Configurational Properties of Polyesters with Cyclohexane Rings Incorporated in the Main Chain

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ABSTRACT: Poly(oxymethylene-1,4-*cis*-cyclohexylenemethyleneoxysebacoyl) (PCCS) and poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxysebacoyl) (PTCS) were synthesized by condensation of the corresponding cis and trans isomers of 1,4-cyclohexanedimethanol with sebacic acid. Values of the mean-square dipole moments $\langle\mu^2\rangle$ of both polyesters were determined from dielectric constant measurements on dilute solutions of the polymers in benzene. The values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ at 30 °C were found to be 0.983 and 0.631 for PCCS and PTCS, respectively, and the temperature coefficient of the dipole moments for the former was significantly lower than for the latter. The values of the temperature coefficient of the unperturbed dimensions $10^3 \mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T$ of the polyesters, determined from thermoelastic experiments carried out on networks obtained by cross-linking hydroxyl-terminated polymers with an aromatic triisocyanate, were -0.93 ± 0.25 and -1.26 ± 0.34 K^{-1} for PCCS and PTCS, respectively. Theoretical calculations carried out with the rotational isomeric state model gave values of $\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T$ in very good agreement with the experimental results. Fair agreement between theory and experiment was also found in the case of the dipole moments of the chains.

Introduction

Owing to the conformational wealth of the cyclohexane ring (twist, boat, and chair forms),[1] the study of polymers with 1,4-disubstituted cyclohexane rings incorporated in the main chain is of great importance for a deeper insight into the correlation between structure and properties. The chair conformation has an energy of 5.5 and 5.0 kcal mol^{-1} lower than the boat and twist forms, respectively. Substituted cyclohexanes in the chair conformation have been used to prepare molecular chains.[1-3] Interconversion between the two possible chair conformations interconverts equatorial into axial substituents and vice versa without changing the configuration cis or trans of the rings.

Alicyclic polyformals have been prepared by condensation of *trans*- and *cis*-1,4-cyclohexanedimethanol with paraformaldehyde.[4] The polymer obtained from the trans isomer (PTCDM) is crystalline and melts[4,5] at 86 °C whereas that obtained from the cis isomer (PCCDM) is amorphous at room temperature.[6] Both polymers, however, have similar polarity. Actually the high preference for $g^{\pm}g^{\pm}$ conformations of the oxymethylene sequences, in which the dipole moments of pairs of COC bonds are nearly antiparallel, is responsible for the relatively low polarity exhibited by both polymers.[5] It would be important to extend these studies to aliphatic polyesters resulting from the condensation of aliphatic acids and 1,4-cyclohexanedimethanol. In contrast with what occurs in alicyclic polyformals, symmetric cis alicyclic polyesters are also crystalline, although the melting points of these polymers are somewhat lower than those of the corresponding trans isomers.[7] Significant differences might also occur in their polarities.

The present study was undertaken with the aim of investigating the dielectric and thermoelastic properties of symmetric cycloaliphatic polyesters prepared from 1,4-cyclohexanedimethanol and sebacic acid. Although the isomer poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxysebacoyl) (PTCS) has a relatively high melting point (70 °C), the high values of the crystallization induction time (at relatively large undercoolings) exhibited by networks prepared from these chains permitted measurement of the temperature coefficient of the unperturbed dimensions of the polymer. Similar measurements were performed on poly(oxymethylene-1,4-*cis*-cyclohexylenemethyleneoxysebacoyl) (PCCS). The dipole moments of both PTCS and PCCS chains, as well as the temperature coefficients of the dipole moments and the unperturbed dimensions, were also theoretically calculated. By comparison of theory and experiment, the values of the energies associated with some conformations were estimated.

Experimental Part

Synthesis of the Polyesters. *trans*-1,4-Cyclohexanedimethanol was isolated from the commercial mixture of cis and trans isomers (Eastman Kodak) by recrystallization from ethyl acetate at −20 °C. *cis*-1,4-Cyclohexanedimethanol was obtained by acetylation of commercial 1,4-cyclohexanedimethanol with acetic anhydride, separation of the *trans*-1,4-cyclohexanedimethanol diacetate by recrystallization from *n*-pentane at low temperature, and hydrolysis of the cis isomer with aqueous sodium hydroxide.[8] The purity of both cis and trans isomers, determined by ^{1}H NMR spectroscopy, was greater than 99%.

PCCS was prepared by dissolving 8.60 g (0.06 mol) of *cis*-1,4-cyclohexanedimethanol and 12.07 g (0.06 mol) of sebacic acid in 100 mL of dry *m*-xylene. The reaction was carried out at 160 °C under a nitrogen atmosphere for 15 h, using 0.2 g of *p*-toluenesulfonic acid as catalyst; the water formed during the reaction was continuously separated by means of a Dean–Stark distillation trap. In order to obtain hydroxyl-terminated chains, a 1% excess of cyclohexanedimethanol was added and the reaction was allowed to proceed for an additional 5 h. The solution was poured into cold methanol, washed three times with methanol, and dried under vacuum for 24 h: yield 93%; η_{inh} (0.5% (w/v) in chloroform) = 0.46 dL/g. PTCS was synthesized in a similar way: yield 92%; η_{inh} = 0.43 dL/g. Both polyesters were fractionated at 35 °C using chloroform/methanol as the solvent/nonsolvent system. The number-average molecular weights of the fractions were determined in chloroform with a Knauer vapor pressure osmometer. The values of the number-average molecular weight for the fractions used in the experimental work were 7200 and 4600 for PCCS and PTCS, respectively.

The ^{1}H NMR spectra of the monomers and the ^{13}C NMR spectra of the polymers were registered on a Bruker WP80SY at 80 and 20.1 MHz, respectively, using deuterated chloroform as solvent and tetramethylsilane as internal standard.

Preparation of the Networks. Networks of PCCS and PTCS were prepared by end-linking the corresponding hydroxyl-terminated polyesters with 2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate. In each case stoichiometric amounts of polymer and cross-linking agent, dissolved in a small amount of ethanol-free dried chloroform, were cast in a Teflon mold. The solvent was removed by evaporation and the mixture of polymer and triisocyanate was kept at 70 °C for 2 days. The networks were extracted with chloroform for 48 h. The soluble fractions of PTCS and PCCS were 10.0% and 11.1%, respectively.

Thermoelastic and Birefringence Measurements. Small strips of cross-sectional area 0.02 cm^2 were cut from the cross-

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linked sheets and mounted between two clamps, the mobile upper clamp being attached to a pressure transducer (Gould Statham, Model UC3) whereas the lower clamp was kept fixed. The sample was surrounded by a double-walled glass jacket, the temperature of which was kept constant (±0.1 °C) by pumping water from a thermostat (Frigomix). The strips were streched at the highest temperature of the experiment, and elastic equilibrium was reached after a short time. Then the temperature was decreased, the equilibrium was reestablished, and the value of the stress was measured. The thermoelastic behavior of the networks was determined in the intervals 40–80 and 50–85 °C for PCCS and PTCS, respectively. The cubic expansion coefficients, measured with a Perkin-Elmer thermomechanical analyzer TMS-2, were found to be 7.2×10^{-4} and 7.6, 10^{-4} K^{-1} for PTCS and PCCS, respectively.

In parallel with the thermoelastic measurements, the birefringence of the elongated networks was determined. The apparatus used is described in detail in the literature.[8-10] The light source was a 2-mW, 632.8-nm He–Ne laser, the polarizer and analyzer were Glan Thompson prisms, and the compensator was a Babinet Soleil type.

DSC Measurements. The melting temperatures of PCCS and PTCS were determined on fractions of number-average molecular weight 7200 and 4600, respectively, with a Perkin-Elmer DSC-4 calorimeter fitted with a Data Station at 5 °C/min. The values of these quantities were 50 and 70 °C, respectively.

Dielectric Experiments. Dielectric constants of solutions of the polymers in benzene were measured at 30, 40, 50, and 60 °C using a capacitance bridge (General Radio) and a three-terminal cell operating[11] at 10 kHz. Values of the refractive indices of the solutions were also obtained at the same temperatures using a Chromatix KHX-16 laser differential refractometer.

Thermoelastic Results

Of great importance in the analysis of the thermoelastic results is the amount of crystallization occurring in the elongated networks. The crystallization behavior of PTCS under strain differs from that observed for PCCS. Thus, whereas in the latter polymer the stress decreases to zero at the end of the crystallization process,[7] the decrease is only 50% of the starting force in the case of the former. This suggests that in the cis isomer, the crystallites are mainly oriented in the direction of the elongation axis and the orientation effect overcomes the reduction in volume that occurs in the network when crystallization takes place; however, in PTCS the crystallites probably form a wide variety of angles with the elongation axis and hence the reduction in stress is lower. This is reflected in the birefringence of the networks. The changes in Δn that take place in PCCS at the beginning of the crystallization process are much higher than those observed in PTCS.

Strain birefringence experiments were carried out on PCCS networks for values of the elongation ratio lying in the range 1.16–1.86. At 10 °C the crystallization induction time decreases as α increases. Times were 120 min for α = 1.16 and 30 min for α = 1.86. This quantity also increases with temperature; for example, for α = 1.86 and t = 23.1 °C, the value of the induction time is 120 min. In the case of strained PTCS, crystallization is developed at temperatures much higher than in the networks prepared from PCCS chains. At 50 °C and for elongation ratios of 1.17 and 1.33, crystallization is not detected in a period of time of 48 h. In view of the results, the thermoelastic experiments were performed in the interval 40–80 and 50–85 °C for PCCS and PTCS, respectively. In these temperature ranges there is certainty that crystallinity that might alter the thermoelastic results will not be developed in the strained networks.

Force–temperature results, expressed in terms of ln (f^*/T), where f^* is the elastic force referred to the undistorted cross-sectional area and T is the absolute temperature, are shown as an example in Figure 1 for PCCS networks. For each value of α the thermoelastic data fit extremely well to straight lines and are highly reversible as is required for subsequent conformational analysis. The results were interpreted in terms of the standard equation[12-14]

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

where f_e/fT is the internal energy component which serves as a measure of nonideality of the elastomeric networks. The values of d ln $\langle r^2 \rangle_0/\mathrm{d}T$, obtained at several elongation ratios, are given in the second and fourth columns of Table I for PTCS and PCCS, respectively. It can be observed that the unperturbed dimensions of the chains exhibit negative temperature dependence and the absolute value of d ln $\langle r^2 \rangle_0/\mathrm{d}T$ is somewhat larger for the trans than for the cis isomer.

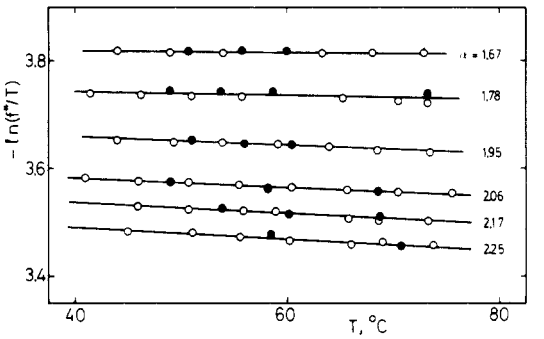

Figure 1. Thermoelastic results for the PCCS network. Open and filled circles refer to experiments carried out at decreasing and increasing temperatures, respectively.

Table I
Thermoelastic Results for PTCS and PCCS Networks

PCCS		PTCS	
α	-10^3 d ln $\langle r^2 \rangle_0/\mathrm{d}T$, K^{-1}	α	-10^3 d ln $\langle r^2 \rangle_0/\mathrm{d}T$, K^{-1}
1.63	1.24	1.17	0.89
1.67	0.40	1.20	0.95
1.78	0.54	1.24	0.94
1.85	0.94	1.27	1.73
1.95	0.86	1.28	1.10
2.06	0.95	1.33	1.57
2.07	1.01	1.33	1.62
2.17	1.08		
2.25	1.08		
2.42	1.16		
	av 0.93 ± 0.25		av 1.26 ± 0.34

Values of the derivatives $\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$ and $\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$ were obtained, as usual, from plots of the dielectric increments of the solution $(\epsilon - \epsilon_1)$ and the increments of the squares of the index of refraction $(n^2 - n_1^2)$ against the weight fraction w of the solute. Illustrative plots of this kind are shown in Figure 2 for PCCS at 30 and 60 °C, and the results obtained for both polymers over the entire temperature range 30–60 °C are given in the second and third columns of Table II. Values of the mean-square dipole moments $\langle \mu^2 \rangle$ of the chains were calculated by the method of Guggenheim and Smith.[15,16] The results, expressed as the dipole moment ratio $\langle \mu^2 \rangle / nm^2$, where nm^2 is the dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed, are shown in Table II. We estimate the uncertainty of these values to be approximately 10%. In the determination of the dipole moment ratio, μ_E = 1.89 D was used for each of the two ester groups of the repeating unit.[17] The experimental results indicate that PTCS is less polar than the cis isomer;

Table II
Summary of Dielectric Results

	PTCS			PCCS		
T, °C	$d(n^2 - n_1^2)/dw$	$d(\epsilon - \epsilon_1)/dw$	$\langle\mu^2\rangle/nm^2$	$d(n^2 - n_1^2)/dw$	$d(\epsilon - \epsilon_1)/dw$	$\langle\mu^2\rangle/nm^2$
30	0.006	1.58	0.631	0.012	2.47	0.983
40	0.01	1.56	0.654	0.020	2.37	0.991
50	0.02	1.55	0.681	0.031	2.27	0.997
60	0.03	1.52	0.709	0.040	2.18	1.004

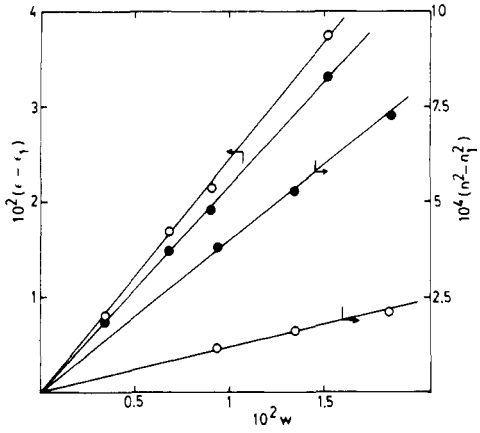

Figure 2. Increments in dielectric constant and squared index of refraction for solutions of PCCS in benzene at 30 (○) and 60 °C (●).

however, the temperature dependence of the dipole moments of the former polyester is significantly larger than that of the latter.

Theoretical Calculations

The isomerization of *cis*- and *trans*-1,4-cyclohexanedicarboxylic acids during the preparation of cycloaliphatic polyesters as well as the isomerization of 1,4-cyclohexanedimethanethiol during its condensation with paraformaldehyde and propionaldehyde have been reported.[18,19] Consequently, the ^{13}C NMR spectra of both PCCS and PTCS chains were registered in order to investigate whether isomerization processes also take place during the synthesis of the polyesters used in this study. Figure 3 shows the spectra obtained for PCCS and PTCS and the assignement of the peaks to the different carbons. As can be seen, the two spectra are clearly different, the differences appearing in the carbons of the cyclohexane rings and in the methylene carbons of the CH_2OOC groups. The carbons of the sebacoyl moiety are not affected by the configuration of the cyclohexane ring. In the case of PCCS the rapid conformational interchange does not allow the differentiation between the axial and the equatorial methylenes (CH_2OOC). For this reason only one peak would be expected for these carbons as well as for the other carbons of the cyclohexane ring. This is confirmed in Figure 3, where it can be seen that the resonances of these carbons appear as single peaks at higher field than the corresponding ones in the trans polymer. It can be concluded that during the polymerization reaction between sebacic acid and both *cis*- and *trans*-1,4-cyclohexanedimethanol, no isomerization occurs and 100% *cis*- and 100% *trans*-poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) are obtained.

In Figure 4 are represented the repeating units of the PCCS and PTCS chains in the all-trans rotational conformation. In order to facilitate the calculations, the cyclohexane ring was substituted by a virtual bond connecting the atoms in the 1,4 positions; assuming bond lengths[20,21] of 1.54 Å and bond angles[21] of 111.5° between the carbon atoms of the ring, the length of the virtual

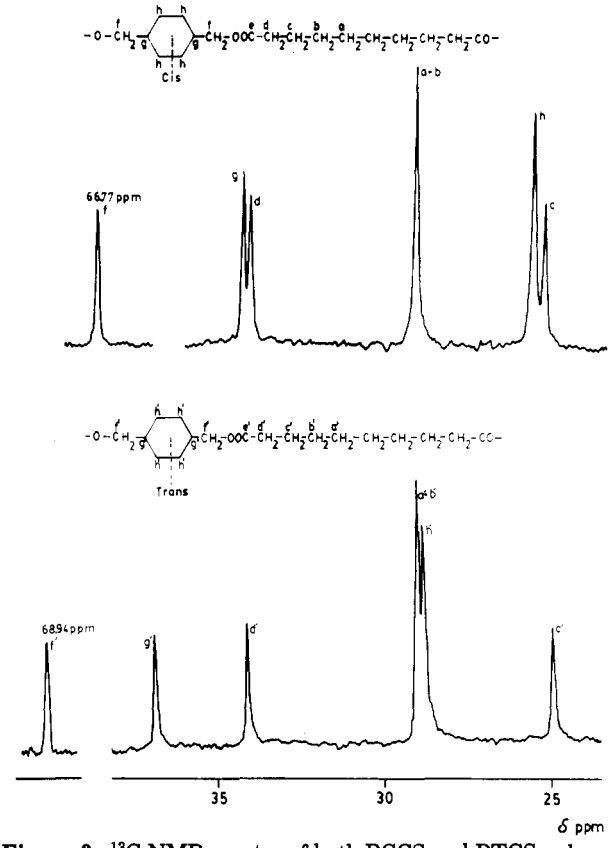

Figure 3. ^{13}C NMR spectra of both PCCS and PTCS polymers.

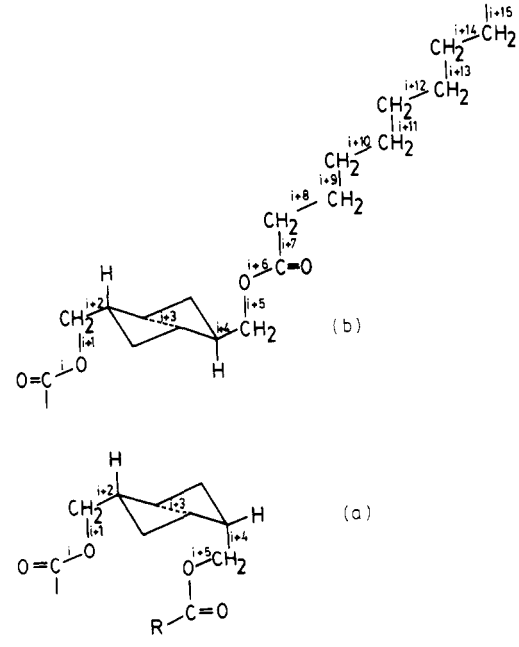

Figure 4. Repeating units of PCCS (a) and PTCS (b) in the all-trans conformation.

bonds is 2.97 Å and its direction makes angles $\theta_e = 148.5°$ and $\theta_a = 101.7°$ with equatorial and axial C–H bonds, respectively.[6] The rest of the skeletal bond angles were

assumed to have the following values:[22] ∠CO–O–CH_2 = 113°, ∠O–CH_2–CH_2 = 110°, ∠O–CO–CH_2 = 114°, and ∠CH_2–CH_2–CH_2 = 110°. Bond lengths of 1.53, 1.33, and 1.43 Å were used for C–C, O–CO, and C–O skeletal bonds, respectively. As stated above, μ_E = 1.89 D for the dipole moment of each ester group; the direction of the dipole was chosen so as to make an angle of 123° with the R–C* bond.[17] The values of the dipole moments associated with the skeletal bonds O–H and O–CH_2 of the end groups ($HOCH_2$) were considered to be 1.7 and 1.07 D, respectively.[11]

With the standard conventions concerning Cartesian coordinate systems,[23] the T matrix required to transform the coordinates from the reference frame $i + 5$ to $i + 4$ or from $i + 2$ to $i + 1$ in Figure 4 will require that 180° be added to the ϕ_v rotation angles of bands $i + 4$ and $i + 2$; in the transformation of the coordinates from $i + 4$ to $i + 3$, ϕ = 0 and 180° for the trans and cis isomers, respectively. Bonds of type i, $i + 3$, and $i + 6$ are restricted to a single state for both trans and cis isomers and the matrix of statistical weights associated with these bonds consists of a column of ones followed by two columns of zeros. For all other skeletal bonds the rotational states were considered to be located at 0 and ±120°, with the exception of the CH_2–O skeletal bonds, whose rotational angles were assumed to be located[23] and 0 and ±95°.

Calculations of intramolecular interactions about bonds of type $i + 1$ (or $i + 5$ in the cis and trans isomers) and $i + 2$ (or $i + 4$ in the trans isomer), carried out with Lennard-Jones potentials, suggest that the energy of the gauche states about these bonds is, respectively, E_{σ_A} = 1.2 and E_{σ_B} = −0.4 kcal mol^{-1} with respect to that of the alternative trans states. The same type of calculation about bonds of type $i + 4$ in the cis isomer indicates that severe interactions between the oxygen atom and the CH_2 groups of the cyclohexane ring occur in the trans conformation which are alleviated in the gauche conformation. The energy of the gauche states about these bonds was found to be ca. 4 kcal mol^{-1} below that of the corresponding trans states and, therefore, the statistical weight matrix for the $i + 4$ skeletal bond was considered to be

$$U_{i+4} = \begin{bmatrix} 0 & 1 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The energy of the gauche states about bonds of type $i + 7$ (or $i + 15$) and $i + 8$ (or $i + 14$) was assumed to be similar to that of the alternative trans states. It should be pointed out that preliminary calculations showed that the configurational properties analyzed in this work are almost insensitive to the energy of the gauche states about these bonds for values of this quantity ranging between −0.5 and +0.9 kcal mol^{-1}. Gauche states about bonds of type $i + 9$ through $i + 13$ give rise to first-order CH_2–CH_2 interactions, which have an energy[23] 0.5 kcal mol^{-1} above that of the alternative trans states. Finally, the ω factor (ω = $\exp(-E_\omega/RT)$) was considered irrelevant for all pairs of bonds with the exception of those in which CH_2···O or CO···CH_2 second-order interactions occur, where its value was assumed to be 0.1 at 30 °C.

Values of the dipole moment ratio and the temperature coefficients of both the dipole moments and the unperturbed dimensions for chains with molecular weight similar to that of the samples studied experimentally were calculated by using standard matrix multiplication methods.[22,23] The calculations were performed at 30 °C for the dielectric quantities and for d ln $\langle r^2\rangle_0/$dT. All of these properties were found to be quite sensitive to E_{σ_A} and E_{σ_B}

Table III
Influence of E_{σ_A} and E_{σ_B} on the Dipole Moment Ratio and Its Temperature Coefficient[a]

		PTCS		PCCS	
E_{σ_A}	E_{σ_B}	$\langle\mu^2\rangle/nm^2$	10^3 d ln $\langle\mu^2\rangle/$dT	$\langle\mu^2\rangle/nm^2$	10^3 d ln $\langle\mu^2\rangle/$dT
0.064	−0.4	0.881	0.539	0.970	−0.145
0.200		0.875	0.559	1.013	−0.109
0.420		0.855	0.674	1.078	−0.314
0.730		0.813	0.932	1.154	−0.453
0.064	−0.56	1.077	0.804	0.956	0.111
0.200		0.839	0.821	0.998	−0.087
0.420		0.825	0.866	1.060	−0.301
0.730		0.785	1.114	1.140	−0.452

[a] E_{σ_A} and E_{σ_B} are given in kcal mol^{-1}.

Table IV
Influence of E_{σ_A} and E_{σ_B} on the Characteristic Ratio and Its Temperature Coefficient[a]

		PTCS		PCCS	
E_{σ_A}	E_{σ_B}	$\langle r^2\rangle_0/nl^2$	-10^3 d ln $\langle r^2\rangle_0/$dT	$\langle r^2\rangle_0/nl^2$	-10^3 d ln $\langle r^2\rangle_0/$dT
0.064	−0.4	6.11	0.592	4.42	0.500
0.200		6.29	0.704	4.51	0.586
0.420		6.57	0.899	4.64	0.705
0.730		6.96	1.070	4.82	0.821
0.064	−0.56	6.19	0.632	4.53	0.547
0.200		6.37	0.733	4.62	0.633
0.420		6.63	0.925	4.74	0.740
0.730		7.06	1.100	4.93	0.857

[a] E_{σ_A} and E_{σ_B} are given in kcal mol^{-1}.

and their values as a function of these conformational energies are given in Table III for the dipole moment ratio and its temperature coefficient and in Table IV for the characteristic ratio $\langle r^2\rangle_0/nl^2$ and is temperature coefficient. The dielectric properties are almost insensitive to the conformational energies associated with the gauche states about the skeletal bonds of the sebacoyl residue; the temperature coefficient d ln $\langle r^2\rangle_0/$dT is slightly sensitive to the gauche population about bonds (CH_2–CH_2) that give rise to first order CH_2···CH_2 interactions.

The theoretical calculations show that the dipole moment ratio of PCCS is somewhat higher than that of PTCS, in agreement with the experimental results. In the planar all-trans conformation of PTCS, presented in Figure 4, the dipole moments of the ester groups are in nearly antiparallel direction and the dipole moment of this conformation is relatively small. Consequently, changes in conformational energies of the skeletal bonds corresponding to the glycol residue should increase the dipole moments of PTCS chains. These qualitative predictions are confirmed in Table III, where it can be seen that in increasing E_{σ_A} from 0.06 to 0.73 kcal mol^{-1}, $\langle\mu^2\rangle/nm^2$ decreases from 0.881 to 0.813 if the value of E_{σ_B} is assumed to be −0.4 kcal mol^{-1}. This change is somewhat larger (from 1.007 to 0.785) if E_{σ_B} = −0.56 is used in the calculations. In the same way, the dipole moment ratio of PTCS also increases as E_{σ_B} decreases for any value of E_{σ_A}. The changes in the dipole moment ratio with E_{σ_A} and E_{σ_B} are relatively small due to the fact that the $i + 4$ skeletal bond is practically restricted to the gauche conformation and, therefore, the all-trans conformation for which the dipole becomes very small is excluded. For this reason the dipole moments of these chains are larger than those of PTCS.

In the case of PTCS chains an increase in temperature gives rise to an increase in the gauche population about both $i + 1$ and $i + 4$ skeletal bonds and a decrease about $i + 2$ and $i + 6$ bonds. Since departure from the trans conformation increases the dipole moments of the chains,

the positive change in temperature causes an increase in the dipole moments in the former case that overcomes the negative effect of the latter. For PCCS an increase in temperature causes a slight decrease in the gauche population about the $i + 2$ and $i + 4$ skeletal bonds. Consequently, the theory suggests a slight decrease of the dipole moments with increasing temperature, in disagreement with the experimental results, which predict a small, but positive, temperature coefficient.

The temperature dependence of the unperturbed dimensions of PTCS and PCCS was evaluated by using the structural parameters and conformational energies given above. The results obtained are shown in Table IV. It can be seen that for both isomers, the characteristic ratio $\langle r^2\rangle_0/nl^2$ is moderately dependent on E_{σ_A} and E_{σ_B} in the sense that $\langle r^2\rangle_0/nl^2$ increases with increasing values of these conformational energies. Moreover, the unperturbed dimensions of these chains are only slightly sensitive to the gauche conformations about the $i + 9$ through $i + 12$ skeletal bonds ($\partial \ln \langle r^2\rangle_0/\partial \ln \sigma = -0.08$). An increase in temperature decreases the characteristic ratio of PTCS and PCCS and, consequently, both polymers exhibit a negative temperature dependence, in agreement with the experimental results. Assuming $E_{\sigma_A} = 0.73$ kcal mol^{-1} (Table IV) the values of 10^3 d ln $\langle r^2\rangle_0/dT$ are -1.1 and -0.86 for PTCS and PCCS, respectively, which compare very favorably with the experimental values (-1.26 and -0.93) found for these polymers. Using this same value for E_{σ_A} and assuming $E_{\sigma_B} = -0.56$ kcal mol^{-1}, we find that the values of the dipole moment ratio are 0.785 for PTCS and 1.14 for PCCS, in fair agreement with the experimental results, whose values are 0.630 for the former polymer and 0.983 for the latter. There is semiquantitative agreement between the theoretical and experimental values of d ln $\langle\mu^2\rangle/dT$ for PTCS chains. The theory predicts for this coefficient a value of 1.1×10^{-3} K^{-1}, which is significantly lower than the experimental one (3.9×10^{-3} K^{-1}). In the case of PCCS chains, the theoretical value of d ln $\langle\mu^2\rangle/dT$ (-0.45×10^{-3} K^{-1}) is small and of opposite sign from the experimental one (0.69×10^{-3} K^{-1}). It should be pointed out that small errors involved in the measurements of the dipole moments may alter significantly the values of d ln $\langle\mu^2\rangle/dT$ and, therefore, this quantity is less suitable than the dipole moment ratio to compare theory and experiment.

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Registry No. PCCS, 96929-57-6; PTCS, 96929-58-7; (*trans*-1,4-cyclohexanedimethanol)·(sebacic acid) (copolymer), 96929-55-4; (*cis*-1,4-cyclohexanedimethanol·(sebacic acid) (copolymer), 96929-56-5; 2,4-bis(4-isocyanatobenzyl)phenyl isocyanate, 4326-63-0.

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