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# Communications to the Editor

## Characterization of the Microvoids in Poly(2,6-dimethyl-1,4-phenylene oxide) by Means of $^{129}$Xe NMR Spectroscopy

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**Introduction.** Microvoids, which exist in the glassy polymers, are considered to be representative of the unrelaxed volume. They are the remaining spaces when polymer becomes glassy and segmental mobility of the main chain is frozen. In some positronium annihilation lifetime measurements for glassy polymers, it has been reported that the mean size of microvoids is the order of angstroms.[1−3]

In recent years, $^{129}$Xe NMR spectroscopy has become a powerful technique to characterize structures of materials.[4−8] Since Xe atom has a very large polarizability, $^{129}$Xe NMR chemical shift sensitively affects its environment.[9,10] Especially, it is expected that induced $^{129}$Xe NMR chemical shift is strongly correlated with the size and nature of microvoids in glassy polymer, because interactions with the host system disturb the electron density of Xe. The $^{129}$Xe NMR chemical shift, $\delta$, of $^{129}$Xe adsorbed by porous materials like zeolites is explained by $\delta = \delta(\mathrm{S}) + \delta(\mathrm{Xe}) + \delta(\mathrm{E})$.[11−14] $\delta$(S), $\delta$(Xe), and $\delta$(E) are the terms explained by collision with porous inner walls, collision among Xe atoms, and the contribution of electric field created by the cations, respectively. In many cases, the contribution of $\delta$(E) can be ignored at glassy polymers because these polymers do not have strong charge groups. Therefore, it is expected that $^{129}$Xe NMR chemical shifts of $^{129}$Xe in glassy polymers show a linear low-field shift with respect to the density of Xe.

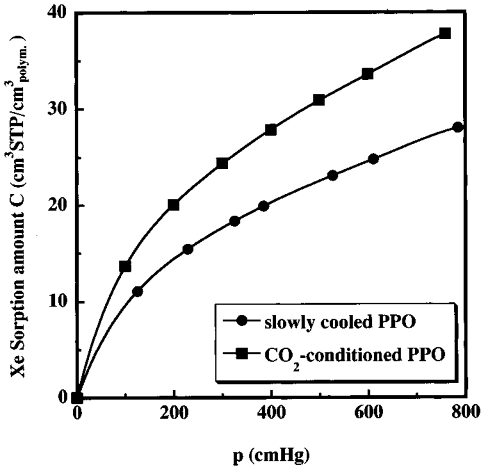

**Figure 1.** Xe sorption isotherms of slowly cooled and CO$_2$-conditioned PPO films at 25 °C.

For the zeolites, there are many reports which state that $^{129}$Xe NMR chemical shift, $\delta$(S), is strongly correlated to the pore size of zeolites.[11−16] Consequently, the technique may be able to characterize the mean size of microvoids in glassy polymers using $\delta$(S). In this study, we investigate the relationship between $^{129}$Xe NMR chemical shifts and Xe sorption properties of glassy polymers and attempt to characterize microvoids in glassy polymers by means of $^{129}$Xe NMR spectroscopy.

**Experimental Section.** Slowly cooled poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and CO$_2$-conditioned PPO were used as glassy polymers. The PPO film was prepared by solution casting method with chloroform and slowly cooled after annealing at 220 °C for 16 h. CO$_2$ conditioning was performed by exposing the slowly cooled PPO film to 60 atm of CO$_2$ at 25 °C for 16 h and then degassed quickly. About 2 g of the film sample was packed into a 10 mm diameter Pyrex NMR sample tube (Wilmad, type 513-7 JYH-7) with the desired amount of Xe (which has a natural abundance of $^{129}$Xe) and sealed with a Teflon valve. $^{129}$Xe NMR spectra were recorded on JEOL GX400 NMR spectrometer set to the

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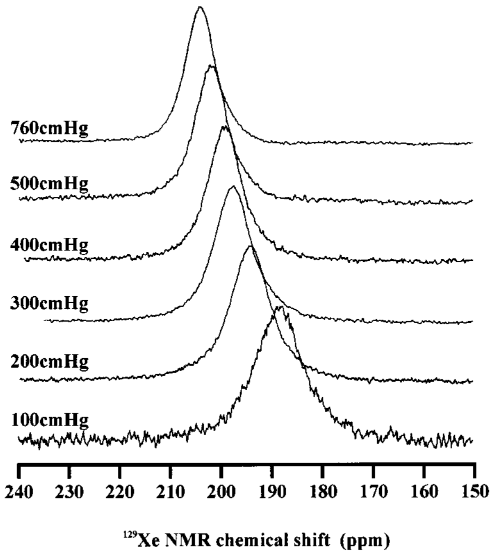

**Figure 2.** $^{129}$Xe NMR spectra of the $^{129}$Xe in slowly cooled PPO film under various pressures of Xe at 25 °C.

frequency of 110 MHz and 25 °C. The $^{129}$Xe NMR chemical shifts were referenced to the NMR signal of $^{129}$Xe gas extrapolated to zero pressure. Xe sorption isotherms of PPO samples were measured by quartz crystal microbalance at 25 °C.[17,18]

**Results and Discussion.** Xe sorption isotherms of slowly cooled and $CO_2$-conditioned PPO films prepared in this study are shown in Figure 1. It is confirmed that sorption amount of Xe for $CO_2$-conditioned PPO is larger than that for slowly cooled one at constant pressure, and similar results have been reported in the case of $CO_2$ sorption measurements.[19] These isotherms are concave toward pressure axis. In general, the dual-mode sorption model represented by following equation is used to interpret gas sorption behavior of glassy polymers.[19,20]

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + bp} \tag{1}$$

Here, $C$ is the equilibrium sorption amount at pressure $p$, $C_D$ is the concentration due to Henry's law contribution, $C_H$ is the concentration due to Langmuir mode contribution, $k_D$ is the Henry's law solubility coefficient, $b$ is the affinity constant of penetrant to Langmuir site, and $C'_H$ is the hole saturation constant in the Langmuir sorption mode. The observed isotherms could be explained successfully on the basis of the dual-mode sorption model, and results of curve fitting are drawn in Figure 1 as solid lines. $C'_H$ values of slowly cooled and $CO_2$-conditioned PPO were determined as 20.6 and 25.1 $cm^3$ STP/$cm^3_{polym}$, respectively, by using the least-squares method. In addition, the corresponding $k_D$ values were $1.7 \times 10^{-2}$ and $2.1 \times 10^{-2}$ $cm^3$ STP/($cm^3_{polym}$ cm Hg), respectively, while $b$ values were $7.8 \times 10^{-3}$ and $8.5 \times 10^{-3}$ cm $Hg^{-1}$, respectively. $C'_H$ is one of the good indicators of microvoids and/or degree of nonequilibrium for glassy polymer. These values indicate that total amount of microvoids was increased by $CO_2$ conditioning.

Figure 2 represents the $^{129}$Xe NMR spectra of $^{129}$Xe in slowly cooled PPO obtained at various pressures of Xe. It is confirmed that the symmetric peaks shift to low magnetic field with increasing pressure of Xe, and similar results were observed for $CO_2$-conditioned PPO. This low-field shift is caused by increasing number of collisions among Xe atoms, i.e., the contribution of $\delta$(Xe). These symmetric peaks indicate that Xe atoms in PPO diffuse fast and exchange rapidly between Henry and Langmuir sites in NMR time scale. We now emphasize the low-field shifts are caused by increasing of Xe density in PPO, which are shown in Figure 2.

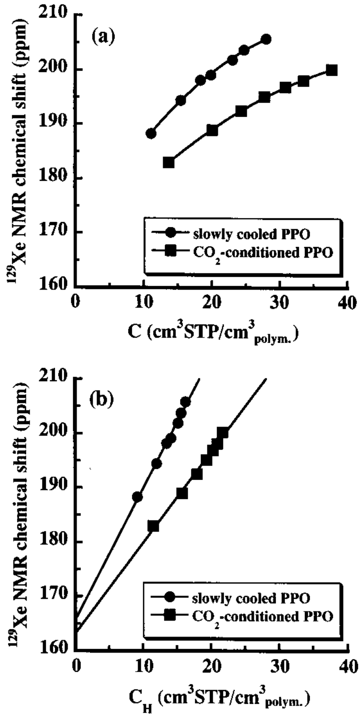

**Figure 3.** Plots of $^{129}$Xe NMR chemical shift vs (a) total sorption amount of Xe ($C$), and (b) the sorption amount of Xe of Langmuir mode contribution ($C_H$), for slowly cooled and $CO_2$-conditioned PPO films at 25 °C.

In general, $^{129}$Xe NMR chemical shift shows linear low-field shift with Xe density. Actually, chemical shift of Xe gas shifts to low-field linearly with pressure, and in some cases, chemical shifts of $^{129}$Xe in zeolites also shift linearly with Xe concentration.[23] Therefore, it was expected that $^{129}$Xe NMR chemical shift of $^{129}$Xe in PPO shifts linearly against the total sorption amount of Xe, $C$, because the contribution of $\delta$(E) can be ignored and the density of Xe in PPO corresponds to $C$. Figure 3a shows the plots of $^{129}$Xe NMR chemical shifts of $^{129}$Xe in slowly cooled and $CO_2$-conditioned PPO films against $C$. In practice, however, they did not shift linearly. This fact consequently suggests that the density of Xe in PPO is not proportional to $C$. Since the amount of $C$ consists of $C_D$ and $C_H$ (see eq 1), it is necessary to evaluate the dependences of $C_D$ and $C_H$ for $^{129}$Xe NMR chemical shift of $^{129}$Xe in PPO. Using the dual-mode sorption parameters, sorption amounts of Xe for Langmuir mode contribution, $C_H$, at each pressure were calculated, and $^{129}$Xe NMR chemical shifts were plotted against $C_H$ (Figure 3b). Linear low-field shifts are clearly recognized. Similar plots against $C_D$ were performed (data not shown), but they were not linear as in the case of $C$. These findings suggest that $^{129}$Xe NMR chemical shift of $^{129}$Xe in PPO can be explained mainly by density of Xe in the Langmuir site and may be attributed to the difference of the increased rate of Xe density between Langmuir and Henry sites. In practice, at low pressure, the proportion of Xe in the Langmuir site is larger than that in the Henry site. Moreover, a rubbery polymer contains "only" the Henry site; the $^{129}$Xe NMR chemical shifts rarely reveal Xe density dependence (data not shown). Soon, more detailed discussions will be reported together with the data for other glassy polymers.

The slope of the $^{129}$Xe NMR chemical shift$-C_H$ plot corresponds to the total amount of microvoids in PPO; it becomes steep with decreasing amounts of microvoids. As shown in Figure 3b, the slope for $CO_2$-conditioned PPO is more moderate than that for slowly cooled one. It indicates that total amount of microvoids has been increased by $CO_2$ conditioning, and it is consistent with the results of Xe sorption measurement mentioned above. Furthermore, it can be said that $^{129}$Xe NMR chemical shift extrapolated to $C_H = 0$ for each sample, i.e. $\delta$(S), reflects the mean size of microvoids. The $\delta$(S) value of $CO_2$-conditioned PPO is smaller than that of slowly cooled one, indicating that mean size of microvoids for $CO_2$-conditioned PPO is larger than that for slowly cooled one.

These results suggest that $^{129}$Xe NMR spectroscopy is a good tool for the characterization of microvoids of glassy polymers.

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