Viscoelastic Relaxation of Guest Linear Poly(dimethylsiloxane) in End-Linked Poly(dimethylsiloxane) Networks

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Received January 30, 2001

ABSTRACT: Dynamics of guest linear polymer trapped in permanently cross-linked network is investigated using the end-linked poly(dimethylsiloxane) (PDMS) networks with well-defined mesh sizes (M_x) containing unattached linear PDMS. Viscoelastic relaxation behavior of the PDMS networks with the unattached PDMS has been examined as a function of the molecular mass of the guest PDMS (M_g) and the end-reactive precursor PDMS. Two host networks with different mesh characters and sizes, i.e., $M_x \approx M_e$ (trapped entanglement dominant) and $M_x < M_e$ (cross-link dominant), were prepared by end-linking the sufficiently longer and shorter precursor PDMS relative to entanglement spacing (M_e), respectively. The dynamic mechanical measurements reveal that the networks containing the guest chains show the definite maxima in loss factor tan δ at certain frequencies which are attributed to the viscoelastic relaxation of the guest chains, and in addition, the location of the tan δ peak shifts to the lower frequencies with increasing in M_g. The characteristic time τ_g, defined by the inverse of the frequency at the tan δ maximum, varies with M_g in good agreement with the predictions of the reptation theories, regardless of M_x. Interestingly, the reptation of the guest chains in the cross-link-dominant network of $M_x < M_e$ is markedly retarded relative to that in the entanglement-dominant network of $M_x \approx M_e$: τ_g in the cross-link-dominant network is larger than that in the entanglement-dominant network by a factor of nearly 10^5. Such remarkable slowing-down of reptation is not simply explained in terms of only the reduction in M_x, which suggests that the effects of the high concentration of cross-link in the network of $M_x < M_e$ on the dynamics of guest chains must be considered.

Introduction

The dynamics of unattached (guest) polymer in (host) cross-linked network has attracted much attention during the past 20 years from the viewpoints of "transport of polymer through gel" as well as reptation concept (tube model).[1−4] The original reptation theory proposed by de Gennes[1,3] and Doi and Edwards[2,4] modeled the diffusion of a probe chain in dense polymer matrix as a reptation in a hypothetical tube representing the "invariant" topological constraints of surrounding polymers. As is evident from the model concept, the guest polymer chain in a cross-linked polymer network corresponding to an invariant topological enviroment provides an experimental model system for tube model. On the other hand, in the case of un-cross-linked polymer melt, unless the polymers are highly entangled, some modifications of the tube theory are necessary due to "variant" topological constraints: The relaxation of the probe chain is promoted by the motion of the surrounding polymers (known as "constraint release process").[5,6] However, it still remains incomplete to confirm experimentally the validity of the original tube model, because some experimental studies[7−11] on the dynamics of unattached chains in cross-linked networks supported the original tube model, but other studies[12−14] reported some appreciable disagreements between the experimental results and the theoretical prediction.

A series of pioneering studies on the viscoelastic behavior of guest chains in cross-linked networks were made by Ferry et al. using some cross-linked rubbers containing unattached macromolecules of "nearly identical" chemical composition.[7−11] However, the different chemical structures between the unattached chains and the network constituents have some drawbacks in quantitative interpretations of experimental results such as miscibility at the molecular level in the two components and the difference between the monomeric friction coefficients of the two polymers. To avoid these difficulties, some polymer networks containing unattached chains with identical chemical composition were prepared using poly(dimethylsiloxane) (PDMS),[15] *cis*-polyisoprene,[12,13] and polybutadiene (PB).[17]

To prepare a host network with well-characterized mesh size, the end-linking method is more advantageous than the conventional random cross-linking method.[18,19] In principle, the end-linking method can control the distance between adjacent cross-links by altering the molecular size of end-reactive precursor chains. One study[15] investigated the viscoelastic behavior of unattached PDMS trapped in some end-linked PDMS networks. However, the derived conclusion remained at a semiquantitative level due to the fairly broad molecular size distribution of the guest chains as well as the difficulty in the quantitative evaluation of the relaxation time (τ) from static stress relaxation experiment as mentioned below.

In most of the earlier studies,[7−11,15] the static stress relaxation experiments at a fixed uniaxial strain were used to investigate the relaxation behavior of unattached chains. However, such stress relaxation techniques needed to subtract the contribution of the host cross-linked network from the total relaxation by assuming the validity of some blending law, which made the evaluation of τ complicated and ambiguous. On the other hand, it was demonstrated for PB networks with unattached PB chains[17] that the dynamic mechanical measurements with oscillatory strains allow a straight-

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10.1021/ma010167s CCC: $20.00

forward evalution of τ on the basis of the maximum of loss modulus in the frequency dependence. Ndoni et al. showed that the dependence of τ on the molecular size of the unattached PB was well explained by the tube model considering contour length fluctuation of tube.[17] The dielectric normal mode relaxation measurement using the *cis*-polyisoprene (PI) (with the Stockmayer's type-A dipoles parallel to the chain contour) is one of the most straightforward techniques to pick up the signal solely from the guest chain. On the basis of the dielectric normal mode relaxation measurements for *cis*-PI trapped in a cross-linked PB network, Adachi et al.[13] reported the fairly stronger dependence of τ on the molecular size of guest chain relative to the cubic power law by the original tube model. The authors obtained the similar strong dependence for *cis*-PI trapped in natural rubber networks using the dynamic mechanical method.[12] However, their dielectric studies showed the validity of the cubic power law for the blends containing a small amount of the probe *cis*-PI in un-cross-linked PB or the *cis*-PI melt with high molecular mass (expected to act as invariant topological constraint).[20,21]

The effect of mesh size (M_x), especially the effect of tight mesh, on the dynamics of guest chains is also an interesting subject to study. De Gennes[22] theoretically considered the self-diffusion of guest linear polymer in host polymer network as a function of the size of guest molecules (M_g) and the mesh size (M_x): For guest linear molecules fairly longer than mesh size ($M_g > M_x$), it was conjectured that if M_x is comparable to or larger than the entanglement spacing (M_e), the self-diffusion of the guest chains obeys reptation; in the case of the tightly cross-linked networks of $M_x < M_e$, the self-diffusion (reptation) is restricted and retarded by tight mesh (*strangulation effect*). Some experimental studies reported the slowing-down in the self-diffusion of guest chains in some tightly cross-linked host networks,[12,16] but the quantification of the effect of tight mesh still remains to be developed because of a broad distribution in mesh size as well as an insufficient trapping of the guest chains in the host networks in the earlier studies,[12,16] the details of which will be discussed in a later section.

In the present study, we have investigated the dynamic mechanical behavior of the two types of end-linked PDMS networks with $M_x \approx M_e$ and $M_x < M_e$ containing unattached linear PDMS chains with relatively narrow molecular size distribution. The meshes of the two host networks of $M_x \approx M_e$ and $M_x < M_e$ are entanglement- and cross-link-dominant, prepared by end-linking sufficiently longer and shorter precursor chains relative to M_e, respectively. The networks of $M_x \approx M_e$ with unattached linear chains can be a model system to assess experimentally the tube theory. The effect of tight mesh on the dynamics of guest linear PDMS has been discussed by comparing the results between the networks of $M_x \approx M_e$ and $M_x < M_e$.

Experimental Section

Materials. Commercial linear vinyl-terminated PDMS and linear (inert) trimethylsilyl-terminated PDMS (Gelest Inc.) were employed as end-reactive precursor chains and unattached (guest) chains, respectively, after the fractionations with a mixture of methanol and 2-butanone to narrow the molecular size distributions. Linear vinyl-terminated oligomeric dimethylsiloxane purchased from Shinetsu Chem. Co. was used without further purification. Number- and weight-average molecular masses (M_n and M_w, respectively) of the PDMS were measured by gel permeation chromatograpy (GPC) using chloroform as solvent at 54 °C under the flow rate of 1 mL/min. Under these conditions, the molecular mass of PDMS is directly obtained from a calibration curve of a series of standard polystyrenes without any further calibrations.[23] The values of M_n and M_w of the precursor and the guest PDMS evaluated from GPC are given in Tables 1 and 2, respectively. The polymeric precursor chain PL, whose molecular mass is much larger than the critical molecular mass for forming entanglement couplings for un-cross-linked PDMS melt ($M_c = 1.66 \times 10^4$),[24] was used for preparing the host network with $M_x \approx M_e$ whose mesh is primarily governed by trapped entanglements. The oligomeric precursor chain PS with M_n less than the entanglement spacing of $M_e = 1.0 \times 10^4$ for PDMS[25] was employed to prepare the host network with a tight mesh of $M_x < M_e$.

Table 1. Characteristics of End-Reactive Precursor PDMS

precursor	M_n (g/mol)	M_w/M_n
PL	84 000	1.3
PS	4550	1.6

Table 2. Characteristic Times (τ_g) and Molecular Masses (M_g) of Guest Linear PDMS in End-Linked PDMS Networks

		guest PDMS		
	precursor of host network	M_g[a] (g/mol)	M_w/M_n	$\log(\tau_g/s)$
NS-29	PS	28 800	1.56	−0.15
NS-71	PS	71 000	1.37	0.78
NS-86	PS	86 400	1.25	1.3
NS-114	PS	114 000	1.20	*b*
NL-114	PL	114 000	1.20	−3.1
NL-138	PL	138 000	1.27	−2.8
NL-285	PL	285 000	1.25	−1.7
NL-354	PL	354 000	1.27	−1.3

[a] Weight-average molecular mass. [b] Beyond the longest experimental time scale in the present study.

Tetrakis(dimethylsiloxysilane) (Chisso Co.), the Spier's catalyst $H_2PtCl_6 \cdot 6H_2O$ (Wako Chem. Co.), and distilled toluene were used as cross-linker, catalyst for hydrosilylation, and solvent, respectively.

Preparation of PDMS Networks Containing Unattached PDMS. The PDMS networks containing unattached PDMS were prepared after the method of Granick et al.[15] The inert guest PDMS was added to the weighed telechelic precursor PDMS such that the volume fraction of the former in the resulting network would be 0.15. To facilitate complete mixing, the mixtures with highly viscous PL were dissolved in distilled toluene. After stirring for 1 week, the toluene was completely removed by evaporation under reduced pressure. The mixtures with PS of low viscosity were stirred without solvent for 1 week. At this stage, the desired amounts of cross-linker and catalyst were added to the mixtures. The molar ratios of reactive groups in the cross-linker to those in the precursor chains were 1.5 and 1.6 for the networks of PL and PS (designated as NL and NS, respectively), respectively. These ratios were obtained in such an optimization that the amount of unreacted materials extracted from the final networks would be minimum. The deviation of the optimized ratio from stoichiometric ratio (unity) was also reported in other studies.[26−29]

The mixtures were poured into a leveled Teflon mold after vigorous mixing and removal of bubbles. The cross-linking reaction hydrosilylation was carried out at 80 °C for 72 h under dry nitrogen atmosphere. The end-linked PDMS networks without unattached chain were prepared in the same way. The resulting networks were used for dynamic mechanical measurements.

The networks without unattached chains were extracted in toluene to measure the weight fractions of the unreacted materials (w_{sol}). The values of w_{sol} for NL and NS without unattached chains were ca. 2 and 8 wt %, respectively.

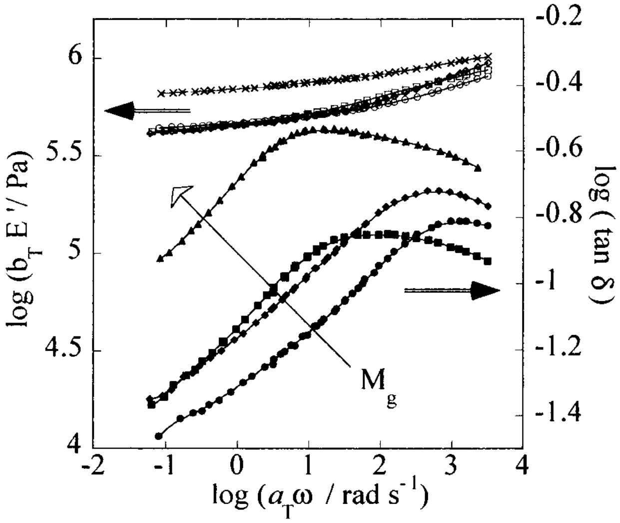

Figure 1. Master curves of angular frequency ω dependence of dynamic storage Young's modulus E' (open symbols) and the loss factor tan δ (closed symbols) for end-linked PDMS networks of the precursor chain PL with $M_n = 8.40 \times 10^4$g/mol containing guest linear PDMS. The reference temperature is 30 °C. The average mesh size estimated from the plateau value of E' is $M_x = 1.2M_e$. The E' data of the pure PDMS networks without guest chains are represented by the × symbol, and the tan δ data are outside the range of the figure due to the small magnitude. The weight-average molecular mass of the guest linear PDMS M_g: circle, 1.14×10^5; diamond, 1.38×10^5; rectangular, 2.85×10^5; triangle, 3.54×10^5 g/mol.

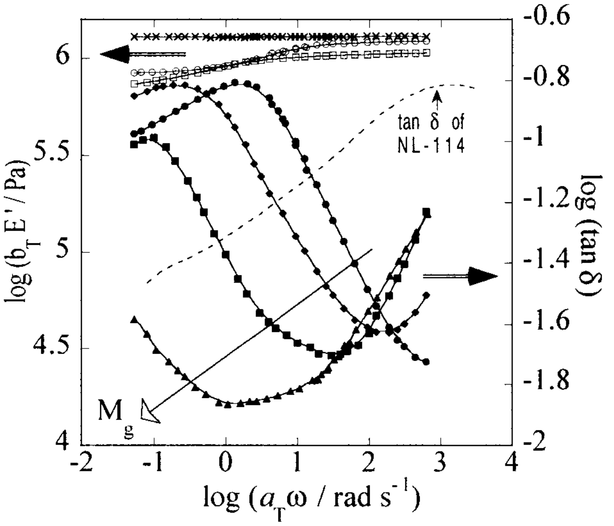

Figure 2. Master curves of angular frequency ω dependence of dynamic storage Young's modulus E' (open symbols) and the loss factor tan δ (closed symbols) for end-linked PDMS networks of the precursor chain PS with $M_n = 4.55 \times 10^3$ g/mol containing guest linear PDMS. The reference temperature is 30 °C. The average mesh size estimated from the plateau value of E' is $M_x = 0.7M_e$. The E' data of the pure PDMS networks without guest chains are represented by the × symbol, and the tan δ data are outside the range of the figure due to the small magnitude. The size (weight-average molecular mass) of the guest linear PDMS M_g: circle, 2.88×10^4; diamond, 7.10×10^4; rectangular, 8.64×10^4; triangle, 1.14×10^5 g/mol. The data for $M_g = 1.14 \times 10^5$ g/mol in the end-linked network of PL are also shown for the comparison.

Dynamic Mechanical Measurements. The dynamic mechanical measurements of rectangular samples of 10 mm width and 5 mm height were conducted with a strain-controlled oscillatory rheometer DVE-V4 (Reoroji) using parallel plates geometry. Frequency sweeps were carried out from 0.1 to 100 Hz, and the temperatures were varied from −30 °C for the networks NL (sufficiently above the crystalline melting temperature ca. −40 °C[30,31]), or 30 °C for NS, up to 180 °C in order to obtain the master curves of rheological data over a wide frequency range using the conventional time−temperature superposition principle.[32] The oscillatory compressive strain amplitudes were within the range of linear viscoelasticity.

Results and Discussion

Temperature Shift Factor. The time−temperature superposition principle was used at a reference temperature $T_o = 30$ °C to obtain the master curves of dynamic Young's strorage modulus (E') and loss tangent (tan δ) as a function of angular frequency (ω). The temperature shift factors a_T for the networks NL and NS with and without unattached chains agreed within the experimental error. The temperature dependence of a_T was approximated by the William−Landel−Ferry equation.[32] The parameters C_1 and C_2 in the WLF equation were estimated to be 5.52 and 522 at $T_o = 30$ °C, respectively. A comparison of a_T for the cross-linked networks and the un-cross-linked melts of PDMS implies that the viscoelasticity of the cross-linked networks is more temperature-dependent.[32,33] Similar results were reported for some PDMS networks and the same networks having pendant chains.[33] For a good superposition, the temperature and density corrections in the vertical direction (b_T) were necessary, and the corrections obeyed the classical dependence[32] $b_T = T_o\rho_o/(T\rho)$ where ρ_o and ρ are the densities at the reference and measurement temperature T, respectively.

Frequency Dependence of *E′*. Figures 1 and 2 show the master curves of the ω dependence of E' for the end-linked networks NL (Figure 1) and NS (Figure 2) with or without guest chains. The mesh of NL is expected to be entanglement-dominant on the basis of about 10 times larger M_n of the precursor PL relative to M_e. Actually, the plateau shear modulus of NL without guest chains ($G_e = E'(\omega\rightarrow 0)/3 = 2.2 \times 10^5$ Pa) is close to the quasi-plateau modulus of un-cross-linked entangled PDMS melt ($G_N^o = 2.4 \times 10^5$ Pa).[25] The magnitude of G_o comparable to G_N^o shows the entanglement-dominant character of NL with $M_x \approx M_e$ ($M_e = 1.00 \times 10^4$).[25] On the other hand, M_x of NS (in which M_n of the precursor PS is less than M_e) without guest chains is smaller than M_e as simply expected, and the value of M_x was estimated as $^3/_5 M_e$ from the plateau shear modulus ($G_e = 4.0 \times 10^5$ Pa) larger than G_N^o by a factor of $^5/_3$.

An increase in E' at high frequencies is observed for the networks containing guest chains, because the guest (unattached) chains behave as elastic chain when the concerning time scale is shorter than the relaxation time of guest chains τ_g, i.e., $\omega > 1/\tau_g$. A finite increase in E' at high frequencies for the pure network of PL is due to the presence of a small amount (ca. 2 wt %) of unreacted precursor chain in the network. The presence of the guest chains slightly reduces the plateau values of E' ($E_e = E'(\omega\rightarrow 0)$) and correspondingly increases M_x relative to the concerning pure networks, because they act as diluent at $\omega \ll 1/\tau_g$. The values of M_x for NL and NS containing guest chains are estimated to be 1.2×10^4 ($=1.2M_e$) and 7.0×10^3 ($=0.7M_e$), respectively, from E_e of each network using the relation for affine network $E_e = 3cRT/M_x$ where c is the network concentration.[32] The estimation of M_x from E_e involves some uncertainity due to the ambiguous front factor resulting from the treatment of thermal fluctuation of cross-links.[32] Therefore, these absolute values of M_x should be viewed with some caution, while the M_x values estimated are very useful as relative values when comparing one network to another.

Frequency Dependence of tan δ. Figures 1 and 2 also illustrate the master curves of the ω dependence of the loss tangent tan $\delta = E''/E'$ where E'' is the loss modulus for the networks NL (Figure 1) and NS (Figure 2) containing guest chains. For both the networks, the definite maxima of tan δ are observed at certain frequencies, and the peak location shifts to the lower frequencies (the longer times) with increasing in M_g. The maxima of tan δ are attributed to viscoelastic relaxations of the guest chains. The single tan δ peak suggests that each network with guest chain is a one-phase system. Ndoni et al.[17] showed that the segregation of guest chains yields the bimodality of the loss peak for the PB networks containing guest PB chains. It is noteworthy that in their study[17] the segregation was observed only for the case of the guest chains with extremely high molecular masses, and in addition, the chemical composition of the host network was slightly different from that of the guest chain due to the presence of epoxy groups for cross-linking.

The values of tan δ of NL and NS without guest chains (outside the range of the figures) were more than 1 order of magnitude smaller than those of NL and NS with guest chains in the entire range of frequencies and temperatures explored. This facilitates the analysis of the viscoelastic relaxation of guest chains, because the height and shape of the tan δ curves around the maximum are not significantly changed by the subtraction of the contribution of host network matrix to the loss tangent. We define the inverse of $\omega_{\max,\tan\delta}$ as characteristic time τ_g for the viscoelastic relaxation of the guest chains as

$$\tau_g = 1/\omega_{\max,\tan\delta} \tag{1}$$

The values of τ_g for each guest chain in the two host networks are listed in Table 2. It can be seen for both the networks that τ_g increases with increasing in M_g. The comparison of τ_g for different M_g on the basis of eq 1 implicitly postulates that the “shapes” of relaxation spectra of different samples are identical. It can be seen in Figures 1 and 2 that the tan $\delta-\omega$ curves of different M_g for identical host network have almost identical shapes, which allows us to discuss the M_g dependence of relaxation time using τ_g defined by eq 1. On the other hand, the shapes of the tan $\delta-\omega$ curves appear to be appreciably different between NL and NS containing guest chains, although a detailed comparison of the curve shapes is difficult because most of the data for NL and NS correspond to the lower and higher frequency regions relative to $\omega_{\max,\tan\delta}$, respectively. However, the definition of τ_g by eq 1 is sufficient for semiquantitative evaluation of τ_g in order to focus on the remarkable difference in τ_g between the two networks as described later.

It is also noticed in Figures 1 and 2 that the relaxation of the unattached chains in the tightly cross-linked network NS is dramatically retarded relative to that in the entanglement-dominant network NL. The difference in the relaxation time between the two networks is so large as to prevent the direct comparison of two experimental values of τ_g for same M_g: The relaxation of the guest chain with $M_g = 1.14 \times 10^4$ in NS (NS-114) was so slow that the maximum of tan δ could not be detected by even the minimum frequency accessible in the present study, while the maximum in NL (NL-114) was close to upper frequency limit, as can be seen in Figure 2. The datails of the marked difference in τ_g between the two networks will be discussed in a later section.

The loss modulus E'' did not have a definite peak and just showed the inflection at around $\omega_{\max,\tan\delta}$ for all the networks of PL and the most of the networks of PS with the guest chains. Also, the ω dependence of E'' at low frequencies was approximately $E'' \sim \omega^{0.2-0.3}$, and the terminal relaxation zone ($E'' \sim \omega^1$) was not achieved in the frequency window covered by the present study. Because of these characteristics of E'', the employment of the definite peak of tan δ is more straightforward for the estimation of relaxation time. The ω dependence of E'', closely related to relaxation spectrum, should provide an important basis for the relaxation mechanism, but we restrict here our attention only to the characteristic time for the relaxation behavior. The detailed analysis of the ω dependence of E'' will be made in a separate publication.[34]

M_g Dependence of τ_g. The original reptation model[1-4] predicts the cubic power dependence of the longest relaxation time τ_L on size of reptative linear chains ($\tau_L \sim M_g^3$) in invariant (fixed) network. The full description of τ_L by the reptation model considering the correction for the contour length fluctuation (CLF) of tube[4,35] is

$$\tau_g \sim \tau_L = \frac{b^2 \zeta_o M_g^{\,3}}{M_x M_o^{\,2} \pi^2 kT}\left[1 - 1.3\left(\frac{M_x}{M_g}\right)^{0.5}\right]^2 \tag{2}$$

where b^2 is the mean-square end-to-end distance per monomer unit, ζ_o is the monomeric friction coefficient, and M_o is the monomeric molar mass. The bracket corresponds to the correction term for CLF. In principle, the characteristic time τ_g based on eq 1 does not strictly coincide with τ_L[32] but should be proportional to τ_L. Actually, τ_L calculated from eq 2 with the molecular parameters of PDMS melt are slightly smaller but close to τ_g for the entanglement-dominant network NL, as can be seen in Figure 3. We employed $b = 6.2 \times 10^{-10}$ m,[32] $M_o = 7.4 \times 10^{-2}$ kg/mol, $\zeta_o = 8.19 \times 10^{-12}$ N s/m for 30 °C calculated from ζ_o at 25 °C with the WLF equation,[32] and $M_x = 12$ kg/mol obtained from $M_x = 1.2M_e$.

Figure 3 shows the double-logarithmic plots of τ_g vs M_g^3 or $M_g^3(1 - 1.3(M_x/M_g)^{0.5})^2$. For the entanglement-dominant network NL, the experimental M_g dependence of τ_g, approximated by $\tau_g \sim M_g^{3.6}$, is appreciably stronger than the cubic power dependence of the original reptation model, but it is well reproduced by considering the CLF correction. This result is in good accordance with the result for the guest linear polybutadiene (PB) trapped in randomly cross-linked entanglement-dominant PB networks:[17] τ_L obtained by dynamic mechanical measurements scaled as $\tau_L \sim M_g^{3.35}$, but after the CLF correction, the data were well described by the reptation theory. For the tightly cross-linked network NS, the M_g dependence of τ_g is more satisfactorily reproduced by the cubic power law than the prediction with the CLF correction. The good agreements in the M_g dependence of τ_g between the experimental results for both the networks and the theoretical predictions suggest that the dynamics of the guest linear polymer chains is well described by the reptation concept, regardless of mesh size of host networks.

Comparison of τ_g for NL and NS. It is found in Figure 3 that in the comparison of τ_g for same M_g between the two networks τ_g for NS is remarkably larger

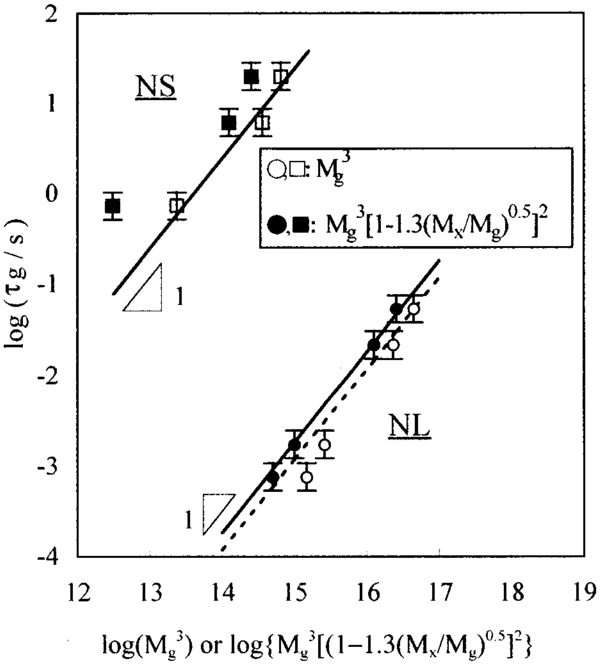

Figure 3. Dependence of characteristic time τ_g on weight-average molecular mass of guest linear PDMS chains M_g in the two end-linked PDMS networks NL (circle) and NS (rectangular), respectively. The average mesh sizes of NL and NS estimated from E_e are $M_x = 1.2M_e$ and $M_x = 0.7M_e$, respectively. The dashed straight line represents the longest relaxation time τ_L predicted by the tube theory with the CLF correction (eq 2) using the parameters of PDMS melt. The slope of the solid straight lines is unity.

than that for NL by a factor of nearly 10^5. The direct comparison using the data of τ_g for same M_g between the two networks is prevented by such marked difference, but the difference in τ_g is easily evaluated by extrapolation using the experimental data at hand.

Some earlier studies reported the slowing-downs in viscoelastic relaxation[12] and self-diffusion[16] of guest polymers for some tightly cross-linked networks, but the slowing-downs observed in both the studies were less than 10-fold. The significantly smaller slowing-down observed in the earlier studies[12,16] will be due to the less entangled guest chains with the network structure as well as the broader size distribution of mesh size, both of which originate from their preparation methods of the networks containing guest chains. Both the studies[12,16] introduced the guest chains into the host networks by swelling (sorption) "after" cross-linking. According to an extraction experiment,[36] the guest chains added after cross-linking were more easily removed from host networks than those present during cross-linking, which clearly suggests that the guest chains introduced after cross-linking are less entangled with the network structure. In addition, their host networks were prepared by the random cross-linking method which inevitably produces a much broader distribution of mesh size relative to end-linking. The guest chains introduced into such a host network after cross-linking will be readily trapped in more porous regions, and they are expected to move preferably in porous regions. Thus, the definitely smaller effect of tight mesh on the dynamics of guest chains in the earlier studies[12,16] is not surprising, and it is difficult to compare directly the results of the present and their studies.[12,16]

De Gennes[22] predicted the slowing-down of reptation in networks of $M_x < M_e$ (what they called strangulation effect) by a factor of M_x^{-1} on the basis of eq 2, considering only the effect of reduction in mesh size, i.e., decrease in "tube diameter" for reptation. However, it is evident that the dramatic slowing-down of reptation in NS cannot be explained only in terms of the reduction in "average" mesh size, since the reduction factor of M_x is only ca. 2. According to eq 2, the remarkable slowing-down of the reptative motion is apparently attributed to a significant increase in segmental friction coefficient ζ_0 in NS. It is to be noted that the temperature shift factors a_T at each temperature employed for constructing the master curves were the same for both the networks NL and NS. This implies[32] that free volume is not appreciably different between the two host networks, and the increase in ζ_0 is not due to a rise in glass transition temperature (T_g).

For the apparent marked increase in ζ_0 in NS, it is very important to consider the significant difference in mesh character between the two host networks, other than the difference in M_x. It is to be noticed that the concentration of chemical cross-link in NS is about 20 times higher than that in NL, while the difference in average mesh size M_x including the contribution of trapped entanglements is not large between the two networks. The mesh of NL is mainly formed by chain entanglements, while that of NS is primarily governed by chemical cross-links. The chemical cross-link in the present study is apparently assumed to have the moiety of PDMS, because the molecular structure of the cross-link is not essentially different from that of the repeating unit of the PDMS network chains. However, some characteristics of tightly cross-linked networks originating from high cross-link density should be considered for the results for NS. The appreciable difference in the ω dependence of tan δ between NL and NS with guest chains (i.e., fairly sharper relaxation peaks of tan δ in NS relative to those in NL in the region of $\omega > \omega_{\max,\tan\delta}$) implies the presence of some effects of network matrix on the dynamics of guest chains.

One is the lowering effect of high cross-link density on the mobility of network chains. Actually, a recent proton NMR study[37] on the dynamics of end-linked PDMS networks demonstrated that the mobility of the network chains in the networks of the precursors with $M_n < M_e$ is remarkably lower than that in the networks of the precursors with $M_n > M_e$, while the mobility is almost independent of M_n of the precursors in the region of $M_n > M_e$. Their results appear to suggest that the significantly lower mobility of the cross-link-dominant network matrix relative to the entanglement-dominant one is an origin of the remarkable retardation in the relaxation of guest chains. As another effect of high cross-link density, one should recall that the precursor PS (with $M_n = 4550$) contains a considerable fraction of short chains "markedly smaller than M_e" due to the finite size distribution ($M_w/M_n = 1.6$). It is expected that the finer meshes formed by such short precursor chains strangle tightly a part of the contours of guest chains, and/or they make the conformation of guest chains more convoluted within the network structure, both of which restrict the motion of the guest molecules. Some numerical simulation studies[38,39] on a polymer chain trapped between regularly or randomly distributed fixed obstacles suggest that in the case of the regular one the dynamics obeys the reptation concept, and the chain statistics are Gaussian; in the latter case, the entropic barriers arising from the presence of the bottlenecks slow the diffusion significantly, and they shrink the chain dimension. The entropic barrier concept may be applicable to the guest chain in tightly cross-linked network, but it is very difficult to quantify how much slowing-down the entropic barrier effect yields in the system investigated here. In addition, the M_g dependence of τ ($\tau \sim M_g^4$) obtained in their simulations for the case of randomly distributed fixed obstacles[38,39] is not in accord with the experimental result ($\tau_g \sim M_g^3$) for the tightly cross-linked network.

Finally, we want to emphasize that the difference in mesh character between the host networks of $M_x \approx M_e$ (entanglement-dominant) and $M_x < M_e$ (cross-link-dominant) is experimentally unavoidable as far as cross-link is necessary for network formation, which precludes us to observe exclusively the pure strangulation effect,[22] i.e., only the effect of tight mesh size, on the dynamics of guest chains. The effect of cross-links on the dynamics of guest chains, which has not been theoretically considered, must be taken into account in understanding the results for the cross-link-dominant host networks of $M_x < M_e$.

Acknowledgment. The authors appreciate helpful comments from Prof. T. Takigawa of Kyoto University and the kind assistance of Dr. T. Kawamura of Kyoto University for sample preparation.

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MA010167S