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# Free volumes and their distribution in crosslinked polysiloxanes probed by positron annihilation lifetime technique

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In order to correlate the size, numerical concentration, and size distribution of free volumes with the nanostructure of crosslinked polysiloxane (cured MQ resin), free volumes of polysiloxanes of different degree of crosslinkage polysiloxanes were observed by positron annihilation lifetime measurements in the temperature range from 30 K to room temperature. The free-volume diameters of the highly crosslinked polysiloxane were found to be larger in the temperature range studied and their distributions become broader above $T_g$ (150 K) than those for the lowly crosslinked polysiloxane, whereas free volume contents (number density) were lower for the highly crosslinked polysiloxane. The results suggest the heterogeneous and distorted nanostructure of prepolymers in the highly crosslinked polysiloxane. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: free volume; positron annihilation lifetime; polysiloxane)**

## INTRODUCTION

Polysiloxanes are a kind of polymer which have Si–O bonds in their main chains and silicon resins; silicon oils and silicon rubbers are included in this category[1,2]. They are widely used as coatings, insulators, release agents, vehicles for paintings and so on. They have advantages in thermal, chemical, and mechanical stability. Because of their good transparency in near infrared region and the flexibility of Si–O–Si bonds in their main chains, they are also used as advanced optical materials.

Crosslinked polysiloxanes, which are one of the silicone resins, have excellent mechanical properties by their hardness. From a structural point of view, crosslinked polysiloxanes contain various constitutional units: M($R_3SiO_{1/2}$), D($R_2SiO_{2/2}$), T($RSiO_{3/2}$) and Q($SiO_{4/2}$) units. The resin is believed to have several higher structures, such as ladder structure and cage structure because their polycondensation reaction proceeds heterogeneously. Thus, the evaluation of size, contents and size distribution of free volumes in three-dimensionally crosslinked polysiloxanes are very important for the characterization of their microstructure.

Since the lifetime ($\tau_3$) and the intensity ($I_3$) due to the pick-off process of ortho-positronium (o-Ps) are correlated well with the average size and contents of free volumes present in the amorphous region of polymers, respectively, positron annihilation lifetime measurement has been applied to various polymers in order to study the physical properties of polymers from the view point of free volumes[3–8].

In the present study, we have clarified the temperature dependence of free volume size, contents and size distribution of highly and lowly crosslinked polysiloxanes (cured MQ resin) by means of the positron annihilation lifetime technique from 30 K to room temperature.

## EXPERIMENTAL

### *Preparation of samples*

The cured MQ resin was prepared by mixing two prepolymers, A and B, in the presence of a platinum crosslinking catalyst. These prepolymers, each with a molecular weight of about 1700, were supplied from Dow Corning Asia Research Centre. The prepolymer A consisted of $M^{vi}$ and Q units (molar ratio 1.5:1), and the prepolymer B consisted of $M^H$ and Q units (molar ratio 1:1). The chemical structures of the constitutional units are shown in *Figure 1*.

The prepolymers were crosslinked upon mixing, without solvent but with the catalyst (20–40 ppm of the prepolymers by weight), at room temperature via the hydrosilylation reaction between vinyl groups and hydrosilyl groups.

The mixture was cured for the further occurrence of crosslinking. Two kinds of samples with different degrees of crosslinking were prepared by different heating curing steps. Lowly crosslinked MQ resin was prepared by heating only at 60°C for 2 h, while highly crosslinked MQ resin was prepared through successive heating steps; at 60°C for 2 h, 80°C for 0.5 h, 100°C for 1 h, and finally 120°C for 2 h.

The degree of the crosslinking was determined from the change in relative intensity of IR absorption assigned to a stretching of Si–H (2100 $cm^{-1}$) to that assigned to a stretching of C–H of methyl groups (2960 $cm^{-1}$). It was

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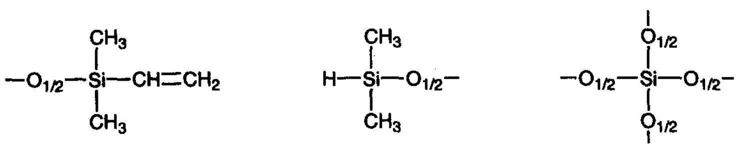

Vinyl type M unit ($M^{Vi}$) Hydrogen type M unit ($M^{H}$) Q unit

**Figure 1** Constitutional units of the MQ resins

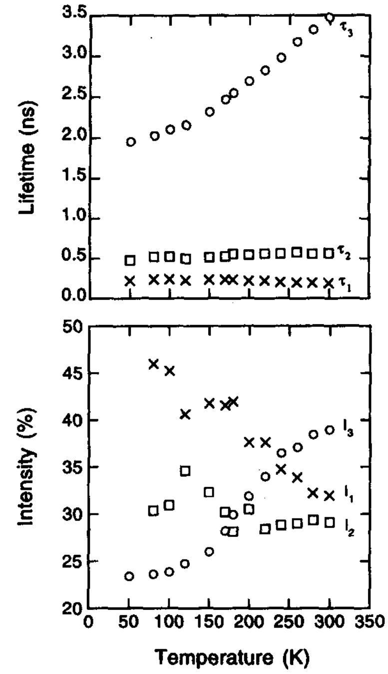

**Figure 2** Change in positron annihilation lifetime parameters of lowly crosslinked polylsiloxanes with an increase in temperature

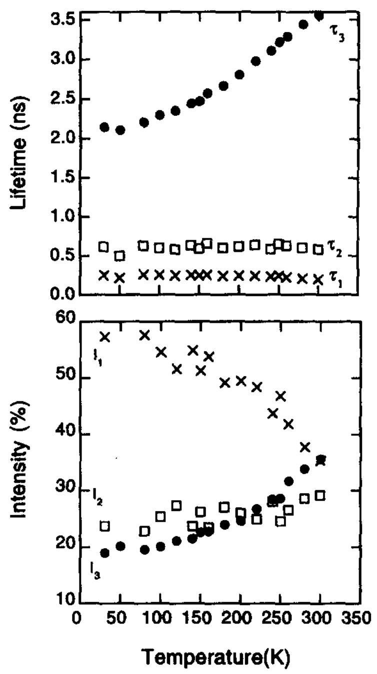

**Figure 3** Change in positron annihilation lifetime parameters of highly crosslinked polysiloxanes with an increase in temperature

30% for the lowly crosslinked MQ resin, and 70% for the highly crosslinked MQ resin.

Sheets of 0.5–1 mm in thickness and 1.0 cm square in dimension were used for the specimen of positron annihilation lifetime measurements.

The penetration depth, $E_{max}$: 546 keV positrons emitted from $^{22}$Na in polymers is less than 1 mm.

### *Apparatus*

High efficiency fast–fast coincidence lifetime measuring equipment with a time resolution of ~220 ps was used. The details are described in a previous publication[8].

The positron source was 7.4 × $10^5$Bq $^{22}$NaCl, deposited on a 7.5 μm Kapton foil and folded. The source was sandwiched between two identical MQ resin specimens. The annihilation curves of positrons were measured in 20-h intervals to collect approximately 4 × $10^6$ counts.

### *Data analysis*

All positron annihilation decay curves were analysed by two methods: a computer program PATFIT[9] (finite-term lifetime analysis), and CONTIN[10,11] (continuous lifetime analysis). The PATFIT procedure determines the mean size and frequency of free volume, while the CONTIN procedure determines a size distribution of free volume.

In the finite-term approach, an experimental datum $y(t)$ is expressed as a convolution of the instrument resolution function $R(t)$ and of finite number ($n$) of linear combination negative exponential:

$$y(t) = R(t) * \{N_t(\alpha_1\lambda_1 e^{-\lambda_1 t} + \alpha_2\lambda_2 e^{-\lambda_2 t} + \alpha_3\lambda_3 e^{-\lambda_3 t}) + B\} \tag{1}$$

where $N_t$ is the normalized total count, $B$ is the background, $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the inverses of the mean lifetimes of the $\tau_1$, $\tau_2$ and $\tau_3$ components, respectively, and $\alpha_1\lambda_1$, $\alpha_2\lambda_2$ and $\alpha_3\lambda_3$ are their intensities. The total number of decay terms for the positron annihilation required for the proper analyses is ~$10^6$ counts for PATFIT analysis. The exact resolution function $R(t)$ is approximated by a linear combination of Gaussian-type functions, and experimental data $y(t)$ are then least-squares fitted to obtain the fitting parameters $\lambda_1$,$\lambda_2$ and $\lambda_3$, and $\alpha_1$, $\alpha_2$ and $\alpha_3$.

$$y(t) = R(t) * \left( N_t \int_0^\infty \lambda\alpha(\lambda)\exp(-\lambda t)\mathrm{d}t + B \right) \tag{2}$$

The CONTIN procedure of a positron annihilation decay curve, equation (1), is a Laplace transformation of the decay probability density function $\lambda\alpha(\lambda)$. The exact solution for $\alpha(\lambda)$ and $\lambda$ in equation (2) is obtained by measuring a reference decay curve as a resolution function $R(t)$ under the same experimental configuration and conditions as used in the sample. We used an extra-high-purity and defect-free single crystal of Cu ($\tau$ = 125 ps) for obtaining the reference decay curve. The deconvolution by a inverse Laplace transformation was developed by using CONTIN offered from Jean's group[12].

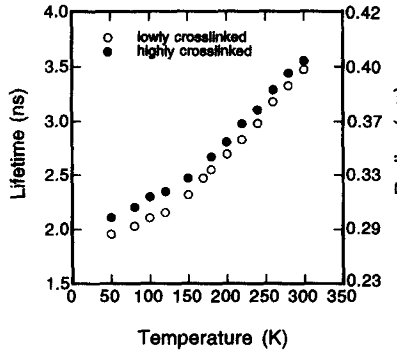

**Figure 4** Change in $\tau_3$ and the size of free volumes, $R$, for lowly and highly crosslinked polysiloxanes with an increase in temperature

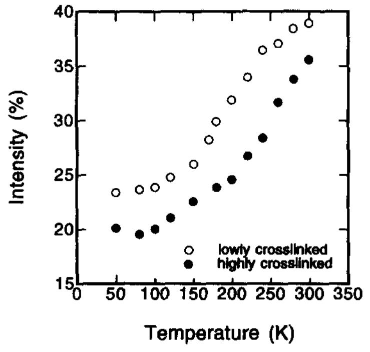

**Figure 5** Change in intensities, $I_3$, for lowly and highly crosslinked polysiloxanes with an increase in temperature

## RESULTS AND DISCUSSION

### *Change in positron annihilation lifetime with temperature*

The positron annihilation lifetime spectrum obtained was resolved into three components by the PATFIT computer programme. Variations of positron annihilation lifetime parameters, $\tau_1$, $\tau_2$, $\tau_3$ and $I_1$, $I_2$, $I_3$, for two kinds of crosslinked polysiloxanes with an increase in temperature from 50 to 300 K are shown in *Figure 2a* and *b* and *Figure 3a* and *b*, respectively. The shortest component, $\tau_1$: ~160 ps, is due to self-annihilation of o-Ps and free annihilations of positron. The second shortest component, $\tau_2$: ~400 ps, is due to annihilation of positrons trapped in various vacancies, possibly present on the surface and between prepolymer particles in the interface or in free volumes. The longest component, $\tau_3$: 1.9–3.5 ns, is due to the pick-off reaction of o-Ps with an electron of free volume wall and can be correlated to free volume hole radius, $R$, by the following semiempirical equation[13].

$$\tau_3 = 0.5\left\{1 - \frac{R}{(R+0.166)} + \frac{1}{2\pi}\sin\frac{2\pi R}{(R+0.166)}\right\}^{-1} \quad (3)$$

where $\tau_3$ and $R$ are expressed in ns and nm, respectively.

### *Change in free volume size with temperature*

Temperature dependences of $\tau_3$ and $R$ for two crosslinked polysiloxane samples are shown in *Figure 4*, which reveals that free volume size in highly crosslinked polysiloxane is larger throughout the temperature range studied. The increases in $\tau_3$ and $R$ below $T_g$ are based on the increase in local chain motion of siloxane chains and the rotation of the methyl group in glassy state, and those above $T_g$ are mainly based on the release of micro-Brownian motion of siloxane chains in rubbery state.

The reason for larger free volumes of the highly crosslinked polysiloxane is attributed to the restriction of vigorous molecular motion of the backbone chains due to many crosslinking points, which may disturb some kind of free movement of the molecular chain resulting in the distorted shapes of larger free volumes. Detailed analyses of data shown in *Figure 4*, indicate that $T_g$'s for lowly and highly crosslinked polysiloxanes are 135 and 150 K, respectively. The evidence indicates that the initiation of the backbone chain motions is more favourable for the less crosslinked polysiloxane.

### *Change in the numerical concentration of free volume with temperature*

The intensity $I_3$ is related to the quantity of free volume in the region where positrons are introduced. The positron forms positronium by picking up an electron produced in the Spur. The area of Spur is ~1 mm in diameter and several hundred micrometres in depth. *Figure 5* reveals that the number density of free volume for highly crosslinked polysiloxane is less than that for lowly crosslinked polsiloxane throughout the temperature range studied. The difference in numerical concentrations is shown in *Figure 5* and suggests that free volumes are generated more easily in the lowly crosslinked polysiloxane with the longer backbone chains between crosslinking points. It should be noted that crosslinking through the curing process occurs only between prepolymers and the average crosslinking density inside prepolymers does not change with the curing process.

The numerical concentration free volume is not supposed to be influenced by the difference in the formation process of o-Ps for these crosslinked polysiloxanes since any chemical species, which affects the formation probability of Ps, cannot be generated in the curing process of the samples. The lower value of the free volume density for the highly crosslinked polysiloxane becomes evident by the analysis of the size distribution profile described in Section 3.5.

### *Change in fraction of free volumes with temperature*

The free volume fraction, $f$, in the polymer increases linearly with temperature at constant pressure as follows,

$$f = 0.025 + \alpha_f(T - T_g) - \beta P \quad (4)$$

where, $\alpha_f$ is the thermal expansion coefficient of free volume and $\beta$ is the compressibility of free volume at a given temperature. Equation (4) has been well discussed and used to estimate the behaviour of free volumes[14]. The expansion coefficients of the calculated free volume radius (free volume size) using data obtained, are $2.6 \times 10^{-4}$ nm/K ($2.7 \times 10^{-4}$ nm$^3$/K) and $3.0 \times 10^{-4}$ nm/K ($3.7 \times 10^{-4}$ nm$^3$/K) at glossy state and $5.4 \times 10^{-4}$ nm/K ($8.7 \times 10^{-4}$ nm$^3$/K) and $4.9 \times 10^{-4}$ nm/K ($8.3 \times 10^{-4}$ nm$^3$/K) at rubbery state for lowly and highly crosslinked polysiloxanes, respectively, and coincide well with the value proposed, ~$4.8 \times 10^{-4}$/K[15]. We are not interested in the absolute value of free volume fraction, but in the temperature dependence of overall variations of calculated free volume fraction[12]. We defined relative free volume fraction ($f_r$) according to:

$$f_r = f_{app}/f_{app.50} \quad (5)$$

where $f_r$ is a ratio of $f_{app}$ to $f_{app}$ at 50 K; $f_{app}$ is calculated

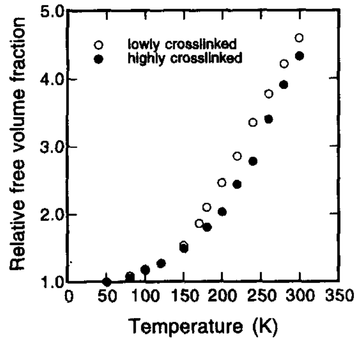

**Figure 6** Change in relative free volumes fraction for lowly and highly crosslinked polysiloxanes with an increase in temperature

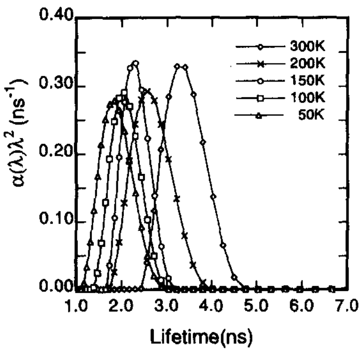

**Figure 7** Change in size distribution of free volume for lowly crosslinked polysiloxane with an increase in temperature

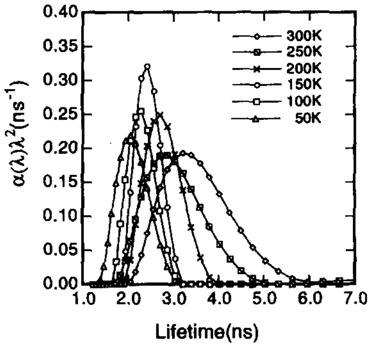

**Figure 8** Change in size distribution of free volume for highly crosslinked polysiloxane with an increase in temperature

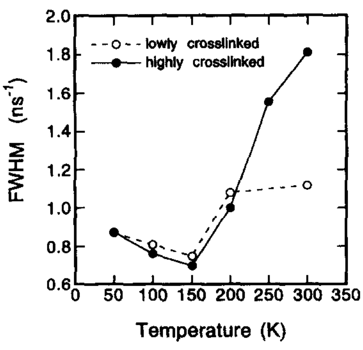

**Figure 9** Full width half maximum (FWHM) of the size distribution profiles for the free volumes of the crosslinked polysiloxanes

according to:

$$f_{\mathrm{app}} = V_{\mathrm{f}}(A \times I_3 + B) \qquad (6)$$

where, $V_f$ is the free volume calculated using equation (3), taking $A$ as unity and $B$ as zero for simplicity.

The changes of relative free volume fraction with temperature are shown in *Figure 6*. The relative free volume fractions for both crosslinked polysiloxanes agree very well below $T_g$ owing to the same crosslinking density inside the prepolymers and the frozen micro-Brownian motion of siloxane chains. The relative free volume fraction for highly crosslinked polysiloxanes is smaller than that for lowly crosslinked polysiloxanes above $T_g$. Comparison of the data shown in *Figure 6* with that in *Figures 4* and *5* reveals that the free volume fraction is more dependent on the numerical concentration of free volume above $T_g$.

### *Variation of size distribution of free volumes*

Inverse Laplace transformation using the CONTIN programme was applied to the decay curve of positron annihilation of lowly and highly crosslinked polysiloxanes. The variations of size distribution of free volume against temperature are shown in *Figures 7* and *8*. The abscissas correspond to the size of free volume, and ordinates express $\lambda^2\alpha(\lambda)$ instead of $\alpha(\lambda)$ probability distribution functions to balance the intensities of $\tau_1$, $\tau_2$ and $\tau_3$ components, where $\lambda$ is the annihilation rate ($\tau = 1/\lambda$). The FWHM (full width at half maximum) for these size distribution profiles are summarized in *Figure 9*.

For the lowly crosslinked polysiloxane, the distribution peak of free volume size shifts from small to large with an increase in temperature, the FWHM of size distribution of free volumes is quite narrow and the rate of increase in size of free volume with temperature is moderate up to $T_g$ (135 K, but observed at ~150 K). The rate of increase in size becomes greater above $T_g$, keeping the FWHM of size distribution almost constant. The narrow distribution of free volume size may be a good indication of relaxed motions of backbone chains, which compose the free volumes. The variation of a FWHM or the peak profile may be determined by various kinematic and dynamic parameters of backbone-chain motions. These parameters are considered to be dependent on the temperature. Thus, FWHM and the peak profile is dependent on temperature. The simulational studies of the size distribution of free volume are initiated for polystyrene by Jean *et al.*[12].

For the highly crosslinked polysiloxane, the profile of size distribution of free volumes is also quite narrow and the size increase with increasing temperature is moderate up to $T_g$ (~150 K). However, the size distribution becomes remarkably broad and the peak becomes larger above $T_g$, suggesting that relaxed and free motions of backbone chains are liberated under the quite restricted condition resulting in the distorted molecular structure. Therefore, free volume size becomes very heterogeneous for the highly crosslinked polysiloxane.

As has already been mentioned in the Section Section 2, the present crosslinked polysiloxanes (cured MQ resin) are prepared by the crosslinking reaction (curing) between two kinds of already crosslinked prepolymers with a molecular weight of 1700 bearing Si–CH=CH$_2$ groups or Si–H bonds on each surface. The mean length of the molecular chain between crosslinkage points of these prepolymers is supposed to be about 2 nm. The photoisomerization probe study of these MQ resins containing azobenzene has revealed that the cured MQ resin still has a heterogeneous structure composed of densely packed parts of siloxane chains inside the prepolymer particle and rather vacant parts at the interface or among the prepolymer particles[16,17]. Based on this picture of the microstructure of the crosslinked polysiloxanes, the results in the present paper suggest that the $\tau_3$ mainly reflects free volumes in the densely packed part of siloxane chains inside the prepolymer particles. The crosslinking between the prepolymer particles creates the stress on the siloxane chains inside the prepolymer particles and greatly influences the shape of the prepolymers. At low temperatures below $T_g$, the micro-Brownian motion of backbone chains of siloxane is frozen, and free volume distributions inside the prepolymer particles are rather narrow regardless of the degree of crosslinking between the particles. At temperatures above $T_g$, the micro-Brownian motion of backbone chains of siloxane exists, and the narrow and equilibrated size distribution profiles are still maintained for free volume inside the prepolymer particle of lowly crosslinked MQ resin. However, in the case of highly crosslinked MQ resin, the chain motion tends to enlarge the free volume, but stress caused by the crosslinking changes the shape of the prepolymer particle and induces microheterogeneity inside the particle. This would be the reason for the remarkable broadening of size distribution of free volumes for the highly crosslinked polysiloxane above $T_g$.

## CONCLUSIONS

Free volumes and their distribution have been studied with a positron annihilation technique. The free-volume radius of the highly crosslinked polysiloxane increased from ~0.295 nm (50 K) to 0.399 nm (300 K), while that of lowly crosslinked polysiloxane increased from 0.281 nm (50 K) to 0.394 nm (300 K). The size distribution of free volume for highly crosslinked siloxane becomes broad and quite heterogeneous above $T_g$, whereas that of lowly crosslinked polysiloxane is rather narrow and smoothly shifts to a larger free volume size with increasing temperature. This can be explained by the heterogeneous structure of the crosslinked polysiloxanes composed of densely packed parts of siloxane chains inside the prepolymer particle and rather vacant parts at the interface or among the prepolymer particles. The values of $\tau_3$ of positron annihilation measurements mainly reflect free volumes in the densely packed part inside the prepolymer particles.

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