Birefringence, Thermoelastic, and Dielectric Studies of Cycloaliphatic Polyesters

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ABSTRACT: Poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) was synthesized by polycondensation of dimethyl 1,4-*trans*-cyclohexanedicarboxylate and diethylene glycol. The mean-square dipole moment $\langle\mu^2\rangle$ of the chains was measured in solutions of the polymer in benzene at several temperatures between 30 and 60 °C. The experimental values of $\langle\mu^2\rangle$, expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/(nm^2)$, changed from 0.588 to 0.608 in the temperature interval indicated above. Elastomeric networks were prepared by cross-linking of cycloaliphatic polyester with an aromatic triisocyanate. From stress–strain birefringence experiments performed on the networks, values of the optical configuration parameter Δa and the temperature coefficient of both Δa, $\mathrm{d}\ln\Delta a/\mathrm{d}T$, and the unperturbed dimensions, $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$, were obtained; the experimental values of these quantities at 30 °C amounted to 7.4×10^{-24} cm^3, ~0, and 1.5×10^{-3} K^{-1}, respectively. Theoretical calculations, carried out by using the rotational isomeric state model, reproduced satisfactorily the experimental values of the dipole moment ratio and the temperature coefficient of both the dipole moments and the unperturbed dimensions, assuming that the two possible planar conformations about C_{cy}–C* bonds have the same energy. The agreement between theory and experiment was not so satisfactory for the optical properties, although the experimental and theoretical results were closer than in other polyesters previously studied.

Introduction

The conformational properties of cycloaliphatic polyesters, prepared by condensation of 1,4-cyclohexanedimethanol with sebacic acid, were recently studied.[1,2] The results obtained showed that the polarity of the chains is very sensitive to the substitution equatorial–equatorial (trans isomers) or equatorial–axial (cis isomers) of the hydrogen atoms bonded to the carbon atoms located at the 1,4-position of the cyclohexane ring. The temperature coefficient of the unperturbed dimensions of both isomers is moderately large and negative, the value of this quantity being larger, in absolute value, for the trans isomer than for the cis.

This work addresses the investigation of the conformational properties of cycloaliphatic polyesters in which the cyclohexane ring is incorporated into the acid residue, using as model poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) (PDGC) chains. Values of the mean-square end-to-end distance and dipole moments were measured, and the results analyzed by using statistical mechanics methods. Since the conformational energies associated with the rotational states of the glycol residue are well-known,[3,4] information was obtained by comparing theory and experiment concerning the energy associated with the rotational states about C_{cy}–C* bonds of the acid residue. In addition, the experimental value of the optical configuration parameter Δa and the temperature coefficient $\mathrm{d}\ln\Delta a/\mathrm{d}T$ was also measured, and the results interpreted by using the valence optical scheme. The optical properties were studied with the aim of investigating whether the discrepancy between theory and experiment found for other polymers[2,4] also holds for the present system.

This work forms part of a more general study in which the capability of polyesters to prepare model networks is currently being investigated.

Experimental Section

Purification of Dimethyl 1,4-*trans*-Cyclohexanedicarboxylate. The commercial mixture of liquid (cis) and solid (trans) dimethyl 1,4-cyclohexanedicarboxylate (Fluka A.G.) was filtered to separate the pure trans monomer from a liquid mixture containing 70/30 cis/trans. The solid trans compound was subsequently purified by recrystallizing three times from 1/2 ethanol/water.

Synthesis of the Polymer. Poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) was obtained by the standard melt-phase procedure from dimethyl 1,4-*trans*-cyclohexanedicarboxylate and excess diethylene glycol in the presence of isopropyl titanate. The reaction was carried at 150 °C for 2 h at 200 °C for 1 h under a nitrogen atmosphere and at 230 °C under vacuum for 2 h. The polymer was fractionated at 35 °C with chloroform/methanol as the solvent/nonsolvent system.

Characterization of the Polymer. The number-average molecular weights of the fractions were determined in chloroform with a Knauer vapor pressure osmometer. A fraction of number-average molecular weight 5300 was used in the dielectric experiments and in the preparation of networks.

The isomerization of the cis and trans forms of dimethyl 1,4-cyclohexanedicarboxylates during the preparation of cycloaliphatic polyesters, as well as the isomerization of 1,4-cyclohexanedimethanethiol during its condensation with aldehydes, has been reported previously.[5,6] Therefore, the ^{13}C NMR spectrum of PDGC was registered on a Bruker WP80SY at 20.1 MHz, by using deuteriated chloroform as solvent and tetramethylsilane as internal standard, and compared with that of the pure dimethyl 1,4-*trans*-cyclohexanedicarboxylate to investigate whether isomerization had taken place during the synthesis of the polyester. Figure 1 shows the spectra of the pure trans monomer and the corresponding polymer. As can be seen, the peaks corresponding to the cyclohexane ring and to the carbonyl groups appear in both cases at the same chemical shift. Furthermore, no peaks can be observed corresponding to the presence of cis isomer, thus indicating that no isomerization had taken place during the reaction.

Dielectric Measurements. Dielectric measurements of solutions of the polymer in benzene were conducted at 30, 40, 50, and 60 °C by using a capacitance bridge operating at 10 kHz and a three-terminal cell.[7] Values of the mean-square dipole moment $\langle\mu^2\rangle$ were obtained by means of the equation of Guggenheim and Smith:[8,9]

$$\langle\mu^2\rangle = (27kTM/(4\pi\rho N_A(\epsilon_1 + 2)^2))((\mathrm{d}\epsilon/\mathrm{d}w) - 2n_1\,\mathrm{d}n/\mathrm{d}w)$$

where k and N_A are the Boltzmann constant and Avogadro's number, respectively, M is the molecular weight of the solute, and ρ is the density of the solvent. The symbols ϵ and n represent the dielectric constant and index of refraction of the solutions, respectively; the symbols with subscript 1 represent the same quantities for the solvent. The derivatives $\mathrm{d}\epsilon/\mathrm{d}w$ were obtained, as usual, from the slopes of the plots of increments of dielectric constant ($\Delta\epsilon = \epsilon - \epsilon_1$) against the weight fraction w of polymer. Values of this quantity at the temperatures of interest are given in the second column of Table I. Increments $(n - n_1)$ of the index of refraction of the solutions with respect to the solvent were measured with a He-Ne laser differential refractometer (Chro-

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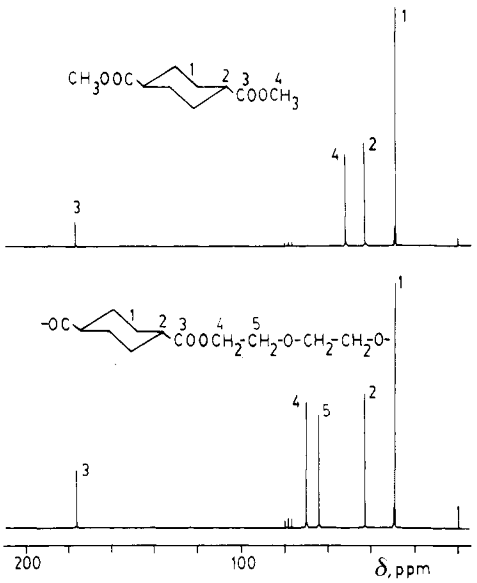

Figure 1. ^{13}C NMR spectra of dimethyl 1,4-*trans*-cyclohexanedicarboxylate (upper) and poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) (lower).

Table I
Summary of Dielectric Results

T, °C	$d\epsilon/dw$	$2n_1\, dn/dw$	$\langle\mu^2\rangle/(nm^2)$
30	2.53	0.04_4	0.585
40	2.44	0.04_7	0.593
50	2.35	0.05_0	0.603
60	2.25	0.05_0	0.608

matix Inc.) operating at 632.8 nm. Values of the derivatives, obtained from plots of $n - n_1$ versus w, are shown in the third column of Table I.

Birefringence–Strain Measurements. Polymer networks were prepared by end-linking hydroxyl-terminated PDGC chains of number-average molecular weight 5300 with 2,4-bis(p-isocyanobenzyl)phenyl isocyanate by using the procedure described elsewhere.[10] Prior to the birefringence–strain experiments the network was treated in a Soxhlet extractor with chloroform for 24 h to extract unreacted chains from the strips. The soluble fraction amounted to 10%.

Strain–birefringence measurements were performed on strips, cut from the networks sheets, at several temperatures the range 20–80 °C. The light source was a 2-mW 632.8-nm He–Ne laser, the analyzer and polarizer were Glan–Thompson prisms, and the compensator was of the Babinet–Soleil type.[11-13] The strips were mounted between two clamps, the lower fixed and the upper attached to a Statham strain gauge. The sample was surrounded by a double-walled jacket in which water was circulated from a thermostat. The strips were stretched at the highest temperature (80 °C) and permitted to relax at this temperature. The temperature was then decreased, and once the force and birefringence remained constant, the values of Δn and the true stress $\tau = f/A$ were recorded. Values of Δn as a function of temperature, for different elongation ratios λ, are given in Figure 2. Thermoelastic results expressed in terms of $\ln (f^*/T)$, where f^* is the equilibrium elastic force referred to the undistorted cross-sectional area, are presented in Figure 3.

Refractive indexes of PDGC chains were measured with a Abbê refractometer at several temperatures. The results obtained are fitted by

$$n = 1.4996 - (3.06 \times 10^{-4})t$$

with t in degrees centigrade. The expansion coefficient β of the chains was obtained from the index of refraction by using the method outlined by Michel et al.[14] The value of this quantity amounted to 5.5×10^{-4} K^{-1}.

General Results

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 column of Table I. The term nm^2 represents the mean-square dipole moment of a chain of n skeletal bonds each of them having an average square dipole moment m^2. In the evaluation of nm^2, dipole moments of 1.07, 0.00, and 1.70 D were assigned to the CH_2–O, CH_2–CH_2, and O–H bonds, respectively:[15] a value of 1.89 D was used for each of the ester groups of the repeating unit.[16] The uncertainty of the values of $\langle\mu^2\rangle/(nm^2)$ was estimated to be ca. 5%.

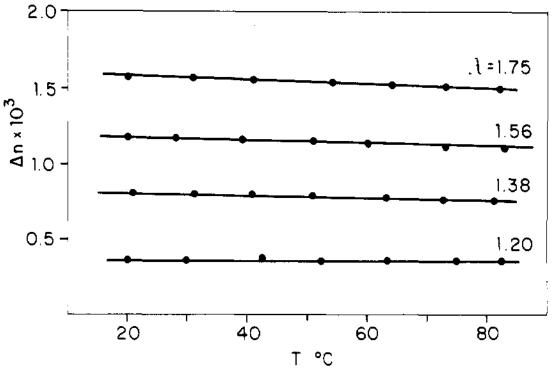

Figure 2. Birefringence versus temperature for poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) networks.

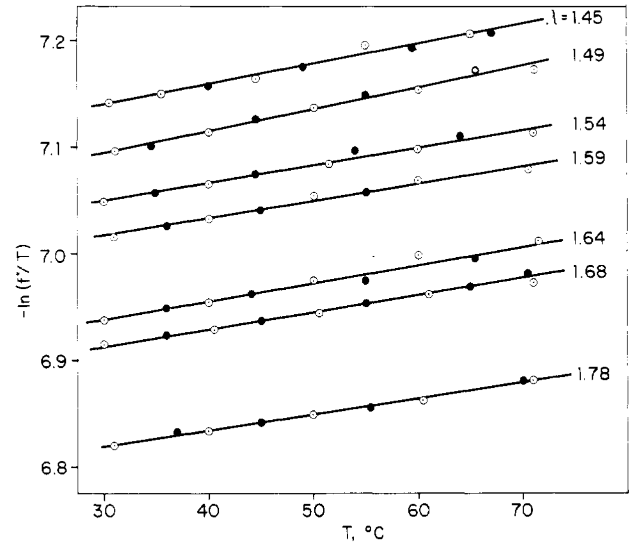

Figure 3. Thermoelastic results, expressed as $\ln (f^*/T)$ against temperature at several elongation ratios.

Table II
Experimental Values at 30 °C of Configuration-Dependent Properties for Poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) (PDGC) and Poly(diethylene glycol terephthalate) (PDET)

property	PDGC chains	PDET chains
$\langle\mu^2\rangle/(nm^2)$	0.585	0.660
$10^3\, d \ln \langle\mu^2\rangle/dT$	1.3	~0
$10^3\, d \ln \langle r^2\rangle_0/dT$	1.5	1.2
$10^{24}\Delta a$, cm^3	7.4	20.7
$10^3\, d \ln \Delta a/dT$	~0	-1.1

The temperature coefficient of the dipole moments $d \ln \langle\mu^2\rangle/dT$ was determined from the slope of the straight line obtained by plotting the natural logarithm of the dipole moment ratio against temperature. The value of $10^3\, d \ln \langle\mu^2\rangle/dT$ was found to be 1.3 K^{-1}. In Table II, for comparative purposes the values of $\langle\mu^2\rangle/(nm^2)$ and $d \ln \langle\mu^2\rangle/dT$ at 30 °C for both PDGC and poly(diethylene glycol terephthalate) (PDET) are shown. It can be seen that the latter polymer exhibits a slightly higher polarity and lower temperature dependence of the dipole moment than the former.

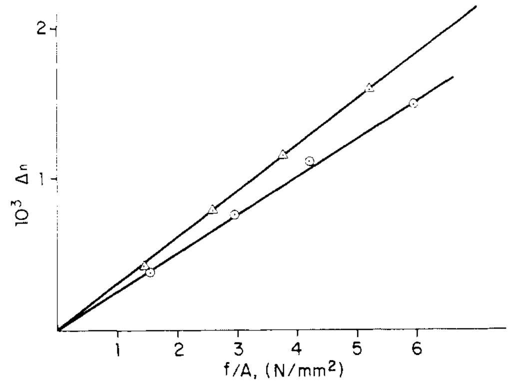

Figure 4. Birefringence (Δn) against true stress (f/A) for poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) networks; (△) 20 °C; (○) 80 °C.

Table III
Stress-Optical Coefficient *C* and Optical Configuration Parameter Δa for Poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) (PDGC)

T, °C	$10^{-10}C$, cm^2/dyn	$10^{-24}\Delta a$, cm^3
20	3.04	7.35
30	2.96	7.42
40	2.87	7.44
50	2.78	7.46
60	2.68	7.43
70	2.60	7.44
80	2.52	7.84

The stress–optical coefficient $C = \Delta n/\tau$ was obtained from the slopes of the straight lines obtained by plotting the birefringence against true stress. Illustrative plots of this kind at two extreme temperatures (20 and 80 °C) are shown in Figure 4. Values of C at different temperatures are shown in the second column of Table III; the temperature coefficient of the natural logarithm of the stress–optical coefficient 10^3 d ln $C/\mathrm{d}T$ amounts to −3.2 K^{-1}.

According to the theory, the optical configuration parameter Δa is related to the stress–optical coefficient by

$$\Delta a = (45kTC/(2\pi))n/(n^2 + 2)^2$$

where k is the Boltzmann constant, T is the absolute temperature, and n is the index of refraction of the isotropic network. Values of the optical configuration parameter at different temperatures in the range 20–80 °C are shown in the third column of Table III. It can be seen that the experimental values of Δa do not show a noticeable temperature dependence. Comparison of the experimental values of Δa and d ln $\Delta a/\mathrm{d}T$ at 30 °C for PDGC and PDET, indicated in Table II, suggests that the former polymer exhibits an optical configuration parameter (7.4×10^{-24} cm^3) significantly lower than that corresponding to the latter (20.8×10^{-24} cm^3), as a consequence of the difference of contribution to Δa from the terephthaloyl and 1,4-cyclohexanedicarboxyl residues. Moreover, 10^3 d ln $\Delta a/\mathrm{d}T$ is almost zero for PDGC, whereas it is −1.1 K^{-1} for PDET.

The temperature coefficient of the mean-square and end-to-end distance, d ln $\langle r^2\rangle_0/\mathrm{d}T$, was obtained from the slopes of the plots of Figure 3, by using the standard equation[11,19,20]

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -[\partial \ln (f^*/T)/\partial T]_{p,L} - \beta/(\lambda^3 - 1)$$

where β and λ are the expansion coefficient and elongation ratio, respectively. Values of d ln $\langle r^2\rangle_0/\mathrm{d}T$, obtained at several elongation ratios, are given in the second column of Table IV. According to these results, 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ = 1.5 ± 0.2 K^{-1}. As can be seen in Table II, the value of the temperature coefficient of the unperturbed dimensions of PDGC seems to be somewhat larger than that of PDET chains.

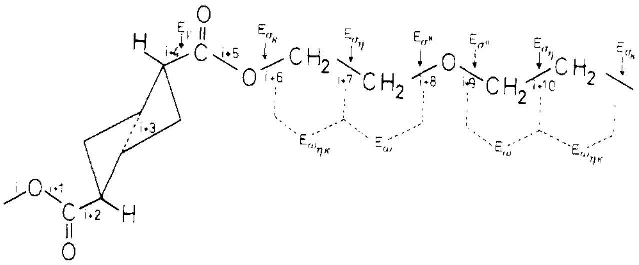

Figure 5. Planar segment of poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate) in the all-trans conformation. First-order and second-order conformational energies are indicated above and below the figure, respectively.

Table IV
Thermoelastic Results for Poly(diethylene glycol 1,4-*trans*-cyclohexanedicarboxylate)

λ	$-10^3\,\partial \ln (f^*/T)/\partial T$	$10^3\,\mathrm{d}\ln \langle r^2\rangle_0/\mathrm{d}T$
1.45	1.90	1.56
1.54	1.66	1.39
1.58	1.41	1.17
1.57	1.62	1.38
1.59	2.05	1.82
1.68	1.61	1.42
1.78	1.46	1.31
		av 1.53 ± 0.21

Theoretical Calculations

The repeating unit of PDGC in all-trans conformation is represented in Figure 5. For purposes of calculations, the cyclohexane ring was substituted by a virtual bond connecting the atoms in the 1,4-positions. With bond lengths of 1.54 Å and bond angles of 111.5° between the C atoms of the rings, the length of the virtual bond is 2.97 Å and its direction makes an angle θ_e = 145.5° with the equatorial C–H bond.[2] Bond lengths and bond angles for the chain were taken from ref 4.

As was indicated above, it was assumed that the modulus of the dipole moment associated to each ester group has a value of 1.89 D, and its direction makes an angle of ca. 123° with the C_{cy}–C* bonds.[16] The dipole moments associated to the ether C–O bonds and to the hydroxyl O–H groups lie along the skeletal bonds and their values are 1.07 and 1.7 D, respectively.

The optical configuration parameter is given by

$$\Delta a = \langle \mathbf{r}^T \hat{\alpha} \mathbf{r} \rangle / \langle r^2 \rangle_0$$

where $\mathbf{r}$ is the end-to-end vector, $\mathbf{r}^T$ its transpose, and $\hat{\alpha}$ the polarizability tensor of the chain. The contribution of the different groups to $\hat{\alpha}$ will be discussed below.

The anisotropic part of the polarizability tensor $\hat{\alpha}_{i+3}$ of a cyclohexane molecule with equatorial–equatorial substitution, having the x axis along the virtual bond, can be expressed by[21]

$$\hat{\alpha}_{i+3} = \Gamma_{CC} \begin{vmatrix} 0.6830 & 0.3357 & 0 \\ 0.3357 & -1.4077 & 0 \\ 0 & 0 & 0.7244 \end{vmatrix}$$

where $\Gamma_{CC} = \Delta\alpha_{CC} - 2\Delta\alpha_{CH}$ and $\Delta\alpha_{CC}$ and $\Delta\alpha_{CH}$ are 0.96 and 0.21 Å^3, respectively. Bonds i through $i + 6$ can be schematically obtained by addition of two molecules of methyl acetate and one molecule of cyclohexane with removal of two molecules of CH$_4$, which because of their symmetry have $\hat{\alpha} = 0$. Consequently, assuming tensor additivity, the contribution of the different bonds of the repeating unit, written in their reference frame, are

$$\hat{\alpha}_i = \hat{\alpha}_{i+1} = \hat{\alpha}_{i+5} = \hat{\alpha}_{i+6} = \mathbf{0}$$

$$\hat{\alpha}_{i+2} = \hat{\alpha}_{i+4} = \hat{\alpha}_{\mathrm{E}}$$

where the contribution of the methyl acetate molecule can be written as[23]

$$\hat{\alpha}_{\mathrm{E}} = \begin{vmatrix} 1.03 & -0.1 & 0 \\ -0.1 & 0.09 & 0 \\ 0 & 0 & -1.12 \end{vmatrix}$$

The remainder of the contributions to the polarizability tensor of the chains are

$$\hat{\alpha}_{i+7} = \hat{\alpha}_{i+10} = \hat{\alpha}_{\mathrm{CC}} - 2\hat{\alpha}_{\mathrm{CH}}$$

$$\hat{\alpha}_{i+8} = \hat{\alpha}_{i+9} = \hat{\alpha}_{\mathrm{CO}} - \hat{\alpha}_{\mathrm{CH}}$$

In these equations

$$\hat{\alpha}_{\mathrm{CC}} = \Delta\alpha_{\mathrm{CC}}\mathbf{K}$$

$$\hat{\alpha}_{\mathrm{CH}} = \Delta\alpha_{\mathrm{CH}}\mathbf{K}$$

$$\hat{\alpha}_{\mathrm{CO}} = \Delta\alpha_{\mathrm{CO}}\mathbf{K}$$

where[22] $\Delta\alpha_{\mathrm{CO}} = 0.58$ Å^3 and $\mathbf{K} = \mathrm{diag}\ (^2/_3, -^1/_3, -^1/_3)$.

According to Flory and co-workers,[16] the sterically favored conformations for dimethyl *trans*-1,4-cyclohexanedicarboxylate molecules are those in which the ester groups are coplanar with the axial CH bonds. The difference between the energies at $\varphi = 180°$ and $\varphi = 0°$, E_γ, about bonds of type $i + 2$ and $i + 4$, was estimated to lie in the range 0–0.2 kcal mol^{-1}. The rest of conformational energy parameters used in the calculations, indicated in Figure 5, were $E_{\sigma\kappa} = 0.4$, $E_{\sigma\eta} = -0.7$, $E_\omega = 0.35$, $E_{\omega\eta\kappa} = 1.4$, and $E_{\sigma''} = 0.57$ kcal mol^{-1}.

Theoretical Results

Values of the configuration-dependent properties were calculated by using standard matrix multiplication methods described in detail elsewhere.[24,25] With the exception of bonds of type $i + 1$, $i + 3$, and $i + 5$, which are restricted to trans states, and bonds of type $i + 2$ and $i + 4$, whose rotational states are located at 0° and 180°, the rotational angles corresponding to the remaining skeletal bonds were assumed to be 0°, ±120°. Following standard conventions, the transformation of coordinates from reference frame $i + 5$ to $i + 4$ and from $i + 3$ to $i + 2$ requires that 180° be added to the rotational angles of $i + 4$ and $i + 2$.

Owing to the uncertainty of the value of the conformational energy E_γ, the dipole moment was calculated as a function of this energy by using the set of conformational energies given above. The results obtained are shown in Figure 6. It can be seen that the dipole moment ratio increases as E_γ decreases reaching a maximum for $E_\gamma = 0$. This behavior is a consequence of the fact that for positive/negative values of E_γ, the favored conformations tctct/ttttt corresponding to $i + 1$ through $i + 5$ in Figure 6 have the dipoles associated with the ester group in a nearly antiparallel direction; hence, the dipole moments ratio decreases as E_γ departs from 0. When E_γ approaches 0, the probability of occurrence of the conformations tcttt and its symmetric tttct, which place the dipole moments in a parallel direction, reaches a maximum, and consequently the value of the dipole moment is also maximum. As a result the dipole moment ratio increases from 0.41 for $E_\gamma = 1$ kcal mol^{-1} to 0.57 for $E_\gamma = 0$. For the same reason the temperature coefficient of the dipole moment increases as E_γ increases.

The temperature coefficient of the unperturbed dimensions also shows a significant dependence on E_γ. In fact $10^3\ \mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ increases from 0.7 to 1.1 K^{-1} when E_γ decreases from 1 to 0.5 kcal mol^{-1}. For values of E_γ in the range 0.5–0 kcal mol^{-1}, the value of the temperature coefficient remains practically constant. PDGC chains exhibit a large value for $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ as a consequence of the fact that the unperturbed dimensions undergo a big increase with decreasing values of the conformational energy $E_{\sigma\eta}$ associated with gauche states about CH$_2$–CH$_2$ bonds of the glycol residue. The value of $10^3\ \mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ changes from −0.084 for $E_{\sigma\eta} = 0.5$ kcal mol^{-1} to 1.28 K^{-1} for $E_{\sigma\eta} = -0.9$ kcal mol^{-1}. However, the sensitivity of the dipole moment ratio and its temperature coefficient to $E_{\sigma\eta}$ is comparatively small. Thus $\langle\mu^2\rangle/(nm^2)$ and $10^3\ \mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ change from 0.55 and 0.58 to 0.60 and 0, respectively, when $E_{\sigma\eta}$ increases from −0.9 to 0.48 kcal mol^{-1}; for values of $E_{\sigma\eta}$ above the latter quantity both $\langle\mu^2\rangle/(nm^2)$ and $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ remain practically constant.

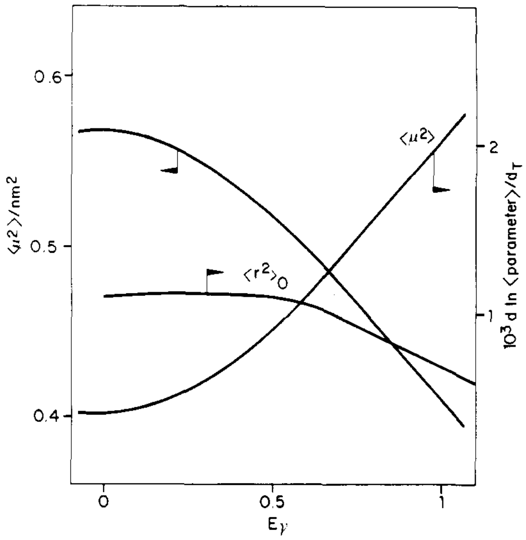

Figure 6. Theoretical values of the dipole moment ratio and the temperature coefficient of both the unperturbed dimensions and the dipole moment, as a *function of the conformational energy* $E_\gamma = E(\pi) - E(0)$ about C$_{\mathrm{cy}}$–C* bonds.

The dipole moment ratio shows a small dependence on the conformational energy associated with gauche rotations of different sign about consecutive pair of bonds of type $i + 6$, $i + 7$. For example $\langle\mu^2\rangle/(nm^2)$ increases from 0.54 to 0.60 when $E_{\omega\eta\kappa}$ decreases from 1.6 to 0.6 kcal mol^{-1}. The sensitivity of the polarity of the chains to the rest of conformational energies is negligible. Accordingly, the use of $E_\gamma = 0$ together with the set of conformational energies indicated above gives a good account of the dipole moment and the temperature coefficient of both the unperturbed dimensions and dipole moments.

Exploratory calculations concerning the dependence of the optical configuration parameter and its temperature coefficient on the conformational energies associated with the rotational states of the skeletal bonds suggest that the optical properties are strongly dependent on $E_{\sigma\eta}$ and E_γ, the sensitivity to the other conformational energies being rather small. The dependence of Δa and $\mathrm{d}\ln\Delta a/\mathrm{d}T$ on $E_{\sigma\eta}$ and E_γ is shown in Figure 7. With the set of conformational energies that successfully interpret the dielectric and thermoelastic results, the values obtained for $10^{24}\Delta a$ and $10^3\ \mathrm{d}\ln\Delta a/\mathrm{d}T$ are 2.32 cm^3 and 2.72 K^{-1}, respectively, in poor agreement with the experimental results 7.42 cm^3 and zero. It can be seen that Δa and its temperature coefficient respectively increase and decrease with increasing value of $E_{\sigma\eta}$, so that to reach a fair agreement between theory and experiment would require that CH$_2$–CH$_2$ bonds are restricted to trans states. It should be pointed out, however, that the value $E_{\sigma\eta} = -0.7$

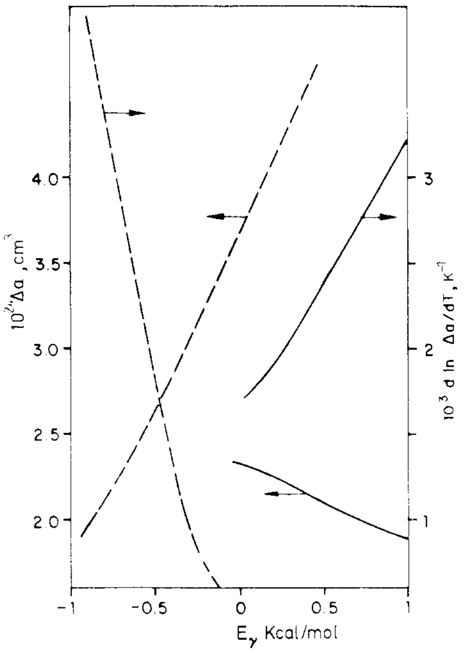

Figure 7. Theoretical values of the optical configuration parameter Δa as a function of the conformational energy $E_\gamma = E(\pi) - E(0)$ about C_{cy}–C* bonds (continuous line) and the conformational energy associated with gauche states about the CH_2–CH_2 bonds of the glycol residue (dashed line).

to −0.8 kcal mol^{-1} is well settled for this magnitude. Both Δa and d ln $\Delta a/dT$ approach the experimental results as the value of E_γ approaches zero.

As can be seen in Table III, the difference between the experimental and theoretical values of $10^{24}\Delta a$ (5.1 cm^3) for PDGC is much lower than the difference obtained for this property (17 cm^3) in the case of PDET chains.[4] These results suggest that intermolecular interactions that presumably enhance the apparent optical anisotropy of the chains are less important in the former polymer than in the latter. Since PDET can schematically be obtained by substituting the cyclohexane in PDGC for benzene, specific intermolecular interactions between terephthaloyl residues may be held responsible for the great discrepancy observed between theory and experiment in the case of PDET chains. It should be stressed that in general better agreement between theory and experiments is obtained for asymmetric chains than for symmetric ones.[26-28] Additional studies that could explain this experimental fact are needed.

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Registry No. (Dimethyl 1,4-*trans*-1,4-cyclohexanedicarboxylate)(diethylene glycol) (copolymer), 114506-20-6; (dimethyl 1,4-*trans*-1,4-cyclohexanedicarboxylate)(diethylene glycol) (SRU), 26523-40-0; (2,4-bis(*p*-isocyanatobenzyl)phenylisocyanate)(diethylene glycol)(dimethyl *trans*-1,4-cyclohexanedicarboxylate) (copolymer), 114506-21-7.

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