Langevin offered an interpretation of this result in terms of a limiting slow relaxation process associated with the transverse viscosity. Our temperature dependence may be similarly explained. Thus, μ depends on frequency and, for example, has a frequency dependence of the form proposed by Mann and Du,[21]

$$\mu = \mu^{\infty} + [\tau\theta/(1 - i\omega\tau)] \quad (4)$$

where τ is the relaxation time, θ is the scaling constant of the non-Newtonian response of the system, and μ^{∞} is the high-frequency limiting viscosity which may be assumed to be zero. According to eq 4, the imaginary part of μ has a maximum value when $\omega\tau = 1$ (i.e., $\tau = 1/\omega$). Thus, since the relaxation time, τ, is expected to become longer as the temperature is decreased, if $\omega\tau < 1$ in the temperature range of interest, μ increases as the temperature decreases; if $\omega\tau > 1$, μ decreases with decreasing temperature. It follows that, if the predominant relaxation time of PVAc is greater than $1/\omega$ and if of PnBMA is less than $1/\omega$, different temperature dependences of μ would be observed. To our knowledge, there is no experimental data to support or test this assumption about the relaxation time. However, since it has been suggested that PVAc is horizontally oriented[19,31] and PnBMA is more nearly vertically oriented,[19] it may follow that the relaxation time, τ, associated with the transverse motion of PVAc is longer than that of PnBMA.

In summary, studies of this sort to probe the transverse viscosity contribution to film viscoelasticity might well bring forth new insight into the chain conformational dynamics at the air-water interface. With the present study, we would suggest that the relaxation processes associated with transverse motions may be of significance in defining the interfacial conformational dynamics; at least we cannot outright ignore it under all circumstances.

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Registry No. PVAc, 9003-20-7; PnBMA, 9003-63-8.

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Influence of the Acid Residue on the Polarity of Cycloaliphatic Polyesters

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ABSTRACT: The cis and trans isomers poly(1,4-cyclohexanedimethanol adipate) (PCCDA and PTCDA) and poly(*trans*-1,4-cyclohexanedimethanol succinate) (PTCDS) were synthesized by condensation of the corresponding cis and trans isomers of 1,4-cyclohexanedimethanol with adipic acid and succinic acid, respectively. The values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ at 30 °C for PCCDA, measured in benzene and dioxane solutions, were found to be 0.950 and 0.914, respectively. The values of the dipole moment ratio of PTCDA and PTCDS, determined from dielectric constant measurements in dilute dioxane solutions at 50 and 70 °C, were 0.596 and 0.454, respectively. In general, the trans isomers exhibit lower polarity than the cis, and the values of the dipole moment ratio of the former polyesters seem to decrease as the number of methylene groups in the acid residue decreases. The trans isomers also exhibit a positive and larger temperature coefficient than the cis isomers. Theoretical calculations carried out with the rotational isomeric state model give a good account of the experimental results, assuming that gauche states about CH_2–CO bonds of the acid residue are preferred over the alternative trans states. The theoretical analysis also suggests that the trans states about the β CH_2–CH_2 bonds of the acid residue are preferred over the corresponding gauche states.

Introduction

Polyesters and polyformals obtained by reaction of cyclohexanedimethanol with aliphatic acids and formaldehyde, respectively, were recently studied with the aim of analyzing the influence of the substitution (equatorial–axial or equatorial–equatorial) of the hydrogen atoms

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located at the 1,4-carbon atoms of the rings on the conformation-dependent properties of these polymers.[1-3] In general the polarity of cycloaliphatic polyformals, expressed by the mean-square dipole moments, was found to be unaffected by the type of hydrogen atoms substituted, but in the polyesters obtained by condensation of cyclohexanedimethanol with sebacic acid, the cis isomer (e–a substitution) was found to be significantly more polar than the alternative trans isomer (e–e substitution).[2]

The theoretical calculations of the conformation-dependent properties of aliphatic and cycloaliphatic polyesters require knowledge of the energies associated to the rotational states about CH_2CH_2–$COOCH_2$ bonds, whose values are at present matter of controversy.[4-8] Thus both positive and negative values can be found in the literature for the energy E_{σ_a} of the C=O/C—H eclipsed form with respect to that of the alternative C=O/C—C eclipsed form. By assuming $E_{\sigma_a} > 0$, theoretical values were obtained for the dipole moment ratio $\langle\mu^2\rangle/nm^2$ and its temperature coefficient of poly(neopentyl glycol succinate) (PNS), which are in disagreement with the experimental results.[9,10] Moreover, negative values were obtained for the theoretical temperature coefficient of the unperturbed dimensions $d \ln \langle r^2\rangle_0/dT$ of both PNS and poly(neopentyl glycol adipate) (PNA), whereas the experimental values obtained from thermoelastic experiments for this quantity are positive in both cases.[9,10] To bring theory close to experiment, it is necessary to assume that gauche states about CH_2CH_2–$COOCH_2$ bonds have equal or lower energy than the alternative trans states.

The conformational energy associated with the central CH_2–CH_2 bonds of the succinyl residue is also controversial. NMR spectroscopic studies on succinic acid and dimethyl succinate[8,11-13] suggest that the gauche conformation is more stable than the trans, at variance with the results obtained for PNS chains.[10]

The aim of this paper is to analyze the influence of the number of methylene groups of the acid residue on the dielectric properties of cycloaliphatic polyesters, using as models the cis and trans isomers of poly(1,4-cyclohexanedimethanol adipate) (PCCDA and PTCDA) and poly(1,4-*trans*-cyclohexanedimethanol succinate) (PTCDS). For this purpose the dipole moments of the chains as a function of temperature were measured and the results discussed in terms of the conformational energies associated to the rotational states about the skeletal bonds of the acid residues.

Experimental Section

Synthesis and Characterization of the Polyesters. *cis*-1,4-Cyclohexanedimethanol was obtained by acetylation of the mixtures of cis/trans (30/70) isomers of commercial cyclohexanedimethanol (Eastman Kodak) with acetic anhydride, further separation of *trans*-1,4-cyclohexanedimethanol acetate by recrystallizaton of *n*-pentane at room temperature, and hydrolysis of the cis isomer with sodium hydroxide.[2] *trans*-1,4-Cyclohexanedimethanol was obtained directly from *cis*/*trans*-1,4-cyclohexanedimethanol by crystallization from ethyl acetate at −20 °C.

PCCDA, PTCDA, and PTCDS were obtained by reaction of equimolecular amounts of the corresponding acids and glycols. The polycondensation was performed at 160 °C in xylene solutions, under nitrogen atmosphere, with *p*-toluenesulfonic acid as catalyst. The water formed during the reaction was separated by means of a Dean-Stark distillation trap. In the final steps of the reaction 1% excess of glycol was added with the aim of obtaining hydroxyl-terminated polyesters. The polymers were precipitated from the reaction medium with methanol, dissolved in benzene, and precipitated again with methanol. Fractions of number-average molecular weights 10 000, 11 000, and 5800 for PTCDA, PCCDA, and PTCDS, respectively, were used in the dielectric measurements. The melting temperatures of the fractions, measured at 5 °C/min with a Perkin-Elmer DSC-4 calorimeter, amounted to 135, 80, and 150 °C for PTCDA, PCCDA, and PTCDS, respectively.

Table I
Summary of Dielectric Results for Poly(*cis*-1,4-cyclohexanedimethanol adipate) (PCCDA), poly(*trans*-1,4-cyclohexanedimethanol adipate) (FTCDA), and poly(*trans*-1,4-cyclohexanedimethanol succinate) (PTCDS)

polymer	solvent	T, °C	$2n_1\, dn/dw$	$d\epsilon/dw$	$\langle\mu^2\rangle/nm^2$
PCCDA	benzene	30	0.00_7	2.86_9	0.950
		40	0.01_8	2.74_1	0.953
		50	0.02_9	2.64_5	0.967
		60	0.03_9	2.53_3	0.972
PCCDA	dioxane	30	0.18_5	3.15_0	0.914
		40	0.19_6	2.99_9	0.916
		50	0.20_4	2.85_0	0.916
		60	0.21_4	2.72_0	0.919
PTCDA	dioxane	50	0.19_3	2.05_1	0.596
		60	0.20_1	2.01_1	0.610
		70	0.20_9	1.94_7	0.615
PTCDS	dioxane	70	0.22_6	1.66_1	0.454

Dielectric Measurements. Dielectric constants ϵ of the polymers in dioxane, and also in benzene in the case of PCCDA, were obtained by using a capacitance bridge (General Radio, type 1620 A) and a three-terminal cell. Differences between the refractive indices of the solutions and of the solvent, n_1, were measured at 638 nm with a Chromatix KXH differential refractometer. Values of the mean-square dipole moments were obtained by means of the equation of Guggenhein and Smith[14,15]

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

where k_B is the Boltzmann constant; T is the absolute temperature; ϵ_1 and ρ are the dielectric constant and density, respectively, of the solvent; M is the molecular weight of the solute; and w is the weight fraction of polymer in the solution. In the evaluation of $\langle\mu^2\rangle$, the contribution of the atomic polarization to the total polarization was considered to be negligible.

Experimental Results

Owing to their high melting points, PTCDA and PTCDS are insoluble in nonpolar solvents at room temperature. For example, dilute dioxane and benzene solutions of PTCDA crystallize below 50 °C and 60 °C, respectively, whereas PTCDS is only soluble in dioxane at temperatures above 60 °C. Consequently, dielectric experiments were conducted at 50, 60, and 70 °C on solutions of PTCDA in dioxane and at a single temperature (70 °C) on solutions of PTCDS in the same solvent. PCCDS is already soluble in benzene and in dioxane at room temperature, and dielectric measurements were performed on solutions of the polymer in each of these solvents at 30, 40, 50, and 60 °C.

Values of the derivatives $d\epsilon/dw$ and $2n_1\, dn/dw$ are shown in the third and fourth columns of Table I, respectively. Values of the mean-square dipole moment ratio $\langle\mu^2\rangle/nm^2$ (nm^2 is the mean-square dipole moment of a chain of n skeletal bonds each having an average dipole moment m) are shown in the fifth column of Table I. In the evaluation of nm^2, it was assumed that the dipole moment associated to each ester group has a value of 1.89 D.[16] As expected, excluded-volume and solvent effects do not seem to affect the dipole moments of the symmetric cycloaliphatic polyesters. Actually, the difference of the values of the dipole moment ratio obtained for PCCDS in benzene and dioxane lies within the experimental error, which was estimated to be ±3%.

For comparative purposes the values of the dipole moments of PCCDA, PTCDA, and PTCDS together with the

Table II
Comparison of Experimental and Theoretical Values of the Dipole Moment Ratio and Its Temperature Coefficient for Poly(*cis*-1,4-cyclohexanedimethanol adipate) (PTCDA), Poly(*trans*-1,4-cyclohexanedimethanol adipate) (PTCDA), Poly(*trans*-1,4-cyclohexanedimethanol succinate) (PTCDS), Poly(*cis*-1,4-cyclohexanedimethanol sebacate) (PCCS), and Poly(*trans*-1,4-cyclohexanedimethanol sebacate) (PTCS)

polymer	T, °C	$\langle\mu^2\rangle/nm^2)_{exp}$	$\langle\mu^2\rangle/nm^2)_{th}$	$(10^3\ d\ln\langle\mu^2\rangle/dT)_{exp}$	$(10^3\ d\ln\langle\mu^2\rangle/dT)_{th}$
PCCDA	30	0.93	0.87	0.4	0.6
PTCDA	50	0.60	0.62	1	1.1
PTCDS	70	0.45	0.49		1.7
PCCS	30	0.98	0.97	0.7	0.1
PTCS	50	0.68	0.74	3.9	0.5

values corresponding to the cis and trans isomers of poly(1,4-cyclohexanedimethanol sebacate) (PTCS and PCCS, respectively) are shown in Table II. It can be seen that the dipole moments of PCCDA and PCCS are significantly higher than the values corresponding to the trans isomers, and in these last isomers the polarity seems to decrease as the number of methylene groups in the acid residue decreases. Moreover, the dipole moments of the cis isomers seem to be less dependent on temperature than those of the trans isomers.

Theoretical Results

The repeating units of PCCDA and PTCDA in planar conformation ($\phi = 0$) are shown in Figure 1. In the theoretical calculation of the dipole moments of PCCDA, PTCDA, and PTCDS, a three-rotational-states scheme was used.[17] The energy minima were assumed to be located at 0 ± 120°, with the exception of the O–CO bonds of the ester groups, which are restricted to trans states,[17] and the O–CH_2 bonds of the glycol residue, for which energy minima are located at[3] $\phi = 0 \pm 75°$. Moreover, the cyclohexane ring was substituted by a virtual bond connecting the carbon atoms in the 1,4-positions. The direction of the virtual bond makes angles $\theta_e = 148.5°$ and $\theta_a = 101.7°$ with equatorial and axial C–H bonds,[1] respectively. The rest of the skeletal angles were assumed to have the following values:[18] ∠CO–O–CH_2 = 113°, ∠O–CH_2–CH_2 =110°; ∠O–CO–CH_2 = 114°, and ∠CH_2–CH_2–CH_2 = 111.5°. The dipole moment corresponding to each ester group of the repeat unit has a magnitude of 1.89 D and its direction makes an angle of 123° with the direction of the CH_2–CO bond.[16] The dipole moments associated to the ether and hydroxyl skeletal bonds of the end groups lie along the bonds and their absolute values are 1.07 and 1.7 D, respectively.[19,20] Finally, the dipole moment associated with the CH_2–CH_2 bond was assumed to be nil.

A brief discussion concerning the conformational energy associated to the rotational states about the skeletal bonds of the repeating units, shown in Figure 1, follows. The analysis of the potential curve corresponding to bonds of type $i + 2$ and $i + 4$ in Figure 1a, obtained by using semiempirical potential functions, suggests that gauche states about these bonds have an energy[3] $E_{\sigma'}$ of ca. 0.4 kcal mol^{-1} below that of the alternative trans states; however, bonds of type $i + 4$ in the cis substitution (Figure 1b) are restricted to $g^{\pm}$ conformations. Gauche rotations about bonds of type $i + 1$ give rise to strong repulsive interactions between the carbonyl group and the methylene groups of the cyclohexane ring; the energy $E_{\sigma''}$ of the $g^{\pm}$ states is ca. 1.2 kcal mol^{-1} above that of the corresponding trans states.[3] Moreover, rotations of the same sign about the consecutive pair of bonds $i + 1$, $i + 2$ in the cis and trans isomers (and $i + 4$, $i + 5$ in the trans isomer) cause strong repulsive interactions between the carbonyl group and the methylene

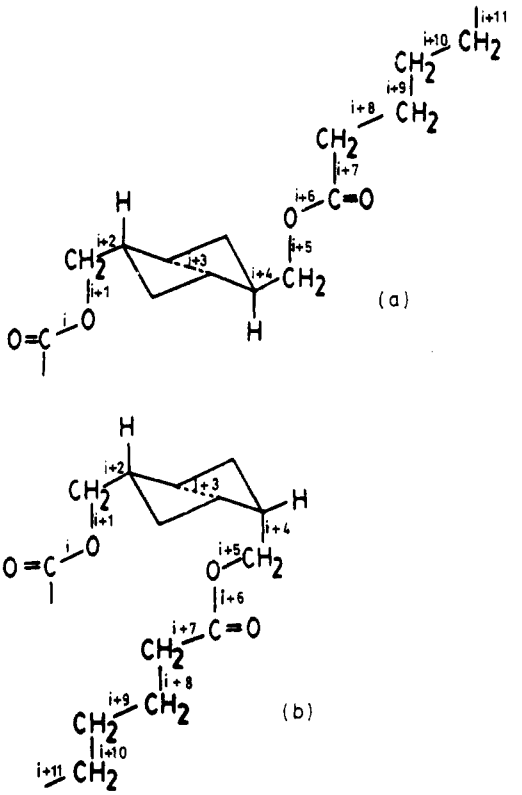

Figure 1. Structural units of PTCDA (a) and PCCDA (b).

groups of the cyclohexane ring and consequently $g^{\pm}g^{\pm}$ conformations about these bonds are not permitted; however, the interactions are alleviated by rotations of opposite sign, so that $g^{\pm}g^{\mp}$ conformations have an energy similar to that of the tt states. Gauche states above bonds of type $i + 9$ in PTCDA and PCCDA have an energy E_{σ} of 0.5 kcal mol^{-1} above that of the alternative trans states.[17]

As was mentioned above, the conformational energy E_{σ_α} associated with gauche states about CH_2CH_2–COO bonds is a matter of controversy. Thus from spectroscopic studies carried out on methyl propionate, positive (1.2, 0.08 kcal mol^{-1}) and negative values have been reported for this energy with respect to that of the alternative trans state.[4-7] Preference for trans states was also reported by Abe[8] from the critical analysis of the dipole moments of dialkyl esters of aliphatic diacids in which the number of methylene groups lies in the range 2–8. However, recent work on the analysis of the conformation-dependent properties of PNA[9] and PNS[10] suggests that gauche states about CH_2CH_2–C-$OOCH_2$ bonds should have similar or lower energy than the corresponding trans states. Conformational studies of succinic acid and dimethyl succinate carried out by using NMR spectroscopy indicate that gauche states about CH_2–CH_2 bonds in the succinyl residue, which cause first-order CO···CO interactions, are preferred over the corresponding trans states.[8,11-13] These results, however, are in conflict with those obtained in the analysis of the configuration-dependent properties of PNS,[10] where gauche states about these bonds have an energy E_{σ_β} of 0.7 kcal mol^{-1} with respect to the trans states if $E_{\sigma_\alpha} = 0$; the analysis also suggests that E_{σ_β} will slightly increase if E_{σ_α} decreases. Finally, gauche rotations of different sign about $i + 7$, $i + 8$ skeletal bonds, which give rise to second-order O···CH_2 interactions, were considered to have an energy E_ω of 0.6 kcal mol^{-1}. Accordingly, the main set of values of the conformational energies used in the calculations were $E_{\sigma'} = -0.4$, $E_{\sigma''} = 1.2$, $E_{\sigma_\beta} = 0.7$ (in PTCS), $E_\sigma = 0.5$, and $E_\omega = 0.6$ kcal mol^{-1}. The values of E_{σ_β} in PTCDA and PCCDA and E_{σ_α} in all the isomers were obtained by com-

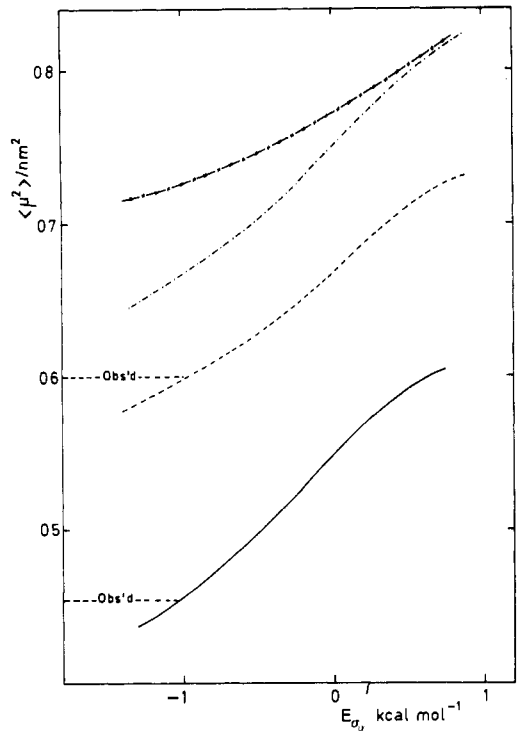

Figure 2. Dependence of the dipole moment ratio on E_{σ_α} for PTCDS (—), PTCDA (- - -) (· · ·), and PTCS (-×-). The curves (—), (- - -), and (-×-) were calculated by assuming E_{σ_β} = 0.7 kcal mol^{-1}. The curve (· · ·) was calculated for E_{σ_β} = 0.3 kcal mol^{-1}.

paring theory and experiment.

Preliminary calculations carried out on the conformational characteristics of cycloaliphatic polyesters showed that the dipole moment ratio of these polymers is very sensitive to the gauche population about the α and β C–C bonds of the acid residue. The dependence of $\langle\mu^2\rangle/nm^2$ on E_{σ_α}, calculated assuming that E_{σ_β} = 0.7 kcal mol^{-1}, is shown for PTCDS in Figure 2. It can be seen that the polarity increases with increasing values of E_{σ_α} and in order to bring theory in reasonable agreement with experiment it is necessary to postulate that gauche states about CH_2–COO bonds are preferred over the alternative trans states. The all-trans conformation places the dipole moment of the two ester groups of the succinyl residue in almost antiparallel directions, and as a consequence departure of the central CH_2–CH_2 bonds from the trans conformation increases the polarity of the chains. The curve of Figure 3, calculated assuming E_{σ_α} = –0.6 kcal mol^{-1}, shows that $\langle\mu^2\rangle/nm^2$ increases from 0.42 to ca. 1.0 when E_{σ_β} increases from –1 to 1 kcal mol^{-1}.

Values of the dipole moment ratio of PTCDA are plotted as a function of E_{σ_α} for two values of E_{σ_β} in Figure 2. With decrease in E_{σ_α} from 0.8 to –1.2 kcal mol^{-1}, the value of $\langle\mu^2\rangle/nm^2$ for E_{σ_β} = 0.3 kcal mol^{-1} diminishes from 0.82 to 0.65. As the trans population about β bonds of the adipoyl residue increases, the dipole moment of the chains is shifted to lower values; thus for E_{σ_β} = 0.7 kcal mol^{-1}, $\langle\mu^2\rangle/nm^2$ increases from 0.60 to 0.74, when E_{σ_α} changes from –1.2 to 0.8 kcal mol^{-1}. In spite of the fact that the two dipoles of the adipoyl residue are separated by five bonds, there is significant correlation between them, as can be seen in Figure 3 where the dipole moment ratio of PTCDA chains is plotted against E_{σ_β}. In this figure, and for comparative purposes, the dependence of $\langle\mu^2\rangle/nm^2$ on E_{σ_β} for PTCS is also represented. Here, the the correlation between the dipoles separated by the sebacoyl residue is very small and consequently the variation of $\langle\mu^2\rangle/nm^2$ is almost negligible.

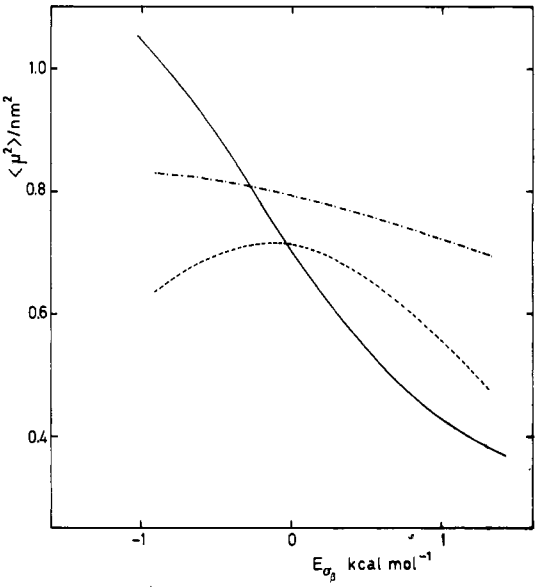

Figure 3. Dependence of the dipole moment ratio on E_{σ_β} for PTCDS (—), (PTCDA) (- - -), and PTCS (· · ·). The curves were calculated for E_{σ_α} = –0.6 kcal mol^{-1}.

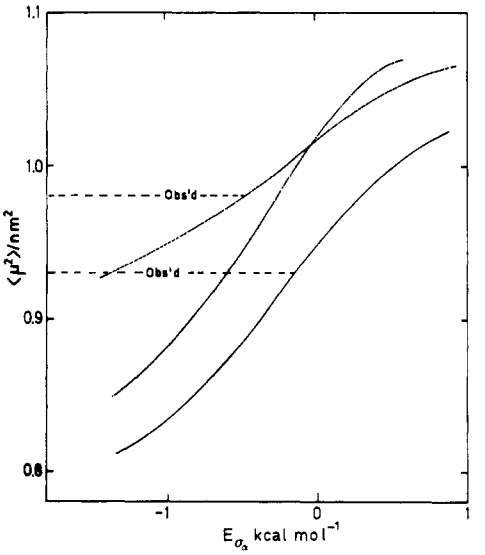

Figure 4. Variation of the dipole moment ratio with E_{σ_α} for PCCDA and PCCS. The lower and middle curves were calculated for PCCDA, assuming E_{σ_β} = 0.7 and 0.3 kcal mol^{-1}, respectively. The upper curve corresponds to PCCS calculated for E_{σ_β} = 0.7 kcal mol^{-1}.

An inspection of the curves of Figure 2 reveals three important facts: (a) the theoretical values of $\langle\mu^2\rangle/nm^2$ for PTCDS, PTCDA, and PTCS are closer to the experimental results as the gauche population about CH_2–CO bonds of the acid residue increases; (b) the lower the gauche population about CH_2–CH_2 bonds, the higher is the value of E_{σ_α} necessary to reach agreement between theoretical and experimental results; (c) values of E_{σ_α} and E_{σ_β} in the vicinity of –0.6 and 0.7 kcal mol^{-1}, respectively, seem to give a good account of the experimental values of the dipole moment ratios of the trans isomers of cycloaliphatic polyesters.

The dipole moment ratio of PCCDA was calculated by using for the skeletal bonds of type i + 4 and i + 5 in Fig.1(b) the following statistical weight matrices:

$$\mathbf{U}_{i+4} = [0 \quad 1 \quad 1]; \qquad \mathbf{U}_{i+5} = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & \omega' \\ 1 & \omega' & 0 \end{bmatrix}$$

The results obtained for $E_{\omega'} = 0$ are plotted as a function of E_{σ_α} in Figure 4, for two values of E_{σ_β}. In the same figure and for comparative purposes the same representation is performed for PCCS for $E_{\sigma_\beta} = 0.7$ kcal mol^{-1}. In both cases agreement between theory and experiment is found for $E_{\sigma_\alpha} < 0$, although the absolute value of this quantity is somewhat lower than that found for the corresponding trans isomers. However, values of $\langle\mu^2\rangle/nm^2$ approaching the experimental results can be obtained, for $E_{\sigma_\alpha} = -0.6$ kcal mol^{-1}, by slightly refining the values of $E_{\omega'}$. Thus by increasing $E_{\omega'}$ from 0 to 0.5 kcal mol^{-1}, the value of $\langle\mu^2\rangle/nm^2$ increases from 0.87 to 0.95 for $E_{\sigma_\alpha} = -0.6$ kcal mol^{-1}.

The temperature dependence of the dipole moment ratio, expressed by d ln $\langle\mu^2\rangle/dT$, is positive for PCCDA and PTCDA, although the value of this quantity is somewhat lower for the former polymer than for the latter. Values of the experimental and theoretical values of d ln $\langle\mu^2\rangle$/dT for PTCDA and PCCDA are shown in the third and fourth columns of Table II. The latter values were calculated by using the following set of conformational energies: $E_{\sigma'} = -0.4$, $E_{\sigma''} = 1.2$, $E_{\sigma_\alpha} = -0.6$, $E_{\sigma_\beta} = 0.7$, $E_\sigma = 0.5$, and $E_\omega = 0.6$ kcal mol^{-1}. An increase of temperature in the trans isomer increases the trans population about bonds of type $i + 2$, $i + 4$, $i + 7$, and $i + 11$, which decreases the polarity of the chains, accompanied by an increase in the gauche population about bonds of type $i + 1$, $i + 5$, $i + 8$, $i + 9$, and $i + 10$, which increases the dipole moment of the chains. Since the latter effect is larger than the former, the temperature coefficient is positive. In the same way, the temperature coefficient of the dipole moment of PCCDA can be explained.

In Table II the experimental and theoretical values of the dipole moment ratio corresponding to PCCDA, PTCDA, PTCDS, PCCS, and PTCS are shown. As can be seen, the rotational isomeric state model gives a good account of the experimental results. Also there is very good agreement between the theoretical and experimental values of d ln $\langle\mu^2\rangle/dT$ corresponding to PTCDA and PCCDA. The agreement is not so good in the case of PCCS and PTCS, presumably as a consequence of small errors in the dielectric measurements that may alter in a significant way the values of d ln $\langle\mu^2\rangle/dT$. Actually, the temperature coefficient is less suitable than $\langle\mu^2\rangle/nm^2$ to compare theory and experiment.

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Registry No. PCCDA (copolymer), 121126-00-9; PCCDA (SRU), 121126-02-1; PTCDA (copolymer), 98845-57-9; PTCDA (SRU), 98773-26-3; PCCDS (copolymer), 121126-01-0; PCCDS (SRU), 121126-03-2; PTCDS (copolymer), 81381-36-4; PTCDS (SRU), 81381-32-0.

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