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# Photoprobe Study of Siloxane Polymers. 3. Local Free Volume of Polymethylsilsesquioxane Probed by Photoisomerization of Azobenzene[†]

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ABSTRACT: We have investigated the local free volume and its thermal fluctuation in an amorphous polymethylsilsesquioxane (PMSQ) consisting only of $T^3$ ($CH_3SiO_{3/2}$) and $T^2$ ($CH_3Si(OH)O_{2/2}$) units using photoisomerization of azobenzene molecularly dispersed in the PMSQ films as a photoprobe over a wide temperature range (4−300 K). Photoisomerization profiles are discussed on the basis of three parameters, i.e., first-order plots, final cis fractions, and three-component analysis, for uncured and silanol-condensation-cured PMSQ's. The final cis fraction in the uncured PMSQ decreases markedly below 250 K, which has never been observed in linear polysiloxanes, MQ resins, or carbon-based polymers. The effect of low-molecular-weight components in the PMSQ was evaluated using fractionated PMSQ's by molecular weight. The effect of hydrogen bonding by a silanol group was also studied by temperature dependence of infrared spectra. These results suggest that the low-molecular-weight components with silanol groups fill local vacant space resulting in the anomalous decrease in the final cis fraction for the uncured PMSQ below 250 K.

## Introduction

Organopolysiloxanes have been investigated as important commercial polymers,[1−3] which have excellent properties including heat resistance, chemical stability, and electric insulation compared to carbon-based polymers. Organopolysiloxanes as commercial polymers are classified into two groups according to their structural units. Silicone oils and elastomers mainly consist of D ($R_2SiO_{2/2}$) units which provide linear polymers in the skeleton, while silicone resins comprise three-dimensionally cross-linked networks, which mainly contain T (units derived from $RSiX_3$) or Q (units derived from $SiX_4$) units in their structure.

Among silicone resins, silsesquioxanes consisting only of $T^3$ ($RSiO_{3/2}$) and $T^2$ ($RSi(OH)O_{2/2}$) units are reported to have ladder structure shown in Figure 1a and cage structures typically shown in Figure 1b,c,[4] although there is no ultimate evidence for the ladder structure in Figure 1a. Among oligosilsesquioxanes, some cage compounds can be synthesized with specific substituents which are incorporated into organic−inorganic hybrid materials to design novel structure giving new properties.[5−10] In contrast to these oligosilsesquioxanes, polysilsesquioxanes in reality are considered to have complicated structure partially containing cage or ladder structures.[11] Porosity in polysilsesquioxanes has been studied with positron annihilation spectroscopy and nitrogen sorption.[12] For the control of the structure to generate new properties which lead to novel performance of silicone resins, information on the microstructure of the polysilsesquioxanes such as local free volume, local chain relaxation, strength of hydrogen bonding, and effects of the presence of various molecular-weight components is important. However, enough knowledge has not been accumulated for three-dimensionally cross-linked polymers such as polysilsesquioxanes.

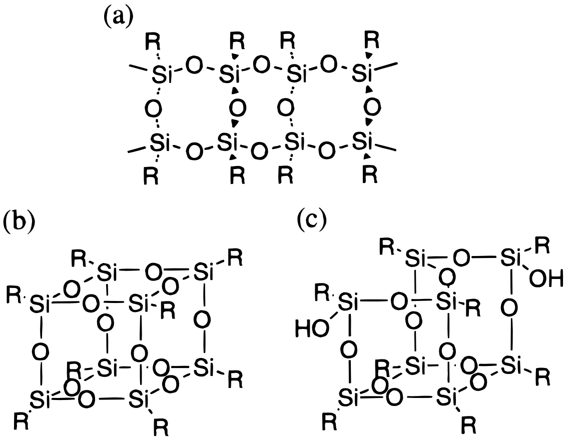

**Figure 1.** Structures of silsesquioxane: (a) ladder structure, (b) completely condensed cage structure ($T^8$), (c) incompletely condensed cage structure.

Various techniques have been used for investigating the microstructure and microenvironments in amorphous polymer solids, including positron annihilation spectroscopy,[13−15] gas sorption,[16,17] solid-state NMR analysis,[18] UV−vis spectroscopy,[19,20] and fluorescent spectroscopy.[20−22] Photochemical and thermal isomerizations of photochromic chromophores[23−32] or photoracemization of chiral molecules[33] molecularly dispersed in polymer matrices or attached to polymer chains have been used as a photoprobe to evaluate the microenvironment including local free volume and its thermal fluctuation. The free volume corresponds to unoccupied volume when the volume of a unit mass of a substance is defined as the sum of van der Waals volume occupied

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[†] Dedicated to Prof. K. Dušek on the occasion of his 70th birthday.

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by the atoms and unoccupied volume. Isomerization reactions in the solid states are different from those in solution due to the local free volume distribution of the matrices and the restriction of chain mobility.[34] Consequently, non-first-order progress of reactions is frequently observed in the solid states. Final conversions and quantum yields in photoisomerization of probe molecules also depend on the amount of the sites where its local free volume is larger than a critical size necessary for isomerization of the probe chromophores. The local free volume can be expanded by thermal fluctuation of the free volume arising from the local relaxation of the matrix.

Photoisomerization of various photochromic probe molecules has been applied to various amorphous carbon-based polymer solids such as polycarbonate (PC),[23,26] epoxy resin,[25] poly(methyl methacrylate) (PMMA),[28] poly(vinyl alcohol) (PVA),[28] phenoxy resin (aromatic polyhydroxyether, PhR),[28] and polystyrene.[30] In our previous studies, linear polysiloxanes and MQ-type silicone resins containing only M ($R_3SiO_{1/2}$) and Q ($SiO_{4/2}$) units were investigated using photoisomerization of azobenzene,[29] as well as fluorescence depolarization[35] and photochemical hole burning.[36] The MQ resin is considered to be an assembly of nanometer-scale particles. The results gave information about drastic restriction of the siloxane-chain flexibility at 4 K.

In the present study, the local free volume and its thermal fluctuation in a polymethylsilsesquioxane (PMSQ) are studied by use of photoisomerization of azobenzene molecularly dispersed in the matrices over a wide temperature range. Photoisomerization profiles were analyzed on the basis of three parameters: the first-order plots, final cis fraction, and three-component analysis for uncured and silanol-condensation-cured PMSQ's. An anomalous decrease in the final cis fraction of azobenzene in an uncured PMSQ below 250 K and its increase with the extent of curing are attributed to the presence of low-molecular-weight components having silanol groups occupying the voids in the uncured PMSQ.

## Experimental Section

**Materials.** *trans*-Azobenzene was purified by recrystallization from ethanol solution. Ethanol, methyl isobutyl ketone (MIBK), methyltrichlorosilane, hexane, chloroform, tetraethyl orthosilicate (TEOS), and magnesium sulfate were used as received.

**PMSQ Synthesis.**[37] MIBK (1.5 L) and 2 L of water were placed in a 5 L four-necked round-bottom flask equipped with a mechanical stirrer, a thermometer, an addition funnel, and a reflux condenser. To this was added dropwise 748 g (5 mol) of methyltrichlorosilane dissolved in 0.5 L of MIBK on an ice–water bath to keep the reaction temperature around 20 °C during the addition. The reaction mixture was then heated at 50 °C for 3 h. The organic phase was washed with water to neutral, followed by drying with magnesium sulfate. The MIBK was then removed in vacuo, giving PMSQ as a white powder, 335 g. This uncured bulk PMSQ is called sometimes simply an uncured PMSQ.

**Fractionation of the PMSQ.** Fractionation of the PMSQ into two fractions was conducted by solvent extraction. PMSQ (10 g) was added with 200 mL of a 7:3 volume ratio of hexane–chloroform mixture. After stirring 30 min, the mixture was allowed to stand overnight, giving a supernatant solution layer and a bottom viscous solution layer. The low-molecular-weight fraction (uncured LPMSQ) was obtained by removing the solvent from the supernatant solution. The high-molecular-weight fraction (uncured HPMSQ) was recovered by removing the solvent from the bottom layer.

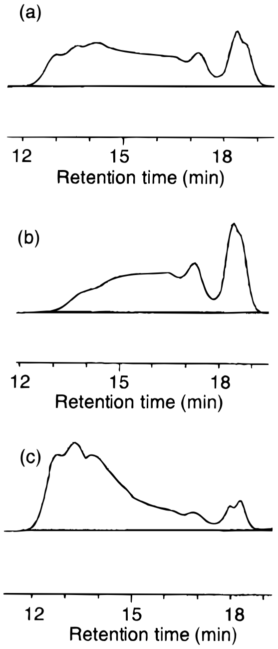

**Figure 2.** GPC curves for various PMSQ's: (a) uncured bulk PMSQ, (b) uncured LPMSQ, (c) uncured HPMSQ.

**PMSQ Characterization.** Gel permeation chromatography (GPC) curves were obtained using a Toso HLC-8020 gel permeation chromatograph equipped with a refractive index detector. A column set TSKgel with $GMH_{XL}$-L×2 was used with chloroform as an eluent. The molecular weight was determined relative to polystyrene standards, of which the molecular weight ranged from $2.66 \times 10^2$ to $3.84 \times 10^6$. Cyclohexane was used as an internal standard. The calibration curves were corrected for each run from the difference in the retention time of the internal standard in each run and the standard curve. Figure 2 shows the GPC curves for each PMSQ.

$^{29}$Si NMR spectra were recorded on a Bruker ACP-300 spectrometer in $CDCl_3$. Chromium acetylacetonate was used as a relaxation agent with concentration of 0.02 M, and a gated decoupling in which the proton was irradiated only during the acquisition of FID was employed with the pulse angle of 70° and the pulse delay of 10 s.

The GPC weight-average molecular weight, $M_w$, of the uncured bulk PMSQ relative to polystyrene was 5820, and the number-average molecular weight, $M_n$, was 1050. The $T^2/(T^3 + T^2)$ ratio determined by $^{29}$Si NMR spectroscopy was 0.226. This $T^2/(T^3 + T^2)$ ratio was simply calculated by assuming that the peaks between −50 and −58 ppm are of $T^2$ and those between −58 and −70 ppm are of $T^3$. It is considered that some $T^3$ silicon in strained rings appear in the traditional $T^2$ region,[11] and as a matter of fact, trimethylsilyl capping of the PMSQ by *N*,*O*-bis(trimethylsilyl)trifluoroacetamide revealed that 75–80 mol % of silicon atoms in the $T^2$ region belong to the real $T^2$ unit (Itoh, M., unpublished result), but comparison of the relative abundance of silanol in resins would be valid by the current $T^2/(T^3 + T^2)$ ratio. The GPC $M_w$ of the uncured LPMSQ was 2080, $M_n$ was 780, and the $T^2/(T^3 + T^2)$ ratio was 0.213. The GPC $M_w$ of the uncured HPMSQ was 8790, $M_n$ was 1880, and the $T^2/(T^3 + T^2)$ ratio was 0.187. The bulk PMSQ used for the fractionation is of different lot from the above bulk PMSQ having the $T^2/(T^3 + T^2)$ ratio of 0.194.

**Sample Preparation.** For the preparation of PMSQ films containing molecularly dispersed *trans*-azobenzene, a chloroform solution of stannous bis(2-ethylhexanoate) (50 $\mu$L, 4.0 wt %) as a cross-linking catalyst (0.1 wt % against the weight of the uncured bulk PMSQ) and that of azobenzene (0.5 mL of 0.014 M solution which corresponds to, for example, $2.0 \times 10^{-3}$ M in cured PMSQ film) were added to a 20% chloroform solution of the uncured PMSQ (2.0 g of uncured bulk PMSQ) at room temperature. At this time, the amount of azobenzene

**Table 1. Extent of Curing Reaction of the Sample Films Prepared with Various Heating Processes**

| condition | sample | curing process[a] | extent of curing reaction[b] (%) |
|---|---|---|---|
| A | bulk PMSQ | 100 °C, 1 h → 120 °C, 2 h | 68 |
| B | bulk PMSQ | uncured | 2 |
| C | bulk PMSQ | 100 °C, 1 h → 140 °C, 1 h | 75 |
| D | bulk PMSQ | 100 °C, 1 h | 20 |
| E | bulk PMSQ | 60 °C, 1 h | 5 |
| F | LPMSQ | 100 °C, 1 h → 120 °C, 2 h | 68 |
| G | LPMSQ | uncured | 2 |
| H | HPMSQ | 100 °C, 1 h → 120 °C, 2 h | 40 |
| I | HPMSQ | uncured | 2 |

[a] After evacuating at room temperature for 6 h. [b] Calculated from the change in the infrared spectra through the curing reaction.

adding to PMSQ films was controlled to be finally OD = 0.4−0.8 at 320 nm by considering that a part of azobenzene molecules sublimate during being dried under vacuum and heating. The mixture was stirred vigorously before being cast onto a poly(ethylene terephthalate) (PET) sheet, followed by standing overnight at room temperature. The sample films were peeled off from the PET sheet after being dried under vacuum at room temperature for 6 h to eliminate the residual solvent. The films (100 $\mu$m in thickness) were then cured by stepwise heating described in Table 1 for the polycondensation on quartz plates. The sample films prepared in condition A in Table 1 were simply named cured PMSQ unless otherwise noted. For the fractionated PMSQ's, the sample films were prepared in a manner similar to the bulk PMSQ films, and the sample films prepared in conditions F and H were denoted as cured LPMSQ and cured HPMSQ, respectively. The concentration of *trans*-azobenzene was determined by ultraviolet absorption spectra. The extent of the polycondensation curing reaction was determined by the change in infrared spectra. The decrease in intensity at 3400 $\text{cm}^{-1}$, O−H stretching of silanol groups, was measured in the course of the curing. The absorption band at 2964 $\text{cm}^{-1}$, C−H stretching of methyl groups, was used as an internal standard.

**Measurements of Photoisomerization.** The sample films set in a cryostat (Oxford DN 1754 for the temperature above 77 K, Iwatani Plantech D 310 below 77 K, and Oxford CF 1204 for 4 K) were irradiated with 360 nm light from a 150 W xenon lamp (Hamamatsu L 2195) with a combination of color filters (UVD 36A and UV 29) for the measurements of trans-to-cis photoisomerization of azobenzene. Photoisomerization of azobenzene was measured with a double-beam system, in which the change in the intensity of transmitted 320 nm light was monitored with a photomultiplier (Hamamatsu R374) through a monochromator (J&Y H-20VIS). The sample films were irradiated until reaching the photostationary state. The absorption spectra of azobenzene in polymer matrices was measured with UV/vis spectrophotometer (JASCO UVIDEC-660). Actinometry for the irradiation light was carried out with an Advantest TQ-8210 type photometer calibrated using a potassium ferrioxalate/*o*-phenanthroline system.[38]

## Results and Discussion

**Kinetics of Photoisomerization of Azobenzene.** When *trans*-azobenzene was irradiated with continuous-wave light at 360 nm with the intensity of $I_0$ (einstein $\text{cm}^{-2}\ \text{s}^{-1}$), the isomerization processes involve photochemical trans-to-cis and cis-to-trans isomerization and thermal cis-to-trans isomerization. The rate of the change in cis-isomer fraction at time $t$, $y_t$, is described by eq 1,

$$\frac{\mathrm{d}y_t}{\mathrm{d}t} = \frac{I_0}{F}\{\Phi_{\mathrm{tr}}\epsilon'_{\mathrm{tr}}(1 - y_t)\} - \frac{I_0}{F}\{\Phi_{\mathrm{cis}}\epsilon'_{\mathrm{cis}}y_t\} - Ky_t \quad (1)$$

where $\epsilon'$ ($\text{L mol}^{-1}\ \text{cm}^{-1}$) is the molar extinction coefficient at irradiation wavelength, $\Phi$ is the quantum yield for photoisomerization, $K$ is the rate constant for thermal cis-to-trans isomerization, and subscripts tr and cis denote trans and cis isomers, respectively. The parameter $F$ is given by $F = (D'_t)/(1 - \mathrm{e}^{-D'_t})$, where $D'_t$ is the optical density at time $t$. The prime for $D'_t$ and $\epsilon'$ denotes that the base is e = 2.7183. The value of $y_t$ is calculated from the optical density of the sample at time $t$, $\mathrm{OD}_t$, from eq 2,

$$y_t = \frac{[\mathrm{cis}]_t}{[\mathrm{tr}]_0} = \frac{1 - \mathrm{OD}_t/\mathrm{OD}_0}{1 - \epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{tr}}} \quad (2)$$

where $[\mathrm{tr}]_0$ denotes the initial concentration of *trans*-azobenzene and $[\mathrm{cis}]_t$ denotes the concentration of the *cis*-azobenzene at time $t$. The final cis fraction, $y_\infty$, is obtained by replacing $\mathrm{OD}_t$ with the optical density at the photostationary state, $\mathrm{OD}_\infty$, in eq 2. The base of OD and $\epsilon$ is 10, and hence $D' = \mathrm{OD} \times \ln 10$ at every time and $\epsilon' = \epsilon \times \ln 10$ for each isomer. As for the value of $\epsilon$, measured values in hexane solution are used ($\epsilon_{\mathrm{tr}} = 2.65 \times 10^4\ \text{L mol}^{-1}\ \text{cm}^{-1}$, $\epsilon_{\mathrm{cis}} = 1.66 \times 10^3\ \text{L mol}^{-1}\ \text{cm}^{-1}$ at 320 nm). The rate of thermal cis-to-trans isomerization of azobenzene is much slower than that of photoisomerization.[23] By neglecting the third term for the thermal isomerization in eq 1 and introducing the cis fraction at photostationary state, $y_\infty$, eq 3 is given as follows:

$$\frac{\mathrm{d}y_t}{\mathrm{d}t} = \frac{A}{F}(y_\infty - y_t) \quad (3)$$

where $A = (I_0\Phi_{\mathrm{tr}}\epsilon'_{\mathrm{tr}})/(y_\infty)$ and $I_0\epsilon'_{\mathrm{tr}}$ is summed over the wavelength region of the incident light. By defining $z = y_\infty - y_t$, eq 3 is rewritten as eq 4,[39]

$$\frac{\mathrm{d}z}{\mathrm{d}t} = -\frac{A}{F}z \quad (4)$$

Blanc proposed the variable $\delta$ as $\delta = D'_\infty - D'_t$.[40] By using the relation of $\mathrm{d}z/z = \mathrm{d}\delta/\delta$, integration can be performed on eq 4. Defining $I(\delta) = \int F(\mathrm{d}\delta)/(\delta)$, eq 5 is obtained,

$$I(\delta) = \int F\frac{\mathrm{d}z}{z} = \int F\frac{\mathrm{d}\delta}{\delta} = -At + b \quad (5)$$

where $b$ is the intercept at $t = 0$ of $I(\delta)$. The slope, $A$, in the plots of $I(\delta)$ vs $t$ gives $\Phi_{\mathrm{tr}}$. The integration in eq 5 is, however, analytically impossible. For the range of $D'$ used in our experiment (0.8−2.0), eq 6 gives a good approximation to the exact value of $F$:[39]

$$F = 1 + \frac{1}{2}D'_t + \frac{1}{12}{D'_t}^2 \quad (6)$$

Using eq 6, eq 7 is obtained,[40]

$$I(\delta) = \left(1 + \frac{D'_\infty}{2} + \frac{{D'_\infty}^2}{12}\right)\ln\delta - \left(\frac{1}{2} + \frac{D'_\infty}{6}\right)\delta + \frac{\delta^2}{24} \quad (7)$$

Thus, $\Phi_{\mathrm{tr}}$ can be obtained from the plots of $I(\delta)$ vs $t$. For convenience, the photoisomerization index, $I'(\delta) \equiv -(I(\delta) - b)$, is used in the present analysis.

Ueda et al.[41] have reported that a new shoulder at absorption between the $\pi$−$\pi$* and n−$\pi$* absorption bands is observed when silanol groups in sol−gel films form hydrogen bonding with the azo group. However,

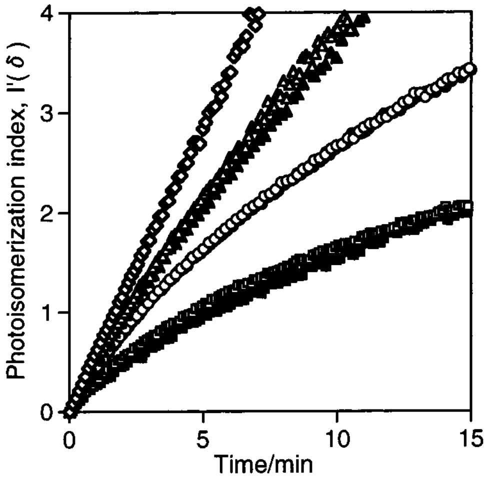

**Figure 3.** First-order plots for the trans-to-cis photoisomerization of azobenzene in the cured PMSQ at various temperatures: (◇) room temperature, (△) 250 K, (▲) 202 K, (○) 150 K, (●) 90 K, (□) 20 K, (■) 4 K.

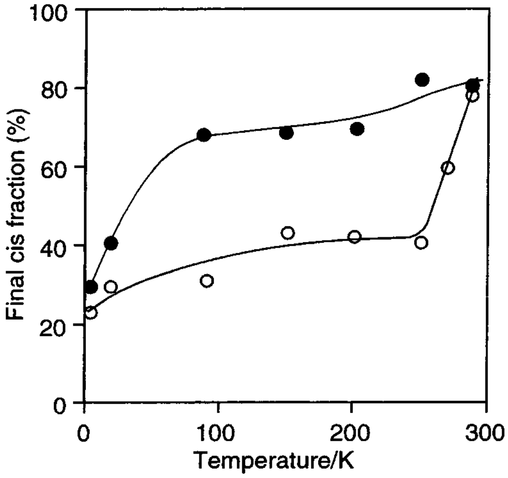

**Figure 4.** Final cis fractions, $[\text{cis}]_\infty/[\text{tr}]_0$, plotted against temperature for the trans-to-cis photoisomerization of azobenzene in the PMSQ films: (●) cured PMSQ, (○) uncured PMSQ.

such absorption spectra of azobenzene were not recognized in the present PMSQ films. This suggests that hydrogen bonding between the azo group and silanol groups is negligible in the present case and has no effect on photoisomerization profiles of azobenzene. The profile of absorption spectra of azobenzene in PMSQ films agreed well with those in dilute hexane and TEOS solutions, suggesting that azobenzene molecules are molecularly dispersed in the PMSQ. The isosbestic points appeared during photoisomerization. This indicates that photoisomerization proceeds without a side reaction.

**Temperature Dependence for Trans-to-Cis Photoisomerization in the PMSQ.** Figure 3 shows the first-order plots for the trans-to-cis photoisomerization of azobenzene at various temperatures, from liquid helium temperature to room temperature, in the cured PMSQ. At room temperature, the reaction proceeds with the first-order kinetics in the cured PMSQ similar to the case in solution. This suggests that most of the azobenzene molecules lie at the sites with a local free volume larger than the critical volume necessary for the isomerization to occur which results from the effect of thermal fluctuation of local free volume at room temperature. This critical volume is determined from the sweep volume of azobenzene. The sweep volume is a volume swept out by the van der Waals area of the isomerizing group. The sweep volume of azobenzene was reported to be 0.127 nm$^3$ based on Bondi's method[42] by Victor and Torkelson.[30]

The deviation from the straight lines in the first-order plots becomes more marked with decreasing temperature, which was previously observed in various amorphous polymer solids, such as PC,[23] PMMA,[28] and MQ-type silicone resins.[29] This deviation from the straight lines can be explained by both the heterogeneous distribution of local free volume at reaction sites and the suppression of chain mobility in the cured PMSQ with decreasing temperature. For photoisomerization in the uncured PMSQ, a similar deviation from the first-order kinetics to that in the cured PMSQ resin was observed.

Figure 4 shows final cis fractions, $[\text{cis}]_\infty/[\text{tr}]_0$, as a function of temperature for the trans-to-cis photoisomerization of azobenzene in the uncured and cured PMSQ's. The final cis fraction is a fraction of cis isomers at the photoequilibrium state. In solid states, the remaining trans fraction, i.e., $1 - ([\text{cis}]_\infty/[\text{tr}]_0)$, includes azobenzene molecules at two kinds of sites. One corresponds to the trans-form site due to backward cis-to-trans photoisomerization. The other is the site where *trans*-azobenzene cannot isomerize owing to a local free volume smaller than the critical volume necessary for isomerization. The value of the final cis fraction reflects both the size of local free volume and its thermal fluctuation arising from the local relaxation of the matrices. The final cis fractions for the cured and uncured PMSQ's are about 80% at room temperature and decrease with decreasing temperature, which can be attributed to the restriction of thermal fluctuation of the local free volume.

The final cis fraction of the uncured PMSQ jumps down at 250 K and is anomalously low (about 30–40%) over the temperature range from 250 to 4 K as shown in Figure 4. This anomalous decrease has never been observed for linear polysiloxanes, MQ resins,[29] or carbon-based polymers.[23–28] At 4 K, only such azobenzene molecules are supposed to isomerize that stay at the local sites where their intrinsic size is larger than a critical size necessary for the photoisomerization to occur, because the thermal fluctuation of local free volume is almost perfectly frozen. Therefore, we suggest from the final cis fraction data that photoisomerization of azobenzene could be restricted mostly due to the suppression of siloxane-chain mobility even at 250 K in the uncured PMSQ.

The final cis fractions in the cured PMSQ were then compared with those in the uncured PMSQ. It is generally considered that curing reaction splits local space, resulting in the decrease in the size of local volume, and restricts the fluctuation of local free volume. The decrease in final cis fractions with the progress of curing reaction was reported in the MQ resin.[29] In contrast, final cis fractions in the cured PMSQ are larger than those in the uncured PMSQ over the wide temperature range from 250 to 90 K as shown in Figure 4. Final cis fractions at 90 K in the PMSQ as a function of the extent of the silanol condensation curing reaction are shown in Figure 5. Final cis fraction increases with increasing degree of curing in the PMSQ and levels off. The increase in final cis fractions with the progress of the curing reaction is a particular

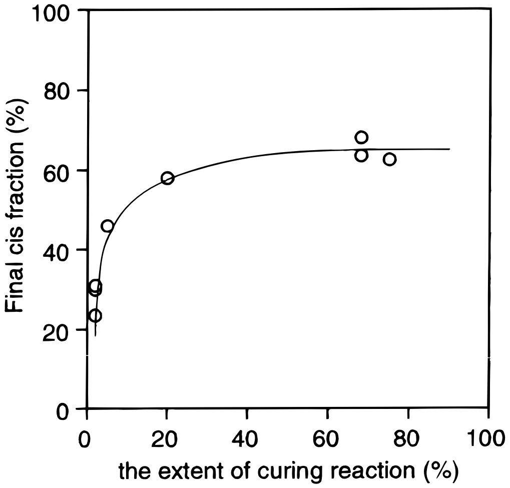

**Figure 5.** Final cis fractions, $[cis]_\infty/[tr]_0$, plotted against the extent of curing reaction for the trans-to-cis photoisomerization of azobenzene at 90 K in the PMSQ.

characteristic among the polymers we have studied to date.

In the following section, we will discuss these two characteristic results: anomalous restriction of photoisomerization in the uncured PMSQ below 250 K and the increase in final cis fractions by the curing reaction of the PMSQ. We will focus on the effects of both low-molecular-weight components existing in the PMSQ and hydrogen bonding by a silanol group as the cause of the characteristic results in the PMSQ.

**Effect of Low-Molecular-Weight Components.** The uncured PMSQ has a broad molecular-weight distribution as shown in Figure 2 containing various low-molecular-weight species, of which GPC $M_w$ is $10^2$–$10^3$. As a matter of fact, 18 compounds (including isomers) ranging from $T^3{}_4T^2{}_2$ to $T^3{}_{10}$ have been detected by GC and GC-MS, of which the sum is ~8 wt % of the PMSQ.[11,43] These molecules do not exist in the cured PMSQ anymore, being a part of cross-linked macromolecules. Therefore, the influence of low-molecular-weight components on photoisomerization of azobenzene should be investigated.

We at first examined the extent of crystallization due to the low-molecular-weight components using the wide-angle X-ray diffraction (WAXD) method with a JEOL JDX-3530 diffractometer with Ni-filtered Cu–Kα radiation. The intensity distribution ($2° < 2\theta < 35°$) was observed in the reflection mode using a goniometer equipped with a monochromator. The WAXD pattern for both uncured and cured PMSQ showed the absence of both macroscopic and microscopic crystallization. Although crystallizable low-molecular-weight compounds exist in the uncured PMSQ, other parts of the PMSQ matrix would disturb the crystallization of low-molecular-weight compounds. The WAXD patterns indicated that there is no crystallization which could influence photoisomerization of azobenzene in the uncured PMSQ.

PMSQ's fractionated by molecular weight were prepared to discuss the effects of low-molecular-weight components on photoisomerization of azobenzene. The lower-molecular-weight fraction of the uncured bulk PMSQ is designated as uncured LPMSQ, and the higher-molecular-weight fraction corresponds to uncured HPMSQ. The GPC curves for each fractionated PMSQ are shown in Figure 2. The uncured LPMSQ has larger amounts of low-molecular-weight components than the uncured bulk PMSQ. The concentration of low-molecular-weight components in the uncured HPMSQ is much lower than that in the uncured bulk PMSQ. Figure 6 shows final cis fractions as a function of temperature for the trans-to-cis photoisomerization of azobenzene in the uncured and cured fractionated PMSQ's. The final cis fractions in the uncured LPMSQ drastically decrease arround 270 K and are anomalously low in the temperature range from 270 to 4 K. The final cis fractions in the cured LPMSQ are much larger than those in the uncured LPMSQ in the temperature range from 250 to 90 K. The curing process dependence of final cis fraction at 270–90 K in the LPMSQ is the same as that for the bulk PMSQ in Figure 4. However, the final cis fractions in the uncured and cured HPMSQ's show almost the same values and are equivalent to those for cured bulk PMSQ and cured LPMSQ's. From these results, we can suggest that the low-molecular-weight components have a great influence on photoisomerization of azobenzene in the bulk PMSQ.

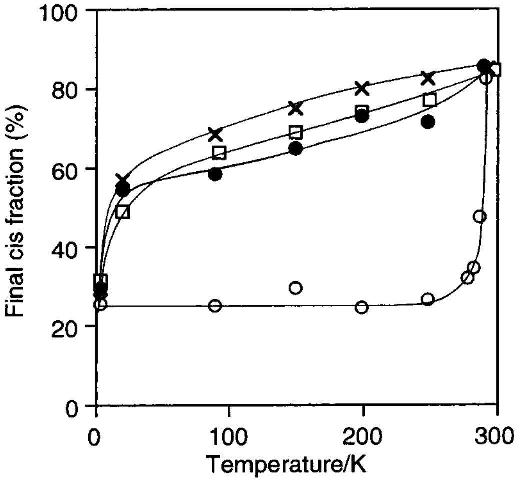

**Figure 6.** Final cis fractions, $[cis]_\infty/[tr]_0$, plotted against temperature for the trans-to-cis photoisomerization of azobenzene in various PMSQ's: (○) uncured LPMSQ, (●) cured LPMSQ, (□) uncured HPMSQ, (×) cured HPMSQ.

**Effect of Hydrogen Bonding.** The uncured bulk PMSQ contains a lot of silanol groups, which form hydrogen bonding with each other or with siloxane chains. Hydrogen bonding will suppress the motion of siloxane chains. Condensation curing reactions consume silanol groups. Therefore, we should discuss the influence of hydrogen bonding on photoisomerization of azobenzene.

To study the effect of hydrogen bonding by a silanol group, we studied the temperature dependence of infrared spectra for the PMSQ. The infrared spectra were obtained with a combination of an IR spectrometer and a cryostat (Oxford DN 1754). The sample was prepared in a manner similar to the sample for photoisomerization except for being cast onto KBr plates and containing no azobenzene. The IR absorption bands assigned to O–H stretching of silanol groups range from 3300 to 3700 $cm^{-1}$. The absorption bands at 3700 $cm^{-1}$, in the vicinity of 3600 $cm^{-1}$, and at 3300–3400 $cm^{-1}$ were assigned to O–H stretching of free silanol groups isolated from other silanol groups, of silanol groups hydrogen bonded to siloxane bonds, and of silanol groups hydrogen bonded to other silanol groups, respectively.[44]

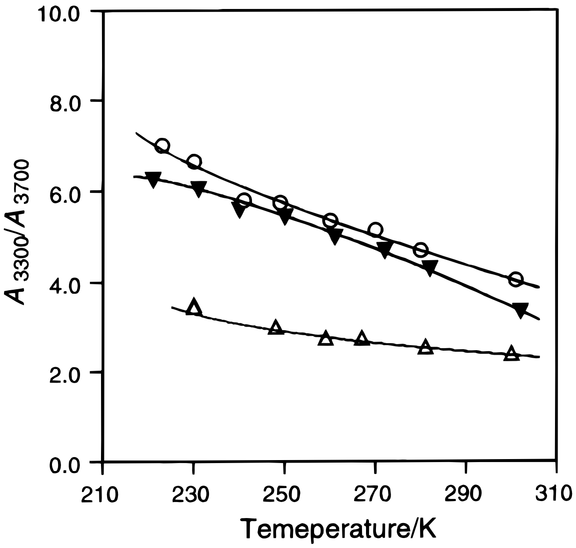

**Figure 7.** Ratios of relative intensity of absorbance, $A_{3300}/A_{3700}$, for various uncured PMSQ's against temperature: (○) uncured bulk PMSQ, (▼) uncured LPMSQ, (△) uncured HPMSQ.

The ratios of relative intensity of the absorbance at 3300 cm$^{-1}$ against that at 3700 cm$^{-1}$, $A_{3300}/A_{3700}$, for various uncured PMSQ's against temperature are shown in Figure 7. The increase in the ratio ($A_{3300}/A_{3700}$) corresponds to the increase in the number of the silanol groups forming hydrogen bonding with each other compared to the case of free silanol groups. The values of $A_{3300}/A_{3700}$ for the uncured bulk PMSQ and LPMSQ are larger than that for the uncured HPMSQ. The $A_{3300}/A_{3700}$ for the uncured bulk PMSQ and LPMSQ increases more markedly with decreasing temperature than that for the uncured HPMSQ does. These differences suggest that hydrogen bonding by a silanol group has an effect on the anomalous decrease of final cis fractions at low temperatures. However, there is no transition near 250 K in the temperature dependence of $A_{3300}/A_{3700}$ for the uncured bulk PMSQ, while the final cis fraction in the uncured bulk PMSQ jumps down at 250 K as shown in Figure 4. We suppose that the presence of low-molecular-weight species itself would strongly work on the transition of final cis fraction at 250 K as compared with the effect of hydrogen bonding.

**Dynamic Structure of the PMSQ.** The uncured bulk PMSQ contains low-molecular-weight components. As mentioned above, 18 compounds were detected by GC and GC-MS analysis, of which the sum is ~8 wt %.[11,43] Also, 97 wt % of these GC-detected species contains silanol. Examples of hypothetical schematic structures for these low-molecular-weight molecules of methylsilsesquioxane (MSQ) are shown in Figure 8 for (a) $T^3{}_6T^2$, (b) $T^3{}_6T^2{}_2$, and (c) $T^3{}_8T^2$. Among them, structure b has been isolated and identified.[45] These low-molecular-weight components could densely lie in the voids of a polysiloxane matrix composed of relatively higher-molecular-weight components. Azobenzene molecules would also lie in the voids of the polysiloxane matrix. At room temperature, the low-molecular-weight species could be able to get in and out of the voids in the polysiloxane matrix owing to the micro-Brownian motion, and the polysiloxane matrix itself could thermally fluctuate. As a consequence, about 80% of azobenzene molecules could finally isomerize despite the presence of low-molecular-weight components.

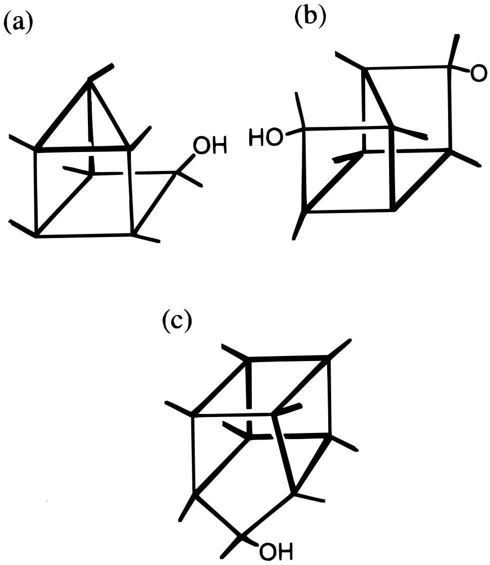

**Figure 8.** Examples of the hypothetical schematic structures for low-molecular-weight molecules of methylsilsesquioxane (MSQ).

At low temperatures, the low-molecular-weight species are occluded in the voids as the restriction of thermal fluctuation causes the shrinkage of the polysiloxane matrix. The presence of low-molecular-weight species in the voids could make the local space smaller. The low-molecular-weight molecules having silanol groups also form hydrogen bonding with each other or with siloxane chains, which suppresses the motion of siloxane chain. Therefore, the synergistic effect of the presence of low-molecular-weight components and the formation of hydrogen bonding could result in the anomalous decrease of final cis fractions in the uncured bulk PMSQ at low temperatures.

Final cis fractions of azobenzene were low also in PhR and PVA having hydroxy groups in the main chain compared to PC and PMMA containing no hydroxy groups.[28] However, final cis fractions in PhR and PVA were still much larger than that in the uncured bulk PMSQ. The difference in the case of uncured bulk PMSQ from those of PhR and PVA could be due to the presence of low-molecular-weight components filling local voids of the polysiloxane matrix.

In the condensation curing reaction, silanol groups change to a siloxane chain. The low-molecular-weight components having silanol groups could form a siloxane chain with relatively higher-molecular-weight components and could be fixed in a position out of the voids with the rearrangement owing to thermal motion. As a consequence, the curing reaction could enlarge the size of local free volumes, leading to the increase in final cis fraction in the bulk PMSQ.

As shown in Figure 5, the decrease in final cis fraction is observed when the extent of curing reaction is below a critical value in the bulk PMSQ. By considering that the concentration of low-molecular-weight components decreases with the progress of the curing reaction, we suggest that the suppressive effect of low-molecular-weight species occurs only when the concentration of low-molecular-weight components in the bulk PMSQ is above a critical concentration. Since low-molecular-weight species could react in the first stage of the curing reaction, there could be no low-molecular-weight species anymore to influence the photoisomerization of azobenzene at a critical concentration.

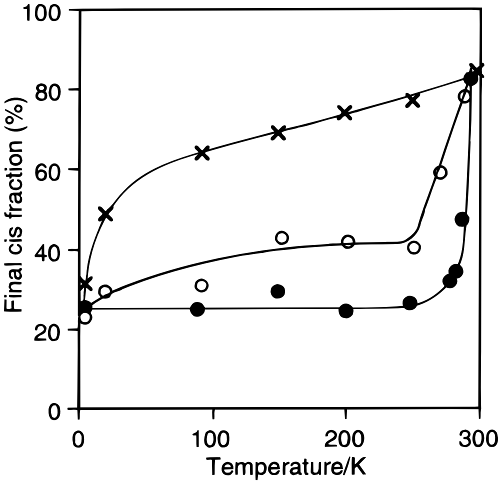

**Figure 9.** Final cis fractions, $[\mathrm{cis}]_\infty/[\mathrm{tr}]_0$, plotted against temperature for the trans-to-cis photoisomerization of azobenzene in various uncured PMSQ's: (○) uncured bulk PMSQ, (●) uncured LPMSQ, (×) uncured HPMSQ.

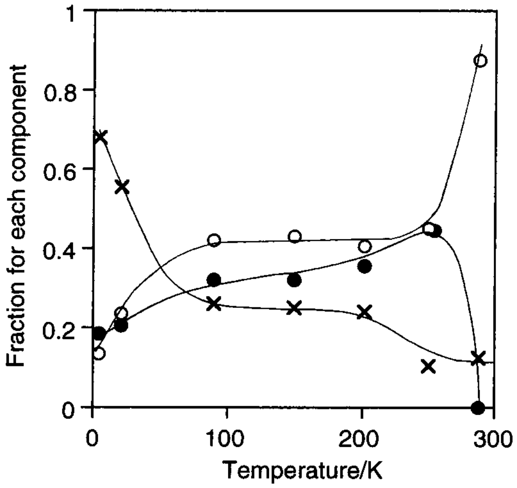

**Figure 10.** Temperature dependence of fractions for each component in the cured bulk PMSQ: (○) fast-rate component, (●) slow-rate component, (×) nonreactive component.

Figure 9 shows final cis fractions, $[\mathrm{cis}]_\infty/[\mathrm{tr}]_0$, against temperature for the trans-to-cis photoisomerization of azobenzene in various uncured PMSQ's. The transition temperature, where the final cis fraction decreases drastically, is around 250 K in the uncured bulk PMSQ, and that in the uncured LPMSQ is near 270 K, about 20 K higher than that in the uncured bulk PMSQ. Final cis fractions in the uncured LPMSQ are a little lower than those in the uncured bulk PMSQ over the temperature range from 250 to 90 K. We suggest from these results that the more the low-molecular-weight components exist in the PMSQ, the more the motion of siloxane chain mobility would be suppressed and the smaller the space for the azobenzene isomerization would become. The absence of low-molecular-weight species in the uncured HPMSQ gave a large final cis fraction similar to that for cured PMSQ's.

The antiplasticization system in thermosetting resins, e.g., in an epoxy resin,[46] has been reported. When polar low-molecular-weight compounds (antiplasticizers) are added to a polymeric material which is relatively rigid and contains polar groups, the doped antiplasticizers make the average radius of free volume smaller.[46,47] The effect of low-molecular-weight components on photoisomerization of azobenzene observed in the bulk PMSQ could be similar to the antiplasticization phenomenon. However, there is a difference between the PMSQ and usual antiplasticized systems. In antiplasticized systems, a low-molecular-weight compound may work as an antiplasticizer for a polar polymer matrix when the concentration of the doped low-molecular-weight compounds is less than a critical value. On the other hand, a low-molecular-weight component in the PMSQ works as a suppressant for siloxane-chain mobility, only when the concentration of low-molecular-weight components is more than a critical value.

**Local Sites in the Cured PMSQ.** The deviation from the linearity in first-order plots of photoisomerization of *trans*-azobenzene in the cured bulk PMSQ in Figure 3 indicates the presence of various-rate sites which could be attributed to the restriction of free-volume fluctuation at low temperatures. The contribution of slow-rate sites could be estimated by the analysis of the deviation. As an approximate approach, we fitted empirically the decay of the photoisomerization with the sum of two processes using eq 8,

$$e^{-I'(\delta)} = \alpha e^{-A_1 t} + (1 - \alpha) e^{-A_2 t} \tag{8}$$

where $A_1$ is the apparent rate coefficient for photoisomerization of azobenzene in the fast-rate site and $A_2$ is that in the slow-rate site, and $\alpha$ is related to the fraction of the fast-rate sites.[29,32] In this study, the sites in the matrix are classified into fast-rate sites, slow-rate sites, and nonreactive sites. We call this "three-component analysis" to analyze the kinetics of the trans-to-cis photoisomerization in amorphous polymer solids by approximating a rate distribution function with three rate components.

The fraction for nonreactive sites is calculated from the final cis fraction data in Figure 4. The final cis fraction in TEOS solution at room temperature (92%) was used as a value of cis fraction of freely photoisomerizable azobenzene at photoequilibrium state. The remainder is divided into fast-rate sites and slow-rate sites on the basis of the curve fitting with eq 8. Figure 10 shows the temperature dependence of fractions for each site in the cured bulk PMSQ. The fraction of nonreactive sites increases with decreasing temperature, which corresponds to the decrease in the final cis fraction with decreasing temperature. The fraction of fast-rate sites decreases with the decrease in temperature. The fraction of slow-rate sites does not exist at room temperature but appears around 250 K and decreases with a decrease in temperature.

The interpretation for the three-component analysis of photoisomerization in the cured bulk PMSQ is the following. The increase in the fraction of the nonreactive sites with a decrease in temperature is due to the restriction of the local free-volume fluctuation. The fast-rate site could change to the slow-rate site, and then to the nonreactive site, because the local free-volume fluctuation becomes suppressed in accordance with a decrease in temperature. As a result, this restriction of the fluctuation also causes the appearance of slow-rate sites and the decrease of the fractions of both fast-rate sites and slow-rate sites with the decrease in temperature.

The quantum yield for trans-to-cis photoisomerization at the fast-rate sites, $\Phi_{\mathrm{fast}}$, was calculated from $A_1$, $I_0$, $\epsilon'_{\mathrm{tr}}$, and $y_\infty$ using $A_1 = (I_0 \Phi_{\mathrm{fast}} \epsilon'_{\mathrm{tr}})/y_\infty$, and the quantum

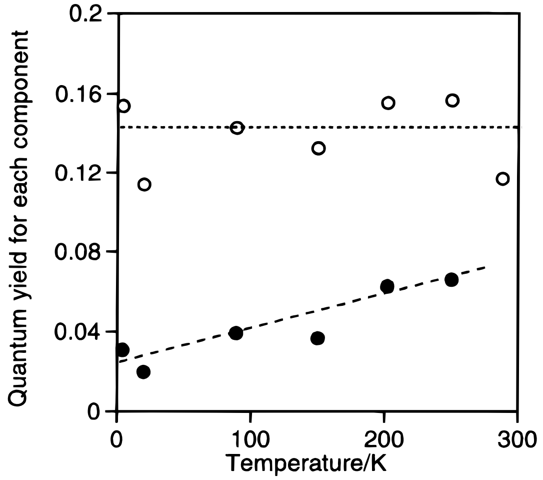

**Figure 11.** Temperature dependence of quantum yields for each component in the cured bulk PMSQ: (○) fast-rate component, (●) slow-rate component.

yield for trans-to-cis photoisomerization at the slow-rate sites, $\Phi_{slow}$, was calculated from $A_2$, $I_0$, $\epsilon'_{tr}$, and $y_\infty$ in the same way. Figure 11 shows the temperature dependence of quantum yields for each site in the cured bulk PMSQ. The quantum yields for fast-rate sites are 0.14 $\pm$ 0.03 independent of temperature. These values agree well with the reported values of 0.09–0.20 for trans-to-cis photoisomerization of azobenzene in organic solvents at room temperature.[48] These results indicate that the fast-rate sites are solution-like sites where the local free volume around azobenzene molecules is much larger than that necessary for the photoisomerization to occur. The quantum yields for slow-rate sites decrease with a decrease in temperature. This decrease in the quantum yields could be due to the restriction of local free-volume fluctuation and chain mobility with the decrease in temperature.

**Conclusion.** We have investigated the local free volume and its thermal fluctuation in the uncured and cured PMSQ's using photoisomerization of azobenzene molecularly dispersed in the matrices as a photoprobe over a wide temperature range. Formation of heterogeneous free-volume distribution is suggested from first-order plots at low temperatures. The drastic decrease in final cis fraction in the uncured PMSQ below 250 K and the increase in final cis fraction by curing reaction are a characteristic feature for PMSQ, which have never been observed in linear polysiloxanes, MQ resins, or carbon-based polymers. For fractionated PMSQ's, the final cis fraction in the uncured LPMSQ also shows a drastic decrease similar to the uncured bulk PMSQ, while the value of final cis fractions in the uncured HPMSQ is the same as that in the cured PMSQ. Besides, hydrogen bonding between silanol groups in the uncured bulk PMSQ and LPMSQ is shown to be considerably strong at low temperatures as compared to that in the uncured HPMSQ. From these results and the known presence of low-molecular-weight species, we suggest that low-molecular-weight species having silanol groups, which form hydrogen bonding with each other or the siloxane chain, make the local vacant space smaller and suppress the siloxane chain mobility. From the comparison between the uncured bulk PMSQ and uncured LPMSQ, we suggest that the increase in the fraction of low-molecular-weight components causes the decrease in the local vacant space and the restriction of the siloxane chain mobility. Photoisomerization reaction is proven to be useful as a photoprobe to investigate the local free volume in silicone resins exemplified by PMSQ.

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