

The Relationship between ^{129}Xe NMR Chemical Shifts and Nanostructure of Polymers

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Introduction

Recently, it has been reported that the ^{129}Xe NMR spectroscopy is one of the powerful techniques for characterization of solid materials. Since Xe atom has a very large polarizability, ^{129}Xe NMR signal of the ^{129}Xe sorbed in a medium is sensitively affected by surrounding environments. For micro porous materials such as zeolites, the NMR chemical shift of the adsorbed ^{129}Xe is explained by following equation;

$$\delta = \delta_{(S)} + \delta_{(Xe)} + \delta_{(E)} + \delta_{(SAS)} + \delta_{(M)} \quad (1)$$

δ is the observed NMR chemical shift of adsorbed ^{129}Xe . $\delta_{(S)}$ is the chemical shift due to interaction between Xe and inner wall of hole. $\delta_{(Xe)}$ corresponds to the interaction between Xe atoms and increases in proportion to concentration of Xe. $\delta_{(E)}$, $\delta_{(SAS)}$, and $\delta_{(M)}$ are terms explained by the contribution of the electric field created by multivalent cations, the interaction of Xe with the strong adsorption site, and the contribution of the magnetic field created by paramagnetic compensation cations, respectively. However, the contributions of $\delta_{(E)}$, $\delta_{(SAS)}$, and $\delta_{(M)}$ can be ignored for most of polymers because of absences of strong charge groups. Observed δ for a polymer, therefore, can be explained as a sum of $\delta_{(S)}$ and $\delta_{(Xe)}$. On the other hand, the microvoids exist in glassy polymers are considered to correlate with unrelaxed volume (so-called as "excess free volume"), which are the space remained when polymer becomes glassy state and is regarded as the segmental mobility of main chains are frozen. Evaluation of gas sorption properties for glassy polymers can provide useful information about the microvoids. Generally, evaluations of gas sorption properties of a glassy polymer can provide some information about unrelaxed-volume or microvoids. Gas sorption behavior of a glassy polymer can be interpreted by the dual-mode sorption model, which is represented by following equation;

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p} \quad (2)$$

where C is the equilibrium sorption amount at pressure p , C_D is the concentration of the penetrant due to the Henry's law contribution, C_H is that held in the Langmuir site, k_D is the solubility coefficient of Henry's law, b is the affinity constant of the Langmuir site, and C_H' is the Langmuir saturation constant. Langmuir-mode sorption is interpreted by the sorption into microvoids of a glassy polymer. Hence, one can obtain prime information about microvoids from evaluations of C_H and parameter C_H' . In this study, the microvoids in glassy polymers were investigated by Xe sorption and ^{129}Xe NMR measurements including our previous data [1-4].

Experimental

The membranes of polyphenyleneoxide (PPO), polystyrene (PS), Tetramethyl-polycarbonate (TMPC), Polycarbonate (PC), poly(ethylene-*r*-vinyl alcohol) (EVOH), and Polyvinylchloride (PVC) were used as glassy polymers. Poly(4-methyl-1-pentene) (PMP) membranes with various crystallinities were used. Xe sorption measurements were carried out using a gravimetric sorption apparatus with an electro-microbalance at 25 °C. Sorption amounts of Xe for the membrane was determined after correction of the contribution of buoyancy. Cut membranes were packed about 1 g into a 10 mm ϕ Pyrex NMR sample tube with thick wall, and degassed for 24 hours. After that, required amount of Xe (with natural abundance of ^{129}Xe) was introduced into the NMR tube with the aid of liquid nitrogen, and the tube was sealed with Teflon valve. ^{129}Xe NMR spectra were recorded at 110 MHz and 25 °C. All of ^{129}Xe NMR chemical shifts were referred to an external standard of gaseous ^{129}Xe at zero-pressure as 0 ppm.

Results and discussion

Xe sorption isotherms of glassy polymers have been successfully interpreted by the dual-mode sorption model, so that, the dual-mode sorption parameters were determined by non-linear least square method from eq. (2). The values of C_H' were listed in Table 1. The ^{129}Xe NMR chemical shift of the ^{129}Xe in the samples showed non-linear low-field shift with increasing sorption amount of Xe because of a fast exchange of Xe atoms between Henry and Langmuir sites, whereas it has showed linear shift against C_H . From this Xe-density dependence of the ^{129}Xe NMR chemical shift, it has been able to estimate mean size of the microvoids in glassy polymer. Results were also listed in Table 1 together with the mean sizes determined by positron annihilation lifetime spectroscopy (PALS) method elsewhere. Furthermore, this methodology was confirmed from the results of crystalline part of PMP whose fine structure and gas transport properties were already characterized. A parameter of dual-mode sorption model, C_H' is the hole saturation constant in the Langmuir sorption site, and a good indicator of total amount of the microvoids, i.e. unrelaxed volume in glassy polymers. Therefore, the C_H' divided by the mean volume of individual microvoid calculated from the ^{129}Xe NMR chemical shift, can be defined as an indication of number of the microvoids. It was found that the mean diameter of the microvoid in PVC is very close to van der Waals diameter of Xe atom, and Xe sorption is not detectable for EVOH whose free space size was smaller than Xe atom according to PALS measurement. Figure 1 shows the relationships between the mean volume of a microvoid calculated with the mean pore size (v) or the number of the microvoids ($N = C_H'/v$) and C_H' value. It is confirmed that there is correlation between C_H' and volume or number of microvoids. From these findings, it is demonstrated that ^{129}Xe NMR spectroscopy is a powerful technique to determine the mean size and number of microvoids in glassy polymers.

Table 1 The values of Langmuir sorption capacities C_H' , ^{129}Xe NMR chemical shifts $\delta_{(S)H}$ and mean pore size of glassy polymer membranes

Sample	C_H' [cm ³ STP / cm ³ polym.]	$\delta_{(S)H}$ [ppm]	mean pore size [Å]	
			^{129}Xe NMR	PALS*
PPO	19.1	165.4	6.34	6.56
TMPC	17.4	169.7	6.18	6.40
PC	13.3	199.7	5.28	5.88
PS	4.9	205.4	5.14	5.76
PVC	3.4	224.0	4.75	4.52
EVOH	impossible	impossible	impossible	4.24
PMP [#]	--	228.1	4.67/4.53	--

*These are literature values. [#]Crystallinity is 96%, and the smaller value of the mean pore size was obtained by assuming cylindrical pore shape.

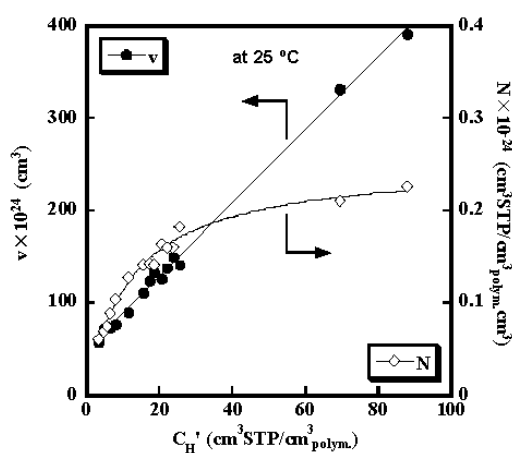


Figure 1 v and N plotted against C_H' of Xe for glassy polymers.

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