Comblike polymers have abnormally high values for the enthalpy $\Delta H_{f,e}$ because of their end group contribution, as can be seen in Table III. This fact can be as a consequence of the n-alkyl side-chain anchorage to the main chain. Comparing columns second and fourth, one notes that this energy is clearly related to the necessity of reaching a minimum length in order that the crystallization would appear, i.e., the number of amorphous methylene groups. In the present case, this fact reveals the influence of the main chain as well as the linking bridge on the critical length to crystallize. As can be seen, there exist a very good correlation between $\Delta H_{f,e}$ and n'_a.

Finally it is useful to draw some conclusions concerning the influence of the location of ester group upon the crystallization, especially from the point of view of the number of methylenes in the inner alkyl side chain. From Table III, the following sequence of n'_a for the different PEMIs is obtained:

$$\text{PEMIs 10} < \text{PMIs 5} < \text{PMIs 1}$$
$$n'_a = 8.9 \quad n'_a = 11.6 \quad n'_a = 12.8$$

Comparison of PEMIs 1, PEMIs 5, and PEMIs 10 lead to the conclusion that for more inner methylenes between the ester group and the main chain fewer outer methylene groups are required to initiate crystallization; in other words the ester group controls the appearance of the crystallinity as well as its situation with respect to the main chain.

Concluding Remarks

The conclusions reached in this paper confirm those advanced[7] for PEMIs 10. It can be summarized that only a part of the outer n-alkyl side chain participates in the crystallization. Thus, crystallization of the inner part of the side chain is hindered by the main chain as well as by the ester group, because its size prevents the side-chain packing of the inner part of the n-alkyl side chain in the typical hexagonal arrays of comblike polymers. Consequently, it is necessary to reach a critical chain length within the external part of the side chain to initiate crystallization. This length is similar to that obtained for many other comblike polymers where the functional group lie near the main chain.

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Registry No. PEMI 1-22, 108292-39-3; PEMI 1-20, 108292-41-7; PEMI 1-18, 108292-43-9; PEMI 1-16, 108292-45-1; PEMI 1-14, 108292-47-3; PEMI 5-22, 108292-49-5; PEMI 5-20, 108292-51-9; PEMI 5-18, 108292-53-1; PEMI 5-16, 108292-55-3; PEMI 5-14, 108292-57-5; PEMI 5-12, 108292-59-7; PEMI 10-22, 73599-08-3; PEMI 10-20, 73593-01-8; PEMI 10-18, 73593-03-0; PEMI 10-16, 73593-05-2; PEMI 10-14, 73593-07-4; PEMI 10-12, 73593-09-6.

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Conformational Characteristics of Phthalic Acid Based Polyesters

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ABSTRACT: Dielectric measurements were performed on solutions of poly(diethylene glycol phthalate) (PDEP) in benzene at different temperatures. The value of the dipole moment ratio, in terms of which the dielectric results were expressed, changed from 0.637 to 0.679 in the temperature interval 30–60 °C. Conformational energy calculations indicated that when the two ester groups of phthaloyl residue are coplanar to the phenyl group, the interaction energy is strongly repulsive; however, the energy becomes attractive when the rotational angles about C^{Ph}–C^* bonds place the ester groups on a plane perpendicular to the phenyl group. By use of the information derived from these calculations, a three-rotational-state model gave values of the dipole moment and its temperature coefficient in good agreement with the experimental results.

Introduction

The critical interpretation of the dielectric and thermoelastic properties of poly(diethylene glycol terephthalate) (PDET) has been useful to obtain information on the conformational characteristics of these chains.[1-3] These studies seem to suggest that gauche states about CH_2–CH_2 bonds, which give rise to first-order $O\cdots O$ interactions, are significantly more favored than similar states

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in poly(ethylene oxide) (POE). The structural analysis (by ^{1}H NMR spectroscopy) of diethylene glycol dibenzoate, a low molecular weight analogue of PDET, shows that the gauche population about CH_2–CH_2 bonds amounts to 0.90 ± 0.05, indicating that the conformational energy associated with these states is ca. 0.8 kcal mol^{-1} below that of the alternative trans states.[4,5]

Crystallographic results[6] obtained in dimethyl terephthalate suggest that the torsional angle $\phi_{C^{Ph}-C^*}$ has a value of ca. 5°. However, conformational calculations[7] carried out by using semiempirical potential functions indicate that the potential energy in the vicinity of the angle at which the carbonyl and phenyl groups are coplanar ($\phi = 0$) reaches a pronounced maximum. Consistency with the small values of ϕ suggested by crystallographic results requires that the delocalization energy of benzoate esters is 3 kcal mol^{-1} or larger.[7] Owing to the large torsional potentials opposing rotations about the C*O*–O bond and the coplanarity of the phenyl and carbonyl groups, the terephthaloyl residue is restricted to cis and trans conformations.[8] The relative fraction of both conformations has a big influence in the polarity of the chains, as a consequence of the fact that the dipole moments associated with the ester groups of the terephthaloyl residue in cis conformation have almost the same direction whereas in trans conformation the direction is opposite.

In the case of the terephthaloyl residue, the ester groups are placed far apart and the van der Waals and Coulombic interactions between them are small. As a consequence, the cis and trans conformations have almost the same probability. It should be important, however, to study how the polarity of the chains changes when the interactions between the ester groups are large, as occurs in phthalic based polyesters. In this work the dipole moment and its temperature coefficient of poly(diethylene glycol phthalate) (PDEP) chains were measured, and the results were interpreted by using statistical mechanics methods. If theory and experiment are compared, information on the relative orientation of the dipoles associated to the ester groups of the phthaloyl residue will be obtained.

Experimental Section

Synthesis of Poly(diethylene glycol phthalate). Commercial dimethyl phthalate (Fluka) was used without further purification. Commercial diethylene glycol was distilled in vacuo under nitrogen atmosphere.

PDEP was obtained by the melt-phase procedure from 97.0 g (0.5 mol) of dimethyl phthalate and 116.6 g (1.1 mol) of diethylene glycol. In the first steps of the reaction, the ester interchange was carried out at 170–190 °C under nitrogen atmosphere in the presence of tetraisopropyl titanate catalyst. In 3 h, 91% of the theoretical amount of methanol was separated, 10 mg of lead oxide was then added to the reaction medium, and the temperature was raised to 220 °C. The polymerization proceeded under vacuum (10 mmHg) for 2 h, and the final step of the polycondensation was carried out under higher vacuum (0.5 mmHg) for an additional 2 h.

The polymer was dissolved in chloroform, filtered through Celite, and precipitated with cold methanol. The polymer was washed several times with methanol and dried under vacuum for 24 h. The yield of the reaction was 92%, and the number-average molecular weight of the polymer amounted to 5300. The polyester was fractionated with chloroform–methanol; eight fractions were obtained whose number-average molecular weights, measured with a Knauer vapor pressure osmometer, ranged from 10 300 to 3200.

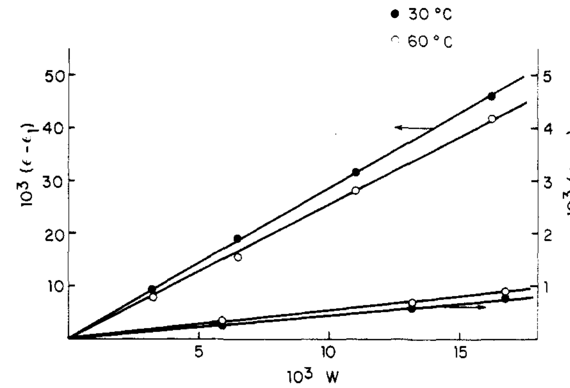

Figure 1. Concentration dependence of the increments in dielectric constant and index of refraction for benzene solutions of poly(diethylene glycol phthalate).

Table I
Dielectric Results for Poly(diethylene glycol terephthalate)

T, °C	$d(\epsilon - \epsilon_1)/dw$	$2n_1(d(n - n_1)/dw)$	$\langle\mu^2\rangle/nm^2$
30	2.84_5	0.13_9	0.637
40	2.76_5	0.14_4	0.652
50	2.69_0	0.15_0	0.667
60	2.61_0	0.15_6	0.679

Table II
Comparison of Dielectric Properties at 30 °C for Poly(diethylene glycol terephthalate) (PDET), Poly(diethylene glycol isophthalate) (PDEI), and Poly(diethylene glycol phthalate) (PDEP)

polymer	$\langle\mu^2\rangle/nm^2$	$10^3[d \ln \langle\mu^2\rangle/dT]$
PDET[a]	0.691	~0
PDEI[b]	0.697	1.1
PDEP	0.637	2.1

[a] Reference 1. [b] Reference 12.

Dielectric Measurements and Results. A fraction of molecular weight 10 300 was used in the dielectric measurements. Dielectric constants of solutions of the polymer in benzene were measured at 30, 40, 50 and 60 °C, with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell[1] operating at 10 kHz. Mean-square dipole moments $\langle\mu^2\rangle$ were obtained by using the method of Guggenheim and Smith which results in the equation[9]

$$\langle\mu^2\rangle = (27kTM/4\pi\rho N_A(\epsilon_1 + 2)^2)((d(\epsilon - \epsilon_1)/dw) - (2n_1(d(n - n_1)/dw))) \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, N_A is Avogadro's number, w is the weight fraction of the solute, and ρ is the density of the solvent. ϵ and n represent, respectively, the dielectric constant and index of refraction of the solutions; the same symbols with the subindex 1 represent the same quantities for the solvent. The terms $d(\epsilon - \epsilon_1)/dw$ and $d(n - n_1)/dw$ were obtained, respectively, from the slopes of the plots of the increments $(\epsilon - \epsilon_1)$ and $(n - n_1)$ against w, in the vicinity of $w \to 0$. Illustrative plots of this kind are shown in Figure 1. Values of $d(\epsilon - \epsilon_1)/dw$ and $2n_1(d(n - n_1)/dw)$ at the temperatures of interest are shown in the second and third 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 column of Table I. The uncertainty of these values is ca. 6%.

In the evaluation of nm^2, the mean-square dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed, it was assumed that the dipole moments associated with each ester group as well as with the ether group and C–C skeletal bonds have values of 1.89, 1.07, and 0.00 D, respectively.[8,10,11]

The value of the temperature coefficient of the dipole moment, $d \ln \langle\mu^2\rangle/dT$, was obtained from plots of the natural logarithm of the dipole moment ratio against temperature; the value thus estimated for this quantity amounts to 2.1×10^{-3} K^{-1}.

In Table II, and for comparative purposes, the experimental values at 30° of $\langle\mu^2\rangle/nm^2$ and $d \ln \langle\mu^2\rangle/dT$ for PDET,[1] poly(diethylene glycol isophthalate) (PDEI),[12] and PDEP are shown. It can be seen that whereas the value of the dipole moment ratio of PDEP is lower than that of PDET and PDEI, the temperature coefficient of the dipole moment is higher.

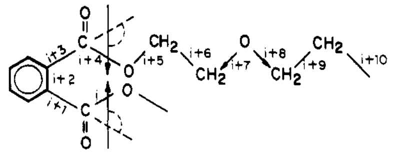

Figure 2. Repeating unit of poly(diethylene glycol phthalate) in an arbitrary planar conformation.

Theoretical Analysis

Rotational States in the Phthaloyl Residue. In Figure 2 we have represented the repeating unit of PDEP in an arbitrary planar conformation, together with the direction of the dipole moments associated with the ester and ether groups. It was assumed that the modulus of the dipole moment of each ester group is 1.89 D, and it makes an angle of 123° with the C^{Ph}–C^* skeletal bond.[8] It is obvious that the polarity of the chains considered will be extremely dependent on both the structural geometry and the potentials affecting torsional rotations of the C^{Ph}–C^* bonds of the phthaloyl residue. Some information relevant to the analysis of the polarity can be obtained from dimethyl phthalate (DP). The available data suggest that the dipole moment of this compound lies in the range 2.6–2.8 D. Thus, Klages and Knobloch[13] have obtained a value of 2.6 D for the dipole moment of DP, whereas values of ca. 2.8 D were also reported by other authors.[14,15]

In the case of DP, which is amorphous, there is no available information concerning the value of the torsional $\phi_{C^{Ph}-C^*}$ angle. In the case of the terephthaloyl residue, coplanarity of the carbonyl group with the phenyl ring guarantees maximum overlapping of electrons of the participating atoms and consequently this residue is restricted to cis and trans conformations.[16,17] For the phthaloyl residue, however, these conformations will probably give rise to strong repulsive interactions among the atoms of the neighbor ester groups that could overcome the stabilizing effects of the coplanarity between carbonyl and phenyl groups.

Calculations of the potential curve around C^{Ph}–C^* bonds were performed using dimethyl phthalate as the model. The molecular energy was evaluated as a sum of nonbonded, delocalization, and Coulombic interactions. The inherent torsional contribution is not required in the calculations since the torsional barrier for rotations about C^{Ph}–C^* bonds is known to be negligible for a group R such as methyl that does not contribute to electron delocalization.[18]

Nonbonded interactions were calculated by using the 6-12 Lennard-Jones potential function

$$V_{ij} = \sum_{i<j} \left(\frac{b_{ij}}{r_{ij}^{12}} - \frac{a_{ij}}{r_{ij}^{6}} \right) \qquad (2)$$

The London dispersion parameters a_{ij} were calculated from atomic polarizabilities,[19] using the Slater–Kirkwood formula,[20] and the constant b_{ij} was assigned as to minimize the potential V_{ij} for a given pair of atoms when the distance r_{ij} is set equal to the sum of the corresponding van der Waals radii. The parameters used to calculate a_{ij} and b_{ij} are given in Table III. The geometric parameters, bond lengths, and bond angles necessary to calculate the distances r_{ij} are represented in Table IV.

Coulombic interactions were calculated from

$$E_{\text{coul.}} = kq_iq_j/\epsilon r_{ij} \qquad (3)$$

where $k = 332.1$ is a conversion factor giving the energy in kcal mol^{-1} when q_i and q_j are in fractional parts of electron charge and r_{ij} is given in Å. Partial charges of $q_{C^*} = -q_{O^*} = 0.318$ and $q_C = -q_O = 0.006$ were used in the calculations. As usual a value of 3 was used for the dielectric constant.[24]

Table III
Parameters for the Lennard-Jones Potential[a]

atom or atomic gp	van der Waals radius, Å	no. of coeff. electrons	polarizability, Å^3
C^{Ph}	1.85	5	1.23
H	1.3	0.9	0.42
O*	1.6	7	0.84
C*	1.8	5	1.23
O	1.6	7	0.70
CH_3	2.0	7	1.77
C	1.8	5	0.93

[a] References 21, 22.

Table IV
Geometric Parameters[a]

bond lengths, Å		bond angles, deg	
C—C	1.53	C^{Ph}—C^{Ph}—C^{Ph}	120
C*—C	1.48	C*—C^{Ph}—C^{Ph}	112
C—H	1.09	C—C—H	110
C*—O	1.33	C^{Ph}—C*—O*	125
C*═O*	1.22	C*—O—C	113
C—O	1.43	C^{Ph}—C*—O	114
C^{Ph}—C	1.39	O—C—C	118.5

[a] Reference 23.

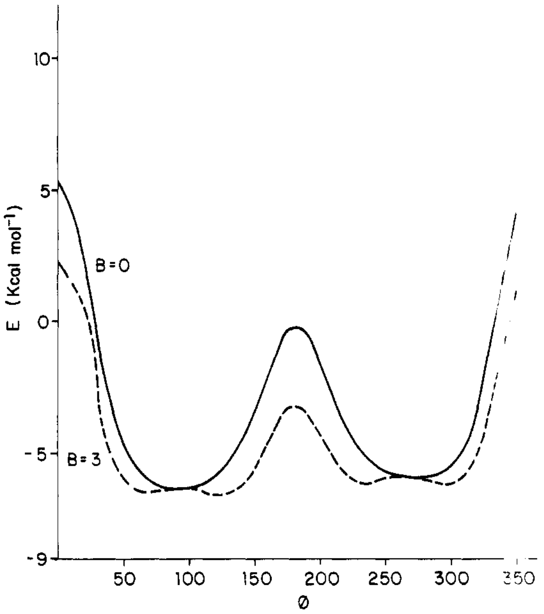

Figure 3. Potential curve for rotation over the $i + 3$ bond of Figure 2, for values of $B = 0$ and 3 kcal mol^{-1}; the rotational angle of the $i + 1$ skeletal bond was kept at 90°.

The electron delocalization energy was assumed to depend on the torsional angle by

$$E_{\text{deloc.}} = -B \cos^2 \phi_{C^{Ph}-C^*} \qquad (4)$$

where higher terms in the Fourier expansion were ignored.[7]

The potential curve $E(\phi_{C^{Ph}-C^*})$ was calculated by restricting one of the C^{Ph}–C^* bonds to $\phi = 0$ while allowing the other one to rotate from 0° to 350° in intervals of 10°. The calculations show that when the two ester groups are coplanar to the phenyl group, the repulsive energy amounts to a few thousands of kcal mol^{-1} and it reaches a value of a few tens at $\phi = \pm 90°$. By restricting now one of the C^{Ph}–C^* bonds to $\phi = 90°$, it was permitted to rotate the other C^{Ph}–C^* bond from 0° to 350°. The results obtained, represented in Figure 3, show two broad minima centered at ±90 if $B = 0$. The minima are even broader for $B = 3$ kcal mol^{-1}, the delocalization energy for which a minimum is obtained in methyl benzoate when $\phi = 0$. As a result of this analysis, it will be assumed that the rotational angles about C^{Ph}–C* bonds are located at ±90°.

Conformational Energies. The energies associated with the rotational states of the different skeletal bonds will briefly be described. The rotational angle about bonds of type i and $i + 4$ is zero; owing to the fact that the $i + 2$ bond is in the cis conformation, the rotational angle corresponding to this bond is 180°. Gauche states about $i + 5$ and $i + 10$ bonds were assumed to have an energy, E_{σ_k}, 0.4 kcal mol^{-1} above that of the alternative trans states.[24] Gauche rotations about CH_2–CH_2 bonds which give rise to first-order O···O interactions have an energy ($E_{\sigma'}$) of ca. 0.8 kcal mol^{-1} below that of the corresponding trans states.[2,4,25] Bonds of type $i + 7$ and $i + 8$ have gauche states approximately 0.9 kcal mol^{-1} higher in energy ($E_{\sigma''}$) than the alternative trans states.[10,24]

It can be seen, at first glance, that the dipole moment of the chains must be very sensitive to the energy E_γ which accounts for the relative fraction of $g^{\pm}cg^{\mp}/g^{\pm}cg^{\pm}$ conformations corresponding to $i + 1$ through $i + 3$ in Figure 2. Preliminary calculations suggest that the $g^{\pm}cg^{\mp}$ conformation should be somewhat disfavored with respect to the $g^{\pm}cg^{\pm}$ one by ca. 0.3 kcal mol^{-1}. However, given the uncertainties involved in the determination of the conformational energies by using semiempirical methods, the value of E_γ was obtained by comparing theory and experiments as will be described below.

The second-order interactions corresponding to the conformations that give rise to pentane-type interferences between O atoms and both CH_2 and carbonyl groups were considered to have energies E_ω and $E_{\omega\eta\kappa}$ of 0.6 and 1.9 kcal mol^{-1}, respectively.[2,4] Rotations of different signs about two consecutive skeletal bonds which cause second-order CH_2···CH_2 interactions were considered to be forbidden.

Dipole Moments. Values of the dipole moment were calculated by using matrix multiplication methods described elsewhere.[24,26] The rotational angles for bonds $i + 5$ through $i + 10$ were considered to be located at 0° ± 120°. Rotational angles about i and $i + 4$ bonds are restricted to 0°, whereas the rotational angles corresponding to $i + 2$ bonds are restricted to 180°. With the usual convention concerning Cartesian coordinate systems, the **T** matrix required to transform the coordinates from the reference frame $i + 4$ to $i + 3$ and from $i + 2$ to $i + 1$ in Figure 2 will require that 180° be added to the rotational angles ϕ_ν (±90°) of bonds $i + 1$ and $i + 3$. In order to include the statistical weight of the $g^{\pm}cg^{\mp}$ conformation with respect to the $g^{\pm}cg^{\pm}$ one corresponding to bonds i through $i + 3$, the partition function corresponding to a chain of x structural units can be written as

$$Z = [\mathbf{U}_i(\mathbf{U}_{i+1}\mathbf{U}_{i+2}\mathbf{U}_{i+3} + \mathbf{U}'_{i+1}\mathbf{U}_{i+2}\mathbf{U}'_{i+3})\mathbf{U}_{i+4}\mathbf{U}\boldsymbol{J}]^x \quad (5)$$

where

$$\mathbf{U}_i = [1] \qquad \mathbf{U}_{i+1} = [1 \quad \gamma] \qquad \mathbf{U}_{i+2} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \mathbf{U}_{i+3} = [1 \quad 0]$$

$$\mathbf{U}'_{i+1} = [\gamma \quad 1] \qquad \mathbf{U}'_{i+3} = [0 \quad 1] \qquad \mathbf{U}_{i+4} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

The matrix **U** in eq 5 embodies the product of the 1 × 3 statistical weight matrix corresponding to bonds $i + 5$ and the 3 × 3 matrices corresponding to $i + 6$ through $i + 10$ in Figure 3. ***J*** represents the column vector to effect the required sum of terms[24] in eq 5.

The calculations performed using the information given above show that the dipole moment ratio of PDEP chains is extremely sensitive to the energy E_γ of the $g^{\pm}cg^{\mp}$ conformation of bonds i through $i + 3$, with respect to that of $g^{\pm}cg^{\pm}$, in the sense that it increases as E_γ decreases. The dependence of $\langle\mu^2\rangle/nm^2$ on E_γ is shown in Figure 4. It should be pointed out that the evaluation of $\langle\mu^2\rangle/nm^2$ was carried out using the following set of conformational energies: $E_{\sigma\kappa} = 0.4$, $E_{\sigma''} = 0.9$, $E_{\sigma'} = -0.8$, $E_\omega = 0.6$, and $E_{\omega\eta\kappa} = 1.9$, all in kcal mol^{-1}. The cause of the strong dependence of the dipole moment ratio on E_γ lies in that in the $g^{\pm}cg^{\pm}$ conformation, the dipole moments associated to the ester group of the phthaloyl residue are in very nearly antiparallel directions and hence the contribution of the residue to the polarity of the chains is small. If E_γ is decreased, the fraction of $g^{\pm}cg^{\pm}$ conformations increases, and since in this conformation the dipole moments of the ester group are almost in parallel directions, the contribution of the phthaloyl residue to the dipole moment of the chain is large. Increasing the temperature also increases the fraction of the energetically less favored conformation ($g^{\pm}cg^{\mp}$), and hence, the dipole moment increases. The dependence of the temperature coefficient on E_γ is shown in Figure 4 where it can be seen that d ln $\langle\mu^2\rangle/dT$ decreases as E_γ decreases as a consequence of the fact that the fraction of the less polar conformation ($g^{\pm}cg^{\pm}$) diminishes.

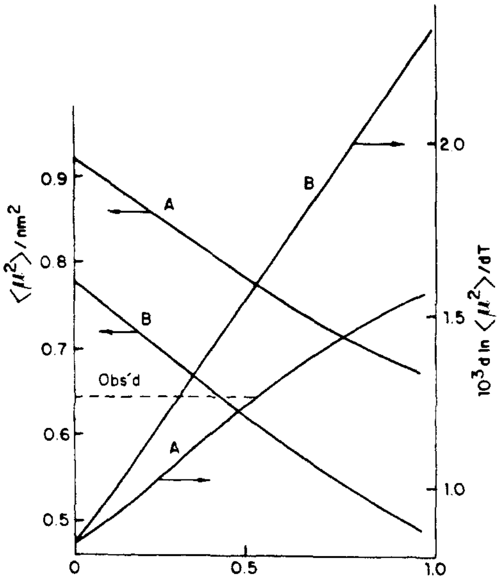

Figure 4. Dependence of the dipole moment ratio and its temperature coefficient on E_γ. A and B curves were obtained for $\phi_{C^{Ph}-C*}$ = ±110° and ±90°, respectively.

The experimental value of the dipole moment ratio was reproduced for values of E_γ lying in the range 0.60–0.35 kcal mol^{-1}; e.g., with $E_\gamma = 0.48$ kcal mol^{-1}, we find $\langle\mu^2\rangle/nm^2 = 0.624$ and 10^3 [d ln $\langle\mu^2\rangle/dT$] = 1.55 K^{-1}, in very good agreement with the experimental results 0.638 and 2.1 K^{-1}, respectively. An increase in the rotational angle, $\phi_{C^{Ph}-C*}$, results in a decrease in the antiparallel orientation of the dipole moments associated to the two neighbor ester groups and consequently a lower fraction of $g^{\pm}cg^{\mp}/g^{\pm}cg^{\pm}$ conformations will be necessary in order to bring agreement between theory and experiment. In other words, the curve representing the value of $\langle\mu^2\rangle/nm^2$ and d ln $\langle\mu^2\rangle/dT$ is shifted to higher values of E_γ. Results of the dipole moment ratio and its temperature coefficient obtained using $\phi_{C^{Ph}-C*}$ = ±110° are represented as a function of E_ν in Figure 4. Agreement between theory and experiment is obtained for $E_\gamma = 1.2$ kcal mol^{-1} a value significantly higher than that obtained for $\phi_{C^{Ph}-C*}$ = ±90°.

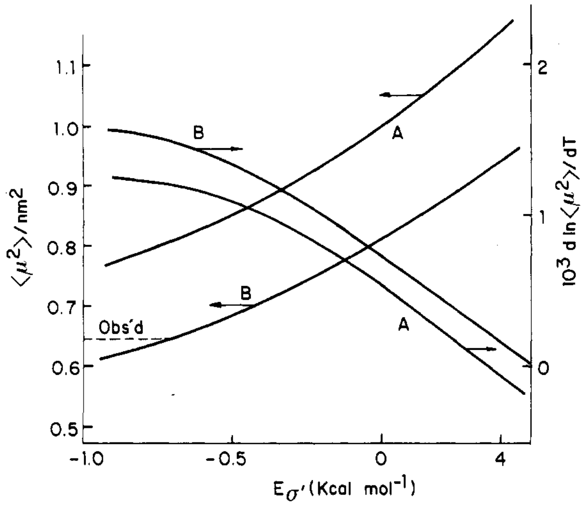

Figure 5. Variation of the dipole moment ratio and its temperature coefficient with the energy ($E_{\sigma'}$) associated with gauche states about CH_2–CH_2 bonds. A and B curves were obtained for $\phi_{C^{Ph}-C*}$ = ±110° and ±90°, respectively.

The dipole moment ratio and its temperature coefficient also show a strong dependence on $E_{\sigma'}$, the energy associated with gauche states about CH_2–CH_2 bonds. Values of $\langle\mu^2\rangle/nm^2$ and d ln $\langle\mu^2\rangle/dT$ as a function of $E_{\sigma'}$ are shown in Figure 5. It can be seen that for $E_\gamma = 0.48$ kcal mol^{-1} and $\phi_{C^{Ph}-C*} = \pm 90°$, $\langle\mu^2\rangle/nm^2$ decreases from 0.95 to 0.617 when $E_{\sigma'}$ changes from 0.42 to −0.91 kcal mol^{-1}. In the same interval of values of $E_{\sigma'}$, the value of 10^3 [d ln $\langle\mu^2\rangle/dT$] increases from 0.05 to 1.6 K^{-1}. The cause of the sensitivity of both the dipole moment ratio and its temperature coefficient to $E_{\sigma'}$ lies in that as the value of $E_{\sigma'}$ rises, the all-trans conformation in which the dipole moment of the ether group is parallel to that of the neighbor ester group increases. Owing to the high percentage for gauche states of the CH_2–CH_2 bonds, an increase in temperature gives rise to an increase of the all-trans conformation fraction, and for the reason outlined above, the dipole moment of the chain goes up.

The dependence of the dielectric conformational properties on the rest of conformational energies is relatively small. Thus, $\langle\mu^2\rangle/nm^2$ decreases 5% when $E_{\sigma\kappa}$ changes from 1.4 to 0.25 kcal mol^{-1}. The variations of the dipole moment ratio with E_ω and $E_{\omega\eta\kappa}$ are even lower than those reported for the latter conformational energy. Finally, the sensitivity of the dipole moment to $E_{\sigma''}$ is negligible.

The reliability of the values $E_\gamma = 0.48$ kcal mol^{-1} and $\phi_{C^{Ph}-C*} = \pm 90°$, suggested by the critical analysis of the dielectric properties of PGDP, was tested in the determination of the dipole moment of dimethyl phthalate. The values of the square dipole moment associated to the $g^\pm cg^\pm$ and $g^\pm cg^\mp$ conformations are 3.4 and 13.2 D^2, respectively. Since the fractions of the former and latter conformations are 0.666 and 0.334, the dipole moment of dimethyl phthalate at 30 °C will amount to 2.57 D, a value which is in very good agreement with that of 2.6 D reported by Klages and Knobloch for this compound.[13]

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References and Notes

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(5) Recent NMR spectroscopic studies carried out on 1,2-dimethoxyethane (Takasaki, K.; Abe, A. Polym. J. 1985, 17, 641) indicate that gauche states about C–C bonds, which causes first-order O···O interactions, tend to be more stabilized as the dielectric constant of the medium increases. Thus, the energy of these states ranges from −0.5 kcal mol^{-1} in deuteriated cyclohexane to 1.2 kcal mol^{-1} in D_2O. The value of −0.8 kcal mol^{-1} obtained for gauche conformations about OCH_2–CH_2O bonds, from the analysis of the ^1H NMR spectrum (in deuteriated chloroform) of diethylene glycol dibenzoate (ref 4), reproduces satisfactorily both the dipole moment (measured in nonpolar solvents) of diethylene glycol dibenzoate and the temperature coefficient of the unperturbed dimensions (obtained from thermoelastic experiments) of poly(diethylene glycol terephthalate) (ref 2 and 3). Consequently, the low value of $E_{\sigma'}$ found for diethylene glycol based aromatic polyesters should not be attributed to solvent effects as in the case of 1,2-dimethoxyethane, but rather to stabilizing effects of the neighbor carbonyl groups.
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