

# Dielectric relaxation in networks of end-linked dimethylsiloxane oligomers

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Networks composed of very short dimethylsiloxane chains were prepared by end-linking dimethylsiloxane oligomers with a tetrafunctional crosslinking agent. Their dielectric properties were studied to elucidate the effects of crosslinks on molecular motion in highly crosslinked networks. The temperature of maximum loss for the primary relaxation process ( $\alpha$  process) shifted greatly to high temperature with decrease in the chain length between crosslinks. The activation energy and the width of the absorption curve increased with decrease in chain length. No linear relation existed between the dielectric properties for the  $\alpha$  relaxation and the crosslink density. On the other hand, the temperature of maximum loss for the secondary relaxation process ( $\beta$  process) shifted to high temperature with decreasing chain length, but the activation energy was almost independent of the chain length. Characteristics for the  $\alpha$ ,  $\beta$  and hypersonic relaxations in the networks are discussed in terms of inter- and intramolecular contributions.

**Keywords** Dielectric constants; endlink; crosslink; dimethylsiloxane; relaxation spectrum; transition map

## INTRODUCTION

Many studies concerning the effects of crosslinks on the glass transition temperature<sup>1-7</sup> and on mechanical and dielectric properties<sup>5,8-11</sup> of polymer networks have been presented. The networks prepared by sulphur vulcanization, peroxide curing, or  $\gamma$ -irradiation have complex structure and their chain length between crosslinks is comparatively long and considerably polydisperse. Recently, new synthetic techniques for preparing rubberlike networks by anionic copolymerization<sup>12</sup> or chemical end-linking of suitably capped oligomers have been developed<sup>13,14</sup>. The end-linking techniques are very important because of the possibility of preparing networks of uniform chain length<sup>15</sup>. Such networks would be valuable in characterizing the effects of chain length and would enable us to clarify the role of crosslinks on molecular motion in networks composed of very short chains between crosslinks.

The purpose of the present study is to elucidate the effects of chain length on the dielectric  $\alpha$  and  $\beta$  relaxation processes in networks formed by end-linking vinyl-terminated dimethylsiloxane oligomers with a cyclic tetrafunctional crosslinking agent. Results are compared with the hypersonic relaxation data<sup>16</sup> measured by the Brillouin scattering method.

## EXPERIMENTAL

The networks were prepared by end-linking of dimethylsiloxane oligomers having vinyl groups— $\alpha,\omega$ -vinyloligo-(dimethylsiloxane),  $C_2H_3(Si(CH_3)_2O)_nSi(CH_3)_2C_2H_3$ —

and a cyclic tetrafunctional crosslinking agent—cyclotetra(methylsiloxane),  $(HSiCH_3O)_4$ —which were provided from Shin-Etsu Chemical Co. The five oligomers ( $n=1,2,3,4,6$ ) and the crosslink agent are the same as those used previously in the Brillouin scattering study<sup>16</sup> and details of the characterizations and the conditions of the reactions are given elsewhere<sup>16</sup>. Some characteristics are again listed in *Table 1*.

The end-linking reactions with platinum compounds as catalyst were carried out for two days at room temperature in a glass mould having interior dimensions of  $5 \times 7 \times 0.1$  cm<sup>3</sup>. Then the partially crosslinked sheets were removed from the mould and cured for 2 h at 150°C, in order to complete the reaction. The network samples prepared in this way were dried for 1 day in a vacuum oven at 120°C. The network samples prepared from dimethylsiloxane oligomers of  $n=1, 2, 3, 4$  and 6 are hereafter designated as S1, S2, S3, S4 and S6, respectively. Since mutual polymerizations between the oligomers are hardly unexpected, the distribution of  $n$  in the networks may result predominantly from the impurities in the oligomer samples, which are smaller than 2%<sup>16</sup>. The fraction of imperfections in end-linking reactions are indicated by the unreacted [SiH] content in *Table 1*. The probabilities of formation of dangling chains and of free chains may be expressed approximately by the unreacted vinyl content listed in *Table 1*.

Dielectric measurements were made with a three-terminal electrode system in conjunction with a General Radio 1620A Capacitance Measuring Assembly. The sample and the electrodes (3 cm in diameter) were set in a cylindrical cavity (3.6 cm diameter and 3 cm depth) of a

Table 1 Characteristics of networks<sup>16</sup>

Sample code	<i>n</i>	Density at 298K (g cm <sup>-3</sup> )	Thermal expansivity × 10 <sup>4</sup> (K <sup>-1</sup> )			Unreacted [SiH] content (%)	Unreacted vinyl content (%)
			$\alpha_{\text{liquid}}$	$\alpha_{\text{glass}}$	$\alpha_{\text{liquid}} - \alpha_{\text{glass}}$		
S1	1	1.032	7.2	3.9	3.3	10	<0.5
S2	2	1.023	7.2	3.3	3.9	5	1.1
S3	3	1.011	8.1	—	—	2	1.3
S4	4	1.008	8.1	2.9	5.2	2	1.0
S6	6	0.994	8.4	2.9	5.5	2	2.0

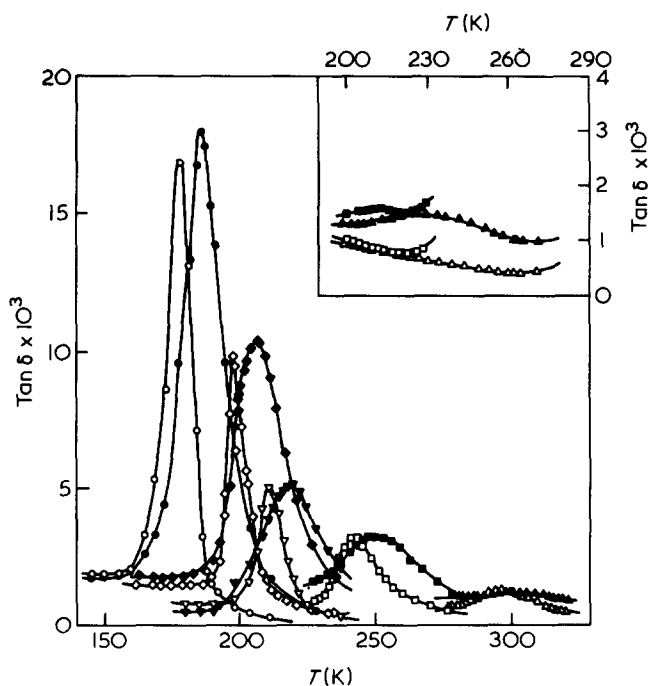


Figure 1 Variations of dielectric loss  $\tan \delta$  with temperature. Open symbols, 120 Hz; closed symbols, 50 kHz;  $\Delta$ , S1;  $\square$ , S2;  $\nabla$ , S3;  $\diamond$ , S4;  $\circ$ , S6

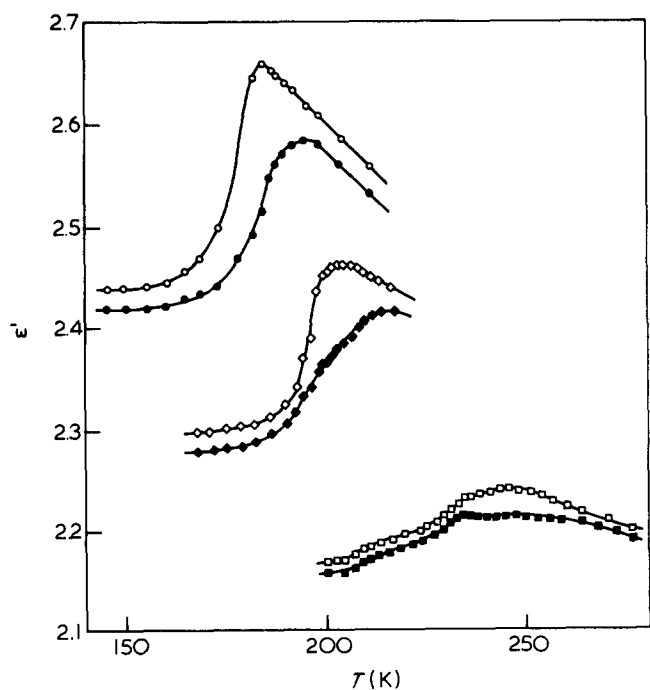


Figure 2 Variations of dielectric permittivity with temperature. Open symbols, 120 Hz; closed symbols, 50 kHz;  $\square$ , S2;  $\diamond$ , S4;  $\circ$ , S6

stainless-steel block (6 cm diameter and 10 cm length), which was immersed in an ethanol bath. Temperature was measured by use of a copper-constantan thermocouple inserted in the cavity of the stainless-steel block. After the temperature was lowered to each desired value by use of liquid nitrogen and a refrigerator (Neslab CC-100), dielectric measurements were carried out under continuous heating at a rate of about 0.09 K min<sup>-1</sup>. The density and the thermal expansivity in Table 1 were used to correct the dielectric constants.

## RESULTS

The dielectric loss tangent ( $\tan \delta$ ) as a function of temperature is shown in Figure 1. In the rubbery (liquid) state, a dispersion is observed for all the samples. In the glassy state, a broad secondary dispersion is observed at high frequency in S1 and S2. Similarly to the loss peaks in amorphous polymers, the relaxation process observed in the liquid region is referred to as  $\alpha$  relaxation and that observed immediately below  $T_g$  is  $\beta$  relaxation. Unfortunately, low-temperature data were not measurable for S3, S4 and S6. The  $\beta$  dispersion of these samples is small and broad and occurs below 150 K, i.e. the region where an accurate temperature control could not be expected in the present dielectric measuring system because of freezing-in of ethanol. At higher temperature above the dielectric  $\alpha$  dispersion region, any anomalous change in the dielectric constants was not observed, and no dispersion process pertaining to the crystallization such as that observed in polydimethylsiloxane (PDMS)<sup>17</sup> could be detected by the present dielectric experiments.

The maximum value of  $\tan \delta$  for the  $\alpha$  process decreases significantly with decreasing  $n$ . This trend correlates with the increment of the thermal expansivity,  $\alpha_{\text{liquid}} - \alpha_{\text{glass}}$ , which decreases rapidly with decreasing  $n$ , as is seen in Table 1. The dispersion temperature of the  $\alpha$  process shifts to higher temperature with decreasing  $n$ . The temperature of the maximum  $\tan \delta$  in the  $\beta$  process shifts to higher temperature with decreasing  $n$  as well as in the  $\alpha$  process, but the maximum value of  $\tan \delta$  in the  $\beta$  process seems to be almost unchanged.

In Figure 2, some examples of the plots of the dielectric permittivity  $\epsilon'$  as a function of temperature  $T$  are shown. Permittivity  $\epsilon'$  decreases with decreasing  $n$ . This is mainly due to the increase in the fractional content of methylene groups with decreasing  $n$ .

The relaxation magnitude, which relates to the number of effective dipoles involved in a particular relaxation process, is given by the dielectric increment,  $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ , where  $\epsilon_0$  and  $\epsilon_\infty$  are the limit values of permittivity at very low and high frequencies, respectively. For the  $\alpha$  process  $\Delta\epsilon$  decreases with decreasing  $n$  in the low  $n$  region as shown in Figure 2. The dielectric increment for the  $\beta$  process, unfortunately, was unobtainable because of the broadness of the  $\beta$  process. However, since the relaxation

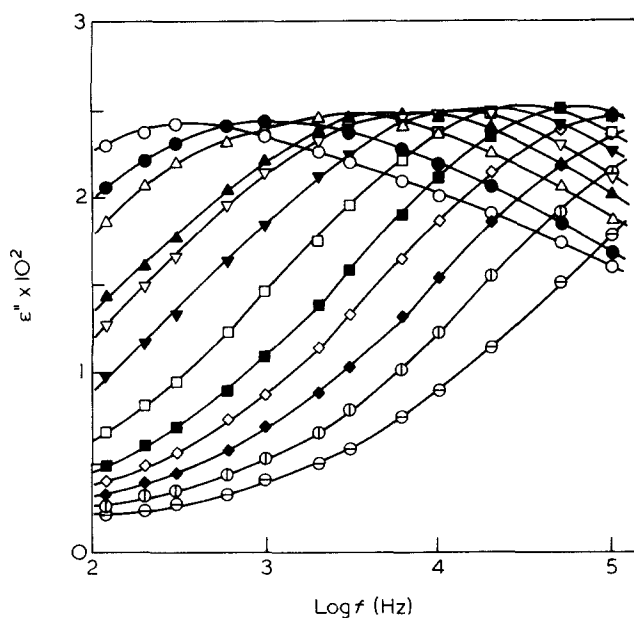


Figure 3 Variations of dielectric loss in S4 with frequency: ○, 198.0 K; ●, 198.8 K; △, 200.3 K; ▲, 201.7 K; ▽, 202.8 K; ▼, 204.4 K; □, 206.0 K; ■, 207.8 K; ◇, 209.6 K; ◆, 211.4 K; ⊕, 216.9 K

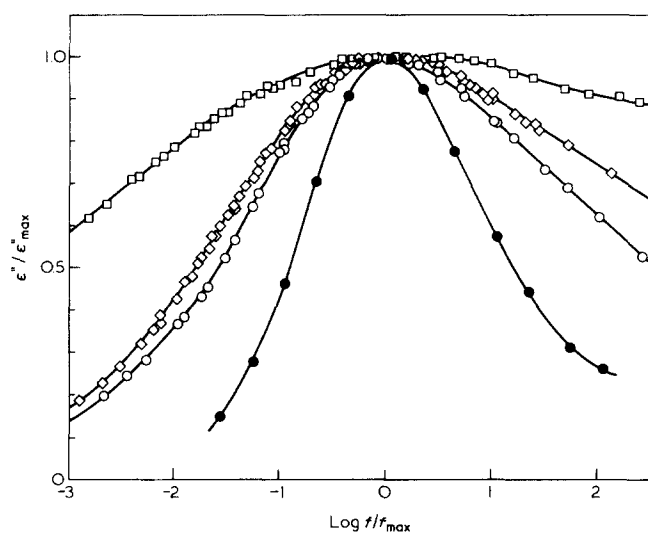


Figure 4 Master curves of reduced dielectric loss as a function of reduced frequency: □, S2; ◇, S4; ○, S6; ●, PDMS, Adachi *et al.*<sup>17</sup>

magnitude may be related to the area enclosed within  $\tan \delta$  curves in Figure 1, the number of effective dipoles in the  $\beta$  process in S1 appears to be somewhat larger than that in S2.

An example of the plots of the dielectric loss,  $\epsilon''$ , against logarithmic frequency,  $\log f$ , is shown in Figure 3. The dispersion region seems to be much broader than that for ordinary polymer liquids and molecular liquids<sup>18</sup>. Master curves, as shown in Figure 4, are obtained by superposition of  $\epsilon''/\epsilon''_{\max}$  against  $\log f$  plots, where  $\epsilon''_{\max}$  is the maximum value of  $\epsilon''$  in the  $\epsilon''$  isotherm against  $\log f$ . The reduced  $\epsilon''$  isotherm for PDMS reported by Adachi *et al.*<sup>17</sup> is also shown in Figure 4 for comparison. The relaxation spectra of the end-linked dimethylsiloxane networks are much broader than that of PDMS, and breadth of the spectra increases significantly with decreasing chain length.

## DISCUSSION

### Location of $\alpha$ relaxation

According to the conventional method for analysis of dielectric relaxation times from dielectric loss data, we have estimated the temperature of maximum loss from isochronal plots of  $\epsilon''$  against  $T$ . At the temperature of maximum loss,  $T_{\max}$ , the frequency employed is taken to correspond to the mean dielectric relaxation time, i.e.  $\tau = 1/2\pi f$ . The locations of the  $\alpha$  process are presented as a transition map in Figure 5, where  $\log f$  is plotted as a function of reciprocal  $T_{\max}$ .

Temperature dependences of the relaxation frequency  $f$  in viscous liquids are well represented by the Vogel-Fulcher-Tammann-Hesse (VFTH) equation<sup>19</sup>:

$$\log f = A - B/(T - T_0) \quad (1)$$

which is equivalent to the WLF equation<sup>20</sup>. The values of the parameters  $A$ ,  $B$ ,  $T_0$  and the standard deviation  $\delta$  calculated by least-squares regression are listed in Table 2. The  $T_{\max}$  data for S1 are represented by the Arrhenius equation:

$$\log f = A - B/T \quad (2)$$

rather than the VFTH equation. This may not indicate superiority of equation (2) rather than equation (1) for S1, but merely means failure to determine a reliable value of  $T_0$  because of uncertainties in estimating  $T_{\max}$  due to an unusual broadness of the relaxation spectrum in S1 and to the narrowness of the frequency region studied.

Uncrosslinked PDMS may be regarded as a network composed of extremely long chains between crosslinks, i.e.  $n = \infty$ . Dielectric properties of PDMS have been reported by Huggins *et al.*<sup>21</sup>, Baird and Sengupta<sup>22</sup> and Adachi *et al.*

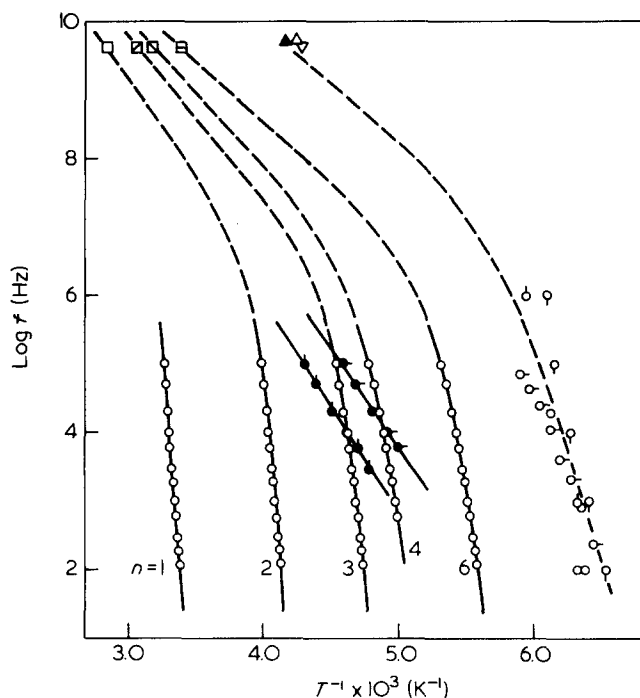


Figure 5 Transition map. Open circles,  $\alpha$  relaxation: ○, S1-S6; ○, Huggins *et al.*<sup>21</sup>; ○, Baird and Sengupta<sup>22</sup>; ○, Adachi *et al.*<sup>17</sup>. Closed circles,  $\beta$  relaxation: ●, S1; ●, S2. Squares and triangles, hypersonic relaxation: □, ▤, ▥, ▦, Kondo and Igarashi<sup>16</sup>; △, ▲, Adshead and Lindsay<sup>36</sup>; ▽, Kondo *et al.*<sup>37</sup>

Table 2 VFTH and Arrhenius parameters

Sample	A	B (K)	$T_0$ (K)	$\delta$
<i><math>\alpha</math> relaxation process</i>				
S1	91.21	26330	0	0.057
S2	19.92	752.3	199.8	0.039
S3	11.40	186.4	190.9	0.036
S4	9.93	136.6	181.1	0.013
S6	11.07	165.4	160.6	0.032
PDMS <sup>a</sup>	53.40	7981	0	0.150
PDMS <sup>b</sup>	10.34	247	124	0.040
PDMS <sup>c</sup>	61.18	9078	0	0.021
<i><math>\beta</math> relaxation process</i>				
S1	18.42	3120	0	0.032
S2	18.71	2993	0	0.016

<sup>a</sup> Huggins *et al.*<sup>21</sup><sup>b</sup> Baird and Sengupta<sup>22</sup><sup>c</sup> Adachi *et al.*<sup>17</sup>

*al.*<sup>17</sup> Locations of the dielectric loss in PDMS estimated from their data (Figure 3 in ref. 21, Figure 1 in ref. 22 and Figure 6 in ref. 17) are also plotted in Figure 5. The data are in good agreement with each other in the lower frequency region, but not in the higher frequency region, i.e. in the higher temperature region. The deviation may be due to a partial crystallization in PDMS<sup>17</sup>. The values of the VFTH or Arrhenius parameters for PDMS have also been calculated by least-squares regression and are listed in Table 2.

Activation energy  $\Delta H^*$  can be calculated from

$$\Delta H^* = 2.303 RBT^2/(T - T_0)^2 \quad (3)$$

$\Delta H^*$  depends on  $n$  to a great extent as shown in Figure 6.\* The values of  $\Delta H^*$  for small  $n$  are approximately equal to those for typical polymers, e.g. poly(vinyl chloride) and poly(vinyl acetate)<sup>23</sup>. The values of  $\Delta H^*$  for large  $n$  and for PDMS are smaller than those for the typical polymers. This implies that dimethylsiloxane chains have a relatively large mobility with small restraint, since the free volume is anticipated to be comparatively large because of the large thermal expansivity of the liquids as listed in Table 1.

In Figure 5, the hypersonic relaxation data,  $T_{\max}$  of the maximum  $\tan \delta$ , obtained from the Brillouin scattering method<sup>16</sup> are also shown, where, to prevent confusion arising from the variety of samples, a broken line is drawn between  $T_{\max}$  from the Brillouin scattering and that from the dielectric measurements for samples of the same  $n$ . The relaxation time estimated from a maximum in  $\epsilon''$  is longer than that estimated from a maximum in  $\tan \delta$  by a factor  $(\epsilon_0/\epsilon_\infty)^{1/2}$ , in the case of the single relaxation time<sup>24</sup>. Since the dielectric increments in the present samples are very small, the difference in the relaxation times is of no significance in the discussion that follows.

#### Location of $\beta$ relaxation

In Figure 5,  $\log f$  is plotted as a function of  $1/T_{\max}$  for the dielectric  $\beta$  relaxation process. The relations of  $\log f$  vs.  $T_{\max}$  are represented by the Arrhenius equation, equation (2). The values of the Arrhenius parameters are listed in Table 2. As shown in Figure 6, values of  $\Delta H^*$  of about

\* Adachi *et al.* reported the value of  $\Delta H^*$  to be 18 kcal mol<sup>-1</sup> in Table 1 of ref. 17. However, their dielectric loss data (Figures 3, 4 and 6 of ref. 17) indicate the value of  $\Delta H^*$  to be 36–42 kcal mol<sup>-1</sup>. Perhaps they missed out the factor 2.303.

14 kcal mol<sup>-1</sup> are approximately equal to those for amorphous polymers, which range from 5 to 20 kcal mol<sup>-1</sup>, and somewhat larger than those for rigid molecules and alcohols<sup>25</sup>, which range from 5 to 12 kcal mol<sup>-1</sup>.

As can be seen in Figure 1, the  $\beta$  peak in  $\tan \delta$  for S1 is comparable to the  $\alpha$  peak, and the  $\beta$  peak for S2 is approximately equal to half the  $\alpha$  peak. With respect to the magnitude of the  $\beta$  process relative to that of the  $\alpha$  process, S1 and S2 are significantly different from ordinary polymer and molecular glasses, in which the  $\beta$  peak in  $\tan \delta$  is about one or two orders of magnitude lower than the  $\alpha$  peak<sup>24,26</sup>. The extreme increase in crosslinks may give rise to an increase in restraint of the cooperative motions involving a large range of network chains. Consequently, the widespread restraints may result in a wide distribution of the localized energy field. This may be responsible for the fact that the thermal expansivity of the glasses increases with decreasing  $n$ . The dielectric  $\beta$  process is characterized by orientational rearrangements of one or a few molecules in such a local region. Thus the magnitude of the  $\beta$  process relative to the  $\alpha$  process may become much larger as the chain length between the crosslinks becomes short.

The Brillouin scattering data reflected in the local density-density correlation function<sup>25</sup> may be characterized by the orientational and translational motions in small local regions. The relaxation process observed in the Brillouin scattering is argued to be a more rapid process than the dielectric  $\beta$  process due to the translational motions<sup>27–29</sup>. The hypersonic relaxation

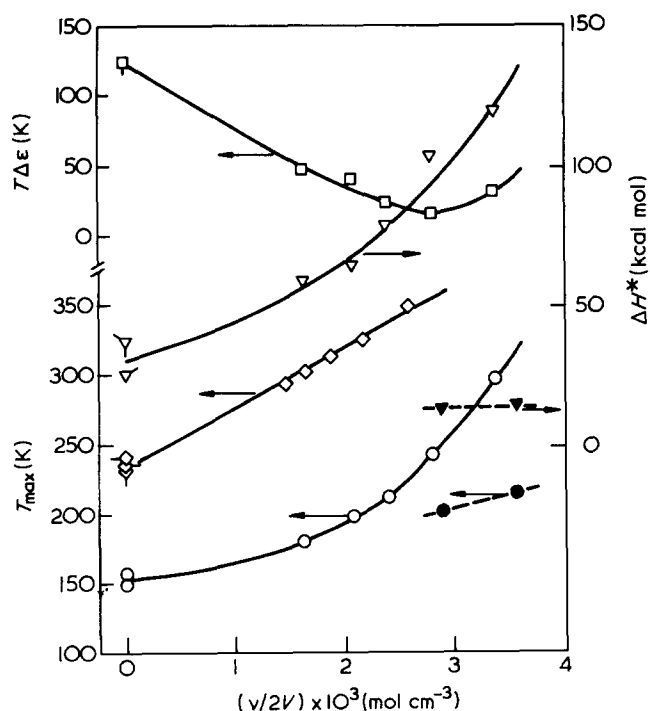


Figure 6 Effects of crosslink density. Open circles,  $T_{\max}$  at 1 KHz in the  $\alpha$  relaxation:  $\circ$ , S1–S6;  $\circ$ , Huggins *et al.*<sup>21</sup>;  $\circ$ , Baird and Sengupta<sup>22</sup>;  $\circ$ , Adachi *et al.*<sup>17</sup>. Open triangles,  $\Delta H^*$  at 1 KHz in the  $\alpha$  relaxation:  $\nabla$ , S1–S6;  $\nabla$ , Huggins *et al.*<sup>21</sup>;  $\nabla$ , Baird and Sengupta<sup>22</sup>;  $\nabla$ , Adachi *et al.*<sup>17</sup>. Squares,  $T_{\max}$  at  $T_{\max}$  of 1 kHz in the  $\alpha$  relaxation:  $\square$ , S1–S6;  $\square$ , Adachi *et al.*<sup>17</sup>. Closed circles,  $T_{\max}$  at 10 kHz in the  $\beta$  relaxation. Closed triangles,  $\Delta H^*$  in the  $\beta$  relaxation. Diamonds, hypersonic relaxation:  $\diamond$ , S2–S6, Kondo and Igarashi<sup>16</sup>;  $\diamond$ , Adshead and Lindsay<sup>36</sup>;  $\diamond$ , Kondo *et al.*<sup>37</sup>

data for S2 seem to lie near the extrapolation of the  $\beta$  process as can be seen in *Figure 5*. This seems to be in accordance with the argument proposed by Patterson<sup>30</sup>. However, the present results may produce little evidence on the identification between the hypersonic relaxation and the dielectric one, because of large uncertainty due to the long extrapolation.

It may be noteworthy that the dielectric  $\beta$  peak in S1 is comparatively large, while no peak was observed in the hypersonic  $\tan \delta$ <sup>16</sup>. The dielectric  $\alpha$  and  $\beta$  processes are usually indistinguishable at higher frequencies<sup>24</sup>. The smallness and broadness of the  $\alpha$  process in S1 might be related to the apparent extinction of the hypersonic relaxation peak observed in the Brillouin scattering.

#### Effects of end-linked chain length

All of the dielectric properties,  $T_{\max}$ ,  $\Delta H^*$  and  $\Delta\epsilon$ , of the  $\alpha$  process depend considerably on frequency (temperature). Here we make comparisons with respect to  $T_{\max}$  at 1 kHz,  $\Delta H^*$  at 1 kHz and  $T\Delta\epsilon$  at  $T_{\max}$  of 1 kHz for the  $\alpha$  process and  $T_{\max}$  at 10 kHz for the  $\beta$  process. In *Figure 6*, effects of chain length on the dielectric properties are summarized as a function of the crosslink density,  $\nu/2V = 2N_A/VM$ , where  $\nu$ ,  $V$ ,  $N_A$  and  $M$  are the number of crosslinks, the specific volume, the Avogadro number and the molecular weight of the repeating group,  $[\text{Si}(\text{CH}_3)_2(\text{Si}(\text{CH}_3)_2\text{O})_n][\text{SiCH}_3\text{O}(\text{CH}_2)_2]_4$  respectively.

The relaxation magnitude  $T\Delta\epsilon$  has a minimum around  $n=2$ . The number density of dipoles in S1 is smaller than that in S2. The group dipole moment of  $[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_2$  for  $n=1$  is much smaller than that for  $n=2$ <sup>31</sup>. The chain flexibility of S1 is considered to be much more suppressed than that of S2. The increment of the thermal expansivity,  $\alpha^{\text{liquid}} - \alpha^{\text{glass}}$ , in S1 is smaller than that in S2. All of these suggest that  $T\Delta\epsilon$  (for S1)  $<$   $T\Delta\epsilon$  (for S2), though this is not really the case. The reason for this contradiction of the relaxation magnitude is not clear. It might be due to imperfections of the network in S1.

$T\Delta\epsilon$  decreases linearly with  $\nu/V$  in the low  $\nu$  region. This is in accordance with the result on  $T\Delta\epsilon$  in poly(acrylonitrile-co-butadiene) crosslinked with dicumyl peroxide reported by Adachi *et al.*<sup>11</sup>

Sullivan *et al.*<sup>10</sup> reported that the viscoelastic  $\tan \delta$  of end-linked PDMS and PDMS crosslinked randomly by  $\gamma$ -irradiation is proportional to  $\nu$  in the  $\nu$  region of the order of  $10^{-4}$ – $10^{-6}$  mol cm<sup>-3</sup>. Similar linear relations between  $T_{\max}$  and  $\nu$  were reported in mechanical<sup>5</sup> and dielectric<sup>11</sup>  $\alpha$  relaxation. However, in the present  $\nu$  region,  $T_{\max}$  increases rapidly with increasing  $\nu$  at high  $\nu$ , and the linear relation between  $T_{\max}$  and  $\nu$  is not observed.

The glass transition temperature  $T_g$  may be closely associated with the dielectric  $T_{\max}$ . Fox and Loshaek<sup>3</sup> proposed a semiempirical equation in which  $T_g$  is proportional to  $\nu$ . Rietsch *et al.*<sup>6</sup> showed that  $T_g$ 's of polystyrene networks (prepared by anionic copolymerization of styrene and divinyl benzene) and star-shaped polystyrene (of varying functionality) are inversely proportional to the molecular weight of chains between crosslinks. For the present samples, this relation leads to  $T_g$  proportional to  $(n+1.54)^{-1}$ . Actually, the dielectric  $T_{\max}$  is approximately proportional to  $(n+0.3)^{-1}$  and is not in conformity with Rietsch's relation. In conclusion, the Fox-Loshaek type linear relation may not be appropriate when the chain length between crosslinks is extremely short.

From many studies on the effects of pressure<sup>32</sup> and elongation<sup>33</sup> on dielectric properties of polymers and

polymer networks, it has been clarified that  $T_{\max}$  and  $T_g$  are approximately determined by the configurational entropy consisting of the intramolecular conformational entropy and the intermolecular configurational entropy. If the intermolecular configuration, which is closely related to the free volume, is a dominant factor, a linear relation may be expected between the average relaxation time and the crosslink density. In the networks composed of extremely short chains between crosslinks, therefore, various steric hindrances may increase and the intramolecular conformations may become a dominant factor governing the cooperative molecular motions.

From the studies on the pressure effects on  $T_g$ ,  $T_g$  is verified to be regarded as an isorelaxation time state, i.e. an isoviscous state<sup>34</sup>. Since the present samples of the end-linked dimethylsiloxane networks with different chain lengths differ in chemical structure with each other,  $T_g$  may not be regarded as the isoviscous state<sup>35</sup>. That is, the dielectric  $T_{\max}$  which corresponds to the isorelaxation time state may not be regarded to be identical with  $T_g$  measured at shorter time scale. However, this difference between  $T_{\max}$  and  $T_g$  scarcely alters the qualitative conclusion of the present study.

As the chain flexibility in the networks reduces, the region of cooperative molecular motions may spread. This may be the reason for the rapid increase in  $\Delta H^*$  of the  $\alpha$  process at large  $\nu$ .  $\Delta H^*$  in the  $\beta$  process, on the contrary, appears to be almost independent of  $\nu$ . The  $\beta$  process is associated with the localized mode of motions of a few molecules confined by the localized energy field. Therefore, the dominant factor governing the  $\beta$  process may be the intermolecular configurations<sup>25</sup>, which may not increase precipitously with  $\nu$  at high  $\nu$ .

At about 4 GHz  $T_{\max}$  obtained from the Brillouin scattering is approximately proportional to  $\nu$ . In such a high frequency region, the relaxation process may be associated with the small local motions in the local energy field, notwithstanding whether its origin is cooperative or not. Therefore, the hypersonic relaxation may depend mainly on the intermolecular configurations rather than the intramolecular conformations.

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