greater in polystyrene than in PSO (cf. Table III) or poly(styrene sulfide)[23], where it is negligible. Although this difference can be attributed in some part to the effects of the protons in vicinal methylene groups, it must also reflect the importance of bond-angle flexing in the backbone motions of polystyrene. The importance of the bond-angle coordinates in conformational entropy calculations has recently been demonstrated by Karplus and Kushick.[37]

Acknowledgment. We thank the National Science Foundation for support of this work: at Dartmouth under Grants DMR 76-22987 of the Polymers Program, Division of Materials Research, and CHE 77-04386; and at Brown under Grant CHE 78-22209-A02. We also thank Professor Robert H. Cole for his interest.

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^{1}H NMR Study of Low Molecular Weight Analogues of Poly(diethylene glycol terephthalate) and Poly(thiodiethylene glycol terephthalate)

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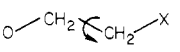
ABSTRACT: The rotameric probability about CH_2–CH_2 bonds in poly(diethylene glycol terephthalate) (PDET) and poly(thiodiethylene glycol terephthalate) (PSDET) was obtained from ^{1}H NMR studies of the respective low molecular weight analogues diethylene glycol dibenzoate (ODB) and thiodiethylene glycol dibenzoate (SDB). The fractions of gauche states X_g about the moiety 1, where X is O for ODB and S for SDB, were 0.89 ± 0.05 and 0.60 ± 0.05, respectively, in deuterated benzene. The fractions X_g in ODB and SDB increase with the polarity of the medium, their values being, respectively, 0.94 ± 0.05 and 0.66 ± 0.05 in deuterated acetone. These results, interpreted in terms of the rotational isomeric state model, suggest that gauche states about CH_2–CH_2 bonds in both PDET and PSDET have an energy ca. 0.5 kcal mol^{-1} lower than similar states about these bonds in poly(oxyethylene) (POE) and poly(thiodiethylene glycol) (PTDG), respectively.



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Introduction

The configuration-dependent properties of polymers can be analyzed within the framework of the rotational isomeric state (RIS) approximation provided that the neighbor-dependent character of the conformational energies is taken into account.[1,2] Experimental values of these energies can be obtained either from spectroscopic studies of model compounds or by comparison between theoretical and experimental values of some configuration-dependent properties.[1,3] In addition, semiempirical potential functions are also used to calculate conformational energy maps which can provide very important information regarding

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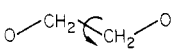
the energy associated with the conformations of minimum and higher intramolecular energies.[4]

The determination of the energy associated with gauche states about



bonds in poly(oxyethylene) (POE) has been widely investigated.[1,3-6] NMR studies[7-9] on the temperature dependence of the couplings in the ^{13}C–H proton satellite sidebands suggest that the gauche conformation is the most stable. A similar conclusion is obtained from the vibrational spectra of dimethoxyethane,[10] CH_3OCH_2-CH_2OCH_3, a low molecular weight analogue of POE. Moreover, the critical analysis of both the unperturbed dimensions and dipole moments of POE chains in terms of the RIS model showed that gauche states about CH_2–CH_2 bonds have an energy ca. 0.5 kcal mol^{-1} below the alternative trans state. It would be interesting to investigate how the nature of the environment influences the population of gauche states about CH_2–CH_2 bonds in which first-order O···O interactions occur. Conformations of this kind with neighbor benzoyl residues appear, for example, in poly(diethylene glycol terephthalate) (PDET), a polyester with repeating unit $OOCC_6H_4COOCH_2CH_2O$-CH_2CH_2. Although the dipole moments of PDET were measured and the results were interpreted in terms of the RIS model,[11] this particular property was not sensitive enough to the gauche population about CH_2–CH_2 bonds, so definitive conclusions regarding the value of the energy corresponding to these states could not be obtained. Other conventional techniques such as light scattering and viscometry which give information concerning the molecular dimensions are not useful due to the relatively low molecular weight of these chains. Therefore, this work examines the use of another technique, NMR spectroscopy, to determine the fraction of the different rotamers about CH_2–CH_2 bonds in the polyesters indicated above.

Poly(diethylene glycol terephthalate) may be schematically converted into poly(thiodiethylene glycol terephthalate) (PSDET) by simply substituting for the ether group a thioether function. Gauche states about CH_2–CH_2 bonds in PSDET bring sulfur and oxygen atoms into close proximity. The effect of the benzoyl residues in the gauche population about these bonds is also studied by means of NMR spectroscopy. For these studies low molecular weight models were used since they provide a better resolution of the resonance signals. In this context, diethylene glycol dibenzoate (ODB) and thiodiethylene glycol dibenzoate (SDB) were utilized as low molecular weight analogues of PDET and PSDET, respectively.

Experimental Section

Preparation of the Polymers. Poly(diethylene glycol terephthalate) (PDET) and poly(thiodiethylene glycol terephthalate) were obtained by using equimolar quantities of purified dimethyl terephthalate and diethylene glycol and thiodiethylene glycol, respectively. Details of the polymerization process as well as of the physical characteristics of PDET and PSDET are given elsewhere.[12-15]

Synthesis of Low Molecular Weight Model Compounds. Diethylene glycol dibenzoate and thiodiethylene glycol dibenzoate were prepared at room temperature by reaction of benzoyl chloride with diethylene glycol and thiodiethylene glycol, respectively. The reaction products were extracted with diethyl ether, dried over calcium chloride, and purified by successive distillations under vacuum. Finally, diethylene glycol dibenzoate was redistilled [bp 157–158 °C (0.5 mmHg), n^{18}_D 1.546; lit.[16] bp 279–281 °C (24 mmHg)] whereas thiodiethylene glycol dibenzoate was crystallized from a mixture of chloroform–*n*-hexane. The melting point of the purified product was 60 °C (lit.[16] mp 65 °C). The molecular weight values of both compounds, determined with a Knauer vapor pressure osmometer, were 305 for ODB and 328 for SDB, in good agreement with their respective theoretical values, 314 and 330.

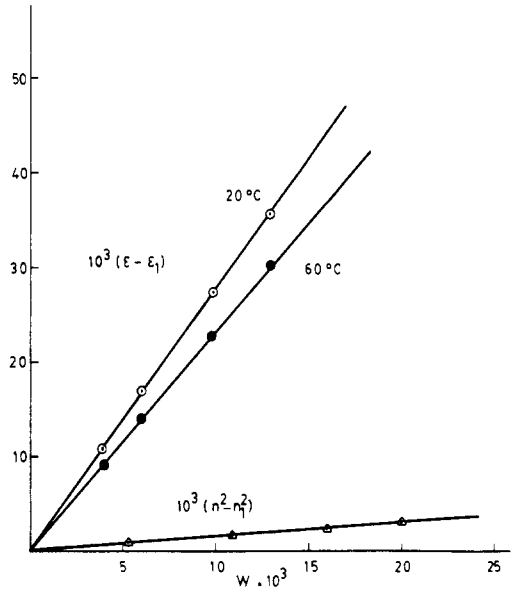


Figure 1. Concentration dependence of the increments in dielectric constant and squared index of refraction for ODB.

Table I
Summary of Dielectric Results for Diethylene Glycol Dibenzoate in Benzene

T, °C	$d(\epsilon-\epsilon_1)/dw$	$d(n^2-n_1^2)/dw$	$\langle\mu^2\rangle^{1/2}$, D
20	2.78	0.14	2.72_4
30	2.66	0.14	2.73_7
40	2.54	0.15	2.73_9
50	2.43	0.16	2.74_0
60	2.30	0.16	2.73_3

Magnetic Resonance Analysis. Fractionated polymers and low molecular weight compounds were analyzed by ^1H NMR spectroscopy with a Varian XL-100 and Bruker HX-90-E spectrometers at 100 and 90 MHz, respectively. The experiments were performed in deuterated chloroform, benzene-d_6, acetone-d_6, and *o*-dichlorobenzene at different temperatures, using tetramethylsilane as an internal reference standard.

Dielectric Measurements. Dielectric constants of solutions of ODB in benzene were measured at 20, 30, 40, 50, and 60 °C with a capacitance bridge operating at a frequency of 10 kHz, using a three-terminal platinum cell.[17,18] Increments in dielectric constants ($\Delta\epsilon = \epsilon - \epsilon_1$) and in squared index of refraction ($\Delta n^2 = n^2 - n_1^2$) were plotted against the weight fraction w of ODB in order to obtain values of the derivatives $d(\epsilon-\epsilon_1)/dw$ and $d(n^2-n_1^2)/dw$. Typical results are shown in Figure 1 and the values of the two derivatives for all five temperatures are given in columns two and three of Table I. Values of the dipole moments then were calculated by means of the equation of Guggenheim and Smith.[19,20] The value of the dipole moment at each temperature of interest is given in the fourth column of Table I. It can be observed that this parameter does not show a noticeable temperature dependence.

Results and Discussion

Figure 2A shows the ^1H NMR spectrum of PSDET recorded at 100 MHz, with deuterated chloroform at 27 °C as solvent. The single sharp peak at 8.09 ppm from Me_4Si corresponds to the four aromatic protons; triplets of intensity ratio near 1:2:1 centered at 4.55 and 3.00 ppm from Me_4Si correspond to the methylene protons next to the ester group and thioether function, respectively.

Figure 2B shows the ^1H NMR spectrum of PDET recorded under the same experimental conditions as PSDET.

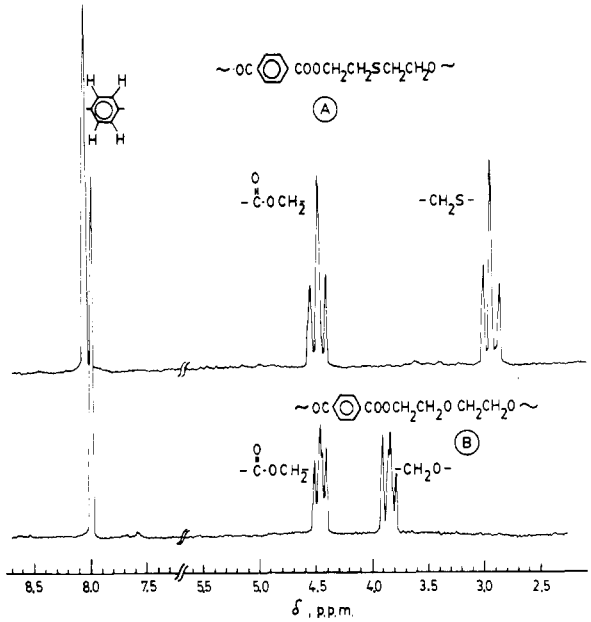


Figure 2. ¹H NMR spectra of poly(thiodiethylene glycol terephthalate) (A) and poly(diethylene glycol terephthalate) (B) in deuterated chloroform at 27 °C.

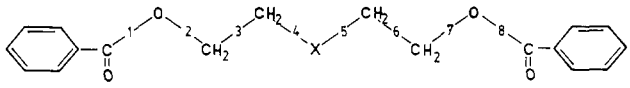


Figure 3. Structure of diethylene glycol dibenzoate (X = O) and thiodiethylene glycol dibenzoate (X = S).

The single sharp peak assigned to the four aromatic protons appears at higher field than the similar signal of PSDET. The resonance signals corresponding to the methylene protons of this polymer (4.45 and 3.82 ppm for the ones next to ester and ether groups, respectively) show an AA'BB' pattern, in contrast with PSDET. This difference in the splittings of the methylene resonances in PDET and PSDET might be satisfactorily explained in terms of different rotamer populations. In order to investigate this and to obtain better resolution in the ¹H NMR spectra, low molecular weight analogues of PDET and PSDET were studied. In this way, ODB and SDB (Figure 3), whose structures are similar to the repeat units of PDET and PSDET, respectively, were used. Figure 4 shows the ¹H NMR spectra of both compounds recorded as chloroform solutions. Similar results were obtained with different solvents, namely, benzene-d_6, acetone-d_6, chlorobenzene, and *o*-dichlorobenzene. It can be observed that the methylene resonance patterns of both spectra are rather similar to those of their corresponding parent polymers, but the resolution of the different signals is enhanced. Actually, the SDB spectrum presents a triplet with intensity ratios about 1:2:1 for the resonance of the methylene protons ($J_{AB} \simeq J_{AB'}$), whereas ODB presents an unsymmetrical multiplet for each one of the methylene groups $COOCH_2$ and CH_2O ($J_{AB} \neq J_{AB'}$). In order to study the possibility of conformational effects on the splitting of the methylene resonance signals, spectra of both model compounds were recorded at several temperatures in *o*-dichlorobenzene solutions. SDB gives methylene resonance signals which are independent of the temperature of the experiment whereas the splittings of ODB resonance signals significantly change with temperature as shown in Figure 5. Thus as the temperature increases the separation between the lines defining the sum $|J_{AB} + J_{AB'}|$ in each one of the CH_2 groups increases. Obviously, this behavior is a consequence of the change of the conformational populations with temperature and so the increase of temperature tends to equilibrate the population of the conformational states.

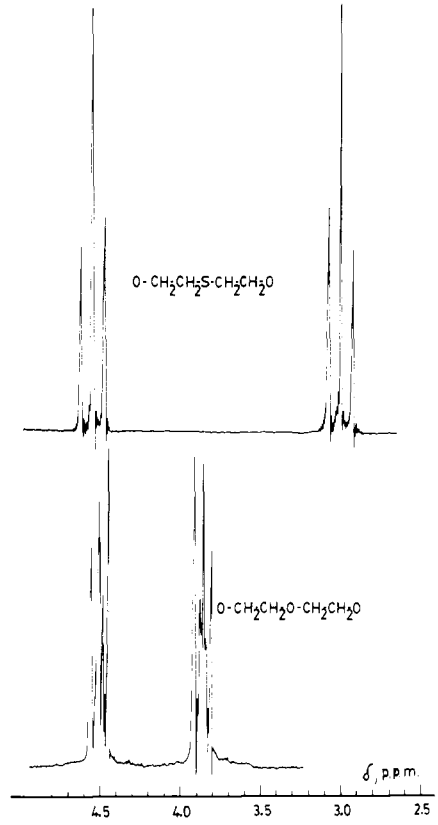


Figure 4. ¹H NMR spectra of ethylene residues corresponding to thiodiethylene glycol dibenzoate (top) and diethylene glycol dibenzoate (bottom) in chloroform at 27 °C.

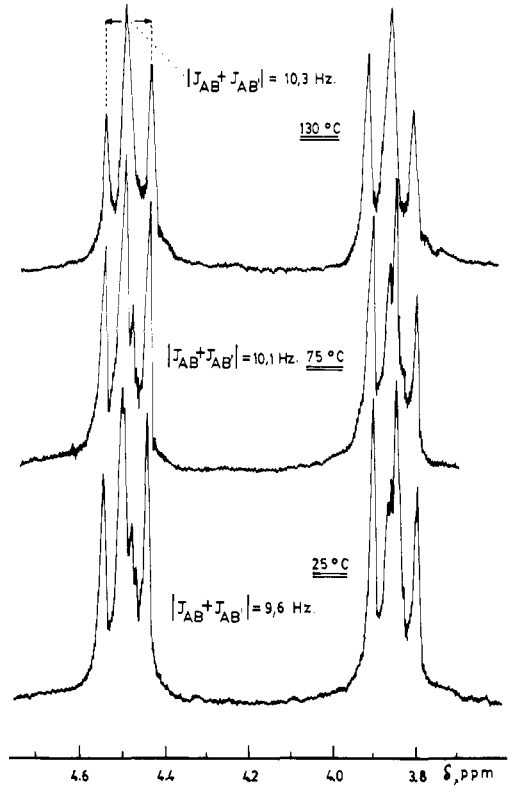


Figure 5. Influence of the temperature on the ethylene pattern of diethylene glycol dibenzoate in *o*-dichlorobenzene.

Each of the ethylene groups of ODB and SDB can be considered to be like 1,2-disubstituted ethanes, which have

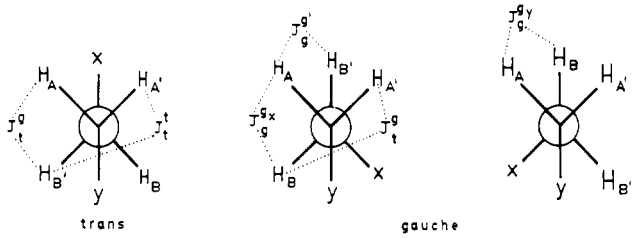


Figure 6. Conformations of 1,2-disubstituted ethanes according to Abraham nomenclature. For SDB, X = S; for ODB, X = O.

Table II
Limiting Couplings[a] for Gauche and Trans Rotamers (Hz), J_{AB} and $J_{AB'}$ Values Obtained from Spectral Analysis (Hz), and Calculated Gauche Molar Fractions for SDB and ODB in Acetone at 27 °C

	SDB	ODB
J_t^t	12.70	11.91
J_t^g	4.97	5.80
J_g^t	12.81	12.27
J_g^{gx}	3.02	2.52
J_g^{gy}	3.94	2.52
$J_g^{g'}$	1.73	0.44
J_{AB}	6.6	3.1
$J_{AB'}$	6.6	6.4
X_g	0.66	0.94

[a] Other coupling values used in the simulation were $J_{AA'} = -11$ Hz and $J_{BB'} = -10.6$ Hz (only the difference $J_{AA'} - J_{BB'}$ can be obtained from analysis). Standard errors in J_{AB} and $J_{AB'}$ were 0.05 Hz. The contribution of this error to the calculated X_g is much less than 0.01.

been described extensively in the literature.[21-23] The molecule XCH_2CH_2Y has three rotational isomers as shown in Figure 6, where the nomenclature of Abraham[22] has been used. Superscripts denote the orientation of the coupled protons and subscripts denote the isomer. In general, the protons of 1,2-disubstituted ethanes give rise to a ^1H NMR spectrum which corresponds to an AA'BB' system. Values for J_{AB} and $J_{AB'}$ coupling constants have been obtained for ODB and SDB from the analysis of their spectra by using LAOCN3 computer program. The values obtained are given in Table II. Values for the molar fractions of each type of conformer can be calculated from

$$X_g = 2(J_t^t - J_{AB})/(2J_t^t - J_g^{gx} - J_g^{gy}) = 2(J_t^g - J_{AB'})/(2J_t^g - J_g^{g'} - J_g^t)$$

$$X_t = 1 - X_g$$

or even better from analogous expressions including $|J_{AB} + J_{AB'}|$ or $|J_{AB} - J_{AB'}|$, if model values for the couplings in the limiting conformations are available. These values can be obtained by using the equation derived by Phillips and Wray,[23] which relates them to the Huggins substituent electronegativities. Values obtained in this way for X_g and gauche and trans couplings in both rotamers for ODB and SDB are also given in Table II.

Figure 7 shows the ethylene spectral pattern of ODB as recorded in acetone-d_6 solution at room temperature together with the corresponding simulated spectrum. It is clear that the agreement between the experimental and the simulated spectra is excellent. The application of the corresponding equations gives for SDB an average value of $X_g = 0.66 \pm 0.05$ and for ODB an average value of $X_g = 0.94 \pm 0.05$ when acetone-d_6 is used as solvent. These values indicate that gauche states about CH_2–CH_2 bonds are strongly preferred over the trans state in the case of ODB; however, SDB presents an equilibrium population of the three rotational states t, g^+, and g^- about the same bonds. In order to evaluate whether there is any solvent

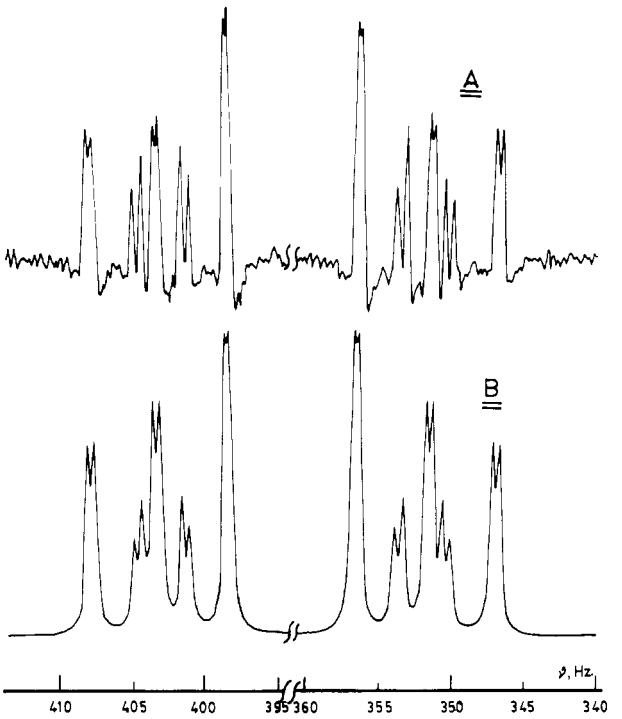


Figure 7. Resolution-enhanced observed spectrum of diethylene glycol dibenzoate (A) and simulated spectrum (B) (90 MHz).

effect on the spectral pattern of methylene resonances of ODB and SDB, spectra of these model compounds were recorded in benzene-d_6 solutions, the concentration being about 10% (v/v). The results obtained under similar experimental conditions to those recorded in acetone-d_6 gave the following values: for SDB, $X_g = 0.60 \pm 0.05$; for ODB, $X_g = 0.89 \pm 0.05$.

In view of the results indicated above, the gauche population about CH_2–CH_2 bonds in both ODB and SDB seems to be dependent on the polarity of the medium in the sense that it increases as the solvent dielectric constant increases. This apparently short-range solvent effect, which frequently has a very marked effect on the dimensions and dipole moments of polar chains,[24] may arise from the dependence of the Coulombic part of the conformational energy on the dielectric constant of the medium. The fact, however, that acetone has a dielectric constant 20.7 at 25 °C, very different from the value of 2.274 corresponding to benzene at the same temperature,[25] and the fact that the fraction of gauche states in both solvents for each model compound differs by only about 0.04, seem to argue against a strong solvent effect. Therefore, it seems reasonable to assume that the values of X_g about CH_2–CH_2 bonds in ODB and SDB free of solvent effects should be in the vicinity of 0.89 and 0.60, respectively.

The three-state RIS model[1] was used to calculate the bond rotation probabilities for CH_2–CH_2 bonds as a function of the energy associated with gauche states $E_\sigma = [E(g^\pm) - E(t)]_{O\cdots X}$, where the subscript X denotes the central heteroatom in the model compound, which is O for ODB and S for SDB. A brief summary of information on the conformational energy associated with the different states of the different bonds follows. Bonds of type 1 and 8 in Figure 3 are restricted to trans states.[1] Bond rotations about bonds of type 2 and 7 bring methylene and carbonyl groups separated by three bonds into proximity; studies based on the molecular dimensions of poly(ethylene terephthalate) (PET) suggest that gauche states about these bonds have an energy 0.4 kcal mol^{-1} higher than the alternative trans states.[1] Bonds of type 4 and 5 have gauche

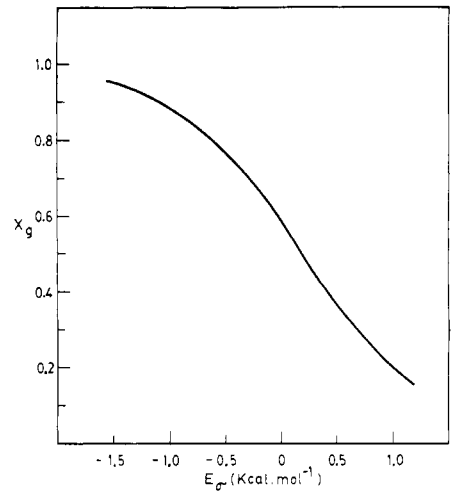


Figure 8. Molar fraction of gauche states X_g about CH_2–CH_2 bonds against E_σ for diethylene glycol dibenzoate.

states approximately 0.9 kcal mol^{-1} higher in energy than the corresponding trans states when X in Figure 3 represents an oxygen atom.[1,3] This value reduces to about −0.1 kcal mol^{-1} for the case in which X represents a sulfur atom.

The second-order interaction energies that give rise to pentane-type interferences between CH_2 groups and O atoms were taken to be[1,3] 0.4 kcal mol^{-1}. In the case of $g^{\pm}g^{\mp}$ conformations in which the interacting species are two CH_2 groups, their steric overlaps cause complete exclusion of these conformations.[1] Finally, gauche states of opposite sign about the pairs of bonds 2,3 and 6,7 cause interactions between a carbonyl group and the central heteroatom X. An energy of about 1.3 kcal mol^{-1} was tentatively used in the calculations.

In Figure 8 we have plotted the value of X_g against E_σ for ODB. It was observed that the curve X_g vs. E_σ for SDB only differs slightly from that shown in Figure 8. In the case of ODB, values of E_σ lying in the range −0.8 to −1.2 kcal mol^{-1} reproduce satisfactorily the value of X_g found for this compound. These values are almost two times lower than the value of the energy associated with gauche states about similar bonds in POE. For SDB, a value of E_σ in the vicinity of zero reproduces the value of X_g obtained by ¹H NMR spectroscopy. This value also is significantly lower than that found for similar states about similar bonds in poly(thiodiethylene glycol) (PTDG), an alternating copolymer of ethylene oxide and ethylene sulfide units, where gauche states about CH_2–CH_2 bonds, which bring oxygen and sulfur atoms into close proximity, have an energy ca. 0.4 kcal mol^{-1} higher than the alternative trans states.[26,27]

The results indicated above suggest, therefore, that O···O as well as S···O first-order interactions are strongly affected by the presence of the benzoyl residue in the sense that it reduces the energy associated with gauche states about CH_2–CH_2 bonds in both SDB and ODB. Given the similarity of the NMR spectra of these compounds with those of their respective parent polymers PSDET and PDET, it can be expected that the gauche population about CH_2–CH_2 bonds in the polymers will be similar to that found for the analogous low molecular weight compounds.

It would be interesting to investigate whether the values of certain experimental conformation-dependent properties of both model compounds, for example, dipole moments,

Table III
Theoretical and Experimental Dipole Moments for ODB and SDB at 30 °C

model compound	$\langle\mu^2\rangle^{1/2}_{theor}$, D	$\langle\mu^2\rangle^{1/2}_{exptl}$, D
ODB	2.66	2.72
SDB	2.73	2.88[a]

[a] Taken from ref 15.

are reproduced with the values of the energetic parameters given above. Thus, the values of the dipole moments at 30 °C for SDB and ODB were calculated by using the RIS model. In the calculations it was assumed that the value of the dipole moment of ethyl benzoate is 1.89 D and its direction makes an angle of 49° with the O–CO bond.[11] Bond dipole moments m_{C-O} and m_{C-S} lie along the bonds and their values are 1.07 and 1.21 D, respectively.[3,28] The values of the theoretical and experimental dipole moments at 30 °C are given in the second and third columns of Table III. Assuming that E_σ = −0.9 kcal mol^{-1}, the theoretical value of the dipole moment of ODB is 2.66 D, in satisfactory agreement with the experimental value (2.72 D). Moreover, the experimental results of Table I indicate that the dipole moment of ODB does not have a noticeable temperature dependence. This is also in agreement with the theoretical results according to which $d \ln \langle\mu^2\rangle/dT = -2 \times 10^{-4}$ K^{-1}. In the case of SDB and for E_σ = 0, the agreement is not so satisfactory although the differences between the theoretical and the experimental results are within the error involved in the experimental determination of the dipole moments.

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