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Nanoscale Cooperative Length of Local Segmental Motion in Polybutadiene

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ABSTRACT: The influence of molecular weight between cross-links, M_c, on the segmental α-relaxation of polybutadiene (PBd) networks was probed using dynamic mechanical spectroscopy. Linear polybutadiene ($M_w = 154$ kg/mol; $M_w/M_n = 1.10$; 60% vinyl) was thermally cross-linked to yield a series of networks encompassing the extensive range of $200 < M_c < 70\,000$ g/mol. Throughout this series, we noted increases in the density, the glass transition temperature, T_g, and the relaxation function breadth which systematically followed the level of cross-link density. However, the T_g-normalized temperature dependence, or fragility, was modified for the networks relative to the response for the linear precursor only when the average distance between confining cross-links was less than approximately 2.4 nm. This dimension was found to be similar to the cooperative length scale of 2.1 nm of linear polybutadiene at its glass transition temperature which was deduced using thermal fluctuation theory. Our findings suggest that the length scale of cooperativity associated with the glass transition temperature of linear polymers is revealed by the segmental dynamics of their networks.

Introduction

A comprehensive picture has yet to emerge concerning the fundamental physics which governs the segmental relaxation of materials and the related kinetic departure from the liquid state into the thermodynamically nonequilibrium glass. Although the glass transition is arguably the most important property for polymer materials in particular, its true basis remains an area of active study and debate. Interpretations of T_g dynamics using thermodynamic/configurational entropy approaches,[1,2] thermal fluctuation theory,[3] the coupling model,[4,5] and mode-coupling theory[6] along with related scaling phenomenology[7] have all been developed in an attempt to address the physics of the glass transition. A common theme, explicit or implied, among these approaches is the general concept of many-particle dynamics or cooperativity.

Cross-links can modify the segmental relaxation behavior of polymer networks.[8−11] The network junctions may be viewed as introducing geometries of restriction similar to polymer nanocomposites and liquids confined in pores.[12,13] Schroeder and Roland[14] studied the dielectric α-relaxation responses of end-linked networks of poly(dimethylsiloxane) (PDMS) where cross-link density was varied by changing the molecular weight of the linear PDMS precursors. All of the networks that were considered exhibited similar variation of segmental relaxation time with temperature (fragility) compared to linear PDMS with the exception of the sample with the highest cross-link density which displayed an increased fragility. The authors interpreted this finding by suggesting the existence of a critical cooperative length scale for segmental dynamics in PDMS which yields an enhanced temperature dependence once impinged upon by the density of cross-link junctions. Fitz and Mijovic[15] investigated the dielectric fragilities for cross-linked poly(methylphenylsiloxane) (PMPS). The network structures were altered by varying the stoichiometry of the cross-linking agent relative to the vinyl functionality on the chain ends of a low molecular weight linear PMPS. The fragility was found to be independent of the average cross-link density for these materials, leading the researchers to conclude that the cooperative domain size for PMPS must be smaller than the distance between cross-links for all of these networks. In this article, we describe the segmental relaxation of cross-linked polybutadiene, as revealed by dynamic mechanical spectroscopy, to further examine any connection between cooperative length and dynamics of networks.

Experimental Section

Polybutadiene (PBd) with $M_w = 154$ kg/mol, $M_w/M_n = 1.10$, and 60% vinyl (1,2-addition) was anionically polymerized. This linear PBd material was cured in cylinder-shaped molds at 553 K in sealed conditions under pressure for times up to 4.5 h. High-temperature curing of polybutadiene without the use of vulcanization agents has been described in the literature,[16,17] and cross-linking is reported to occur at the vinyl unsaturation. The final cylindrical specimens were characterized by a length of 35 mm and a diameter of 9.1 mm. The cured samples were checked under an optical microscope before testing, and only those samples without visible bubbles or cracks were used.

Densities were measured at room temperature (296 K) by comparative weighing of the samples in air and in 2-propanol. Equilibrium swelling of the networks was performed in THF solvent. Cross-link densities were evaluated from the swelling data using the Flory−Rehner expression[18] with an interaction parameter estimated from solubility parameters[19] ($\chi = 0.37$).

Linear dilatometry was used to construct volume vs temperature plots for the polybutadiene networks. Contraction of a 35 mm long PBd cylinder with 9.1 mm diameter was monitored during cooling at 0.6 K/min in a Rheometrics ARES. Volume vs temperature responses were constructed by referencing the results to measured densities at 296 K and by assuming isotropic contraction of the samples. A small compressive load of 100 g force was applied during measurements to maintain contact with the sample. A glass rod with known

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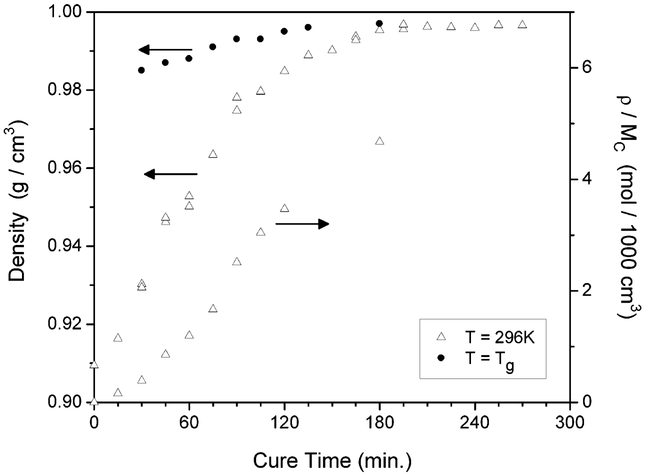

Figure 1. Density and cross-link density (ρ/M_C) vs cure time for PBd networks.

thermal contraction characteristics and similar dimensions to the polybutadiene samples was tested in the ARES under the same cooling cycle. This allowed the thermal contraction contribution of the rheometer fixtures to be eliminated from the length vs temperature data for the polybutadiene network samples.

Dynamic oscillatory shear was employed to probe the mechanical α-relaxation, or segmental relaxation, at temperatures within the equilibrium state just above the glass transition region. A Rheometrics RDA II with a spring transducer (2000 g cm maximum torque) was used to make these measurements. Testing was performed on cylindrical specimens with diameter of 9.1 mm and height of ca. 5 mm. The samples were glued between 10 mm diameter parallel plate fixtures to eliminate slipping during testing. The influence of the glue was found to be negligible for the uncured PBd material which could be adequately tested both with and without the gluing procedure. Oscillatory rates were in the range $0.001 < \omega < 63$ rad/s, and typical strains used were from 0.1 to 0.4% (maximum strain defined at outer edge). Values of segmental relaxation time, τ, were defined at most temperatures from the inverse of the frequency corresponding to where the loss modulus, $G''(\omega)$, displayed a maximum in the segmental region ($\tau = 1/\omega_{max}$). Frequency–temperature superposition was used to evaluate τ for the highest temperatures where relaxation times were <0.02 s.

Modulated differential scanning calorimetry (MDSC) was performed using a TA Instruments Modulated DSC (model 2920). Samples (ca. 5 mg) were cooled into the glassy state at 5 K/min and then tested using an underlying heating rate of 5 K/min with a superimposed temperature modulation having an amplitude of 0.5 K and a period of 40 s. Prior to these measurements, a sapphire sample was used to calibrate the heat capacity signal of the instrument at the same modulated temperature profile.

Results and Discussion

A series of cross-linked networks were formed by thermal treatment of the polybutadiene at 280 °C for various lengths of time. A regular buildup of average cross-link density, ρ/M_C, with cure time was noted for these materials as shown in Figure 1. The volume–temperature responses during cooling were also used to characterize the progression of the cross-linking process, and these results are plotted in Figure 2. From this information, it is clear that the glass transition temperature (Figure 3) and the density at $T = T_g$ (Figure 1) both systematically increase with increasing cross-link density, although the entire range of the latter is not large. These cross-linked PBd materials were created in order to observe the influence of M_C on the breadth and temperature dependence of the mechanical α-relaxation and on the glass transition region surveyed by modulated differential scanning calorimetry. These effects will now be discussed.

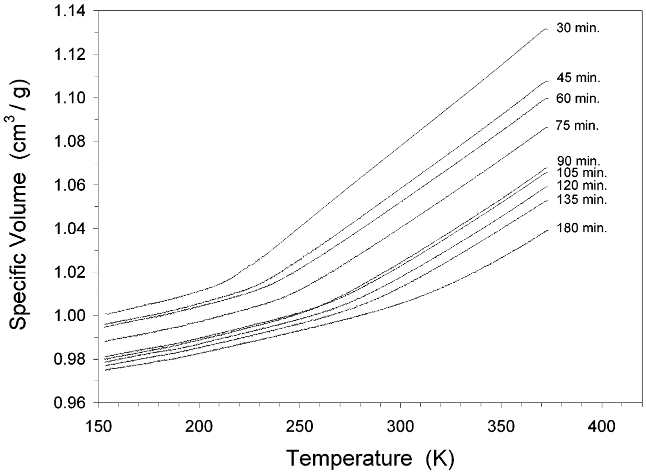

Figure 2. Volume–temperature responses during cooling at 0.6 K/min for the networks cured for the times shown.

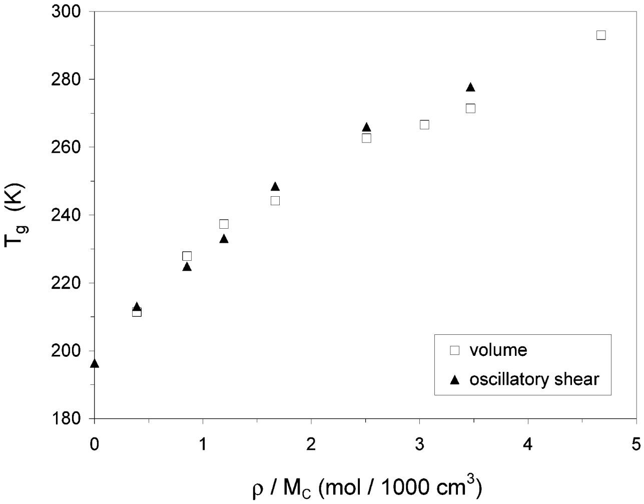

Figure 3. T_g from volume–temperature data (0.6 K/min cooling) and oscillatory shear results (temperature at which $\tau = 10$ s).

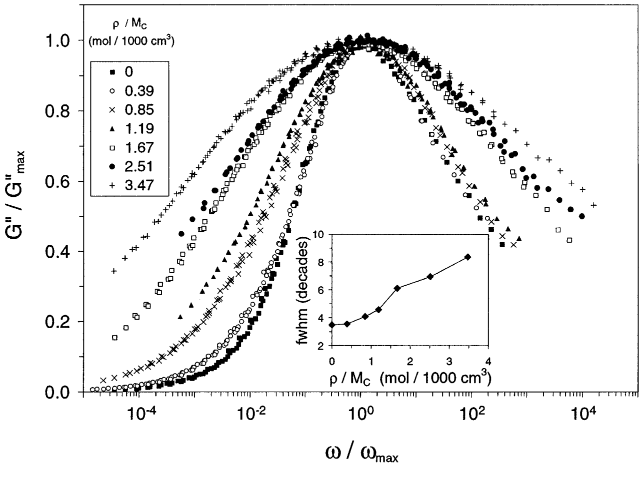

Figure 4. Normalized segmental loss dispersion peaks for the indicated networks. The inset plot illustrates the full width at half-maximum vs cross-link density.

Dynamic Mechanical α-Relaxation. Reduced α-relaxation spectra from dynamic mechanical analysis are

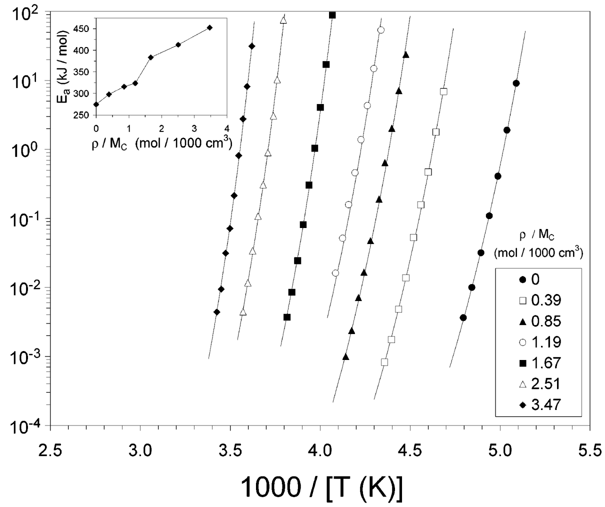

Figure 5. Temperature dependence of segmental relaxation times for the networks with the indicated cross-link densities. The solid lines are the VFTH fits to the data. The inset plot shows the variation of apparent activation energy at $T = T_g$ with increasing cross-link density.

Table 1. Temperature Dependence of Segmental Relaxation

cure time (min)	M_C (g/mol)	τ_0 (s)[a]	T_∞ (K)	B (K)	T_g (K) [$\tau = 10$ s]	fragility, m
0	n/a	1.0E−14[b]	156.1	1393	196.4	73.0
30	2390	1.0E−14	169.3	1511	213.1	73.0
45	1110	1.0E−14	178.9	1589	224.9	73.3
60	798	1.0E−14	184.9	1666	233.2	72.5
75	578	1.0E−14	202.2	1597	248.5	80.6
90	390	1.0E−14	216.8	1700	266.0	81.0
120	284	1.0E−14	228.8	1692	277.8	85.1

[a] Constant value used during VFTH fitting. [b] Read as 1.0×10^{-14}.

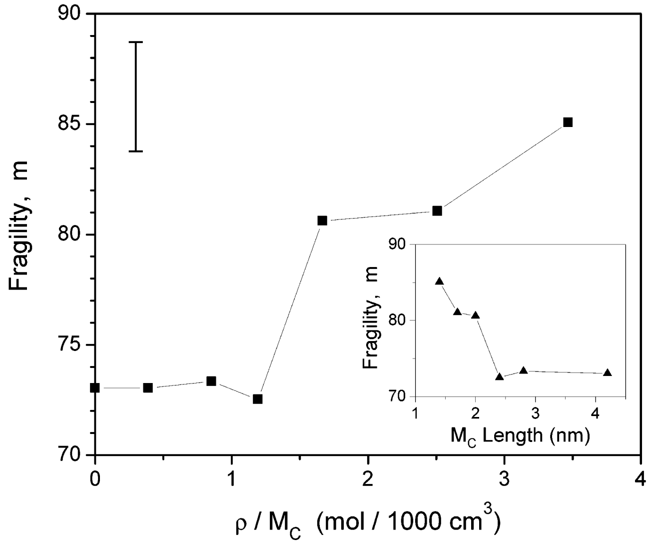

Figure 6. Changes in fragility with increasing cross-link density. The inset shows the dependence of fragility on M_C length which is the calculated distance $\langle R^2\rangle_0^{1/2}$ between cross-links. A typical error bar for the fragility is given in the upper left corner.

illustrated in Figure 4 for the PBd networks. Using the maximum in $G''(\omega)$ as a reference point, results from different temperatures are approximately superimposed for each material. This was necessary to provide some indication of relaxation breadth, and it does not necessarily imply complete validity of time−temperature correspondence. For the highly cross-linked materials, in particular, it was not possible to experimentally access enough of the peak shape at a single temperature. The dispersion widths are provided in the inset to Figure 4 where it is evident that the full width at half-maximum (fwhm) increases in a somewhat steady manner with increasing cross-link density.

A distribution of local mobility can cause extra spectral broadening of the segmental dispersion beyond the usual expectation based on the general correlation between fragility and width of the relaxation function,[20] the latter often characterized by the inverse of the Kohlrausch−Williams−Watts[21,22] (KWW) β parameter. Anomalous breadth contributions can include concentration fluctuations in miscible blends,[23] restrictions such as crystallinity[24] and cross-links,[9,14] and even high concentrations of mobile chain ends.[25] The inhomogeneous broadening is typically weighted toward the low-frequency side for cross-linked polymers; hence, the $G''(\omega)$ peaks are not well represented by the KWW expression. For this reason, we used the full width at half-maximum as a means to quantify the breadth of the segmental relaxation response for the PBd networks. A later discussion will further address the asymmetry of the relaxation responses.

The dependence of the segmental relaxation time on temperature was determined as a function of cross-link density (Figure 5). These relaxation times were determined as mentioned previously in the Experimental Section. The solid lines represent fits to the familiar Vogel−Fulcher−Tammann−Hesse (VFTH) expression:[26−28]

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_\infty}\right) \tag{1}$$

In this expression, τ_0 is the relaxation time in limit as $1/T$ approaches zero, T_∞ represents the temperature where relaxation times diverge to infinity, and B is a parameter which is related to an activation energy. Here, a constant value of $\tau_0 = 1.0 \times 10^{-14}$ s was used for fitting experimental data according to recommendations of Angell.[29]

The slope of a plot of log(τ) vs T_g/T evaluated at $T = T_g$ is called fragility, m. Quantifying the temperature dependence of the local segmental motion in materials using fragility allows valid comparisons to be made by normalizing for T_g-related effects which exert constant frictional drag but do not contribute to the dynamics. We define the mechanical T_g according to the temperature at which the segmental relaxation time assumes a value of 10 s. This temperature was determined by interpolation of the relaxation time data in Figure 5 via the VFTH equation fits. As indicated in Figure 3, these mechanical glass transition temperatures are comparable to the T_g values from dilatometry. Fragility can be defined from the VFTH parameters as follows:[30]

$$m = \left.\frac{\mathrm{d} \log \tau}{\mathrm{d}(T_g/T)}\right|_{T=T_g} = \frac{B/T_g}{(\ln 10)[1 - (T_\infty/T_g)]^2} \tag{2}$$

The VFTH parameters and values of m are listed in Table 1. The changes in fragility with increasing cross-link density, ρ/M_C, are given in Figure 6. Fragility displayed nearly constant values and then was found to increase at the higher levels of cross-linking. This unique dependence will now be interpreted on the basis of an apparent critical length scale between cross-link junctions.

The length scale defined by adjacent cross-link points was estimated from M_C using reported results for the molecular weight (M) dependence of the mean-squared distance between chain ends for an unperturbed linear PBd coil with similar microstructure via[31]

$$\langle R^2\rangle_0/M = 0.727\ \text{Å}^2\ \text{mol/g} \tag{3}$$

Values of the M_C length scale $\langle R^2\rangle_0^{1/2}$ were accordingly calculated using $M = M_C$. These results were used to replot the fragility data in the inset in Figure 6. A transition in fragility response was noted with respect to this length. The fragility was enhanced compared to uncured linear PBd only for networks which had average lengths between cross-linking sites which were less than approximately 2.0−2.4 nm. For distances between network junctions which were greater than this size, the T_g-normalized temperature dependence of segmental dynamics was not altered.

There are other subtle signs that the dynamic behavior was modified differently for cure times of 75 min and greater (M_C < 600 g/mol). A noticeable change in slope, or "bend", in the T_g vs cross-link density relationship can be noted from Figure 3 in the vicinity of $\rho/M_C = 1.7$ (cure time = 75 min). The relaxation function breadth also suggests that a change occurred within the same region of cross-link density. While increases in the full width at half-maximum of the loss modulus dispersion proceeded somewhat continuously as the number of cross-link junctions increased, the majority of this broadening was exerted on the low-frequency side for low cure times. For networks that were cured for 75 min or greater, however, additional broadening was also manifested at the high-frequency end of the spectrum as can be observed in Figure 4. The breadths for these PBd networks with higher levels of cross-linking were influenced not only by the inhomogeneous contributions of the cross-link junctions[9,14] but also by the additional input associated with the usual connection between fragility and breadth.[20]

Cooperative Length Scale from MDSC. Thermal fluctuation theory was used by Donth to derive an expression for a length scale of cooperativity, ξ_α, and its temperature dependence from calorimetry:[3,32,33]

$$\xi_\alpha = \left(\frac{kT^2\Delta(1/C_v)}{\rho(\delta T)^2}\right)^{1/3};\quad \Delta(1/C_v) \approx \Delta(1/C_p) \tag{4}$$

In the above equation, $\Delta(1/C_p) = (1/C_{p,\text{glass}}) - (1/C_{p,\text{liquid}})$ and δT is the half-width of the thermal response which is regarded as the mean thermal fluctuation associated with the cooperatively rearranging regions.

The MDSC results for linear PBd are provided in Figure 7 and Table 2, from which $\xi_{\alpha.g}$ (i.e., ξ_α at $T = T_g$) was calculated using eq 4. A value of $\xi_{\alpha.g}$ equal to 2.1 nm was found for this polymer. It was interesting to find that the two networks cured at 60 and 90 min had cooperative length scales nearly identical to $\xi_{\alpha.g}$ of the uncured PBd (see Table 2) when estimates of δT were used versus the experimental half-widths which have additional inhomogenenous contributions from cross-link junctions.[35] Compared to the linear PBd, cross-linking reduced $\Delta(1/C_p)$, increased T_g, and broadened the transition region, but these changes all combined to yield the same $\xi_{\alpha.g}$ via thermal fluctuation theory once the extra breadth was eliminated. Thus, the calorimetric signature of cooperative length at T_g for linear polybutadiene appears to underlie the MDSC behavior of its networks.

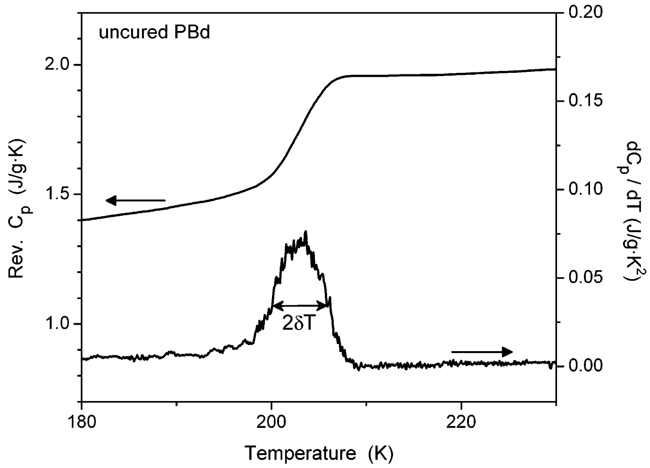

Figure 7. Reversing heat capacity data for the uncured PBd. A sinusoidal temperature modulation with an amplitude of 0.5 K and a period of 40 s was applied relative to the underlying average heating rate of 5 K/min.

Table 2. Thermal Fluctuation Parameters at $T = T_g$ from MDSC

cure time (min)	ρ_g (g/cm^3)	T_g (K)	δT (K)	ΔC_p[a] (J/(g K))	$\Delta(1/C_p)$[b] ((g K)/J)	$\xi_{\alpha.g}$ (nm)
0	0.983	203.1	2.9	0.382	0.134	2.1
60	0.988	235.2	3.4 [8.2][c]	0.273	0.130	2.1
90	0.993	262.9	3.8 [14.6][c]	0.226	0.108	1.9

[a] $\Delta C_p = C_{p,\text{liquid}} - C_{p,\text{glass}}$. [b] $\Delta(1/C_p) = (1/C_{p,\text{glass}}) - (1/C_{p,\text{liquid}})$. [c] Values in brackets are actual breadths from MDSC; see ref 35.

We can now compare the $\xi_{\alpha.g}$ from calorimetry for the uncured linear polybutadiene with the apparent connection between the α-relaxation dynamics of the networks and a critical length scale. The fragilities of the network were increased compared to linear PBd only for lengths between cross-links that were less than 2.0−2.4 nm (Figure 6). This critical length between cross-links was very similar to $\xi_{\alpha.g} = 2.1$ nm from thermal fluctuation theory. Therefore, the assertion by Schroeder and Roland[14] that fragility enhancement in networks is dictated by a critical cooperative length scale appears to be well-founded.

Conclusions

Systematic changes in the glass transition temperature and density at T_g followed from cross-linking polybutadiene to increasing levels. It was only after M_C was decreased below ca. 600 g/mol, however, that the fragility displayed increases compared to the uncured polymer. Changes in the symmetry of the relaxation dispersions also signified modified dynamics for M_C < 600 g/mol. The length between cross-links where this transition occurred was estimated to be 2.0−2.4 nm. This inferred network length scale, below which fragility was enhanced, was very similar to the cooperative length scale for linear PBd, $\xi_{\alpha.g} = 2.1$ nm, which was determined from modulated differential scanning calorimetry using Donth's thermal fluctuation approach.

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(35) The measured δT is only useful in calculating $\xi_{\alpha.g}$ when it is not additionally influenced by the same features which can unduly broaden dielectric and dynamic mechanical spectra as discussed earlier. Direct calculation of $\xi_{\alpha.g}$ using δT from MDSC results is not appropriate for the networks. Therefore, it is necessary to estimate δT for the cross-linked polybutadienes in the absence of the extra broadening. In the glass transition region, the isochronal half-width of calorimetric relaxation, δT, can be related to its isothermal counterpart, δq, using the apparent activation energy at T_g, Δh^*, according to[3] $\delta T = \delta q R T_g^2/\Delta h^*$. The calorimetric analogue to fragility, $m_{\Delta h}$, can be defined according to[34] $m_{\Delta h} = \Delta h^*/[\ln(10) R T_g]$. If δq is proportional to $m_{\Delta h}$ in the same way that breadth and fragility are correlated for the α-relaxation,[20] then δT is simply proportional to T_g based upon the above expressions. Hence, the δT for the networks can be estimated as follows: $\delta T_{\text{network}} = \delta T_{\text{uncured}}(T_{g,\text{network}}/T_{g,\text{uncured}})$.

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