constant, C_H', which corresponds to the unrelaxed volume, was determined by curve fitting. The values of C_H' increased linearly with decreasing temperature, and the obtained temperature was almost identical to the glass transition temperature, T_g, of PPO when the C_H' value was extrapolated to 0. The ^{129}Xe NMR chemical shift of ^{129}Xe in the PPO showed a nonlinear, low-field shift with increasing Xe pressure at temperatures below the T_g. The mean volumes of individual microvoids were determined at each temperature based on the ^{129}Xe NMR chemical shift analysis, assuming a fast exchange of the Xe atoms between the Henry and Langmuir sorption sites. The temperature dependence of the individual microvoid volumes was similar to that of C_H'.

INTRODUCTION

Determining the higher order structures of glassy polymers in detail is notably important, not for only academic purposes but for solid polymeric material applications in many fields. Microvoids form in dense polymer matrices as interspaces between molecular chains, when the polymer becomes glassy and the segmental mobility of the main chains is frozen. Figure 1 schematically represents both a specific volume–temperature, V–T, and occupied volume curve typical of an amorphous polymer. The total amount of microvoids corresponds to the unrelaxed volume, as defined in Figure 1. The unrelaxed volume in the glassy state increases with decreasing temperature until the temperature, T_2, reaches the intersection between the hypothetical equilibrium supercooled liquid- and occupied volume–temperature curves. Temperature T_2 is defined in thermodynamics as the configuration where entropy becomes zero (that is, it is the temperature where the smallest number of possible configurations form). Generally, evaluating the gas sorption properties of a glassy polymer provides information about the unrelaxed volume and microvoids.

The free volume of polymers determined by their gas sorption properties has also been discussed by many researchers.[1–5] The mechanisms of gas sorption below and above T_g are different, which reflects the difference in the microscopic structure of the respective thermodynamic state, namely, the non-equilibrium nature of the glassy state and the equilibrium liquid-like nature of the rubbery state. The sorption isotherms of gases to glassy polymers are interpreted using the dual-mode sorption model, which is based on the assumption that the gas is sorbed via both Henry and Langmuir sorption mechanisms.[6] The former sorption mechanism behaves similarly to gas sorption to rubbery polymers, whereas in the latter mechanism, the gas sorbs in microvoids that exist in the glassy polymer, and saturation only occurs at high pressures. Therefore, it is possible to understand the behavior of the unrelaxed volume by examining the Langmuir sorption mechanism. The presence of unrelaxed volume in glassy polymers has an important role in the gas sorption of microvoids.

^{129}Xe NMR spectroscopy is a powerful technique for measuring the micropore size of a material.[7–16] The ^{129}Xe NMR signal is sensitively influenced by its environment, and the induced ^{129}Xe NMR chemical shifts strongly correlate to the microvoid size because certain interactions with the host system disturb the Xe electron density. It has been reported by our research group that the mean microvoid size in glassy polymers can be determined based on the Xe density dependence of the ^{129}Xe NMR chemical shift.[17–23] Therefore, the behavior of the unrelaxed volume can be studied via the microvoid size by investigating the ^{129}Xe NMR spectra below the T_g.

To elucidate the thermal behavior of the unrelaxed volume in poly(2,6-dimethyl1,4-phenylene oxide), PPO, the Xe sorption isotherms of PPO were measured using a quartz crystal microbalance[24,25] across the temperature range of –55 °C to +80 °C.

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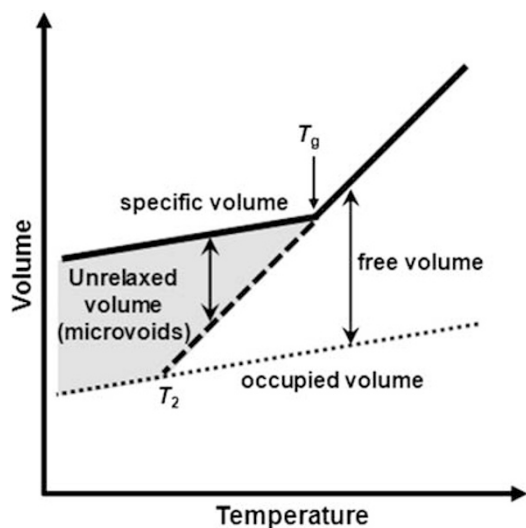E-mail: yoshimizu.hiroaki@nitech.ac.jp

Figure 1 Schematic representation of typical specific volume–temperature (bold line) and occupied volume (dotted line) curves for an amorphous polymer. The free volume is defined as the difference between the specific and occupied volumes, and, in the glassy state, includes the unrelaxed volume, which is defined as the gap between the specific and hypothetical equilibrium supercooled liquid (dashed line) volumes. The temperature T_2 is defined as the intersection between the volumes of a hypothetical equilibrium supercooled liquid- and the occupied volume–temperature curves.

Furthermore, we investigated the relationship between the ^{129}Xe NMR chemical shift and Xe sorption properties across a similar temperature range and attempted to characterize the PPO microvoids.

EXPERIMENTAL PROCEDURE

PPO (Japan GE plastics Co., Osaka, Japan; $T_g = 216\,^{\circ}$C) was used after a standard purification as the glassy polymer in this study. Xe purchased from Nagoya Kosan Co. (Nagoya, Aichi, Japan) ($>99.9\%$ purity) was used for the gas sorption. A thin film was prepared by casting a chloroform solution of PPO onto the quartz crystal oscillator. This oscillator was annealed at $220\,^{\circ}$C for $3\,$h, to remove a portion of the residual tension caused by casting. This annealing condition was nearly identical to that in the investigations of PPO by dilatometry reported elsewhere.[26,27] The PPO-coated quartz oscillator was subsequently installed inside a home-made quartz crystal microbalance cell with a metallic seal. After drying at approximately $10^{-3}\,$mm Hg, Xe was introduced into the cell at various pressures. The resonant frequency was measured by a frequency counter. The frequency change because of gas sorption was converted into a weight variation. The sorption cell was immersed in methanol as a refrigerant, and the temperature variation inside the system was controlled to at least $\pm 1\,^{\circ}$C. ^{129}Xe NMR measurements were performed using the following steps. Approximately, $1\,$g of a film sample was packed into a 10-mmϕ Pyrex NMR tube with thick walls, and the desired pressure of Xe (with the natural abundance of ^{129}Xe) was subsequently introduced into the NMR tube. This tube joined a long stainless tube attached to a home-made apparatus equipped with a gas supplier and pressure gauges. The internal pressure was monitored in real time by this apparatus. After a sufficient time to reach sorption equilibrium, the ^{129}Xe NMR spectra were recorded via a single pulse method at $110\,$MHz on an INOVA 400 plus NMR spectrometer (Agilent Technologies, Ltd., Santa Clara, CA, USA) equipped with a temperature controller. All of the ^{129}Xe NMR chemical shifts were referenced to an external standard of zero-pressure ^{129}Xe gas at each temperature.[28]

RESULTS AND DISCUSSION
Estimation of the unrelaxed volume using an equation of state
From a thermodynamics viewpoint, the temperature dependence of the total amount of microvoids at low temperatures is related to the
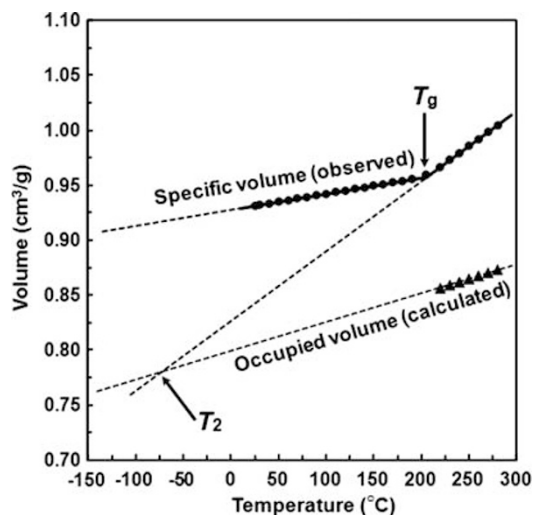

Figure 2 Temperature dependence of the observed specific volume[refs 26,27] and calculated occupied volume for PPO.

specific volume of the glassy polymer. The unrelaxed volume is defined as the difference between the specific volume of the glassy state and the volume of the supercooled liquid state. Figure 1 shows a schematic representation of the specific and occupied volumes. The occupied volume was calculated in the present study using Sanchez–Lacombe's equation of state[29,30] based on the V–T curve observed for PPO in the liquid state from published data.[26,27] The calculated temperature dependence of the occupied PPO volume is shown in Figure 2 with its V–T curves. The characteristic temperature, T_2, was predicted to be $-75 \pm 20\,^{\circ}$C from the intersection between the temperature dependence of the occupied and specific volumes at the hypothetical equilibrium supercooled liquid state, as shown in Figure 2. A discontinuous change is expected for the temperature dependence of the unrelaxed volume at approximately T_2. The temperature dependence of the unrelaxed volume in PPO will be discussed in the following section.

Temperature dependence of sorption properties
The Xe sorption isotherms of PPO at various temperatures are shown in Figure 3. It was observed that the amount of Xe sorption increased with decreasing temperature, and all of the sorption isotherms obtained were concave toward the pressure axis, which is common in glassy polymers. The solid lines through the experimental data in Figure 3 represent the nonlinear least-square curves fit using the dual-mode sorption model.[6] The dual-mode sorption model is given by the following equation:

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p}, \qquad (1)$$

where C is the concentration of the penetrant into the polymer at pressure p. In all equations, the subscripts D (Dissolved) and H (Hole) correspond to the Henry and the Langmuir sites, respectively. C is composed of the concentrations at Henry site, C_D, and Langmuir site, C_H. Henry's law parameter, k_D, characterizes sorption to the densified equilibrium matrix of the glassy polymer, whereas the Langmuir saturation parameter, C_H', characterizes sorption into the microvoids related to the non-equilibrium unrelaxed volume of the glassy state and b is the Langmuir affinity parameter.

At low temperatures, the sorption isotherm in the high-pressure region is nearly a straight line because nearly all of the microvoids had
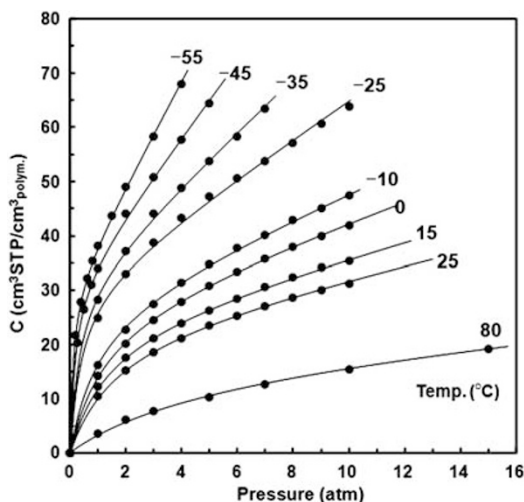
Figure 3 Xe sorption isotherms of PPO at various temperatures. The solid lines represent the nonlinear least-square curve fit using the dual-mode sorption model.

Table 1 Dual-mode sorption parameters, C_H' and k_D, and heat of solution, ΔH_s, for Xe in polyphenyleneoxide at various temperatures

Temperature	C_H'	$k_D \times 10^2$ $(cm^3 STP\, cm^{-3}_{polym.}$	ΔH_s[a]
$(^\circ C)$	$(cm^3 STP\, cm^{-3}_{polym.})$	$cm\, Hg^{-1})$	$(kcal\, mol^{-1})$
80	16.4	0.61	
25	23.5	1.49	
15	24.8	1.79	
0	27.0	2.37	
−10	28.1	2.89	−3.44
−25	31.2	4.58	
−35	31.8	6.29	
−45	31.8	9.04	
−55	31.2	12.51	

[a]Value was determined from Arrhenius plot of k_D as shown in Figure 4.

already saturated with the penetrant atoms at relatively low pressures. The dual-mode sorption parameters estimated by the fitted nonlinear least-square curve are shown in Table 1. The Arrhenius plot of k_D indicates a linear relationship with the measured temperature (Figure 4). The heat of solution for a Henry-type sorption mechanism is obtained from the above plot and tabulated in Table 1. This value is comparable to that of carbon dioxide.[31,32]

The C_H' value corresponding to the total amount of microvoids in a glassy polymer at a temperature, T, can also be represented by the following equation:[33]

$$C_H' = 22\,414 \cdot \left(\frac{V_g - V_l}{V_g}\right)\frac{1}{V_{gas}} = 22\,414 \cdot (\alpha_l - \alpha_g)(T_g - T) \cdot \frac{1}{V_{gas}}, \quad (2)$$

where V_g and V_l are the specific volumes of the polymer in the glassy and supercooled liquid states, respectively, V_{gas} is the molar volume of the sorbed gas in a liquid-like state, and α_l and α_g are the thermal expansion coefficients above and below the T_g, respectively. Equation 2 indicates that C_H' is proportional to the difference between the T_g and T. The C_H' value was plotted against the temperature as shown in Figure 5. It can be observed that the C_H' value for PPO increased linearly with decreasing temperature above a certain temperature. When the straight line obtained for PPO was
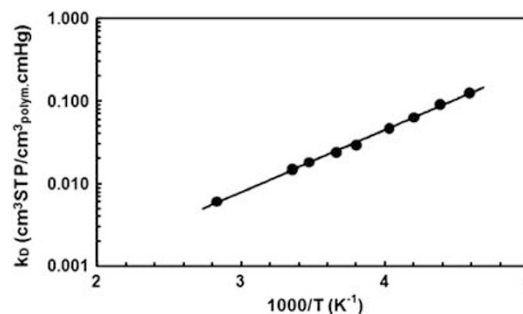

Figure 4 The Arrhenius plot of k_D for Xe in PPO.
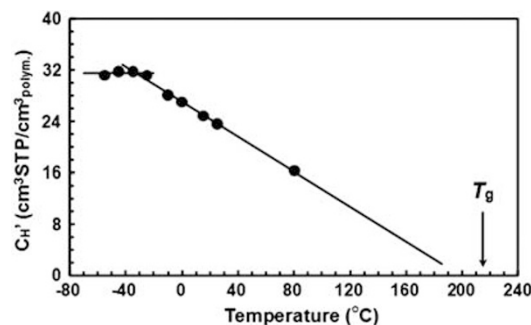

Figure 5 Temperature dependence of C_H' for Xe in PPO.

extrapolated to $C_H' = 0$ (the solid lines in Figure 5), the obtained temperature was notably close to the T_g of PPO. This finding indicates the C_H' value is related to the unrelaxed volume.

Though few data are available, Figure 5 suggests that C_H' corresponds to the unrelaxed volume, which becomes nearly constant below approximately −30 °C. Although this temperature is markedly different from the value of T_2 as shown in Figure 2 (−75 °C), we equate this characteristic temperature for PPO to T_2. This suggestion should at least be confirmed by observing Xe sorption at lower temperatures in the near future.

Temperature dependence of the microvoid size, as determined by ^{129}Xe NMR

Figure 6 shows the ^{129}Xe NMR spectra of ^{129}Xe in PPO obtained at various pressures using −25 °C as an example. It is obvious that the peak position of the ^{129}Xe in PPO shifts to a low magnetic field with increasing Xe pressure. The peak width narrows with increasing Xe pressure. Similar results were obtained at the other temperatures used in this study. The two diffusion coefficients of the carbon dioxide in PPO were determined elsewhere[26] according to the dual-mode sorption and partial immobilization[27] models. The diffusion coefficient for the Henry site, D_D is larger than that for the Langmuir site, D_H. If a similar phenomenon occurs with Xe, the obtained results shown in Figure 6 are reasonable. Specifically, the narrowing of ^{129}Xe NMR peak should be caused by the increasing mean diffusivity of Xe in PPO at higher pressures because the concentration contribution from Henry's law is larger than that of the Langmuir sorption site.

In this study, the symmetrical line shapes and downfield shifts were used to analyze the glassy state based on the microvoid size. The downfield shift was caused by increasing the interactions between Xe atoms. The symmetrical peaks indicate that the Xe atoms quickly dissolve and diffuse throughout the PPO and subsequently exchange
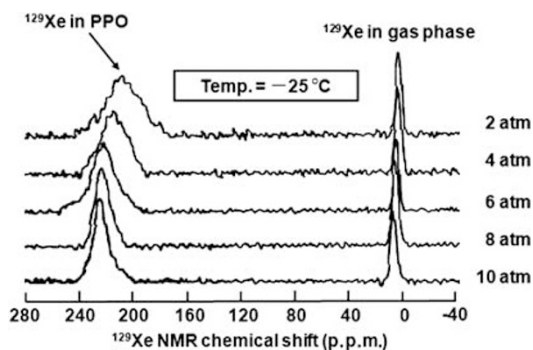
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Figure 6 ^{129}Xe NMR spectra of ^{129}Xe in both PPO and the gas phase for various pressures of Xe at $-25\,^{\circ}$C.
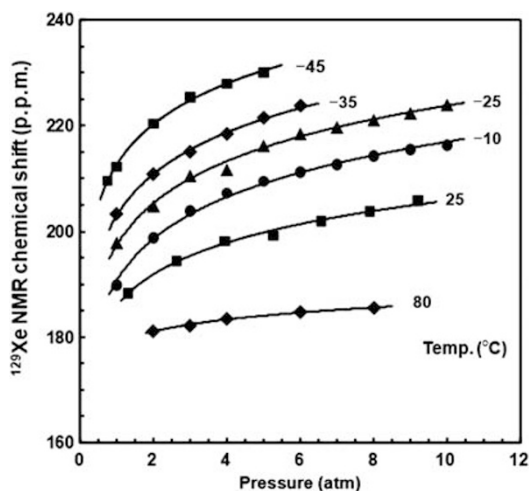

Figure 7 Pressure dependence of the ^{129}Xe NMR chemical shift of ^{129}Xe in PPO at various temperatures.

rapidly between the Henry and the Langmuir sites on the time scale of these NMR observations. We plotted the observed downfield shifts against the pressure in Figure 7 at each of the temperatures examined. The chemical shift of the gaseous Xe moves downfield linearly with increasing pressure. A similar linear dependence was observed for the NMR chemical shifts of ^{129}Xe in zeolites with no strong charges.[34,35] Therefore, one would observe a linear dependence, assuming the density of Xe is proportional to C. However, Figure 7 shows a linear dependence in the higher pressure/temperature regions but not the lower pressure/temperature regions. These findings show that the Xe density in glassy polymers is not proportional to C. Because the total sorption amount, C, of a glassy polymer consists of the partial sorptions, C_D and C_H (see Equation 1), it is necessary to evaluate the dependence of the NMR chemical shifts of ^{129}Xe in glassy polymers on C_D and C_H.

The NMR chemical shifts for the Henry and Langmuir sites were calculated using the dual-mode sorption parameters and assuming a rapid exchange of the Xe atoms between each site (Table 1).

$$\delta_{obs.} = \varphi_D \delta_D + \varphi_H \delta_H \tag{3}$$

$$\varphi_D + \varphi_H = C_D/C + C_H/C = 1 \tag{4}$$

where $\delta_{obs.}$ is the observed NMR chemical shift, ϕ_D and ϕ_H are the fractional concentrations of Xe at the Henry and Langmuir sites at
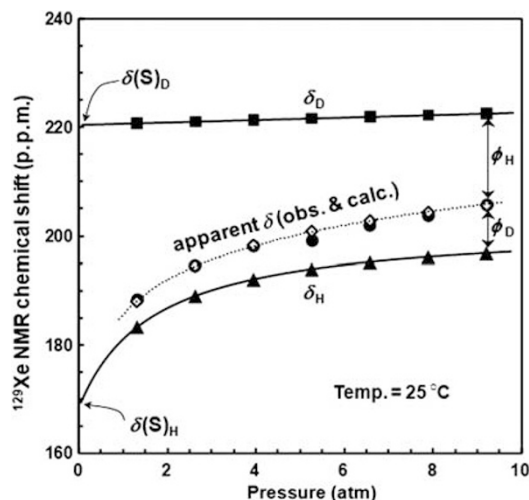

Figure 8 ^{129}Xe NMR chemical shifts of ^{129}Xe in PPO plotted against the Xe pressure at $25\,^{\circ}$C. The symbols □, ●, ■, and ▲ are the observed δ, calculated δ, δ_D and δ_H, respectively.

each pressure, respectively, and δ_D and δ_H are the NMR chemical shifts at the Henry and the Langmuir sites, respectively. Thus, the ^{129}Xe NMR chemical shift for each site is explained using the following equations, assuming a linear low-field shift in the Xe sorption amount:

$$\delta_D = \delta(Xe)_D + \delta(S)_D = A_D C_D + \delta(S)_D \tag{5}$$

$$\delta_H = \delta(Xe)_H + \delta(S)_H = A_H C_H + \delta(S)_H \tag{6}$$

where A_D and A_H are constants proportional to the Xe concentration at each site, C_D and C_H are the sorption amounts of Xe at each site, and $\delta(S)_D$ and $\delta(S)_H$ are the NMR chemical shifts caused by interactions between Xe atoms and the porous inner walls at each site, respectively. Using these equations, the Xe concentration dependence of the NMR chemical shifts of both the Henry and Langmuir sites were calculated. Figure 8 illustrates the result at $25\,^{\circ}$C using pressure (atm) as the unit of the horizontal axis. The fractional Xe concentration for the Langmuir site, ϕ_H, is larger than that for the Henry site, ϕ_D, in the low-pressure region, whereas the opposite is true in the high-pressure region. These observed nonlinear low-field shifts can thus be explained using the two-site model.

The NMR chemical shift extrapolated to $C_H = 0$, that is, $\delta(S)_H$, reflects the mean hole size of the microvoids in the glassy polymer. According to Fraissard and Ito[34] and Demarquay and Fraissard,[36] when the NMR chemical shift of the ^{129}Xe in zeolites is determined only by collisions with the walls, and disturbances from paramagnetic species or electric fields are either absent or negligible, the mean free path λ is linked to $\delta(S)$. Therefore, the mean hole size in the glassy polymer can be estimated using following relation:

$$\delta(S)_H = 243 \times \frac{2.054}{2.054 + \lambda} \tag{7}$$

where λ is a function of both the hole's shape and dimensions. Assuming the shape of the hole in the glassy polymer is spherical, the following relation can be derived:

$$\lambda = \frac{(d_s - d_{Xe})}{2} \tag{8}$$

where d_s is diameter of the sphere and d_{Xe} is the van der Waals diameter of Xe $= 4.4$ Å. The calculated $\delta(S)_H$ and d_s values at each temperature are shown in Table 2. It appears that the d_s value

Table 2 ^{129}Xe NMR chemical shifts due to the interaction between Xe atoms and inner walls of microvoids, $\delta(S)_H$ and the mean diameter of the spherical microvoids, d_s of polyphenyleneoxide at various temperatures

Temperature (°C)	$\delta(S)_H$ (p.p.m.)	d_s (nm)
80	177.1	0.593
25	168.4	0.622
−10	161.4	0.648
−25	157.0	0.665
−35	156.3	0.668
−45	157.4	0.663
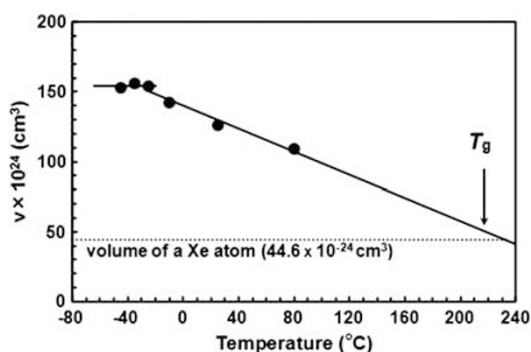
Figure 9 Temperature dependence of the mean volume of individual microvoids, v, in PPO determined by analyzing the ^{129}Xe NMR chemical shifts (details were described in the text).

increases with decreasing temperature. The mean volume of individual microvoids, v (cm^3), was calculated from d_s. Figure 9 shows the plot of v versus temperature. The extrapolated volume at the T_g was close to the van der Waals volume of a Xe atom (44.6×10^{-24} cm^3). Notably, the temperature-independent regions in Figures 5 and 9 indicate that the value of v remains constant below approximately −30 °C. These findings support the interpretation of the unrelaxed volume as shown in Figures 1 and 2 above.

In this study, we tried to estimate quantitatively the degree of temperature dependence for the unrelaxed volume, C_H', and v for PPO. The ratio of the unrelaxed volume at −25 °C to that at +25 °C was 1.28 based on the experimental and calculated data shown in Figure 2. The ratios for C_H' and v at the same temperature, that is, $C_{H'\,at\,-25\,°C}/C_{H'\,at\,+25\,°C}$ and $v_{at\,-25\,°C}/v_{at\,+25\,°C}$, were 1.32 and 1.22, respectively. It can be observed that these ratios coincide with each other within the error bounds. As the unrelaxed volume (nearly identical to C_H') is the product of both the individual volume and number of microvoids, we conclude that the thermal changes result primarily from the individual sizes of the microvoids.

CONCLUSIONS

Sorption of Xe to PPO as a glassy polymer was measured at various temperatures below its T_g. The observed sorption isotherms at each temperature were analyzed using the dual-mode sorption model characteristic of glassy polymers. The Langmuir saturation parameter, C_H', which corresponds to the unrelaxed volume, increased proportionally with decreasing temperature. And then this parameter became a constant value below approximately −30 °C, whereas the Henry's law parameter, k_D, obeys the Arrhenius relation. After

analyzing the ^{129}Xe NMR chemical shifts of ^{129}Xe in PPO at various temperatures, the mean volume of the individual microvoids was determined. The temperature dependence of the microvoid size was notably similar to that of the unrelaxed volume and C_H'. These findings show that the gas sorption properties of glassy polymers should be interpreted based on the temperature dependence of their unrelaxed volume and microvoids in addition to the thermodynamics of dissolution. Therefore, the ^{129}Xe NMR spectroscopy is a good tool for characterizing microvoids in glassy polymers.

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