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Conformational Characteristics of Polyesters Based on Terephthalic Acid with an Ether Group in the Glycol Residue

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ABSTRACT: Poly(ditrimethylene glycol terephthalate), prepared by the melt-phase procedure from dimethyl terephthalate and ditrimethylene glycol, was studied with regard to its unperturbed dimensions and polarity. From viscometric and osmotic results obtained in tetrahydrofuran solutions, the unperturbed dimensions ratio $\langle r^2\rangle_0/M$, where $\langle r^2\rangle_0$ is the mean-square end-to-end distance in the unperturbed state and M the molecular weight, was found to be ca. 0.90 Å^2 mol g^{-1} at 30 °C. From dielectric measurements carried out on benzene solutions the mean-square dipole moment of the chains was determined; this quantity, expressed in terms of the dipole moment ratio $\langle \mu^2\rangle/nm^2$, where nm^2 is the mean-square dipole moment of the chain in the idealization that all the skeletal bonds are freely jointed, amounts to ca. 0.80 at 30 °C and it exhibits a slightly negative temperature dependence. Both the unperturbed dimensions and the dipole moments were interpreted by using the rotational isomeric state model. The principal conclusion of this analysis is that these conformational properties are extremely dependent on the gauche population about CH_2–CH_2 bonds of the glycol residue and the dimensions are also very sensitive to the second-order interactions arising from gauche rotations of different sign about two consecutive CH_2–CH_2 skeletal bonds. Stabilizing gauche effects about CH_2–CH_2 bonds reported in poly(trimethylene oxide) were not detected in the present system.

Introduction

The configuration-dependent properties of polyesters with repeating unit $OOCC_6H_4COO(CH_2)_n$ are strongly dependent not only on the number of methylene groups of the glycol residue but also on the nature of the acid (terephthalic, isophthalic, or phthalic) residue. In polyesters based respectively on terephthalic and isotphthalic acids, coplanarity between the carbonyl and phenyl groups guarantees maximum overlapping of electrons of these groups[1] and consequently the rotational angles about C^{Ph}–CO bonds are restricted to 0 and 180°.[2] The planar conformation of the terephthaloyl and isophthaloyl residues favors the molecular packing of the chain in the crystal and enhances the attractive intermolecular interactions between the ester groups of neighboring chains. As a result, the polyesters exhibit high melting points whose values decrease as the number of methylene groups in the glycol residue increases,[3] reaching a minimum, and then increase eventually reaching the T_m of polyethylene for $n \to \infty$. In contrast, large repulsive intramolecular interactions between two ester groups of the phthaloyl residue overcome the stabilizing effects of the coplanarity between the carbonyl and phenyl groups and the critical interpretation of conformation-dependent properties of polyesters based on phthalic acid[4] suggests that the rotational angles about C^{Ph}–CO bonds are ±90°. Consequently, the molecular packing of the chains in the crystal seems to be disfavored, hindering the possibility that crystallinity is developed in phthalate-based polyesters in which the number of methylene groups in the glycol residue is small.

The structure of the glycol residue also has a big effect on the physical properties of polyesters based in aromatic diacids, and this work is part of a more general investigation dealing with the influence of ether glycol residues on the conformational properties of polyesters based on aromatic diacids, specifically, on terephthalic acid.[5-10] Results have been reported that indicate that poly(diethylene glycol terephthalate) (PDET) hardly crystallizes from the bulk and only crystallizes from dilute solutions.[7] The closeness of the glass-transition temperature (~20 °C) to the melting temperature (~90 °C) in PDET seems to enhance the transport term in the crystallization process, slowing down the development of crystallinity in the bulk polymer. An important conformational characteristic of PDET is that gauche states about CH_2–CH_2 bonds of the glycol residue are 0.8 kcal mol^{-1} below that of the alternative trans state.[11] It seems that the presence of neighboring carbonyl groups enhances the gauche population about CH_2–CH_2 bonds with respect to that of similar bonds in poly(ethylene oxide) (PEO) where gauche states about

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CH_2–CH_2 bonds, which give rise to first order O···O interactions, have only an energy of −0.5 kcal mol^{-1} with respect to that of the corresponding trans states.[12] The possibility that effects of this kind occur in other structures was investigated in the present work by using as a model poly(ditrimethylene glycol terephthalate) (PDTT). With this aim, the experimental values of the unperturbed dimensions and the dipole moments of PDTT were obtained from viscometric and osmotic measurements on the polymer dilute solutions in the former case and from dielectric measurements on solutions of the polymer in nonpolar solvents in the latter. By critical analysis of these experimental quantities, information was obtained concerning the relative value of the conformational energy associated with gauche states about CH_2–CH_2 bonds which gives rise to first-order CH_2···O interactions, in comparison with the value of similar conformations in poly(trimethylene oxide) (POM_3). The effect of increasing the number of ethylene groups in the ether glycol residue on the physical properties of polyesters was also investigated by comparing the conformation-dependent properties of PDTT and PDET.

Experimental Section

Materials. Trimethylene oxide (Merck) and trimethylene glycol (Merck) were dried with sodium and distilled in vacuo. Methylene chloride (Merck) was shaken with sulfuric acid, washed with water, separated, dried with calcium hydride, and distilled. Dimethyl terephthalate (Ferosa) was purified by crystallization from ethanol, and tetraisopropyl titanate (Carlo Erba) was used as received. Tetrahydrofuran (THF) was refluxed overnight over potassium hydroxide and distilled from sodium.

Synthesis of Ditrimethylene Glycol. Ditrimethylene glycol was obtained by cleavage of oxetane with trimethylene glycol in the presence of sulfuric acid, using methylene chloride as solvent.[13] The reaction was carried out at 30 °C for 24 h and the products were neutralized with sodium bicarbonate; the excess of glycol was separated from the reaction products by fractional distillation. The characterization of the ether glycol was made by ^1H NMR and its molecular weight, determined by vapor pressure osmometry in chloroform at 37 °C, coincided with the theoretical value.

Synthesis of Poly(ditrimethylene glycol terephthalate) (PDTT). The polyester was prepared by the melt-phase procedure from ditrimethylene glycol and dimethyl terephthalate with tetraisopropyl titanate as catalyst. A molar ratio of 1:2 of ester to glycol was used and the reaction was allowed to proceed under nitrogen atmosphere in two steps. In the first step the interchange proceeded at 170 °C, with elimination of the theoretical amount of methanol; the second step, polycondensation, started at 220 °C and was carried out under vacuum and vigorous agitation. In order to remove the excess diol, the temperature was increased to 240 °C in the final steps of the reaction. The polymer was dissolved in a phenol/tetrachloroethane mixture (40/60) and precipitated with methanol. The polymer was characterized by ^1H and ^{13}C NMR spectroscopy. Nine fractions were obtained by fractionating the polyester using toluene/methanol as a solvent/nonsolvent system.

Viscometry, Osmometry, and GPC. Viscometric measurements were carried out in THF solutions at 30 °C, using an Ubbelohde viscometer in which kinetic energy corrections were lower than 3%. Osmotic pressure of THF solutions of the four fractions of higher molecular weight were measured in a high-speed membrane osmometer (Hewlett-Packard 502) containing a gel cellophane membrane conditioned for use in THF. Values of the number-average molecular weight of the other fractions were measured in a Knauer vapor-pressure osmometer. Values of the number-average molecular weight of the fractions were also determined in a GPC apparatus (Waters Associates 150-C) with five columns of μstyragel whose pore size lies in the range 500–10^6 Å. The solvent was THF, the elution rate at 30 °C was 2 mL/min, and the injection volume was 400 mL. The apparatus had previously been calibrated with standard fractions of polystyrene.

Dielectric Measurements. Dielectric constants of solutions of a fraction of M_n = 15 500 in benzene were measured with a capacitance bridge (General Radio, Type 1620 A) operating at 10 kHz, using a three-terminal cell. Calibration of the cell was carried out at 30, 40, 50, and 60 °C using benzene (Merck), cyclohexane (Merck), and carbon tetrachloride (Merck), all of known dielectric constant.[14] Increments of the refractive indices of the solutions were determined at the temperatures of interest with a Chromatix KHX laser differential refractometer working at 632.8 nm.

Table I
Summary of Dielectric Results for Poly(ditrimethylene glycol terephthalate) at Different Temperatures

T, °C	$d\epsilon/dw$	$2n_1\,dn/dw$	$\langle\mu^2\rangle/mn^2$
30	3.185	0.123	0.805
40	2.999	0.136	0.795
50	2.870	0.147	0.798
60	2.753	0.149	0.798

Table II
Viscometric, Osmotic, and GPC Results

fraction	$[\eta]$, dL g^{-1}	10^4M_n(osm), g mol^{-1}	10^4M_n(GPC), g mol^{-1}
1	0.64	4.80	3.60
2	0.68	4.10	3.20
3	0.52	3.05	3.20
4	0.46	2.40	1.80
5	0.38	1.55	1.90
6	0.39	1.10	1.40
7	0.27	0.80	1.10
8	0.22	0.70	0.80
9	0.21	0.45	0.40

Experimental Results

(A) Dipole Moments. Increments ($\Delta\epsilon = \epsilon - \epsilon_1$) of the static dielectric constant of the solutions ϵ with respect to that of the solvent ϵ_1 were plotted against the weight fraction w of the polymer and the derivatives $d\epsilon/dw$ at 30, 40, 50, and 60 °C were obtained from the slope of the plots in the limit $w \to 0$. Values of these quantities are given in the second column of Table I. In a similar way, values of the derivative dn/dw were obtained from the slopes of the plots $\Delta n = n - n_1$ vs w at the temperatures indicated above and the values of the derivatives dn/dw obtained are listed in the third column of Table I.

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were determined by means of the equation of Guggenheim and Smith[15,16]

$$\langle\mu^2\rangle = (27kTM)(4\pi\rho N_A)^{-1}(\epsilon_1 + 2)^{-2}[(d\epsilon/dw) - 2n_1(dn/dw)] \qquad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, ρ and n_1 are the density and index of refraction of the solvent, respectively, and N_A is Avogadro's number. The dipole moment of polymer chains are customarily expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where nm^2 is the mean-square dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed. In the evaluation of nm^2 it was assumed[2] μ_{es} = 1.89 D and μ_{CH_2O} = 1.07 D[12,17] for the ester and ether groups of the repeating unit, respectively. Values of the dipole moment ratio thus obtained, with an uncertainty of 5%, are shown in the fourth column of Table I. The results suggest that the dipole moment ratio of PDTT chains should have a slight negative temperature dependence.

(B) Unperturbed Dimensions $\langle r^2\rangle_0$. Values of the number-average molecular weight obtained by osmometry and GPC for the fractions used in this study are shown in the third and fourth columns of Table II, where it can be seen that there is fair agreement between the values of

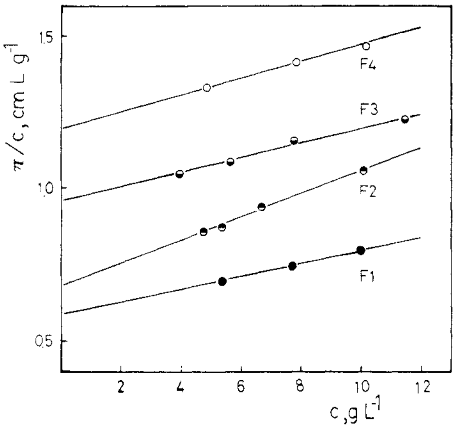

Figure 1. Reduced osmotic pressure dependence of PDTT benzene solutions on concentration.

Table III
Second Virial Coefficient A_2, Expansion Factor $\alpha = \langle r^2\rangle/\langle r^2\rangle_0$, Characteristic Ratio $\langle r^2\rangle_0/nl^2$, and Dimension Ratio $\langle r^2\rangle_0/M$

fraction	10^3A_2, mol cm^3 g^{-2}	α	$\langle r^2\rangle_0/nl^2$	$\langle r^2\rangle_0/M$, Å^2 mol g^{-1}
1	1.03	1.199	4.57	0.932
2	1.32	1.261	4.22	0.861
3	1.05	1.196	4.33	0.883
4	0.99	1.163	4.59	0.935

the quantities obtained by the two techniques.

In the analysis of the osmotic pressures π obtained at 30 °C for the four fractions of higher molecular weight, the ratio π/c was found to vary linearly with the concentration c, as shown by a typical plot represented in Figure 1. These data fit the linear relationship[18]

$$\pi/c = RT(M_n^{-1} + A_2c) \qquad (2)$$

where R is the gas constant, T the absolute temperature, and A_2 is the second virial coefficient whose values are given in the second column of Table III.

The values of the parameter $\alpha = \langle r^2\rangle/\langle r^2\rangle_0$ which characterize perturbations due to exclude-volume effects were obtained by using the Orofino–Flory equation[19]

$$\ln\,[1 + (\pi^{1/2}/2)(\alpha^2 - 1)] = (27\Phi/2^{5/2}\pi N_A)(A_2M_n/[\eta]) \qquad (3)$$

which is specially suitable for those systems in which α is close to unity. In eq 3 Φ is a hydrodynamic constant equal to 2.1×10^2 dL cm^{-3} mol^{-1}, N_A is Avogadro's number, and π is here the numerical constant 3.1416.

The ratio $\langle r^2\rangle_0/M_n$ was obtained from the equation[18]

$$[\eta] = \Phi(\langle r^2\rangle_0/M_n)^{3/2}M_n^{1/2}\alpha^3 \qquad (4)$$

using the values of $[\eta]$ and α given in the second column of Table II and the third column of Table III, respectively.

The ratio $\langle r^2\rangle_0/M$ can also be expressed in terms of the characteristic ratio $\langle r^2\rangle_0/nl^2$, where nl^2 is the mean-square end-to-end distance of the chains in the idealization that all the skeletal bonds are freely jointed. In the evaluation of nl^2 it was assumed that the length of the virtual bond l_γ that joins the two carbonyl groups of the terephthaloyl residue is 5.74 Å; the lengths of the other skeletal bonds were taken to be[20,21] $l_{C^*-O^*} = 1.33$ Å, $l_{CH_2-O} = 1.43$ Å, and $l_{CH_2-CH_2} = 1.53$ Å. The values of $\langle r^2\rangle_0/M$ and $\langle r^2\rangle_0/nl^2$ obtained from eq 4 are shown in the fifth and fourth columns of Table III. They seem to be independent of molecular weight and the average values for $\langle r^2\rangle_0/M$ and $\langle r^2\rangle_0/nl^2$ are 0.903 Å^2 mol g^{-1} and 4.43, respectively.

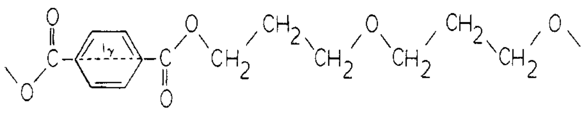

Figure 2. Structural unit of PDTT in all-trans conformation.

Theoretical Results

Theoretical values of the dipole moment ratio and the dimensions ratio were evaluated by using standard matrix multiplication methods discussed in detail elsewhere.[22,23] The values of the skeletal bond angles were assumed to be[21] COC* = 113°, C*C*O = 114°, OCC = 110°, COC = 111°, and CCC = 112°. The bond lengths used in the evaluation of the mean-square end-to-end distance were given above. The dipole vector associated with each ester group, μ_{es}, has a value of 1.89 D and its direction makes an angle of 123° with the C^{Ph}–C* bond,[2] whereas two dipole moments μ_{CH_2-O} each having a magnitude of 1.07 D and the direction of the O–CH$_2$ bonds were assigned to the ether parts of the molecule.[12] The dipole moment associated with the CH$_2$–CH$_2$ bonds was considered to be nil.

With the exception of the O–C*O* bonds of the ester group that are restricted to trans states and the virtual bonds l_γ of the terephthaloyl residue in which the potential minima are located at 0 and 180°, the rotational angles of the remaining skeletal bonds of the repeating unit in Figure 2 were assumed to be 0, ±120°. A brief discussion concerning the conformational energies used in the calculations follows. Thus the trans and cis conformations in the terephthaloyl residue were assumed to have the same energy. Gauche states about O–CH$_2$ bonds of the ester group have an energy E_{σ_k} = 0.3 kcal mol^{-1} above that of the alternative trans states.[22] Semiempirical calculations performed by Abe and Mark[12] on POM$_3$ suggest that gauche rotations about CH$_2$–CH$_2$ bonds that give rise to first-order CH$_2$···O interactions have an energy $E_{\sigma'}$ of ca. –0.15 kcal mol^{-1} with respect to that of the corresponding trans states. Similar rotations about O–CH$_2$ ether bonds in which first-order interactions between two methylene groups occur have an energy $E_{\sigma''}$ = 0.9 kcal mol^{-1} above that of the alternative trans states.[12,22] It was assumed that gauche rotations of different sign about two consecutive CH$_2$–CH$_2$ bonds that give rise to pentane-type interferences between two oxygen atoms have an energy[12] E_ω of 0.45 kcal mol^{-1}, whereas similar rotations about O–CH$_2$ bonds of the ester group and the adjacent CH$_2$–CH$_2$ bond that cause second-order interactions between carbonyl and methylene groups were considered to have an energy[22] of 1.4 kcal mol^{-1}. Accordingly, the conformation-dependent properties studied in this work were calculated by using as a first approximation the following set of conformational energies: $E_{\sigma_k} = 0.31$, $E_{\sigma'} = -0.15$, $E_{\sigma''} = 0.9$, $E_\omega = 0.45$, and $E_{\omega_k} = 1.4$ kcal mol^{-1}.

An inspection of the structure of PDTT reveals that the polarity of the chains should be very sensitive to $E_{\sigma'}$. For this reason and because of the uncertainties involved in the value of $E_{\sigma'}$ given above (since it was obtained from semiempirical potential functions), the dependence of the dipole moment ratio on $E_{\sigma'}$ was calculated and the pertinent results are shown in Figure 3. The calculations show that the value of $\langle\mu^2\rangle/nm^2$ decreases as $E_{\sigma'}$ increases. This is a consequence of the fact that a larger $E_{\sigma'}$ increases the fraction of all-trans conformations in which the dipole associated with the ether group of each repeating unit is almost in an antiparallel direction to the dipoles associated with the two neighbor ester groups. For example, the dipole moment ratio changes from 0.70 up to 1.0 when $E_{\sigma'}$ changes from 0.15 down to –1.0 kcal mol^{-1}; as can be seen

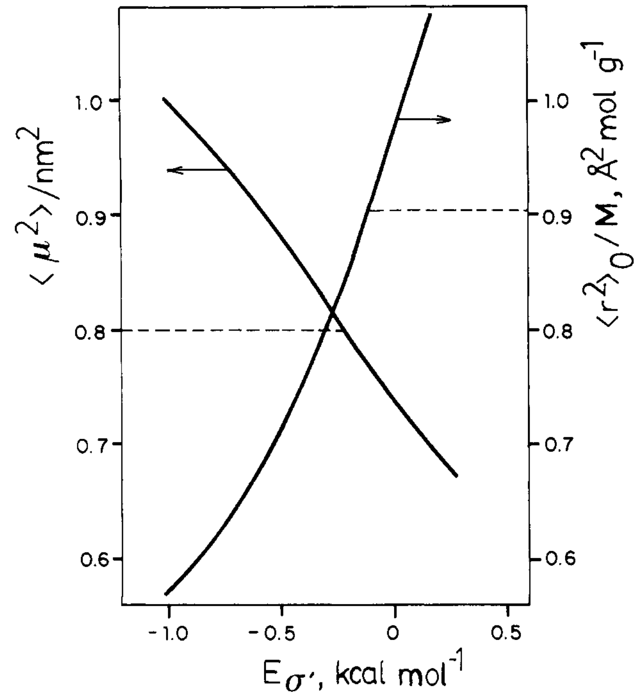

Figure 3. Variation of the dipole moment ratio and the dimension ratio with $E_{\sigma'}$ for PDTT chains at 30 °C.

Table IV
Comparison of Experimental Conformation-Dependent Properties of PDET and PDTT

property	PDET	PDTT
$\langle\mu^2\rangle/nm^2$	0.66	0.80
10^4 d ln $\langle\mu^2\rangle/\mathrm{d}T$, K^{-1}	0.97	−2.40
$\langle r^2\rangle_0/M$	0.60^a	0.90
10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$, K^{-1}	1.10	−0.30^b

^{a}Calculated by assuming that gauche states about CH_2–CH_2 bonds have an energy of 0.8 kcal mol^{-1} below that of the alternative trans states.[9] ^{b}Calculated value (see Figure 4).

in Figure 3, agreement between theoretical and experimental results is found for $E_{\sigma'} = -0.2$ kcal mol^{-1}. Moreover, since departure from the all-trans conformation increases the dipole moment of the chains, an increase in temperature should decrease the dipole moment for negative values of $E_{\sigma'}$; this means that d ln $\langle\mu^2\rangle/\mathrm{d}T$ should be negative for $E_{\sigma'} < 0$ and its absolute value should be larger the lower is $E_{\sigma'}$. This behavior is reflected in Figure 4, where it can be seen that d ln $\langle\mu^2\rangle/\mathrm{d}T \simeq -4.6 \times 10^{-4}$ for $E_{\sigma'} = -0.2$ kcal mol^{-1}, a value somewhat higher in absolute value than that found experimentally (Table IV).

With the dimensions expressed in terms of the characteristic ratio $\langle r^2\rangle_0/nl^2$, certain ambiguity can arise from the fact that in the evaluation of nl^2 we can use either the virtual bond $l_\gamma = 5.74$ Å indicated in Figure 2 or the virtual bond of 3.67 Å connecting the set of atoms C^{Ph}–CO–OC, the value of nl^2 being higher in the former case than in the latter. In order to avoid this ambiguity it is covenient to express the calculated values of the mean-square end-to-end distance in terms of the ratio $\langle r^2\rangle_0/M$. The variation of this ratio with E_σ, is shown in Figure 3. It can be seen that the dimensions of the chains show a strong dependence on $E_{\sigma'}$, the value of $\langle r^2\rangle_0/M$ changing from 0.57 to 1.07 Å^2 mol g^{-1} when $E_{\sigma'}$ increases from −1 to 0.15 kcal mol^{-1}. Agreement between theory and experiment is found for $E_{\sigma'} = -0.1$ kcal mol^{-1}, a value that is very close to that found in the analysis of the dipole moment of the chains.

The unperturbed dimensions are also very sensitive to E_ω as can be seen in Figure 5, where $\langle r^2\rangle_0/M$ was calculated by assuming that $E_{\sigma'} = -0.15$ kcal mol^{-1}, the intermediate value found for this parameter from the analysis of the unperturbed dimensions and dipole moments of the chains. In contrast, the dependence of the dipole moment on E_ω is rather small. The big decrease observed in $\langle r^2\rangle_0/M$ with decreasing values of E_ω is caused by the fact that the fraction of $g^\pm g^\mp$ states about two consecutive CH_2–CH_2 skeletal bonds of the glycol residue increases, leading to the folding of the repeating unit on itself, thus decreasing the dimensions of the chains. Good agreement between theoretical and experimental results is found for $E_\omega = 0.55$ kcal mol^{-1}, a value that is very close to that found for this parameter from the critical interpretation of the conformation-dependent properties of POM_3.[12]

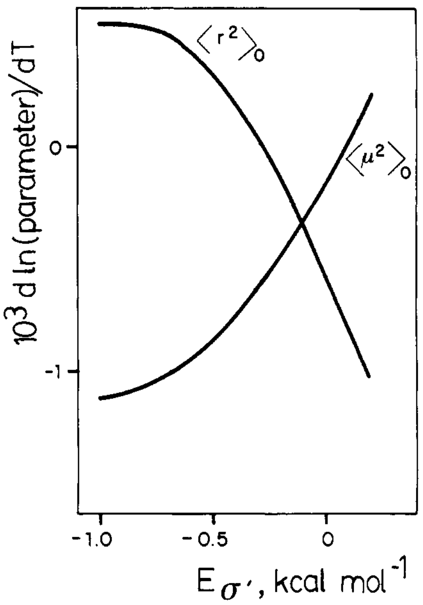

Figure 4. Dependence of the temperature coefficient of both the dipole moment and the dimension ratio at 30 °C on $E_{\sigma'}$.

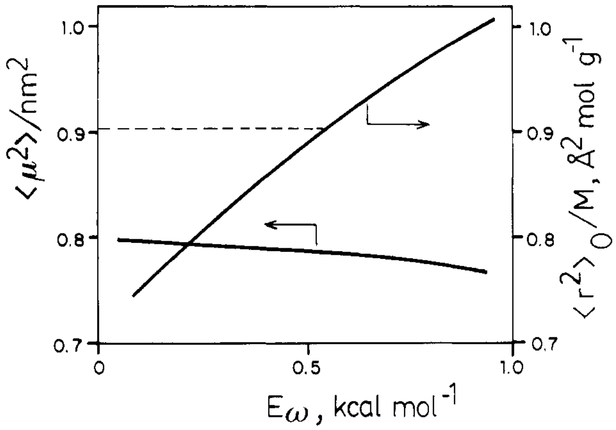

Figure 5. Dependence of the dipole moment ratio and the dimension ratio at 30 °C on the second-order interactions E_ω for PDTT chains.

The dependence of d ln $\langle r^2\rangle_0/\mathrm{d}T$ on $E_{\sigma'}$ is shown in Figure 4, where it can be seen that the value of this quantity decreases as $E_{\sigma'}$ increases. The theoretical analysis suggests that the unperturbed dimensions should have a small but negative temperature coefficient.

Discussion

The sensitivity of the conformation-dependent properties to $E_{\sigma''}$, $E_{\omega_{\eta k}}$, and E_{σ_k} in comparison with the sensitivity to $E_{\sigma'}$ and E_ω is rather small. The theoretical calculations indicate that the value of $E_{\sigma'} = -0.15$ kcal mol^{-1} gives a good account of the dipole moment ratio and dimensions ratio of PDTT chains. Accordingly, the experimental value of $E_{\sigma'}$ is in complete agreement with the value obtained for this quantity in POM_3 by using semiempirical potential functions but is somewhat larger than the value of −0.4 kcal mol^{-1} obtained by Abe and Mark[12] from the critical interpretation of the dipole moments and unperturbed dimensions of this polymer. Therefore, it seems that the carboxyl group cancels the stabilizing effects of the gauche states about CH_2–CH_2 bonds that appear in POM_3.

By comparing the conformation-dependent properties of PDET[6,9] and PDTT (see Table IV) important differences can be detected. Thus PDET is less polar than PDTT presumably owing to the difference in gauche population about CH_2–CH_2 bonds between the two polymers. In the all-trans conformation the dipole associated with the CH_2OCH_2 group in PDET is in a nearly parallel direction with the two neighbor ester groups, so that departure from the trans conformation will diminish the polarity of the chains; in PDTT, on the other hand, the polarity will increase. The fact that the gauche population fraction about CH_2–CH_2 bonds is ca. 90% in PDET,[12] whereas the bonds are almost freely rotating in PDTT, explains the higher polarity of the latter polymer with respect to the former. It also explains why the temperature coefficient of the unperturbed dimensions is large and positive in PDET,[8] whereas it is negative in PDTT. Actually, an increase in temperature causes an uncoiling effect in PDET as a result of the transition of the gauche state about CH_2–CH_2 bonds to trans, which overcomes the coiling effect of the change of trans to gauche that takes place in the CH_2–O ether bonds. However, the latter effect is dominant in PDTT and hence the negative temperature coefficient of the dimensions of this polymer.

The high preference for gauche states about CH_2–CH_2 bonds in PDET is nearly as strong as the preference for trans states about CH_2–O bonds, and as a consequence, these chains are less flexible than PDTT chains, where, as indicated above, CH_2–CH_2 bonds are almost freely rotating. This qualitative argument suggests that the glass transition temperature of the former polymer should be higher than the T_g of the latter. The low preference for the gauche state of the CH_2–CH_2 bonds in PDTT would also favor the packing of the chains in the all-trans conformation that apparently should be the conformation of the chains in the crystal.

Acknowledgment. This work was supported by the CICYT through Grants PB-86-0620 and 568.

Registry No. PDTT (copolymer), 115563-51-4; PDTT (SRU), 115563-52-5.

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