SHORT COMMUNICATIONS

Effects of Aging on Molecular Motion of Poly(1-trimethylsilyl-1-propyne) Membranes Synthesized Using Various Catalysts

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Poly(1-trimethylsilyl-1-propyne) (PMSP) is a typical glassy polymer at room temperature that was first synthesized by Masuda and Higashimura in 1980s.¹ Recently, membranologists have focused their research on this polymer's high gas permeation properties.

The biggest problem of this glassy polymer is a decrease in its gas permeability with age. Therefore, we have been studying the aging process and the stabilization of the gas permeability of this PMSP membrane.^{2–7} It has been found that membrane contamination is a dominant factor causing the change in gas permeability; and, in the absence of contaminants, aging is due to the relaxation of the unrelaxed volume (the unrelaxed free volume in the glassy state or excess free volume below glass transition temperature). Relaxation can be attributed to physical aging, which is most likely related to a change in molecular motion.

In this study, we describe the effects of physical aging on the molecular motion of the PMSP membranes synthesized using various catalysts.

EXPERIMENTAL

Materials

The PMSP materials were the same polymers previously synthesized^{6,7} utilizing Masuda *et al.*'s method.^{8–10} Polymerization catalysts included tantalum (V) chloride (TaCl₅), niobium (V) chloride (NbCl₅), and TaCl₅–triphenyl bismuthine (Ph₃Bi) as a cocatalyst (TaCl₅:Ph₃Bi=1:1). The weight-average molecular weights (M_w) of the PMSPs were 86×10^4 (TaCl₅), 260×10^4 (TaCl₅–Ph₃Bi), and 35×10^4 (NbCl₅). The intrinsic viscosities ($[\eta]$, dL g⁻¹) were 6.0 (TaCl₅), 9.3 (TaCl₅–Ph₃Bi), and 0.7 (NbCl₅), which were measured in toluene at 30°C.

Membrane Preparation

PMSP membranes with a thickness of between 100 and 200 μ m were cast on a horizontal glass plate from a toluene solution of the polymer. To prevent physical aging and contamination,^{6,7} all the membranes were immersed in methanol just prior to NMR measurements.

The PMSP was aged by sorbing vacuum pump oil vapor.^{3,6,7,11,12} In this work, an oil vacuum pump was

used and a cold trap with liquid nitrogen was placed between the pump and the membrane. The vacuum pressure was maintained at between 10^{-2} and 10^{-3} mmHg. The vacuum pump oil used was Sanvac oil No. 160 (Asahi Vacuum Chemical Industry Co., Ltd.), having a vapor pressure of 4.1×10^{-6} mmHg at 10°C.

NMR Measurements

High resolution, solid-state NMR measurements were performed at 30°C using a JEOL JNM 400 spectrometer. Sample membranes were cut into small pieces measuring about 5 mm $\times$ 5 mm and packed into each sample tube. The spin-lattice relaxation times (T_1) of the carbons were obtained by the CP T_1 pulse sequence, using a spinning speed of 6 kHz. The same T_1 measurements were carried out on at least three separate membranes, prepared at the same time from the same cast solution.

RESULTS AND DISCUSSION

No thermal change occurred up to 250°C during the DSC measurements of all synthesized PMSPs.^{6,7} These samples were glassy under the conditions used in this study. The solid state ¹³C NMR spectra were the same as those reported by Costa *et al.*¹³ The catalyst dependence was not clearly observed in the solid state spectra of the PMSPs synthesized with TaCl₅ and NbCl₅. The solution state ¹³C NMR spectra revealed that the Nb-catalyst produced a more regular configuration compared to the Ta-catalyst.¹³ In addition, the PMSP synthesized with NbCl₅ had a *cis*-rich structure.¹⁴ The catalysts used for polymerization affect the solubility of the PMSP in various solvents. For example, the PMSP synthesized with TaCl₅ was soluble in hexane, whereas the PMSP synthesized with NbCl₅ was insoluble in the same solvent.^{8,10} The same solubility differences were observed for samples prepared in this study. This is because of a difference in the configuration of the PMSPs.^{8,10}

Figure 1 shows the ¹³C T_1 of each carbon in both the initial and aged PMSP membranes. The aged membranes were prepared by storing them in a vacuum vessel for 14 days at 30°C. Costa *et al.*¹³ reported that the T_1 values

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Figure 1. ^{13}C T_1 of $\text{C}_a\text{--C}_d$ in the initial and aged PMSP membranes. Aging conditions: stored in a vacuum vessel for 14 days at 30°C . (a) C_a ; (b) C_b ; (c) C_c ; (d) C_d .

of the PMSP synthesized with TaCl_5 , T_1 [s]; C_a , 1.6; C_b , 4; C_c , 16; and C_d , 16. Since T_1 has a frequency dependence, the T_1 values in this study cannot be simply compared with them. However, the same tendency of the ^{13}C T_1 values of each carbon were observed. The side chain protonated carbons of C_a and C_b have smaller T_1 values compared to the backbone chain non-protonated carbons of C_c and C_d . The T_1 values of C_c and C_d were almost same in each catalyst case, indicating the same molecular motion. The T_1 of C_a bonding a silicon atom is also smaller than that of C_b , suggesting that the C_a has a faster molecular motion rather than C_b . From the theoretical basis it is difficult to directly compare the molecular motion between the protonated and non-protonated carbons (*i.e.*, between the side chain and backbone carbons) in terms of T_1 . The reason is that the dipolar interaction between the carbon spins and directly bonded proton spins is dominant for the former carbons, while the latter case depends on the long range carbon-proton dipolar interaction. Moreover, chemical shift anisotropy effects may also be included for the latter case.

During aging, the change in the T_1 values of the side chain carbons (C_a and C_b) was smaller than those of the backbone chain carbons (C_c and C_d). The NbCl_5 catalyst produced PMSP with the largest T_1 values of the backbone chain carbons, compared to $\text{TaCl}_5\text{-Ph}_3\text{Bi}$ and TaCl_5 . In the case of the PMSP synthesized with NbCl_5 , no change in the T_1 values of the backbone carbons was observed during aging. After aging, the T_1 values of the backbone carbons of the PMSPs synthesized with TaCl_5 and $\text{TaCl}_5\text{-Ph}_3\text{Bi}$ increased, whereas those of the PMSP synthesized with NbCl_5 stayed almost constant.

The former PMSPs may be in a more unstable glassy state compared to the unchanged carbons. During aging under this condition, the unrelaxed volume estimated by the gas sorption method decreased in the PMSP membrane synthesized using a Ta-catalyst.^{6,7} In other words, the chain packing increased. On the other hand, the unrelaxed volume of the PMSP synthesized with NbCl_5 was stable under the same aging condition in this study.⁷ An increased chain packing will reduce the molecular motion. This change may affect not only the backbone chains but also the side chains; but the T_1 values of the side chain carbons hardly changed during aging. Although relaxation of the unrelaxed volume occurred, the PMSP maintained a larger unrelaxed volume compared to other conventional glassy polymers. Based on this result, the larger molecular scale gaps between polymer segments did not affect the molecular motion of the side chain carbons.

Only the backbone carbons changed with age. This result may be due to a change in the degree of twisting of the backbone chains during aging, since a configurational change, such as *cis-trans* isomerization of the non-substituted polyacetylene,¹⁵ was not observed in the PMSP case.¹⁶ This change probably caused the relaxation of the unrelaxed volume of the PMSPs synthesized with a Ta-catalyst.

An immersion of aged PMSP in methanol caused the restoration of the properties of the PMSP such as the gas permeability and the unrelaxed volume due to the swelling of the membrane.⁶ Figure 2 displays the ^{13}C T_1

Figure 2. ^{13}C T_1 restoration of backbone carbons (C_c and C_d) in the aged PMSP membranes synthesized with $\text{TaCl}_5\text{-Ph}_3\text{Bi}$. Restoration, immersed the aged membrane in methanol for 24 h.

restoration of backbone carbons (C_c and C_d) in the aged PMSP membranes synthesized with $\text{TaCl}_5\text{-Ph}_3\text{Bi}$. The aged PMSP membrane was immersed in methanol for 24 h. After immersion, the T_1 values were restored, especially C_d was perfectly restored to the initial value.

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