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Thermoelasticity of Acrylic Copolymers in Simple Shear

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ABSTRACT

Thermoelastic measurements were carried out for acrylic copolymers in simple shear. Samples were synthesized by UV photopolymerization. It is shown that the energy contribution to rubber elasticity (f_e/f) can be readily calculated from the temperature coefficient of shear modulus. The value of f_e/f for poly(n-butyl acrylate) thus obtained is in excellent agreement with that determined in uniaxial elongation. Energy contributions were found to vary as a function of temperature. Values of f_e/f for the copolymers are intermediate between those of the parent homopolymers as long as thermoelastic measurements were carried out at a temperature sufficiently greater than the glass transition temperature of the polymer.

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INTRODUCTION

In previous publications [1-3] we have demonstrated that the relative energy contribution to rubber elasticity (f_e/f) can be calculated from the temperature coefficient of shear modulus (G) through the following equation:

$$\frac{f_e}{f} = 1 - \frac{d \ln G}{d \ln T} - \frac{\beta T}{3} \qquad (1)$$

where β is the cubic thermal expansion coefficient. Equation (1) is useful in that f_e/f can be obtained independent of strain as long as the statistical theory of rubber elasticity is obeyed. However, in these works we have obtained values of the shear modulus indirectly through uniaxial tensile measurements.

According to the statistical theory [4, 5]

$$f = GA_0(\lambda - 1/\lambda^2) \qquad (2)$$

where A_0 is the cross-sectional area, λ is the elongation ratio, and

$$G = NkT\langle r^2\rangle/\langle r_0^2\rangle \qquad (3)$$

In Eq. (3), N is the number of network chains per unit volume of rubber, k is the Boltzmann constant, and $\langle r^2\rangle$ and $\langle r_0^2\rangle$ are the mean square end-to-end distances of network and free chains, respectively. In previous thermoelastic experiments, shear moduli were determined from slopes of f/A_0 vs $(\lambda - 1/\lambda^2)$ plots. We now wish to report a new thermoelastic experimental technique which determines values of G directly by simple shear [6]. This technique is used in studying the effects of copolymerization and extended temperature range on values of f_e/f. A series of acrylic polymers were synthesized for these investigations.

EXPERIMENTAL METHODS

Monomers of n-butyl acrylate (NBA), ethyl hexyl acrylate (EHA), methoxyethyl acrylate (MEA), methoxybutyl acrylate (MBA), and methoxyethyl methacrylate (MEMA) were purchased from the Borden Chemical Co. Polymers were prepared by UV photopolymerization, benzoin being added as photosensitizer. In all monomer mixtures, 1% tetramethylene glycol dimethacrylate was added as cross-linking agent.

Samples of the dimension of 0.7 × 2.5 × 2.5 cm^3 were cut by a high-speed rotating blade. Two equal size samples were glued together with one aluminum tab between them, with two other tabs on the outside of the sample assembly (Fig. 1). Stress was introduced by placing known weights on a pan connected to the middle aluminum tab (Fig. 2). A linear variable differential transformer (LVDT), manufactured by the Schavitz Engineering Co., was used to measure the displacements from which shear strains can be calculated. Electronic signals from the LVDT were amplified by a Daytronic Model 300D-70 Transducer-Amplifier-Indicator, and displayed on a two pen strip-chart recorder. The other pen simultaneously recorded the sample temperature through a copper-constantan thermocouple. Even though the LVDT is located more than 15 cm away from the temperature chamber for the sample, it is still very sensitive to room temperature fluctuations. Special precautions were taken to insulate the

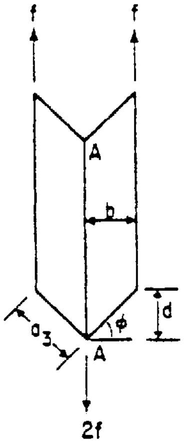

FIG. 1. The deformed sample in simple shear experiment. a_3 = unstrained thickness. d = absolute displacement of Point A. b = final thickness. 2f = load.

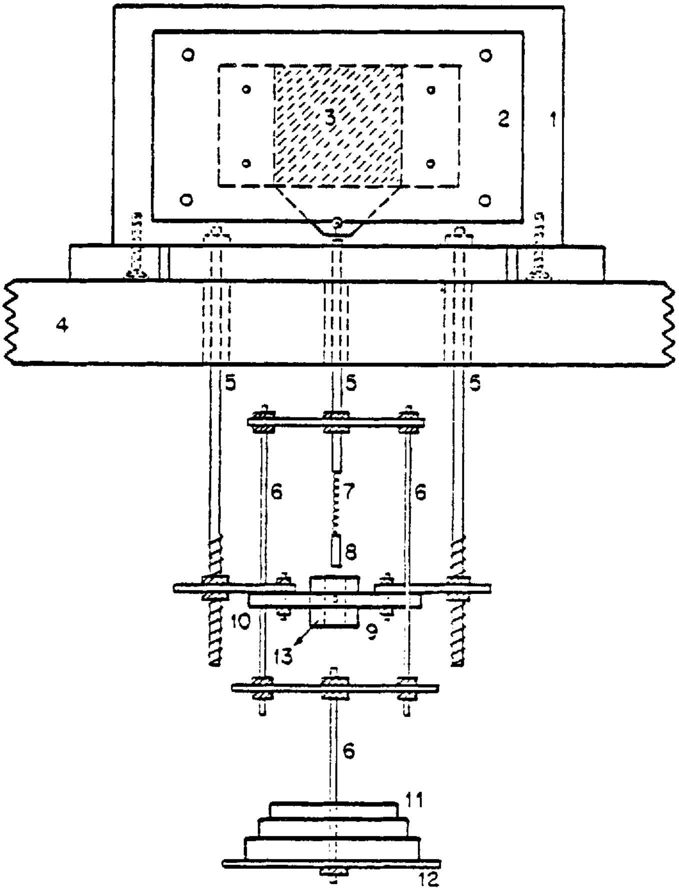

FIG. 2. Schematic diagram for constant stress, simple shear apparatus. (1) Stand, (2) rack, (3) samples, (4) bottom of the temperature chamber, (5) invar rods, (6) aluminum rods, (7) bronze-ring chain, (8) core, (9) LVDT, (10) Teflon block, (11) weights, (12) pan, and (13) to amplifier.

LVDT from these fluctuations during the experiment. The schematic diagram of the constant stress, simple shear apparatus is shown in Fig. 2.

The sample was permitted to reach its equilibrium strain at the highest temperature and under the highest load to be used in the experiment. After no further creep was observed between successful measurements (generally within 3 days), the temperature was decreased by approximately 10°C intervals. At least 2 hr were given for each temperature to insure the achievement of thermal equilibrium. After this temperature cycle, part of the load was removed. The sample was left standing overnight before the next set of thermoelastic measurements were made.

The unstrained sample position was obtained by extrapolation to zero load. Shear strain was calculated by

$$\gamma = d/b \tag{4}$$

where d is displacement and b is sample thickness (Fig. 1). Shear modulus is defined in the Appendix, where stress is computed by dividing the total load by the cross-sectional area of the sample.

Computer calculations were employed to find the values of dG/dT by least-square fit and then to calculate $d \ln G/d \ln T$. Values of f_e/f were calculated by Eq. (1). The thermoelastic analysis in simple shear is given in the Appendix. Because of the lack of information on linear thermal expansion coefficients of these elastomers, the average value of $2.5 \times 10^{-4}/°C$ was used in Eq. (1) to get the relative energy contribution to rubber elasticity.

RESULTS AND DISCUSSION

Figure 3 shows the modulus-temperature curves for the n-butyl acrylate—ethyl hexyl acrylate (NBA-EHA) system. All of these curves are linear, in agreement with the prediction of the statistical theory of rubber elasticity. On the basis of these data, values of f_e/f were calculated by Eq. (1). These results are given in Fig. 4. It is clear that the energy contributions thus computed vary with temperature. This observation is not surprising in view of the fact that moduli of most rubbers vary linearly with temperature, thus necessitating a nonlinear relationship between log G and log T, and consequently a nonlinear f_e/f dependence on T through Eq. (1).

It is important to note that in Fig. 4 our results are presented as f_e/fT, which is the negative temperature coefficient of the

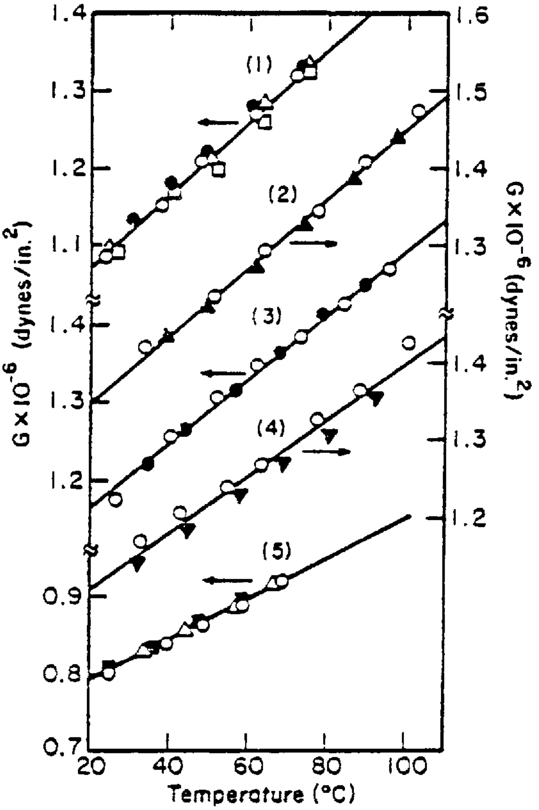

FIG. 3. Shear modulus vs temperature for NBA-EHA copolymers. (1) NBA; (○) 4.60 dynes/in.^{2} (= shear stress × 10^{-4}); (□) 8.40 dynes/in.^{2}; (△) 12.20 dynes/in.^{2}; (●) 15.99 dynes/in.^{2}. (2) 75% NBA + 25% EHA; (○) 12.40; (▲) 17.51. (3) 50% NBA + 50% EHA; (○) 10.29; (●) 15.99. (4) 25% NBA + 75% EHA; (○) 11.06; (▼) 16.06. (5) EHA; (○) 8.41; (△) 12.20; (■) 16.01.

unperturbed dimensions of network chains. In other words [7, 8],

$$f_e/fT = -d\ln\langle r_0^2\rangle/dT = \epsilon'/R \qquad (5)$$

where ϵ' is the intrachain folding energy [8]. ϵ' is related to the thermodynamic potential energy difference between the

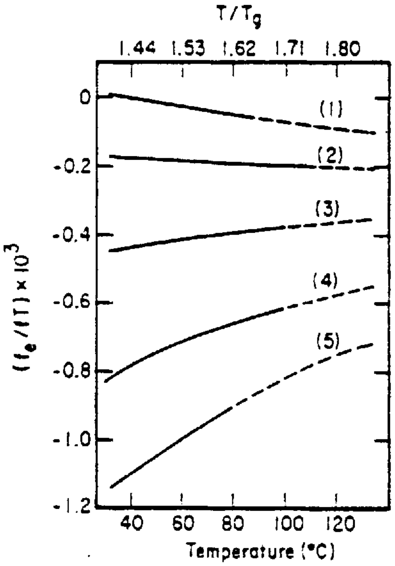

FIG. 4. Variation of energy contribution with temperature: NBA-EHA copolymers. (1) NBA, (2) 75% NBA + 25% EHA, (3) 50% NBA + 50% EHA, (4) 25% NBA + 75% EHA, and (5) EHA. Solid lines are actual data; broken lines are extrapolated.

rotational isomeric states of the chain backbone [9, 10].

In a previous paper [11] we have reported thermoelastic measurements by uniaxial elongation for poly(n-butyl acrylate). It was found that $f_e/f = -0.68$ at 120°C. In that work, d ln G/d ln T was first determined at 30°C. Then assuming that the logarithmic temperature coefficient of shear modulus remains constant to 120°C, f_e/f was calculated by Eq. (1). In order to compare this with our new results, it would be appropriate to shift it back to 30°C. At this temperature, f_e/f is -0.35 for PNBA from uniaxial elongation experiments, in excellent agreement with the value of -0.36 from simple shear measurements of this work. This agreement is gratifying in that it reinforces the utility of Eq. (1) in computing the energy contribution to rubber elasticity from thermoelastic data.

In a recent paper, Cirlin, Gebhard, and Shen [12] investigated the thermoelastic behavior of a number of rubbery copolymers.

It was found that $f_e/fT = -0.13 \times 10^{-3}/°C$ for a one-to-one random copolymer of ethylene and propylene. This value is in poor agreement with the calculated result [13] of $-1.1 \times 10^{-3}/°C$, though in satisfactory accord with the experimental result of Opschoor [14]. On the other hand, for homopolymers, f_e/fT is $0.11 \times 10^{-3}/°C$ for polyethylene [15] and $0.40 \times 10^{-3}/°C$ for polypropylene [14]. In the case of SBR, a styrene-butadiene copolymer, $f_e/fT = 0.39 \times 10^{-3}/°C$. In contrast, these values were reported in the literature to be $-0.33 \times 10^{-3}/°C$ for polybutadiene [16], and $-0.37 \times 10^{-3}/°C$ for polystyrene [17]. There is apparently no correlation between the energy contributions of copolymers and their homopolymers.

This apparent lack of correlation provided the motivation for us to study the acrylic copolymers. Figure 5 shows a plot of f_e/fT as a function of %EHA in the NBA-EHA copolymer system

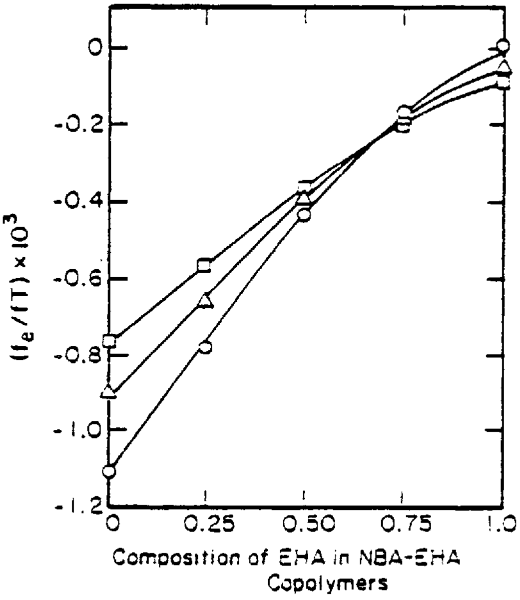

FIG. 5. Variation of energy contribution with temperature and composition: NBA-EHA copolymers. (○) 40°C, (△) 80°C, and (□) 120°C.

for three temperatures. Here it is found that energy contributions for the polymers are intermediate between those of the homopolymers, and no reversals in signs are evident. It is not clear at present if the source of discrepancy between our current and previous results is attributable to the difference in materials. One possible reason may be that we have used Eq. (1) in calculating the energy contribution, while most of the other workers used [18]

$$f_e/f = 1 - (\partial \ln f/\partial \ln T)_{P,L} - \beta T/(\lambda^3 - 1) \tag{6}$$

Values of f_e/f computed by Eq. (6) are often dependent on λ, as previously discussed [1-3].

In order to further study the effect of copolymerization on energy contribution, we chose the copolymer system of methoxyethyl methacrylate-methoxyethyl acrylate (MEMA-MEA). Figure 6 shows the modulus-temperature data of this system. Here we note that the G-T curves become increasingly nonlinear with increasing concentration of MEMA. Values of f_e/fT calculated from these data are shown in Fig. 7. No apparent correlation between the homopolymers and the copolymers appears to exist. We note, however, that the glass transition temperature [19] for MEMA is 290°K, while that for MEA is 223°K. Even though we have carried out our thermoelastic measurements for those samples containing a high MEMA content to 200°C, it is possible that even at this temperature the sample is still not sufficiently rubbery. In Fig. 8 we replot the f_e/fT data of Fig. 7 as a function of the reduced temperature T/T_g. Here T_g's of the copolymers were computed by the equation of Fox [20]. It is seen here that the curves for the low MEMA samples are only slightly curved, while those for the high MEMA samples show considerable variation with T/T_g until the latter ratio is greater than about 1.6. Above $T/T_g = 1.6$ there appears to be relatively constant f_e/fT values, and those of the copolymers fall in between the homopolymers. The implication here is that for the more rigid chain methacrylates a higher T/T_g ratio is required in obtaining meaningful thermoelastic data. By contrast we note

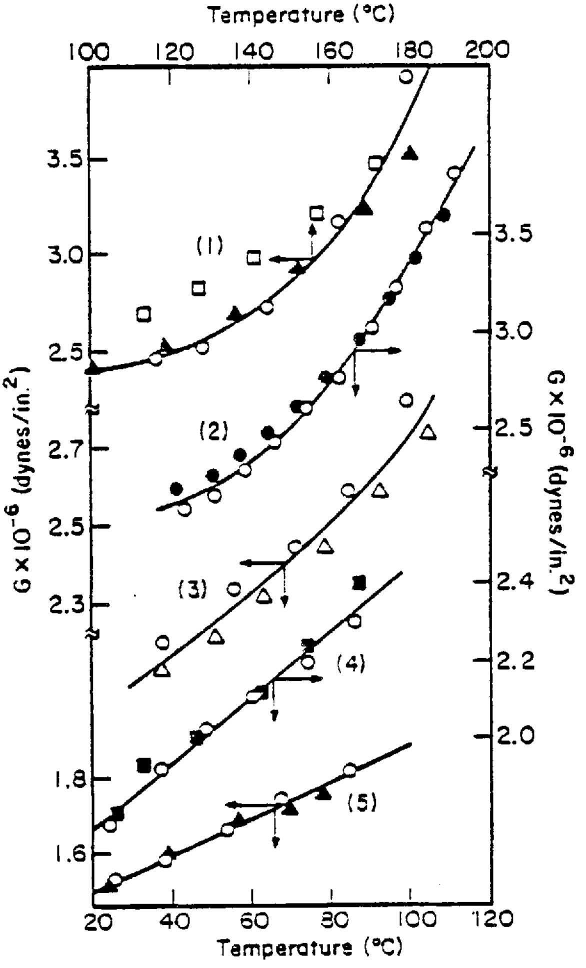

FIG. 6. Shear modulus vs temperature for MEA-MEMA copolymers. (1) MEMA; (○) 8.39 dynes/in.^{2} (= shear stress × 10^{-4}); (▲) 14.09; (□) 18.20. (2) 70% MEMA + 30% MEA; (○) 12.20; (●) 18.28. (3) 50% MEMA + 50% MEA; (○) 10.30; (△) 16.00. (4) 30% MEMA + 70% MEA; (○) 12.19, (■) 17.51. (5) MEA; (○) 8.39; (▲) 14.09.

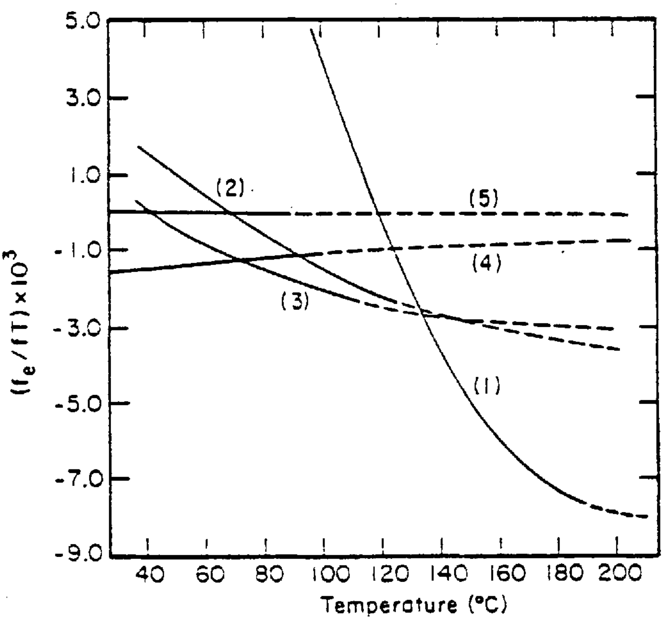

FIG. 7. Variation of energy contribution with temperature: MEMA-MEA copolymers. (1) MEMA, (2) 70% MEMA + 30% MEA, (3) 50% MEMA + 50% MEA, (4) 30% MEMA + 70% MEA, and (5) MEA. Solid lines are actual data; broken lines are extrapolated.

that T_g's for poly(n-butyl acrylate) and poly(ethyl hexyl acrylate) are 218 and 223°K, respectively [19]. The f_e/fT data for copolymers of NBA and EHA, presented in Fig. 5, are in the temperature range of $T/T_g > 1.4$.

In conclusion, we can state that Eq. (1) is found to be valid in computing energy contributions to rubber elasticity by either uniaxial elongation or simple shear measurements. Values of f_e/f for copolymers are intermediate between those of the parent homopolymers as long as thermoelastic measurements were carried out at a temperature sufficiently higher than the glass transition temperatures of the polymers.

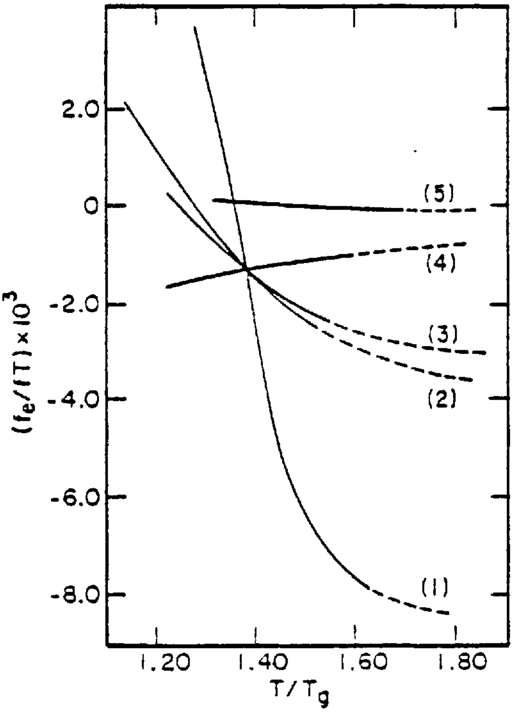

FIG. 8. Variation of energy contribution with reduced temperature (T/T_g): MEMA-MEA copolymers. Numerals have the same meanings as in Fig. 7. Solid lines are actual data; broken lines are extrapolated.

APPENDIX

Thermoelastic Analysis in Simple Shear

Simple shear is a type of deformation which may be represented by the sliding of planes parallel to a given plane by an amount proportional to their distance from the given plane [21] (Fig. 9). It is by definition a constant-volume deformation, whether or not the material is incompressible. The lateral faces of a cube are transformed by simple shear into parallelograms, and the amount of the

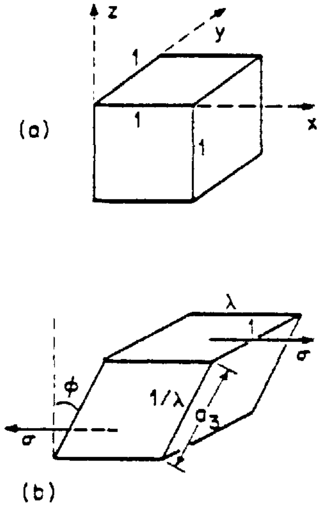

FIG. 9. Deformation of a unit cube. (a) Unstrained cube. (b) Simple shear.

shear strain (γ) is measured by the tangent of the angle φ through which a vertical edge is titled, thus

$$\gamma = \tan \phi \tag{7}$$

And the shearing stress σ is

$$\sigma = G\gamma \tag{8}$$

which means that Hooke's law is obeyed in simple shear.

The first and second laws of thermodynamics in this case is

$$dE = TdS - PdV + Md\phi \tag{9}$$

where M is the moment produced by the shear stress σ, and φ is the angular displacement. The moment M produced by the shear stress when the sample has undergone a deformation by the amount dφ at constant temperature, volume, and a_3 is

$$M = \left(\frac{\partial E}{\partial \Phi}\right)_{T,v,a_3} - T\left(\frac{\partial S}{\partial \Theta}\right)_{T,v,a_3} \tag{10}$$

where a_3 is the length of the tilted edge of the lateral faces, as shown in Fig. 9.

The energy component of the moment is

$$M_e = \left(\frac{\partial E}{\partial \Phi}\right)_{T,v,a_3} \tag{11}$$

The entropy component of the moment is

$$M_s = -T\left(\frac{\partial S}{\partial \phi}\right)_{T,v,a_3} \tag{12}$$

And the Helmholtz free energy function in this case is

$$dA = -\ SdT - Pdv + Md\phi \tag{13}$$

It follows that

$$\left(\frac{\partial S}{\partial \phi}\right)_{T,v,a_3} = -\left(\frac{\partial M}{\partial T}\right)_{v,\phi,a_3} \tag{14}$$

Combining Eq. (14) with Eqs. (1) and (11),

$$M_e = M - \left(\frac{\partial M}{\partial T}\right)_{v,\phi,a_3} \tag{15}$$

or

$$\frac{M_e}{M} = -\ T\left[\partial \ln\left(\frac{M}{T}\right)/\partial T\right]_{v,\phi,a_3} \tag{16}$$

And by definition,

$$M = \sigma a_3 \cos \phi = G a_3 \sin \phi \tag{17}$$

By substituting the definitions of M and G into Eq. (16), one obtains the relation between the energy contribution to the elastic moment and the temperature coefficient of the unperturbed chain dimensions:

$$\frac{M_e}{M} = -T \frac{d \ln \langle r_0^2 \rangle}{dT} \tag{18}$$

The result represented by Eq. (18) is a special case of the general result enunciated by Flory [18] that for any type of distortion the logarithmic temperature coefficient of the stress is equal to $-d \ln \langle r_0^2 \rangle / dT$. Equation (18) is identical to the one derived by Treloar [22, 23] for torsional measurements.

If we differentiate $\ln(M/T)$ with respect to temperature at constant pressure instead of constant volume (see Eqs. 3 and 17), we get

$$\left[\frac{\partial \ln(M/T)}{\partial T}\right]_{P,\varphi,a_3} = -\frac{d \ln \langle r_0^2 \rangle}{dT} - \frac{\beta}{3} \tag{19}$$

Combination of Eqs. (16), (18), and (19) yields

$$\frac{M_e}{M} = -T\left[\frac{\partial \ln(M/T)}{\partial T}\right]_{P,\phi,a_3} + \frac{\beta}{3} \tag{20}$$

Although Eq. (20) can, in principle, be used in determining the relative energy contribution, the condition of holding a_3 constant against thermal expansion is impractical. It is much more expedient to use Eq. (1) since shear moduli are much easier to measure as a function of temperature. Having been satisfied that Eqs. (1) and (20) (or Eqs. 18 and 5) produce equivalent results, we thus exclusively used Eq. (1) throughout the text of this paper.

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