mation prior to publication.

Registry No. (Butadiene) (homopolymer), 9003-17-2; (butadiene)·(styrene) (copolymer), 9003-55-8.

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Expansion Factor of a Part of a Polymer Chain in a Good Solvent Measured by Small-Angle Neutron Scattering

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ABSTRACT: The radii of gyration of deuterium-labeled sections of polystyrenes with narrow molecular weight distributions were determined in a good solvent (carbon disulfide) by small-angle neutron scattering (SANS). The expansion factors of the labeled sections were calculated from the measured radii of gyration using unperturbed dimensions estimated from literature radius of gyration–molecular weight relationships for polystyrenes. The expansion factors of the labeled sections are smaller than those of the whole chains but are larger than that of a whole chain with the same molecular weight as the labeled section. Both results are reasonable in comparison with a Monte Carlo calculation in the literature and also with the perturbation theory.

Introduction

It is well-known that the mean square radius of gyration of nonionic polymers in good solvents $\langle s^2 \rangle$ is proportional to the $(1 + \epsilon)$th power of the molecular weight, $M^{1+\epsilon}$, where ϵ is about 0.2. This implies that the conformation of the polymer coils does not follow Gaussian statistics. In their calculation of the scattering factor $P(\theta)$, Peterlin[2] et al.[3,4] took into account this non-Gaussian distribution of segments by assuming that the mean square distance between the ith and jth segments $\langle r_{ij}^2 \rangle$ is proportional to $|i - j|^{1+\epsilon}$, as in the mean square radius of gyration–molecular weight relationship for whole molecules.

Experimental determinations of $P(\theta)$ by light scattering, however, showed that $P(\theta)$ does not agree with the function of Peterlin et al. but is better approximated by the Debye function based on the Gaussian distribution of segments, if the scattering angles are low enough.[5] To understand the conformation of polymers in good solvents more clearly, therefore, it is desirable to determine the expansion factors for portions of polymer chains relative to those of the entire chain.[6-9]

In the present work, we determined the radii of gyration of deuterated sections of polystyrenes by small-angle neutron scattering, using block copolymers of ordinary and deuterated polystyrenes having narrow molecular weight distributions both in each block and in the whole molecule.[10] The samples were prepared carefully, as previously described, in view of the fact that scattering from block copolymers is very sensitive to heterogeneities in both molecular weight and composition.

Experimental Section

Materials. A deuterated styrene homopolymer and partially labeled polystyrenes used as samples in this work were prepared by a sequential monomer addition method in anionic polymerization. The polymerization was carried out in benzene with *sec*-butyllithium. Sample TUN-01 is a homopolymer of d styrene, TUN-14 is a diblock copolymer of d and h styrenes, and TUN-15 is a triblock copolymer of h, d, and h styrenes. The polymers obtained were purified by fractional precipitation. Their number- and weight-average molecular weights were determined by membrane osmometry and light scattering. The contents of d styrene in the two block copolymers were determined by pyrolysis–gas chromatography.[11] The molecular weights of the deuterated sections were calculated from the total molecular weights and the d styrene content of the purified samples. Molecular characteristics of the samples are listed in Table I.

Spectrograde CS_2 was used as a good solvent for polystyrenes without further purification. Since the scattering length of CS_2 is nearly equal to that of ordinary polystyrene, the observed coherent scattering is due to the deuterated portions of the samples.

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Table I
Molecular Characteristics of the Samples

sample code	mol wt of whole molecule $M_n \times 10^{-4}$	$M_w \times 10^{-4}$	d styrene content, %	$M_d \times 10^{-4}$ [a]
TUN-01 (d)	2.7		100	2.5
TUN-14 (dh)	41.6 (2.7–38.9)	42.6 (2.7–39.9)	6.3	2.5
TUN-15 (hdh)	29.3 (14.0–3.1–12.2)	28.6 (13.6–3.1–11.9)	10.7	2.9

[a] Molecular weight of d parts. M_d are converted to the values of ordinary h polystyrenes having the same degrees of polymerization.

SANS Measurement. The new SANS instrument[12,13] at the National Bureau of Standards, with a two-dimensional position-sensitive detector, was used for all measurements.[27] The thermal neutron source is a direct beam from the reactor which passes through a liquid-nitrogen-cooled filter to remove core γ rays and fast neutrons. The beam is further refined by a helical-channel velocity selector. The average wavelength $\langle\lambda\rangle$ is 5.46 Å with a distribution $\Delta\lambda/\lambda$ of about 0.25. To estimate radii of gyration from the angular dependence of the scattered intensity, we used the inverse square average of λ defined by

$$1/\bar{\lambda}^2 = \int \lambda^{-2} I(\lambda)\, d\lambda / \int I(\lambda)\, d\lambda \qquad (1)$$

where $I(\lambda)$ is the intensity of the incident beam as a function of λ. The value of $\bar{\lambda}$ thus determined is 5.38 Å and $\bar{\lambda}/\langle\lambda\rangle$ is 0.985. Two collimation geometries were used in this experiment. One involved two apertures (27 and 12 mm; regular resolution, $q_{min} \simeq 1 \times 10^{-2}$ Å^{-1}) and the other consisted of a series of 12 masks, each with nine focusing apertures (high resolution; $q_{min} \simeq 4 \times 10^{-3}$ Å^{-1}). The evacuated presample flight path was 4.5 m, and the sample-to-detector distance was 3.6 m. The detector has an active area of 65 × 65 cm^2 with 5-mm spatial resolution. A dedicated DEC 11/23 minicomputer processes the signals from the detector and provides real-time imaging of the data. Complete data sets are then transferred to a DEC VAX 11/780 computer for analysis.

The measurements were carried out at room temperature (about 20 °C) with a quartz cell 1 cm thick. Measurements were made at three concentrations of each sample in CS_2: 0.8%, 1.5%, and 2.5% by weight of polymer. The scattering intensity of the deuterated sections was obtained by subtracting the scattering intensities of the empty cell and the solvent from that of the sample solution. The close match in coherent scattering length of hydrogenated polystyrene and CS_2 was also checked.

Results

The radius of gyration of a polymer can be obtained from the initial slope in the angular dependence of the particle scattering factor, irrespective of the polymer conformation. The scattering intensities from the present samples, however, were not high enough to obtain reliable radii of gyration by this method since the deuterated parts were only one-tenth or less of the total polymer. Furthermore, the number of data points in the range of $\langle s^2\rangle q^2 < 1$ was not sufficient to obtain $\langle s^2\rangle$ with good precision. Therefore, we evaluated the apparent radii of gyration of the deuterated sections by fitting the Debye function (2) to the scattering data at scattering angles higher than the angle where the intensity maximum due to the correlation hole appears.[14]

$$I(\theta) = A + \frac{B}{x^2}(e^{-x} - 1 + x) \qquad (2)$$

with

$$x = q^2\langle s^2\rangle$$

and

$$q = (4\pi/\lambda)\sin(\theta/2)$$

where $\langle s^2\rangle$ is the mean square radius of gyration, λ is the wavelength (5.38 Å), and θ is the scattering angle. A and B are parameters for the incoherent base line and an arbitrary intensity scaling factor, respectively. The curve fitting was carried out by nonlinear regression with the three parameters A, B, and $\langle s^2\rangle$. In Figure 1, the scattering curve for the 2.5% solution of sample TUN-01 is presented. It can be seen that the Debye function can describe the scattering data over a wide range of scattering angle. In Figure 2 are shown scattering curves for the 2.5% solution of TUN-15, in both the regular and high-resolution runs. It is clear that the data taken with the two different collimation geometries at the NBS-SANS facility can be normalized together and are also well described by the Debye function. Though the Debye function is strictly applicable only to a Gaussian coil, experimental and theoretical studies have shown that the shape of the scattering factor for a polymer in a good solvent is very similar to the Debye function.[9,15]

The apparent radii of gyration of the deuterated portions of the three samples thus determined at various concen-

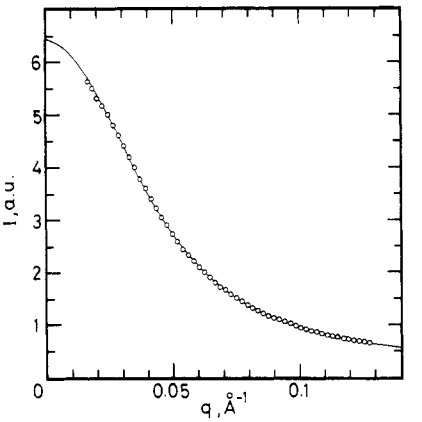

Figure 1. Scattering curve for TUN-01, 2.5% in CS_2. The solid line denotes the best-fit Debye function.

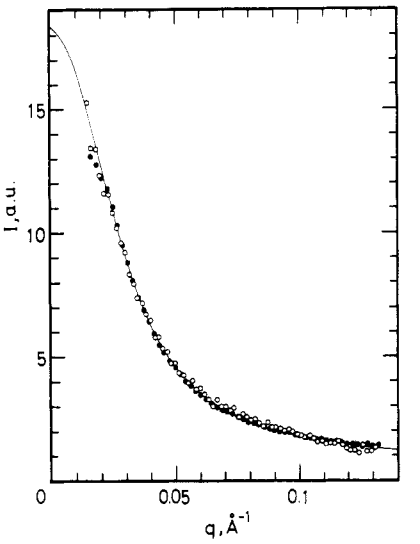

Figure 2. Scattering curves for TUN-15, 2.5% in CS_2. Open circles were obtained by a collimation geometry with high resolution, while closed circles were obtained with the regular resolution geometry. The solid line denotes the best-fit Debye function.

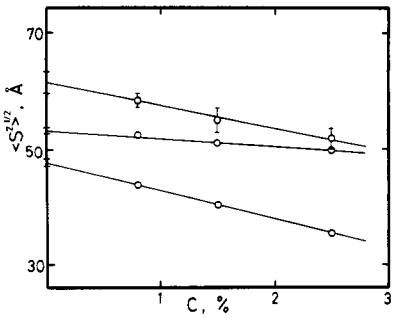

Figure 3. Extrapolation of apparent radii of gyration to infinite dilution. Samples are TUN-15, TUN-14, and TUN-01 from top to bottom.

Table II
Radii of Gyration and Expansion Factors of Deuterated Parts

sample code	M_d × 10^{-4} [a]	$\langle s^2 \rangle_0^{1/2}$,[b] Å	$\langle s^2 \rangle^{1/2}$,[c] Å	α_d	α (whole molecule) in CS_2	α (whole molecule) in C_6H_6
TUN-01 (d)	2.5	45.2	47.7 ± 0.6	1.06 ± 0.03	1.17	1.13
TUN-14 (dh)	2.5	45.2	53.3 ± 0.6	1.18 ± 0.03	1.56	1.47
TUN-15 (hdh)	2.9	48.7	61.5 ± 1.9	1.26 ± 0.05	1.50	1.42

[a] Molecular weight of d parts. [b] The unperturbed radius of gyration $\langle s \rangle_0^{1/2}$ was calculated from eq 3. [c] Observed.

trations are plotted in Figure 3, together with their estimated uncertainties. The uncertainties in the apparent radii of gyration of TUN-15 are larger than those of TUN-14 and TUN-01. This is mainly because the experimental points in the low $q^2\langle s^2 \rangle$ region govern the accuracy of the nonlinear regression fit. There are less experimental points for TUN-15 than for TUN-01 and TUN-14 in the same region of low $q^2\langle s^2 \rangle$, since q_{min} is determined by the instrument characteristics and $(q^2\langle s^2 \rangle)_{min}$ for TUN-15 is larger than those of the others. The extrapolation of the apparent radii of gyration to infinite dilution was carried out by least squares, taking into account the respective uncertainties in the apparent radii of gyration. The radii of gyration thus obtained are listed in Table II, together with their possible errors.

The fact that the three slopes in Figure 3 are different may seem unusual. It is noted, however, that the concentration axis refers to the whole polymer, and thus the TUN-14 and TUN-15 solutions are considerably more dilute in deuterated polymer than the TUN-01 solutions. In this case, the apparent radius of gyration obtained by fitting eq 2 to the experimental data at a finite concentration may be affected by the intermolecular interference of scattering from deuterated portions of molecules, of which the radial distribution is determined by the excluded volume of the "whole" molecule. It can be pointed out that in Figure 3 the slope decreases with increasing molecular weight of the "whole" molecule.

The expansion factors of the deuterated sections, α_d, were calculated as the ratios of the observed radii of gyration of the labeled parts $\langle s^2 \rangle^{1/2}$ to their values in the unperturbed state $\langle s^2 \rangle_0^{1/2}$. The unperturbed radii of gyration were estimated from the following equation:

$$\langle s^2 \rangle_0^{1/2} = 0.286M^{0.50} \quad (3)$$

Equation 3 was determined by applying the least-squares method to all experimental values published for polystyrenes with narrow molecular weight distributions in cyclohexane at 34.6–36.0 °C as shown in Figure 4.[16-18] At the Θ temperature, we make the reasonable assumption that the radius of gyration of a part of a chain is equal to that of a whole polymer having the same molecular weight. The expansion factors of the deuterated sections thus calculated are listed in Table II, together with their uncertainties. The uncertainty in the expansion factors arises from the uncertainties in determining $\langle s^2 \rangle^{1/2}$ and M. The uncertainties for $\langle s^2 \rangle^{1/2}$ are given in Table II and in Figure 3, and those for M were estimated as ±5%.

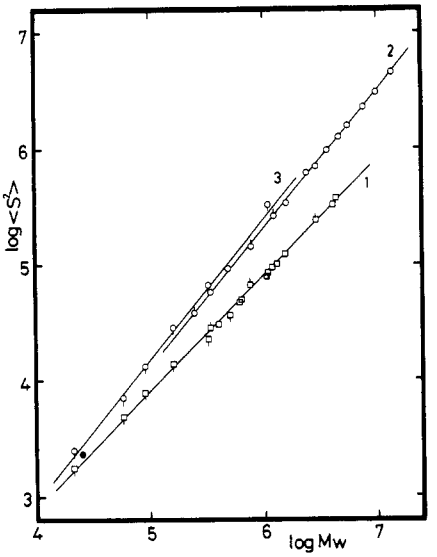

Figure 4. Double-logarithmic plots of mean square radii of gyration $\langle s^2 \rangle$ vs. molecular weight M for whole molecules. Line 1: poly(h styrenes) in cyclohexane at 34.8 °C (□)[17] and 34.6 °C (⊡)[18] by light scattering (LS). Poly(d styrenes) in cyclohexane at 36 °C (⊡)[16] by neutron scattering (NS). Line 2: Circles (○)[18] and (◎)[19] denote the data of poly(h styrenes) in benzene at 30 °C by LS. Line 3: Poly(d styrenes) in CS_2 at room temperture (◎)[16] by NS. The filled circle denotes the present experimental data (TUN-01) in CS_2 by NS.

The radii of gyration and expansion factors of the whole chains TUN-14 and TUN-15 in benzene and CS_2 are also listed in Table II. These values were estimated from the following two equations:

$$\langle s^2 \rangle^{1/2} = 0.123M^{0.595} \quad \text{in benzene by LS} \quad (4)$$

$$\langle s^2 \rangle^{1/2} = 0.122M^{0.60} \quad \text{in } CS_2 \text{ by NS} \quad (5)$$

Equations 4 and 5 were determined by applying the least-squares method to the experimental data published for polystyrenes with narrow molecular weight distributions in benzene[18,19] and CS_2,[16] and as shown in Figure 4, there is not a large difference between the $\langle s^2 \rangle^{1/2}$–$M$ relationships of polystyrenes in benzene and in CS_2.

It can be concluded from Table II that the expansion factor of a part of a chain α_d is smaller than that of the whole chain α, i.e., $\alpha_d < \alpha$, but larger than the expansion factor of a molecule having the same molecular weight as the labeled section, i.e., α_d(TUN-14, TUN-15) > α_d(TUN-01). Moreover, it appears that the labeled portion in the middle of the chain has a larger expansion factor than that at the end, i.e., α_d(TUN-15) ≥ α_d(TUN-14), but the difference is close to the limit of our experimental reliability.

Discussion

The question of intrachain expansion has been considered by several groups, using perturbation theory,[20] Monte Carlo calculation,[21-23] and renormalization group methods.[24,25] In this paper we compare our results with the first-order perturbation theory analysis of Kurata et al. and also with Monte Carlo results of Wall and Erpenbeck.

Table III
Comparison of Experimental Expansion Factors with Theories

sample code	α_d	α_p	α_M
TUN-01	1.0_6	1.06	1.13
TUN-14	1.1_8	1.08	1.24
TUN-15	1.2_6	1.14	1.27

[a] α_d, experimental expansion factor; α_p, first perturbation theory; α_M, Monte Carlo calculation.

According to the first-order perturbation theory,[22] the expansion factor of the radius of gyration of a whole polymer composed of N segments is given by

$$\alpha_s^2 = 1 + 1.276Z \tag{6a}$$

where

$$Z = (3/2\pi a^2)^{3/2}\beta N^{1/2} \tag{6b}$$

with a the segment length and β the binary cluster integral. The expansion factor α_p of the mean square distance between the ith and jth segments in a polymer chain is given by

$$\alpha_p^2 \equiv \frac{\langle r_{ij}^2\rangle}{(j-i)a^2} = 1 + X(N,i,j)Z \tag{7a}$$

where

$$X(N,i,j) = \tfrac{4}{3}N^{-1/2}\{\tfrac{8}{3}(j-i)^{1/2} - 4(N-i)^{1/2} - 4j^{1/2} + N^{-1/2}(j-i) - \tfrac{8}{3}(j-i)^{-1}[(N-j)^{3/2} - (N-i)^{3/2} - j^{3/2} + i^{3/2}]\} \tag{7b}$$

If we let n be the number of segments in the deuterated homopolymer (TUN-01) and N be the total numbers of segments of the other two samples (TUN-14 and TUN-15), the positions of the deuterated parts along the chains can be expressed in terms of n; i.e., $N = 16.6n$, $i = 0$, and $j = n$ in TUN-14 and $N = 11.6n$, $i = 5.6n$, and $j = 6.8n$ in TUN-15. Introducing these numbers into eq 7b, we obtain $X = 0.435$ and 0.896 for TUN-14 and TUN-15, respectively.

To evaluate theoretical expansion factors for the deuterated blocks from the first-order perturbation theory (7a), the relationship between the excluded volume function Z and molecular weight M must be determined. Various methods for determining the Z–M relationship have been reported. In general, application of the first-order perturbation method to highly expanded coils cannot be recommended. However, it is self-consistent if we estimate the Z–M relationship by introducing the present experimental value for TUN-01 ($\alpha_s = 1.06$) into eq 6a and calculate the expansion factors of deuterated blocks α_p in the other two samples from eq 7a. Introduction of the data for TUN-01 into eq 6a gives $Z = 6.13 \times 10^{-4} M^{1/2}$ and we have the values of α_p as listed in Table III.

Using a Monte Carlo calculation, Wall and Erpenbeck[20] presented an empirical equation for the mean square distance between the ith and jth segments $\langle r_{ij}^2\rangle$ in a chain composed of N segments and having the mean square end-to-end distance $\langle r_N^2\rangle$. Their equation is

$$\langle r_{ij}^2\rangle = I(N,i,j)\langle r_N^2\rangle \tag{8a}$$

where

$$I(N,i,j) = 1.09\left|\frac{i-j}{N}\right|^{1.13+\nu(i,j)} \tag{8b}$$

and

$$\nu(i,j) = 0.36\left|\frac{i-j}{N}\right|\left|1 - \frac{i+j}{N}\right| \tag{8c}$$

If we assume that the ratio $\langle s^2\rangle/\langle r^2\rangle$ for a part of a chain is equal to that for a whole chain, we can convert eq 8a to

$$\langle s_{ij}^2\rangle = I(N,i,j)\langle s_N^2\rangle \tag{9a}$$

and

$$\alpha_M^2 \equiv \frac{\langle s_{ij}^2\rangle}{\langle s_{ij}^2\rangle_0} = I(N,i,j)\frac{\langle s_N^2\rangle}{\langle s_{ij}^2\rangle_0} \tag{9b}$$

The values of $I(N,i,j)$ are 0.043 for TUN-14 and 0.080 for TUN-15. In eq 9b, $\langle s_N^2\rangle$ is the perturbed square radius of gyration of the whole chain composed of N segments and $\langle s_{ij}^2\rangle_0$ is the unperturbed square radius of gyration of a part of the chain. Therefore, using the $I(N,i,j)$ values and also eq 3 and 4, we can calculate α_M for TUN-14 and TUN-15 from eq 9b. The values of α_M are also listed in Table III.

In Table III, it can be seen that the experimental values are in reasonable agreement with the Monte Carlo calculations. Moreover, both the first-order perturbation theory and the Monte Carlo calculation show that the expansion factor of a part in a chain is larger than that of the whole molecule having the same molecular weight. That is, the mean square end-to-end distance–molecular weight relationship for a part of chain is not the same as that determined for whole chains. For example, in the Peterlin theory of the particle scattering factor $P(\theta)$ for polymers expanded due to the excluded volume effect, the mean-square end-to-end distance of a part of a chain is given by $\langle r_{ij}^2\rangle \propto |i-j|^{1+\epsilon}$, where ϵ is assumed to be the same as that for whole molecules. The present experimental results show that a part of a chain is expanded more than assumed in the theory of Peterlin et al.; in other words, the expansion factor of a part in a chain approaches that of the whole chain. This conclusion is consistent with our previous conclusion concerning $P(\theta)$ of polystyrenes with extremely high molecular weight and narrow molecular weight distribution in toluene.[9]

In the blob model,[26] it is assumed that the conformation of a part of a chain is Guassian (i.e., $\langle r_{ij}^2\rangle \propto |i-j|$) if the number of segments in that part is smaller than a critical number, while fully developed excluded volume is operative between segments (i.e., $\langle r_{ij}^2\rangle \propto |i-j|^{1+\epsilon}$, where ϵ is a constant independent of $|i-j|$) if the segments are further apart than the critical number of segments. Thus this model gives the same value for the expansion factor of a chain independent of whether the chain is a part of a molecule or an isolated molecule and independent of its position in the chain. Therefore, the blob model cannot explain the present experimental results.

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(27) Disclaimer: Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Electron Paramagnetic Resonance Studies of Amine-Cured Epoxy Resins: Dependence of Nitroxide Spin-Probe Mobility on Cross-Link Density, Free Volume, and Temperature

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ABSTRACT: Studies were made of the electron paramagnetic resonance line shapes of the nitroxide spin probes TANOL and TEMPENE in amine-cured epoxy resin matrices above their glass transition temperatures. The rotational correlation times deduced from these line shapes were measured as a function of temperature and matrix cross-link density. Fractional free volumes, glass transition temperatures, and cross-link densities of the matrices were determined by linear expansion measurements, differential scanning calorimetry, and dynamic mechanical analysis and/or sample stoichiometry, respectively. The rotational correlation times were dependent on the fractional free volume and temperature. The dependence on the free volume was in the form of a modified WLF equation and yielded values of $\sim$0.4 for the Doolittle parameter. The explicit temperature dependence had an Arrhenius form with a preexponential factor of $\sim 10^{-12}$ s and an activation energy of $\sim$19 kJ mol^{-1}. At a constant temperature the logarithm of the rotational correlation time was a linear function of matrix cross-link density. This relationship appears to be a direct consequence of the linear dependence of the glass transition temperature on cross-link density.

Introduction

Amine-cured epoxy resins are thermosetting polymers that are widely used in the aerospace industry as matrix materials for fiber-reinforced composite structural components. Molecular mobility and the associated free volume are important parameters in such thermosetting polymers since they can determine mechanical and transport properties and the value of the glass transition temperature. In this study we have used the techniques of dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) (linear expansion measurement), differential scanning calorimetry (DSC), and electron paramagnetic resonance (EPR) spectroscopy to investigate the dependence of molecular mobility on temperature and cross-link density for a series of chemically similar amine-cured epoxy resin polymers. In the EPR experiments the spin-probe method was used. This technique entails the use of stable nitroxide free radicals as probes of their dynamic environments in the polymer network.

Experimental Section

Materials. The samples investigated were prepared from the diglycidyl ether of bisphenol A (DGEBA) epoxy in the form of the DER 332 commercial resin obtained from Dow Chemical Co. This resin had a nominal average equivalent weight of 172–176 compared with 170 for pure DGEBA monomer, indicating that small amounts of higher order oligomers were present.

The aliphatic amine curing agents *N,N'*-dimethyl-1,6-diaminohexane (DDH) and 1,4-diaminobutane (DAB) obtained from Aldrich Chemical Co. had ≥97%

The nitroxide spin probes 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL) and 2,2,6,6-tetramethyl-1,2,3,6-tetrahydropyridine-1-oxyl (TEMPENE) were obtained from Eastman Kodak Co. and Molecular Probes, respectively. All materials were used as received. Their chemical structures are shown in Figure 1.

Sample Preparation. Amine-cured epoxy samples having different average cross-link densities were prepared by using mixtures of the tetrafunctional amine DAB and the difunctional amine DDH. The samples contained the following ratios (by equivalents) of DAB:DDH:DGEBA: 0:5:5, 2:3:5, 3:2:5, and 5:0:5. The amines were first mixed in the desired ratios and then added to a stoichiometric amount of DGEBA containing less than 0.03 wt % nitroxide. EPR, DSC, and TMA samples were cast in glass tubes. Separately prepared DMA samples were cast in silicone rubber molds. All samples were cured for at least 15 h at room temperature followed by postcuring above the glass transition temperature, T_g.

Measurements. Torsional dynamic mechanical measurements were made with a Rheometrics dynamic spectrometer (Model RDS

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