Macromol. Symp. ***146**, 25–31 (1999)*

Relaxation Study of Poly[(4-Oligodimethylsiloxanyl)styrene]s by Solid State ^{29}Si NMR

Yusuke Kawakami

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

SUMMARY: Quantitative evaluation of spin-lattice relaxation time (T_1) was made at each silicon atom of the side chains by solid-state ^{29}Si NMR. It was found that the closer the silicon atoms were to main chain, the more the motion was restricted. Such local mobility of side chains was correlated to the gas permeation behavior through the polymer membrane.

Introduction

Poly(dimethylsiloxane) (PDMS) membranes have the highest permeability coefficient among industrial membranes, and they are important starting materials for the construction of gas permeable membrane materials. However, they also have the lowest O_2 / N_2 permeation selectivity value for membrane polymers *i.e.* $\alpha = 2$. Many attempts have been made to improve the shortcomings of non-self-supporting PDMS by strengthening through cross-linkage or copolymerization with hard segments. Although block copolymers of polycarbonate and PDMS or PDMS based cross-linked polymers are satisfactory in film-forming property, they usually exhibit poor permeation selectivity$^{1)}$, because the gases seem to permeate through the phase-separated easily permeable PDMS domain.

The permeability (P) of a gas through a homogeneous film at rubbery state is controlled by the diffusion (D) and the solubility (S) coefficients of a gas in or through the film.

$$P = DS \qquad (1)$$

CCC 1022-1360/99/$ 17.50+.50/0

We reported enhanced permeation through surface-modified polymeric membrane by hydrophobic polymer additives. Importance of *S* of gases at the surface in permeation was pointed out[2,3]. Meanwhile, polymers consisting of dimethylsiloxane side chains, which contributes to permeation, and main chain component with high glass transition temperature (T_g), which lends high permeation selectivity and gives film-forming properties, should demonstrate well-balanced permeation properties of non phase-separated membrane[4-13]. Importance of diffusibility of a gas, which is controlled by the local motion of the side chain siloxane segment, was pointed out[12]. Thus, permeation behavior of a gas through polymeric membrane must be closely related to the nature and relaxation behavior of the polymer segments, at surface and in bulk, which control the solubility and diffusibility of the permeating gas[14]. In this study, relaxation study by solid state NMR was carried out to obtain insights about the segmental motion of oligosiloxane side chains of polystyrene which presumably control the diffusibility of gases in the solid state[15, 16].

Property of Polymers

Properties of the polymers are listed in Table 1. The polymers show only one T_g, which clearly indicates that oligosiloxanes do not phase-separate from the main chain component. The absolute T_g is lowered dramatically by the introduction of the siloxane linkage (PS1 → PS2). Introduction of more siloxane linkages lowers the T_g, however, branched structure of the siloxane prevents the drop of the T_g. PS*t*4 shows the T_g at 114° C.

The permeability coefficients (PO_2) increased with the increase in the number of trimethylsiloxyl groups in the substituent. PO_2 of PS*i*3 and PS*n*5 are 71 and 110 ($\times 10^{-10}$ cm^3 (STP) • cm/cm^2 • sec cmHg), respectively. The values are about 1.8 and 2.8 times

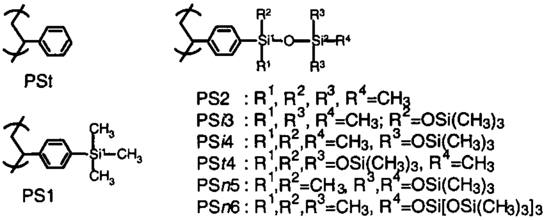

Fig. 1: Structure of Poly(4-oligodimethylsiloxanylstyrene)s

Table 1. Properties of Poly(4-oligodimethylsiloxanylstyrene)s.

Polymer	T_g [K]	Δν [kHz]	T_1 [msec] 303 K	T_1 [msec] 338 K	PO_2	α	DO_2	SO_2
PSt	373	31.25	---	---	1	5.5	1	2.2
PS1	409	13.23	695	916	14	3.4	---	---
PS2	309	9.97	892	890	40	3	18	2.2
PS*i* 3	325	8.27	1131	1026	71	2.8	32	2.3
PS*i* 4	364	2.33	643	661	74	2.8	35	2.1
PS*t* 4	387	5.52	896	1011	---	---	---	---
PS*n* 5	314	5.21	837	934	110	2.6	49	2.2
PS*n* 6	256	2.76	733	866	141	2.6	64	2.2

Δν, T_1: half-amplitude width of the CH_3 signal and spin-lattice relaxation time in solid state ^{1}H NMR (90 MHz).
PO_2: 10^{-10} cm^3 (STP)·cm/cm^2·sec·cmHg. DO_2: 10^{-7} cm^2/sec. SO_2: 10^{-3} cm^3 (STP)/cm^3·cmHg.

higher compared with that of PS2. The change in S was small. PO_2 is mainly controlled by D, whereas D depends on its frequency factor. Accordingly, permeation behavior of a gas through these polymeric membrane must be closely related to the relaxation behavior of the polymer side chains. The change in magnetization in 180°-t-90° pulse sequence in solid state ^{1}H NMR of PS*n*5 is shown in Fig. 2. Here the following equation holds.

$$\log[(M_\infty - M_t)/2M_\infty] = -t/2.303T_1 \qquad (2)$$

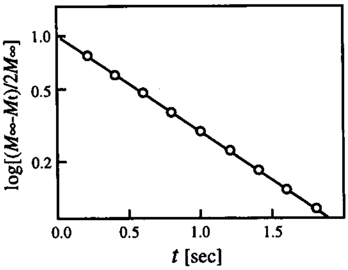

Fig.2: Decay of the Magnetization of PS*n*5 at 303 K

Where M_∞ and M_t are equilibrium magnetization and magnetization time, at a given static magnetic field

All methyl protons in side chain obeyed a single exponential decay, and from the slope, single spin-lattice relaxation time T_1 was determined, which indicates that spin-lattice relaxation of each methyl proton is averaged by the spin diffusion. Information about segmental motion at each silicon atom is lost under such situation.

Except PS*i*3, T_1's are longer at higher temperature. This trend is characteristic for glassy polymers below and near $T_g$$^{17)}$. At higher temperature, polymer segments, including side chains, become more mobile and lose thermal contact with lattice and result in slow relaxation and longer relaxation time. The relatively long T_1 compared with spin-spin relaxation time T_2 reflects very local mode of motion of the side chain like rotation of methyl group. T_1 of PS1 (695 ms) is shorter than that of PS2 (892 ms) at 30 °C. Similarly to ^{1}H NMR, only one T_1 was observed for methyl groups of PS2 also in ^{13}C NMR. The T_1 of PS2 (3.90 sec) is longer than that of PS1 (3.28 sec). These facts might imply that the rotational motion of pentamethyldisiloxanyl groups in PS2 is faster than that of trimethylsilyl groups in PS1.

Discussion, about the local motion of a side chain as a whole which seems to relate closely to the gas permeability of the polymer, can be made more adequately by the consideration of the line width of the methyl signal at half-height which is reciprocally proportional to T_2*, the measured spin-spin relaxation time:

$$\Delta\nu = 1/\Pi T_2^* \qquad (3)$$

T_2* reflects slow segmental motion of 4-6 bonds. By the introduction of siloxane linkage (PS1 → PS2), the line width at half-height became narrow. This fact suggests the higher mobility of the pentamethyldisiloxanyl side chains than the trimethylsilyl side chains. PS3, which has trisiloxane linkage, shows T_g at 263 K and has the narrowest line width at half-height (2.15 kHz) almost comparable with that of rubbery polybutadiene (0.72 kHz). Among PS3, PS*i*4 and PS*n*5, the line width becomes wider in this order, which reflects the slower motion of the side chains by the introduction of bulkier substituents at 3-position of the trisiloxane linkage. In PS*n*6, tris(trimethylsiloxy)silyl group is attached to phenyl group with tetramethyldisiloxane spacer. While in PS*t*4 and PS*n*5, they are directly attached to the phenyl groups, or with dimethylsiloxane spacers. The order of the narrowness of the line width at half-height reflects the mobility of side chains of these polymers. The side chains of PS*n*6, namely 5,5-bis(trimethylsiloxy)heptamethyltetrasiloxanyl groups are the most mobile. Tris(trimethylsiloxy)silyl groups of PS*t*4 are the least mobile, and 3,3-bis(trimethylsiloxy)pentamethyltrisiloxanyl side chains of PS*n*5 are intermediate. The faster motion of the side chains will result in the higher diffusion coefficient of a gas in permeation. The role of trimethylsiloxyl groups in the side chains are considered to give large free volume and good mobility of the side chains.

As already discussed, T_1 reflects the rotational motion of methyl groups along the Si-C bond. T_1 of Si^1 which attaches directly to phenyl ring as shown in Fig. 1 might have strong correlation with the mobility of the side chain as a whole, since contrary to ^1H NMR, spin diffusion does not occur in ^{29}Si nuclei$^{15-19)}$. The solid state ^{29}Si NMR spectra of PS*i*3 are shown in Fig. 3.

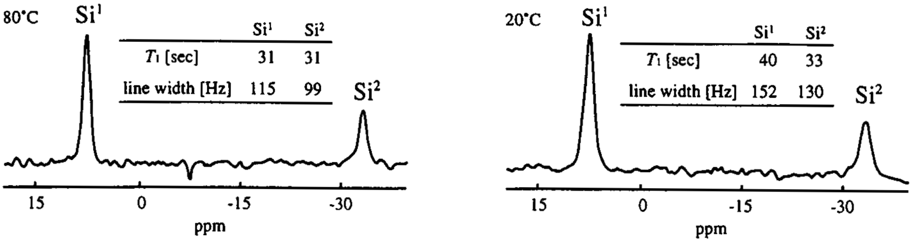

Fig. 3: Change of T_1 of Si^1 and Si^2 of PS*i*3 Estimated by 79.6 MHz ^{29}Si Solid State NMR

Each silicon atom in the side chain gives not only different chemical shifts, but independent T_1 in ^{29}Si NMR. Line width and T_1 become narrower and shorter with elevating the temperature. Although, it is rather meaningless to compare T_1 of polymers with different degree of polymerization or T_g at a given temperature, it is concluded that it is not necessary to take the difference of the molecular weight into consideration if it is in the similar range. T_1's of each Si atom of the polymers with disiloxane linkage are shown in Fig. 4.

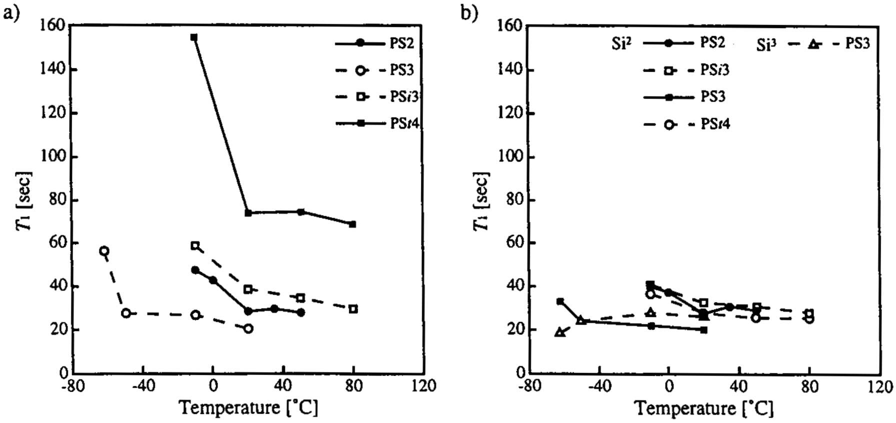

Fig. 4: Change in T_1 of Si^1 (a) and Si^2 and Si^3 (b) of Poly(4-dimethylsiloxanylstyrene)s with Temperature

T_1 of Si^1 became shorter in the order of the decreasing T_g of the polymers, and showed a tendency to sharply decrease with the elevation of the examined temperature to room temperature. The T_1 of Si^2 of PS2, PS*i*3, PS3 (second silicon atoms from phenyl ring separated by siloxane linkage), and PS*t*4 also decreased with increasing temperature. However, the change was quite moderate. Shorter T_1 can be taken to mean higher mobility of the side chains in this temperature region for these polymers having T_g around the temperatures of the measurement. For reference, the T_1 of inner Si atoms of poly(dimethylsiloxane) (PDMS) was reported to be 27.3 sec$^{20)}$, which is similar to those of Si^2 of presently reported polymers. The Si^2 atoms in these polymers seem to have similar mobility with Si atom of siloxane units in PDMS.

For a more quantitative discussion, T_1 of polymers having different T_g must be compared at similar thermal condition for each polymer. It is worthwhile to point out that the terminal trimethylsiloxyl group (Si^2) has shorter relaxation time than silicon nuclei located closer to main chain (Si^1) and relaxes easier for all of the polymers.

Table 2. Solid-state ^{29}Si T_1 of Poly(4-oligodimethylsiloxanylstyrene)s Measured at a Temperature 35 Degree below the T_g ($T_{1,-35}$).

Polymer	Temp. [℃]	$T_{1,-35}$ [sec]		
		Si^1	Si^2	Si^3
PS2	0	43	38	
PS3	-62	57	33	19
PS*i* 3	20	39	33	
PS*t* 4	79	69	26	

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