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Dynamic Viscoelasticity of Poly(butyl acrylate) Elastomers Containing Dangling Chains with Controlled Lengths

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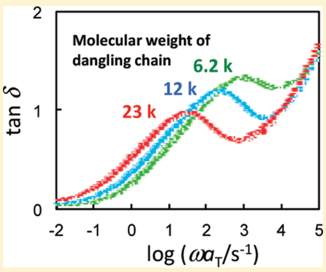
ABSTRACT: We demonstrate that the poly(butyl acrylate) (PBA) elastomers containing considerable amounts of dangling chains with uniform lengths exhibit pronounced viscoelastic relaxation ($\tan\delta > 1$) at characteristic frequencies. The elastomers are obtained by the copolymerization of monoacryloyl- and diacryloyl-terminated precursor PBA with narrow size distributions. The molecular weights of the precursors are smaller than the critical molecular weight for the onset of entanglement coupling. The relaxation time of the elastomers (τ_D) is proportional to the square of the molecular weight of the dangling chains equivalent to the monofunctional PBA (M_D), and τ_D is about 2.5 times larger than the relaxation time of the corresponding free guest chains in the elastomers (τ_G). These observations are close to the expectations from the Rouse-chain dynamics without entanglement effect ($\tau_D \sim M_D^2$ and $\tau_D = 4\tau_G$). These results provide an important basis for the understanding of the dynamics of the unentangled chains whose one end is tethered to the permanent networks. The results also offer a route of molecular control of characteristic frequency and strength of mechanical damping of elastomers.



INTRODUCTION

There has been a lot of industrial demand for elastomers with high damping properties to suppress the vibration and noise. The loss tangent ($\tan\delta$), defined by the ratio E''/E' where E' and E'' are the storage and loss modulus, respectively, is often employed as a measure of the dissipation of the input deformation (vibration) energy,[1,2] when the materials are used in extensional (free-layer) and constrained-layer damping systems. Much effort has been made to enhance the magnitude of $\tan\delta$ of elastomers in the desired ranges of frequency and temperature. The earlier studies tackling this issue are roughly classified into the two approaches. One approach utilizes a large mechanical loss at the glass−rubber transition, and they tune the location of the glass transition temperature (T_g) or broaden the transition region by blending the polymers with different T_g.[3−5] A marked change in E' inevitably accompanies the glass−rubber transition, which often limits the availability of the materials in industrial use. The other approach introduces the relaxation components into elastomers. The dangling chains,[6−13] whose one end is tethered to permanent networks, or the unattached free chains[14−18] are employed as the relaxation components. The relaxation times of these chains are located in the rubbery region of elastomers, and the relaxation accompanies no significant change in E'. The elastomers containing the dangling chains are of all solid type in contrast to those containing the unattached free chains which act as solvents (diluents). In the latter case, the bleeding of the free chains in the long time use may be disadvantageous in industrial applications.

The elastomers containing small amounts of dangling chains have been employed to investigate the dynamics of a single tethered chain in fixed polymer networks.[9,10,19] Most of these elastomers have been prepared by end-linking the mixture of bi- and monofunctional precursor chains (designated as B_2 and B_1, respectively) with low B_1 concentrations via multifunctional cross-linker (C_n) whose functionality is typically $n = 3$ or 4. The species B and C_n have different functional groups, and C_n reacts with B_1 or B_2 while no reaction between B_i ($i = 1, 2$) occurs in this end-linking system. Our previous study[11] showed that $\tan\delta$ of the elastomers increased with an increase in B_1 concentration in the mixtures. The polydimethylsiloxane elastomers with high B_1 concentrations exhibited relatively high $\tan\delta$ (ca. 0.3), which was nearly constant in the wide temperature range (ca. 150 °C). The temperature-insensitive damping feature reflects a nearly flat relaxation spectrum over a broad time range with finite relaxation strength. The origin of this peculiar relaxation spectrum was attributed to an irregular network structure made of the pendant branched components with various shapes and a wide size distribution.

The copolymerization of the B_2/B_1 mixtures also results in permanent networks, i.e., elastomers, when the B_2 concentrations are sufficiently high. Importantly, the copolymerization of the B_2/B_1 mixtures enables us to introduce much more amounts of dangling chains into the elastomers than the end-linking reaction [$B_2 + B_1 + C_n$] using cross-linker with modest functionality (such as $n = 3, 4$) because B_1 chains undergo polymerization themselves without cross-linker in the copolymerization.

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Table 1. Characteristics of Precursor PBA

precursor	M_n	M_w/M_n	F_n[a]	T_g (°C)
B12	1.19×10^4	1.19	1.94	–[b]
M06	6.23×10^3	1.22	1.00	−54
M12	1.16×10^4	1.10	0.92	−49
M23	2.27×10^4	1.12	0.94	−51
N13	1.28×10^4	1.30	0	–[b]
N24	2.40×10^4	1.18	0	–[b]

[a] Number of acryloy group per chain. [b] Not measured.

In particular, in the case of high B_1 concentrations, the copolymerization yields the elastomers with many dangling chains equivalent to B_1: The comb-shaped polymers with long side chains, which are formed by sole polymerization of B_1, are loosely cross-linked by B_2. The copolymerization of the B_2/B_1 mixtures provides a route to prepare the elastomers having many dangling chains with uniform lengths. This elastomer is expected to exhibit pronounced viscoelastic relaxation at a characteristic time because many dangling chains with uniform length result in high relaxation strength at the corresponding relaxation time. This will offer an important basis of the molecular control of the characteristic frequency (ω_c) showing the maximum mechanical damping because ω_c is governed by the length of dangling chains. The results also significantly contribute to the understanding of the dynamics of the polymer chains whose one end is tethered to permanent networks. To our knowledge, the elastomers with high damping at characteristic frequencies utilizing the viscoelastic relaxation of dangling chains have not yet been reported.

The present study demonstrates this concept using the elastomers obtained by the copolymerization of monoacryloyl- and diacryloyl-terminated poly(*n*-butyl acrylate) (PBA) with narrow size distributions. We investigate the dynamic viscoelasticity of the PBA elastomers as functions of the length and content of monofunctional precursor. We also compare the relaxation times of the dangling chains with those of the corresponding free guest chains in the elastomers.

■ EXPERIMENTAL SECTION

Materials. The monoacryloyl- and diacryloyl-terminated linear PBA (Kaneka Corp.) were employed as end-reactive precursor chains, i.e., dangling chains and bridge chains in elastomeric networks, respectively. The inert linear PBA (Kaneka Corp.) were used as unattached guest chains. These PBA were synthesized by atom transfer radical polymerization, and they have narrow size distributions of $M_w/M_n < 1.3$ where M_w and M_n are the weight- and number-average molecular weights, respectively. The monofunctional, bifunctional, and inert PBA are designated as *MX*, *BX*, and *NX*, respectively, where *X* denotes the value of M_n. Table 1 lists the characteristics of each PBA. The values of M_n and M_w were measured by gel permeation chromatography (GPC) using chloroform as solvent at 40 °C. Under this condition, the molecular weight of PBA is directly obtained from a calibration curve of a series of standard polystyrenes without any further calibration. The number of the acryloyl groups per single chain was estimated by ^{1}H NMR.

Sample Preparation. The elastomers containing dangling chains or unattached chains were prepared by the photopolymerization of B12/*MX* or B12/*NX* mixtures. A mixture of 2-hydroxy-2-methyl-1-phenylpropane-1-one (Darocure 1173, Ciba Specialties Chemicals) and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819, Ciba Specialties Chemicals) was employed as photoinitiator. The reactant liquid mixtures were poured into a metal mold with a thickness of 2 mm.

Table 2. Characteristics of PBA Elastomers

elastomer	ϕ_{B12}[a]	ϕ_D[b]	ϕ_G[c]	T_g (°C)
D0	1			−44
D82-M12	0.18	0.82		−48
D70-M12	0.30	0.70		−48
D50-M12	0.50	0.50		−48
D82-M06	0.18	0.82		−52
D82-M23	0.18	0.82		−49
G75-N13	0.25		0.75	−49
G75-N24	0.25		0.75	−49

[a] Weight fraction of B12. [b] Weight fraction of monofunctional PBA. [c] Weight fraction of inert PBA.

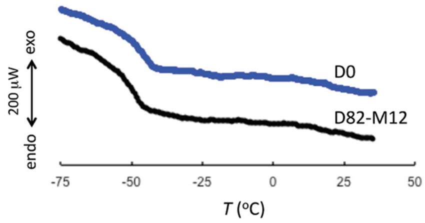

Figure 1. DSC curves of D0 and D82-M12 obtained with a heating rate of 5 °C min^{-1}.

The reactant mixture was irradiated using Light Hammer 6 (Fusion UV Systems Japan) with emission at a peak wavelength 260 nm with an irradiance of 1.5 W cm^{-2} for 10 s. The compositions of the mixtures are summarized in Table 2. The sample code D*Y*-*MX* or G*Y*-*NX* represents the elastomer containing dangling chains composed of *MX* or the elastomer containing unattached guest chains *NX*, respectively, and *Y* denotes the weight fraction of *MX* or *NX*. The elastomer D0 was prepared by the photopolymerization of only B12.

After the irradiation of UV light, the resultant elastomers (excepting the elastomers containing *NX*) were allowed to swell in toluene for 1 week in order to wash out the unreacted materials. The toluene was renewed every day. The swollen elastomers were gradually deswollen in the toluene/methanol mixtures by increasing stepwise the methanol content. The deswollen elastomers in pure methanol were dried in vacuum. The fully dried elastomers were employed for the measurements. The elastomers before and after the washing procedures will have no significant difference in the composition of the B12/*MX* mixtures because B12 and *MX* are similar in reactivity. The elastomers containing *NX* were used for the measurements without this washing procedure.

Measurements. The thermal properties of the precursor chains and elastomers were investigated using a differential scanning calorimeter (DSC-6200, Seiko Instruments) at a heating rate of 5 °C min^{-1}.

The dynamic viscoelasticity of the elastomers was measured by a solids analyzer RSA-G2 (TA Instruments). In the frequency scan measurements, the angular frequency (ω) was varied from 0.1 to 100 s^{-1} at each temperature (T), and T was altered between −25 and 75 °C with an interval of 10 °C. The master curves at a reference temperature of 25 °C were constructed on the basis of the conventional time−temperature superposition principle. The T scan measurements were conducted at ω = 5 s^{-1} and a heating rate of 5 °C min^{-1} in the range of $-60\ °C < T < 40\ °C$. The oscillatory strain amplitudes were within the range of linear viscoelasticity in all measurements.

■ RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of D0 and D82-M12. No thermodynamic transition other than the glass transition was

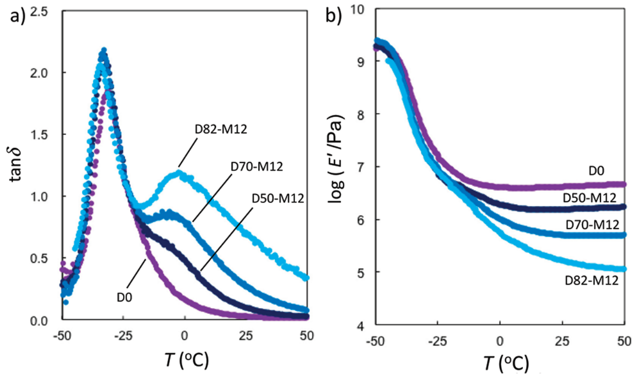

Figure 2. Temperature dependence of (a) loss tangent (tan δ) and (b) storage modulus (E') obtained with a heating rate of 5 °C min^{-1} and an angular frequency of 5 s^{-1} for the elastomers containing the dangling chains of $M_D = 1.16 \times 10^4$ with various contents.

observed in the T range of interest. The glass transition temperature (T_g) was taken as the summit of the peak of the differentiated DSC curve, and T_g of each sample is summarized in Tables 1 and 2. The temperatures T_g of the elastomers are about −50 °C, which is similar to T_g of the precursor chains, and they are almost independent of the molecular weight of dangling chains (M_D). Further, no appreciable difference in T_g is observed among the elastomers with various weight fractions of dangling chains (ϕ_D), when ϕ_D is higher than 0.5. The elastomers with finite ϕ_D exhibit slightly lower T_g than D0, which is because they are smaller in number of cross-links and larger in number of free chain ends than D0.

Figure 2 illustrates the T dependence of loss tangent (tan δ) and storage Young's modulus (E') for the elastomers with various ϕ_D of M12. The peak of tan δ at ca. −35 °C for each sample is assigned to the glass transition on the basis of the results of DSC. The elastomers with finite amounts of dangling chains exhibit an appreciable relaxation at ca. 0 °C which is absent in D0, and the corresponding peak of tan δ becomes more pronounced as ϕ_D increases. D82-M12 shows a large maximum of tan δ which exceeds unity. As is evident from the DSC results, the peak of tan δ at ca. 0 °C are not attributable to thermodynamic transition such as crystalline melting. The rubbery plateau modulus decreases with an increase in ϕ_D because an increase in ϕ_D results in not only an increase in the number of dangling chains but also a decrease in the number of cross-links.

Figure 3 displays the master curves of the ω dependence of tan δ, E', and E'' for the elastomers containing the same amount of dangling chains ($\phi_D = 0.82$) with various lengths. These elastomers contain the same amount of B12 in feed ($\phi_{B12} = 0.18$). In fact, they are almost similar in equilibrium modulus E_0 [$E_0 \equiv E'(\omega \rightarrow 0) = 2.6 \times 10^4$ Pa]. This indicates that these elastomers are dissimilar in length of dangling chains but similar in the density of elastically effective cross-links. All curves for each viscoelastic parameter are well overlapped in the high ω regime corresponding to the segmental relaxation (the glass−rubber transition). In the middle ω range, each elastomer shows a definite peak of tan δ, and the peak position (ω_D) shifts to the lower ω side as M_D increases. Each curve of E' or E'' exhibits an appreciable shoulder at the frequencies near ω_D. The tan δ peak at log $\omega_D \approx 2.4$ for D82-M12 corresponds to that at $T \approx 0$ °C in Figure 2. These results obviously indicate that the tan δ peak originates from the viscoelastic relaxation of dangling chains.

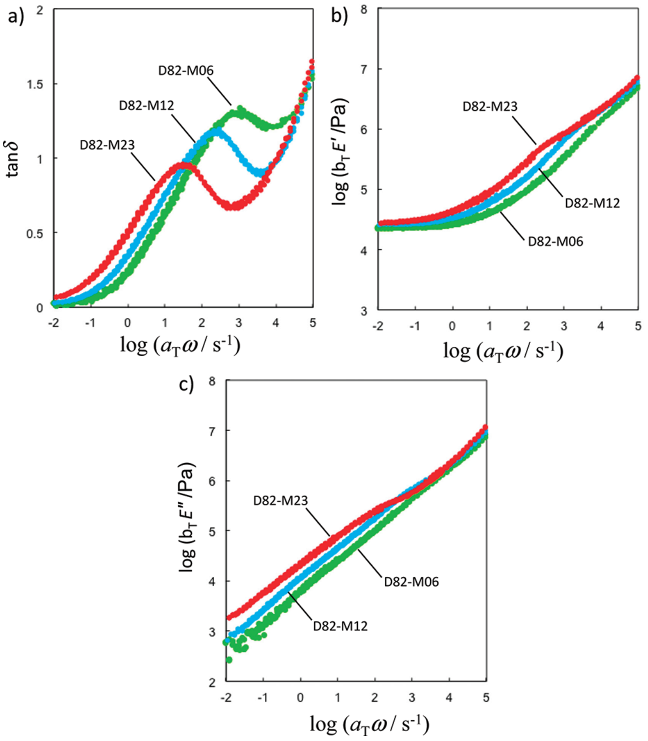

Figure 3. Master curves of the angular frequency (ω) dependence of (a) loss tangent (tan δ), (b) storage Young's modulus (E'), and (c) loss Young's modulus (E'') for the elastomers containing the dangling chains of a weight fraction of $\phi_D = 0.82$ with various lengths. The master curves are obtained by the time−temperature superposition principle at a reference temperature of 25 °C. The quantities a_T and b_T are the horizontal and vertical shift factors, respectively.

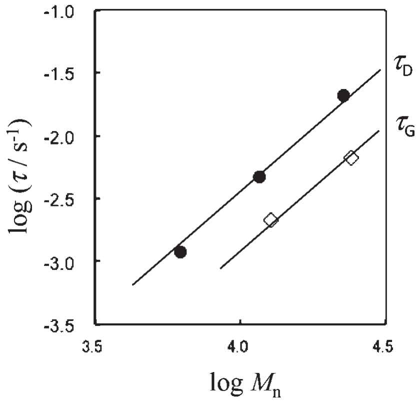

Figure 4. Double-logarithmic plots of the characteristic times of dangling chains (τ_D) and unattached guest chains (τ_G) versus molecular weight (M_n). The slope of the lines is two.

The characteristic time (τ_D) is defined by the inverse of ω_D as $\tau_D \equiv {\omega_D}^{-1}$. The shift of the tan δ peaks in Figure 3a demonstrates that τ_D increases with an increase in M_D. In addition, the large values of tan δ at ω_D (tan δ > 1) indicate that these elastomers have high damping performance for the vibrations with the frequencies near ω_D. The height of the tan δ peak decreases with an increase in M_D as a result of a reduction in the number of the dangling chains ($\sim \phi_D/M_D$). The details of the M_D dependence of the relaxation strength will be discussed later.

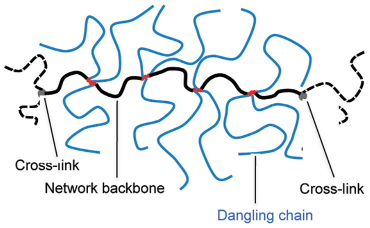

Figure 5. Schematic of the structure of a network strand between adjacent cross-links for D82-M23. The network strand is composed of five bridge chains (B12) and 12 dangling chains (M23).

Figure 4 represents the double-logarithmic plots of τ_D vs M_D for the data in Figure 3. The data fall on the straight line with a slope of two. The dependence $\tau_D \sim M_D^2$ agrees with the expectation from the dynamics of Rouse chains without entanglement interaction.[1] The molecular weight of network backbone (*excluding the dangling chains*) between neighboring junctions (M_c) for the elastomers in Figure 3 was evaluated to be 5.6 × 10^4 g/mol from the equilibrium modulus (E_0) using the relation of rubber elasticity[20] $M_c = 3\rho(1 - \phi_D)RT/E_0$, where ρ is the density of PBA ($\rho = 1.08$ g/cm^3) and R is the gas constant. The molecular weight between neighboring entanglements (M_e) in PBA melts is 2.9 × 10^4 g/mol, which was estimated from the rubbery plateau modulus of the un-cross-linked entangled PBA melt with a high molecular weight measured in our separate experiments. Importantly, M_D of all dangling chains employed here are smaller than both of M_c and M_e. This indicates that these dangling chains are too short to form definite entanglement coupling with themselves and network strands. The relations $M_D < M_c$ and $M_D < M_e$ support the Rouse-type behavior observed. In addition, the relation $M_c > M_e$ shows that M_c corresponds to the molecular weight of network backbone between chemical cross-links without including entanglements.

Figure 5 shows the schematic of the network structure for D82-M23. For the three elastomers in Figure 3, the number of the bridge chains B12 ($M \approx 1.2 \times 10^3$ g/mol) between neighboring cross-links is estimated to be about 5 from the value of M_c ($\approx 5.6 \times 10^4$ g/mol). The number of dangling chains between adjacent cross-links (N_D) is evaluated to be ca. 12 from the molar ratio [M23]/[B12] ($\approx$ 7/3). The values of N_D for D82-M12 and D82-M06 are obtained likewise as $N_D \approx 20$ and $N_D \approx 45$, respectively, from the molar ratios [M12]/[B12] $\approx$ 4/1 and [M06]/[B12] $\approx$ 9/1. It should be noted that the number densities of dangling chains on a network strand in these elastomers are considerably lower than those in typical comb-shaped polymacromonomers:[21,22] for even D82-M06 with the highest N_D among all samples, the fraction of the butyl acrylate (BA) unit having dangling chain in all BA units comprising a single network strand is as large as 0.1. The high side-chain densities reduce the flexibility of the polymacromonomers,[21,22] but the number densities of dangling chains in these elastomers are too small to have finite stiffening effect on the network strands.

Figure 6 compares the master curves of the ω dependence of tan δ for D82-M23 and G75-N24. G75-N24 contains the unattached guest chains with almost the same molecular weight as the dangling chains in D82-M23. These elastomers are almost similar in mesh size because the values of E_0 are comparable: $E_0 = 2.0 \times 10^4$ Pa for G75-N24 and $E_0 = 2.6 \times 10^4$ Pa for D82-M23. The amount of B12 in feed (ϕ_{B12}) for G75-N24 is larger than that for D82-M23 because no sufficient gelation occurred for the B12/N24 mixtures with $\phi_{B12} = 0.18$. G75-N24 also exhibits a prominent peak of tan δ, but the peak frequency of G75-N24 (ω_G) is higher than ω_D of D82-M23. This indicates that a polymer chain in elastomer matrix relaxes faster in the free state than in the tethered state. The characteristic times for the free guest chains, which is defined by $\tau_G \equiv \omega_G^{-1}$, were obtained for G75-N24 and G75-N13. In Figure 4, τ_G are also plotted against the molecular weight of the free guest chain (M_G). The Rouse-type behavior, $\tau_G \sim M_G^2$, is also observed for the free guest chains, although only two data points are available. The relaxation time of the dangling chains is larger than that of the corresponding free chains by a factor of ca. 2.5, i.e., $\tau_D = \alpha\tau_G$ with $\alpha \approx 2.5$. This difference is slightly smaller than but close to the expectation ($\alpha = 4$) for the relaxation of the Rouse chains in the free and tethered states.[23] To the author's knowledge, this is the first experimental comparison of the relaxation times of the Rouse chains in the free and tethered states.

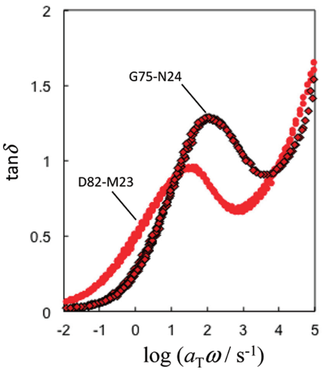

Figure 6. Comparison of the master curves of the angular frequency (ω) dependence of loss tangent (tan δ) for the elastomers containing the dangling chains (D82-M23) and unattached guest chains (G75-N24) with almost the same length.

For comparison, the Rouse relaxation times (τ_R) for the un-cross-linked melts of M12 and M23 were evaluated from the zero-shear viscosity (η_0) using the relation $\tau_R = 6\eta_0 M/(\pi^2\rho RT)$ where the values of η_0 after isofriction correction were employed due to the low molecular weights.[1,24] These polymer melts showed the Rouse-type behavior, i.e., $\eta_0 \sim M$ and $\tau_R \sim M^2$, and the relations $\tau_D \approx 20\tau_R$ and $\tau_G \approx 8\tau_R$ were obtained. The Rouse model expects that the terminal relaxation time of the unattached Rouse chains in fixed networks, whose mesh size is larger than M_G, is comparable to τ_R, because the Rouse chains have no explicit interaction with surroundings. The quantitative discussion about these relations, however, is not straightforward here because the characteristic times (τ_D and τ_G) determined from the peak positions of tan δ are proportional but not equivalent to the terminal relaxation times to be directly compared with τ_R.

In the case of the Rouse-type relaxation, the relaxation strength is linearly proportional to the number of the chains.[1,24] As a simple estimate of relaxation strength, we employ here the height of the shoulder (E''_X) in the log E''−log ω curve at around ω_D (Figure 3c): E''_X is a quantity not equivalent but proportional to relaxation strength. The value of E''_X for each sample was estimated as the intersection of the linear extrapolations from the high and low ω regions. Figure 7 shows E''_X as a function of mole concentration (c_N) of dangling chains or free guest chains.

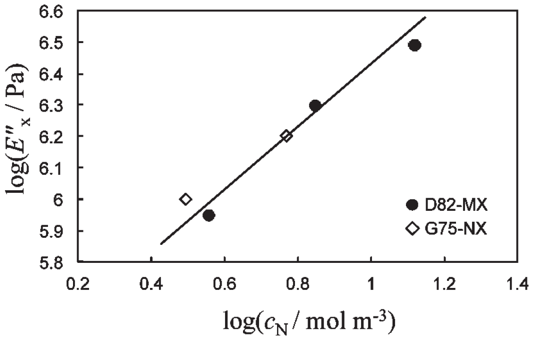

Figure 7. Dependence of the quantity proportional to relaxation strength (E''_x) on the mole concentration of dangling or unattached chain (c_N). The slope of the line is unity.

The c_N dependence of E''_X is approximated as $E''_X \sim c_N^1$, which further confirms the Rouse-type relaxation of the dangling chains and free guest chains.

The pronounced relaxation at ω_D originates from the relaxation of the dangling chains, but the viscoelastic spectra (in particular, in the regime of $\omega < \omega_D$) do not purely reflect the dynamics of the dangling chains equivalent to the monofunctional precursors. In the spatial scale far beyond the size of the dangling chains, the networks are expected to have a treelike structure composed of branched components with various sizes and shapes. In fact, a power law behavior $E'' \sim \omega^\beta$ with $\beta \approx 0.6$ observed in the low ω regime of $\omega < \omega_D$ (Figure 3c) is different from the terminal relaxation behavior ($\beta = 1$). This behavior is due to the viscoelastic contributions of the branched components with larger sizes than the monofunctional precursors. The contributions of these components are not negligible but very small in magnitude because no appreciable gradient in E' is observed in the low ω region. The relaxation strength of the dangling chains equivalent to the monofunctional precursors is considerably higher than those of other viscoelastic components in the networks because the corresponding dangling chains are much larger in number. This is in contrast to the damping properties of irregular end-linked networks composed of dangling parts with broad size distribution: tan δ is relatively high, but its dependence on T and ω is very weak and has no definite peak.[11]

We have demonstrated that the introduction of many dangling chains with uniform lengths into elastomers results in high mechanical damping (tan $\delta > 1$) at a characteristic frequency via their viscoelastic relaxation. We have also shown that the characteristic frequency and strength of damping can be controlled by the chain length and content of dangling chains, respectively. The fabrications of elastomers by the copolymerization of end-reactive precursor chains with uniform lengths provide a route of the molecular control of mechanical damping of elastomers. The dynamic viscoelasticity of the elastomers with many long dangling chains which form entanglement couplings remains to be investigated. The entanglement coupling is expected to provide a marked effect on the M_D dependence of τ_D as in the case of the effect of arm length on the viscoelastic relaxation of entangled star polymer melts.[9,25] This will be investigated in our future work.

■ SUMMARY

The elastomers containing considerable amounts of dangling chains with uniform lengths were prepared by the copolymerization of monoacryloyl- and diacryloyl-terminated PBA with narrow size distributions. The elastomers exhibit pronounced viscoelastic relaxation (tan $\delta > 1$) at the characteristic frequencies regarding the relaxation of the dangling chains equivalent to the monofunctional PBA. The relaxation time τ_D depends on the molecular weight of the dangling chains (M_D) as $\tau_D \sim M_D^2$, and τ_D is about 2.5 times larger than the relaxation time (τ_G) of the corresponding guest free chains in the elastomers. These results are close to the expectations of the Rouse-chain dynamics. This agreement is also supported by the fact that M_D is smaller than both the critical molecular weight for the onset of entanglement coupling and the molecular weight of the network backbone between adjacent cross-links. The copolymerization of the mono- and difunctional polymers with uniform lengths provides a route of molecular control of the frequencies and strength of mechanical damping in the elastomers.

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