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Configurational Properties of Polyesters Derived from Aliphatic Diacids and 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propane

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ABSTRACT: The dipole moment ratio, $\langle\mu^2\rangle/nm^2$, and the temperature coefficient of both the dipole moment, d ln $\langle\mu^2\rangle$/dT, and the unperturbed dimensions, d ln $\langle r^2\rangle_0$/dT, of polyesters derived from aliphatic diacids and 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane were measured. Polyesters with adipoyl and sebacoyl residues yield values of $\langle\mu^2\rangle/nm^2$ at 30 °C of 0.624 and 0.689, respectively. The experimental value of d ln $\langle r^2\rangle_0$/dT shows an anomalous dependence on the elongation ratio of the networks at which the thermoelastic measurements were performed. Although the rotational states scheme gives a fairly good account of the polarity of the chains, it fails in reproducing the experimental values of d ln $\langle r^2\rangle_0$/dT; the causes of this disagreement are discussed.

Introduction

The physical properties of polyesters depend on the conformational characteristics of both the acid and the glycol residues. Studies on the configurational properties of polyesters prepared from aliphatic diacids and 2,2-bis-[4-(2-hydroxyethoxy)phenyl]propane (dyanol-22) are attractive because of the conformational characteristics of the glycol residue. Actually, interactions between aromatic hydrogens and the two neighboring methyl groups cause the rotational angles about the C^{Ph}–$C(CH_3)_2$ bonds to be located at[1,2] $\pm\Delta\phi$ and $180 \pm \Delta\phi$, where $\Delta\phi \approx 45°$.

Recent ^1H NMR studies carried out on dyanol-22 diacetate indicate that gauche conformations about CH_2–CH_2 bonds in this compound are strongly favored over the alternative trans states.[2] In addition to the NMR studies, the critical interpretation of the equilibrium dielectric conformation-dependent properties of this diester has permitted the development of a conformational statistics[2] whose reliability will be tested in this study by the theoretical analysis of the dipole moment and the temperature coefficient of both the dipole moment and the mean-square end-to-end distance of aliphatic polyesters with the dyanol-22 residue in their structure. To our knowledge, no information on the statistics of polyesters of this kind is available in the literature.

Another goal of this work is to investigate how the rotational population about CH_2–C^*O^* of the acid residue will affect the conformation-dependent properties of polyesters with dyanol-22 residue in their structure, specifically the temperature coefficient of the unperturbed dimensions of poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane adipate] (PDA) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (PDS). Earlier studies[3,4] on the temperature coefficient of poly(neopentyl glycol succinate) (PNS) and poly(neopentyl glycol adipate) (PNA) seem to suggest that gauche states about CH_2–C^*O^* bonds have an energy similar to or below that of the alternative trans states. However, it should be pointed out that the information at hand concerning the relative energy of the gauche states with respect to the corresponding trans states of these bonds is highly controversial, the values reported in the literature being positive,[5–7] nearly zero,[8] and even negative.[9]

Experimental Section

Synthesis of the Polyesters. Poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane adipate] (PDA) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (PDS) were obtained by reaction of equimolar amounts of dyanol-22 and the corresponding diacids by using p-toluenesulfonic acid as catalyst. The step condensation reactions were conducted in refluxing toluene solutions, utilizing a high concentration of reactants (~50% w/w), with the aim of avoiding the formation of high molecular weight cycles.[10] The reaction time was 24 h, and the water formed during the reaction was separated by means of a Dean–Stark distillation trap. In the final steps of the reaction a slight excess of dyanol-22 was added to the reaction medium, with the aim of obtaining hydroxyl-terminated chains, and the reaction was permitted to proceed for another 5 h. The polyesters were precipitated with n-hexane, and then they were washed several times with water in order to eliminate the catalyst. The polymers were fractionated at 25 °C with chloroform/n-hexane with the purpose of eliminating low molecular weight cycles. Two fractions of number-average molecular weight M_n 5700 and 5400 were used for PDA and PDS, respectively, in the thermoelastic studies. The values of M_n for the two fractions utilized in the dielectric experiments were, respectively, 5700 and 2000. The glass transition temperatures of the polymers, measured at the heating rate of 5 °C/min with a DSC-4 Perkin-Elmer calorimeter, amounted to 27 and 16 °C for PDA and PDS, respectively.

Thermoelastic Experiments. PDS and PDA networks were prepared by casting a chloroform solution (methanol free) of the corresponding hydroxyl-terminated polyester and an equivalent amount of tris(p-isocyanatophenyl) thiophosphate (Bayer) into a Teflon mold, where the solvent was evaporated off. Then the cross-linking reaction was carried out at 80 °C for 2 days. The networks exhibited rather poor mechanical properties as a consequence of their high soluble fraction, which amounted to 0.18 and 0.30 for PDS and PDA, respectively.

Thermoelastic measurements were carried out on unswollen amorphous strips by using standard techniques. Thus elastic forces of the strips, under a constant elongation ratio, were measured with a pressure transducer (Gould Statham Model UC3) in the temperature range 35–70 °C. In all the cases the strips were stretched at high temperature and held at this temperature until the relaxation was complete. The measurements were performed from high to low temperature, with an occasional reverse of order to test for reversibility. The determination of the cubic expansion coefficient β of the networks was carried out by means of refractive index measurements. Actually the Lorenz–Lorentz relationship[11] relates the refractive index n to the density ρ by the expression

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\rho P \qquad (1)$$

where P is the molecular polarization. Assuming that the dependence of P on temperature is small in comparison with that of ρ, eq 1 can be written as[12]

$$\frac{n^2+2}{n^2-1} = aT + b = kv_0(1 + \beta T) \qquad (2)$$

where v_0 is the specific volume at the temperature of reference,

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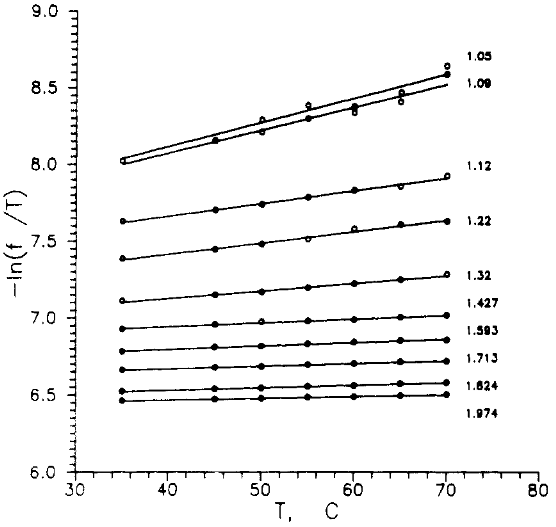

Figure 1. Thermoelastic results for poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (PDS) networks.

and $\beta = a/b$. The values of $10^4\beta$ in the temperature range 20–60 °C amounted to 5.4 and 5.8 K^{-1} for PDA and PDS, respectively. It should be pointed out that the networks are amorphous and they apparently do not crystallize under elongation. A similar behavior was found in poly(diethylene glycol terephthalate) networks.[13]

Dielectric Measurements. Values of the mean-square dipole moment $\langle\mu^2\rangle$ of the polyesters were determined by using the equation of Guggenheim and Smith[14,15]

$$\langle\mu^2\rangle = \frac{27\kappa TM}{4\pi\rho N_A(\epsilon_1 + 2)^2}\left(\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right) \tag{3}$$

where ϵ and n represent the dielectric constant and the index of refraction of the solutions, whereas these quantities with subindex 1 refer to the solvent; T is the absolute temperature, M the molecular weight of the solute, N_A Avogadro's number, ρ the density of the solvent, and w the weight fraction of polymer in the solutions. Experimental values of ϵ for different solutions of the polymers in benzene were obtained at 30, 40, 50, and 60 °C with a capacitance bridge (General Radio, type 1620 Å) and a three-terminal cell operating at 10 kHz. The derivative $d\epsilon/dw$ was obtained at each temperature of interest from the slope of the plot ϵ versus w, in the limit $w \rightarrow 0$. Experimental values of $n - n_1$ were also measured for different solutions with a He–Ne KMX-16 laser differential refractometer (Chromatix Inc.) operating at 632.8 nm. The derivative dn/dw in eq 3 was obtained, as usual, from the slope of the plot $n - n_1$ versus w, at $w \rightarrow 0$.

Dielectric and Thermoelastic Results

According to the Gaussian network theory developed by Flory, the temperature coefficient of the mean-square end-to-end distance is given by[16,17]

$$\frac{d \ln \langle r^2\rangle_0}{dT} = -\left[\frac{\partial \ln (f/T)}{\partial T}\right] - \frac{\beta}{\alpha^3 - 1} \tag{4}$$

where β is the expansion coefficient, α is the elongation ratio, and f is the elastic force at equilibrium referred to the undistorted cross-sectional area A of the strip. Thermoelastic results expressed in terms of $\ln (f/T)$ versus T are shown in Figure 1 for the PDS elastomer. Values of $\partial \ln f/\partial T$ are represented in terms of the elongation ratio in Figure 2, where it can be seen that thermoelastic inversion occurs at rather high elongation ratios, the values of these quantities at the inversion point amounting to $\approx$1.40 and 1.32 for PDS and PDA, respectively. By introduction of the values of the thermoelastic results represented in Figure 1 into eq 4, an unreasonable dependence of $d \ln \langle r^2\rangle_0/dT$ on α is obtained. This can be seen in Figure 3 where the temperature coefficient is plotted against α; for example, the value of $d \ln \langle r^2\rangle_0/dT$ for PDS decreases from 0.014 to 2.0×10^{-4} when α increases from 1.08 to 2. Similar changes are found for PDA.

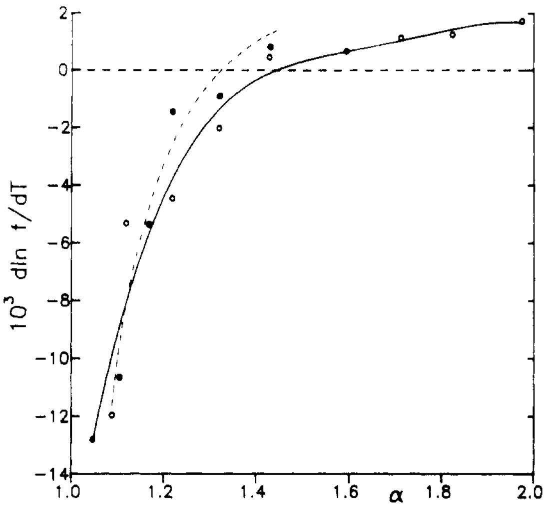

Figure 2. Variation of the natural logarithm of the elastic force, over the undistorted cross-sectional area, with the elongation ratio for poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (open circles) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane adipate] (PDA) (filled circles) networks.

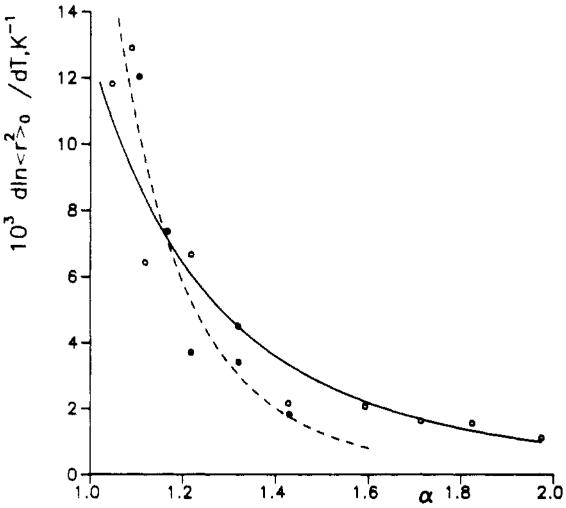

Figure 3. Influence of the elongation ratio on the temperature coefficient of the unperturbed dimensions of poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane adipate] (filled circles) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (open circles).

Table I
Summary of Dielectric Results for PDA and PDS at Several Temperatures

T,	PDA			PDS		
°C	$d\epsilon/dw$	$2n_1dn/dw$	$\langle\mu^2\rangle/nm^2$	$d\epsilon/dw$	$2n_1dn/dw$	$\langle\mu^2\rangle/nm^2$
30	2.03	0.16	0.624	2.10	0.11	0.689
40	1.96	0.17	0.631	2.04	0.13	0.702
50	1.90	0.18	0.640	2.00	0.14	0.722
60	1.83	0.19	0.643	1.95	0.15	0.735

Values of $d\epsilon/dw$ at 30, 40, 50, and 60 °C are represented for PDA and PDS, respectively, in the second and fifth columns of Table I. The increments of the refractive indexes of the solutions with respect to those of the solvent are positive, and they slightly increase with temperature. The results for the term $2n_1dn/dw$ are given in the third and sixth columns of Table I. Values of the mean-square dipole moment expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ are shown in the fourth and seventh columns of Table I. In the evaluation of nm^2 the mean-square dipole moment of the chains in the idealization

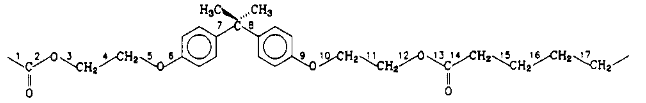

Figure 4. Section of poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane adipate] in the all-trans conformation.

that the skeletal bonds are freely jointed, it was assumed that the dipoles associated with the ester group,[2] the ether C–O bond, and the C–C and O–H bonds[18] are 1.89, 1.07, 0.00, and 1.7 D, respectively. The uncertainty of the values of $\langle \mu^2 \rangle / nm^2$ was estimated to be ±5%. By plotting the natural logarithm of the mean-square dipole moment against temperature, values of 1.1×10^{-3} and 1.8×10^{-3} K^{-1} were obtained for the temperature coefficients of PDA and PDS, respectively.

Discussion

The conformational statistics of the glycol residue of the polyesters have recently been discussed, taking as a basis the statistics developed by Hutnik and Suter[1] for bisphenol-based polycarbonates. A four-state scheme was used for bonds 6–9 in Figure 4 with rotational angles located at 45, 135, 225, and 315°. The corresponding statistical weight matrices are[1,2]

$$\mathbf{U}_6 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix} \quad \mathbf{U}_7 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix} \tag{5}$$

$$\mathbf{U}_8 = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix} \quad \mathbf{U}_9 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix} \tag{6}$$

whereas the rotational angles for bond 10 were considered to be located at 0, ±120°, its statistical weight matrix being[2]

$$\mathbf{U}_{10} = \begin{pmatrix} 1 & 0 & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \\ 1 & \sigma & 0 \end{pmatrix} \tag{7}$$

where σ is the statistical weight or Boltzmann factor associated with gauche states about CH_2–O bonds of the glycol residue, which give rise to first-order interactions between a hydrogen atom of a phenyl group and the hydrogen atoms of a methylene group.

Gauche states about CH_2–CH_2 bonds of the glycol residue cause first-order interactions between two oxygen atoms; earlier NMR studies carried out on dyanol-22 diacetate suggest that the energy of these states is ca. 0.8 kcal mol^{-1} below that of the alternative trans states. On the contrary, gauche states about O–CH_2 bonds of both the ester group and the ether groups of the glycol residue have energies 0.3 and 0.9 kcal mol^{-1}, respectively, above those of the respective trans states.[2,19]

The values reported for the energy of gauche states about CH_2–C*O* bonds, E_{σ_a}, vary in the range 1.2–0 (or below) kcal mol^{-1}, with respect to that of the alternative trans states.[3-9] Moreover, gauche states about CH_2–CH_2 bonds, which cause first-order CH_2...C*O* interactions, have energies lying in the range 0.3–0.7 kcal mol^{-1} above that of the corresponding trans states.[3,20] Finally, gauche states about the CH_2CH_2–CH_2CH_2 bonds are disfavored by ca. 0.5 kcal mol^{-1} with respect to the trans states.[19]

Theoretical values of the dipole moment ratio and the temperature coefficient of both the dipole moment ratio and the unperturbed dimensions were calculated by using matrix multiplication methods described in detail elsewhere.[19,21] It was assumed that the dipole moment associated with the ester group is 1.89 D and its direction makes an angle of 123° with the CH_2–C*O* bond,[22] whereas the dipole moments of CH_2–O, CH_2–CH_2, and O–H lie along the bonds, their values being 1.07, 0.00, and 1.7 D, respectively.[18] A virtual bond of 3 Å was used for the phenyl group, and the lengths of C–C, C–C*, O–C*C, and C–O bonds were considered to be 1.53, 1.51, 1.30, and 1.43 Å, respectively. Values of 144 and 111° were used for the OC*C and C*OC skeletal bond angles and 111.5° for the rest. The rotational angles about bonds 6–9 were given above; O–C*O* bonds of the ester group are restricted to trans states[19] whereas the rotational angles of the other bonds were assumed to be located at[18] 0,±110°.

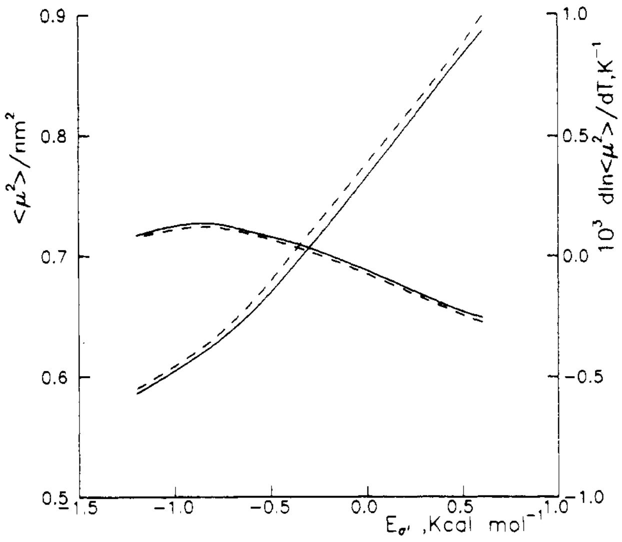

Figure 5. Dependence of the dipole moment ratio and the temperature coefficient of the dipole moment on the conformational energy $E_{\sigma'}$ of gauche states about CH_2–CH_2 bonds of the glycol residue for poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane adipate] (solid line) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane sebacate] (broken line).

The theoretical calculations showed that the dipole moment ratio is very sensitive to the gauche population about CH_2–CH_2 bonds of the glycol residue. This can be seen in Figure 5 where the values of $\langle \mu^2 \rangle / nm^2$ for PDS and PDA are plotted against $E_{\sigma'}$, the energy of gauche states of these bonds with respect to the alternative trans states. An increase in $E_{\sigma'}$ also increases the dipole moment ratio of the chains, probably as a consequence of the fact that it decreases the all-trans conformation fraction in the repeating unit for which the dipoles associated with the polar groups have similar orientation. The dependence of $\langle \mu^2 \rangle / nm^2$ on the relative population of rotational states about CH_2–O ether bonds is very small. However, the dipole moment ratio is rather sensitive to the energy E_{σ_k} of gauche states about CH_2–O bonds. Actually, in changing E_{σ_k} from −0.5 to 1 kcal mol^{-1}, $\langle \mu^2 \rangle / nm^2$ increases in nearly 42% its value.

The dipole moment ratio is quite insensitive to the relative population of rotational states about each skeletal bond of the acid residue. This is the reason why both PDS and PDA should have similar polarity. Strictly speaking, the dipole moment ratio of PDS chains is slightly higher than that of PDA (see Figure 5), because the larger number of methylene groups in the acid residue in the former case presumably diminishes the correlation between the ester groups of each repeating unit. In general, the calculations reproduce in a satisfactory way the dipole moment ratio of the polyesters for values of $E_{\sigma'}$ lying in the range −0.5 to −0.8 kcal mol^{-1}.

The influence of the gauche population about CH_2–CH_2 on the temperature coefficient of the dipole moments

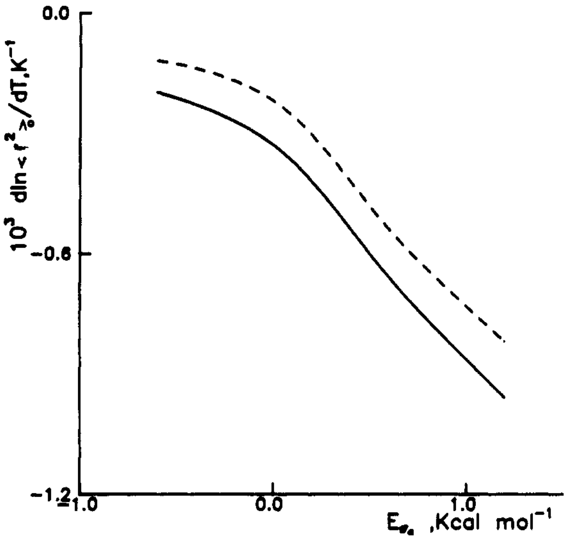

Figure 6. Variation of the temperature coefficient of the unperturbed dimensions with the conformational energy E_{σ_α} of gauche states about the CH_2–C^*O^* bond of the acid residue for poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane adipate] (solid line) and poly[2,2-bis[4-(2-hydroxyethoxy)phenyl]propane sebacate] (broken line).

of the polyesters is represented in Figure 5, where it can be seen that the values of this quantity decrease as $E_{\sigma'}$ increases. The changes on d ln $\langle\mu^2\rangle$/dT with the conformational energies of other bonds are in comparison small. On the contrary, the temperature coefficient of the unperturbed dimensions is only slightly sensitive to $E_{\sigma'}$, but it shows a high dependence on E_{σ_α}, the energy associated with gauche states about CH_2–C^*O^* bonds. As can be seen in Figure 6, d ln $\langle r^2\rangle_0$/dT for both polyesters increases as E_{σ_α} decreases, approaching zero for values of this energy below −1 kcal mol^{-1}. This theoretical analysis seems to rule out the high value of the temperature coefficient of the unperturbed dimensions obtained from thermoelastic experiments at low strains.

Flory's method has been criticized on the grounds that it gives unreasonably high values for the temperature coefficient of the unperturbed dimensions of many systems. Some authors[23-25] have argued that the term $2C_1$ in the Mooney–Rivlin equation[26,27]

$$[f] = 2C_1 + 2C_2\alpha^{-1} \tag{8}$$

$$[f] = \frac{f}{(\alpha - \alpha^{-2})A} \tag{9}$$

should be used to determine d ln $\langle r^2\rangle$/dT. According to this approach

$$\frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} = -\frac{\partial\ln(C_1/T)}{\partial T} \tag{10}$$

Although the validity of this method has not yet been settled, the results of the present analysis suggest that the temperature coefficient decreases rather smoothly as α increases (see Figure 3) for values of this quantity above the inversion point. Tentative calculations of d ln $\langle r^2\rangle_0$/dT by means of the values of $2C_1$ obtained by extrapolation of $[f]$ versus α^{-1}, as the Mooney–Rivlin formalism suggests, give for the coefficient of these polymers values of ca. -0.7×10^{-3} K^{-1}. It should be pointed out, however, that these results are only slightly reliable, owing to the fact that $[f]$ could not be obtained for elongation ratios larger than 2, and, consequently, the extrapolated values of $2C_1$ are somewhat uncertain.

Another criticism made to the thermoelastic method in the determination of the temperature coefficient of the unperturbed dimensions is that hysteresis perturbations may cause a failure of the elastomer to attain mechanical equilibrium within the time scale of the experiment. In order to avoid this, a new method of temperature-induced creep was formulated by McCrum[28,29] in which it is assumed a priori that equilibrium under stress is never obtained. This author claims that with this method it is possible to obtain the true values of the temperature coefficient of the unperturbed dimensions. However, reexamination of this approach led Smith and Mark[30] to the conclusion that McCrum's approach is misguided and very seriously flawed. We should point out that, although hysteresis perturbations may be important in the case of networks prepared from high molecular weight chains randomly cross-linked, they are not in networks prepared from low molecular weight chains as those used in this study; in this case mechanical equilibrium is attained at rather low times, on the order of a few minutes, even at temperatures not far above T_g.

Summing up, the theoretical values come close to the experimental results obtained for d ln $\langle r^2\rangle_0$/dT at moderate elongations by assuming that gauche states about CH_2–C^*O^* are favored over the corresponding trans states, in agreement with the conclusions obtained from earlier analysis of the temperature coefficient of the unperturbed dimensions of poly(neopentyl glycol succinate) and poly(neopentyl glycol adipate).

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