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Comparative Study of the Conformational Characteristics of Partially Fluorinated Polyesters and Their Hydrogenated Counterparts

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ABSTRACT: From a comparative study of the polarity of poly(neopentyl glycol hexafluoroglutarate) (PNFG) and its hydrogenated counterpart, poly(neopentyl glycol glutarate) (PNG), the influence of the presence of the fluorine atoms on the conformational characteristics of polyesters is investigated. At 30 °C, the experimental values of the mean-square dipole moment per repeating unit of PNG and PNFG chains, $\langle \mu^2 \rangle / x$, are 5.25 and 9.16 D^2, respectively. A critical interpretation of the experimental results using the rotational isomeric state model suggests that the conformational energies associated with the gauche states about both the $C^{\alpha}H_2{-}C^*(O^*)$ and $C^{\beta}H_2{-}C^{\alpha}H_2$ bonds of the acid residue of PNG have, respectively, lower and higher energy than the alternative trans states. Similar conclusions are reached for the conformational energies associated with the skeletal bonds of the $C^{\beta}F_2{-}C^{\alpha}F_2{-}C^*(O^*)$ segment of the acid residue of PNFG chains. This study leads us to conclude that differences in the orientations of the dipoles associated with the ester groups, rather than differences in the rotational populations about the skeletal bonds of the chains, may be responsible for the significant higher polarity of the fluorinated polyesters.

Introduction

Besides poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride), important fluorine-containing polymers (molecular chains with fluorinated moieties in their structure) also include some organic[1] and inorganic rubbers,[2] polyacrylates,[3,4] polyurethanes,[5−8] polyesters,[9−11] polyamide−imides,[12] epoxy resins,[13] high-temperature fluorinated polymers,[14] etc. The presence of several consecutive CF_2 groups in the molecular chains confers on them some of the desirable properties of PTFE, such as lower water absorption, better chemical resistance, lower refractive indices, lower coefficients of friction, and lower energy surfaces. As a consequence of this latter property, fluorine-containing comonomers incorporated into copolymers tend to migrate to the surface, thus affecting the physical properties of the resulting materials. It should be noted that the surface properties of fluorine-containing polymers make them suitable for applications as biomaterials.

Earlier efforts to synthesize fluoroaliphatic polyesters met with only limited success.[10,11] The principal reason is that polyesters of this kind derived from fluoroaliphatic diacids are easily degradable. Only polyesters derived from hydrogenated aliphatic diacids and fluoroaliphatic diols met the stability requirements necessary for practical applications. However, the inductive effects of the fluorine atoms lead to highly acidic OH groups in the diol, thus decreasing their reactivity and promoting the formation of oligomers. In order to overcome this difficulty, it is necessary to use diols in which the CF_2 groups are separated by at least two methylenes from each terminal OH group. The CH_2 group spacers decrease the acidity of the diol, thus allowing the synthesis of chemically stable polyesters of relatively high molecular weight.[11]

In spite of the limited stability of polyesters containing fluorine atoms in the acid residue, a comparative study of the conformational properties of these polymers with respect to those of their hydrogenated counterparts is important because it contributes to a better understanding of the effect of structure on the conformational properties of polymer chains. For example, it is interesting to investigate how the CF_2 groups affect the magnitude and orientation of the dipoles associated with bonds or groups of bonds of the polyester chains. Moreover it is also important to study how the CF_2 groups affect the rotational populations about the skeletal bonds of partially fluorinated polyesters.

In this article we present a conformational study of the dipolar correlation coefficient of poly(neopentyl glycol hexafluoroglutarate) (PNFG). Owing to the lack of information on the effects of the fluorine atoms on the dipoles of bonds and/or groups of bonds of the chains, the distribution of residual charges in molecular model compounds with structural characteristics similar to those of the chains under investigation was calculated. The conformational energies associated with gauche states about both the $C^{\alpha}F_2{-}C^*(O^*)$ and $C^{\alpha}F_2{-}C^{\beta}F_2$ bonds of the acid residue of PNFG were determined by comparing the dipolar correlation coefficient, calculated as a function of these energies, with experimental results.

It is important to note that in spite of the efforts devoted to the study of the conformational characteristics of completely hydrogenated aliphatic diesters and polyesters, the elucidation of the distribution of rotational populations about the $C^{\beta}H_2{-}C^{\alpha}H_2{-}C^*(O^*)$ bonds of the acid residue remains highly controversial. For example, from a critical interpretation of IR, ^1H NMR, and Raman spectra of aliphatic esters and diesters, values ranging from 1 to −1 kcal mol^{-1} with respect to that of the alternative trans state have been reported for the energy of gauche states about the $C^{\alpha}H_2{-}C^*(O^*)$ bonds.[15−19] Similar disagreement was obtained from both the interpretation of the dipole moments of aliphatic diesters and the temperature coefficient of the unperturbed dimensions of aliphatic polyesters.[17,20−22] As for the energy associated with gauche states about $C^{\beta}H_2{-}C^{\alpha}H_2$ bonds, values of −0.6, 0.3, and 0.8 kcal

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mol^{-1} over those of the corresponding trans states were reported, respectively, for dialkyl esters of succinic, glutaric, and adipic acids.[17] In this study, these energies were determined by comparing the dipolar correlation coefficient of poly(neopentyl glycol glutarate) (PNG), calculated as a function of these energies, with experimental results.

Experimental Section

Materials. Glutaric acid (Aldrich) was recrystallized from benzene, the melting point of the purified product being 99 °C (lit. mp 98−100 °C). Hexafluoroglutaric acid (Aldrich) was distilled at reduced pressure (bp 140 °C at 10^{-2} mmHg), and the melting point of the distilled diacid was 89 °C. Neopentyl glycol was purified by successive crystallizations in a mixture of acetone−hexane (1/1, v/v), mp 131 °C (lit. mp 130 °C). Toluene was washed three times with a 10% solution of sulfuric acid to eliminate thiophenes, refluxed for 6 h in the presence of NaOH, and finally distilled over 4,4-diphenylmethane diisocyanate. *p*-Toluenesulfonic acid and tetraisopropyl titanate (Aldrich) were used as received.

Synthesis of Poly(neopentyl glycol glutarate). The polyester was synthesized by condensation of neopentyl glycol and glutaric acid in refluxing toluene, under a nitrogen atmosphere and stirring. The condensation process was catalyzed with *p*-toluenesulfonic acid (1−1.5% of the weight of the reacting products). Water formed during the process was azeotropically separated from the reaction medium with a Dean−Stark distillation trap. Toluene was periodically replaced in the reactor to avoid hydrolytic reactions, and the evolution of the polycondensation with time was followed by determining the acid index. In order to obtain hydroxyl-terminated chains, in the final steps of the process (acid index close to zero) a slight excess of glycol was added to the reaction medium. The polymer was dissolved in chloroform, precipitated several times with methanol, and dried in vacuum at 100 °C for 72 h.

Synthesis of Poly(neopentyl glycol hexafluoroglutarate). The synthesis proceeded by melt condensation of neopentyl glycol and hexafluoroglutaric acid for 4 h at 130 °C, under a nitrogen atmosphere. Tetraisopropyl titanate was used as catalyst in a ratio of 0.01% of the total weight of the reacting products. Water formed during the polycondensation was continuously eliminated by a nitrogen stream, and the evolution of the process with time was controlled by determining the acid index. In the final steps of the polycondensation, an excess of neopentyl glycol was added to obtain hydroxyl-terminated chains, and the process was allowed to proceed for a further 6 h. The polymer was dissolved in chloroform, precipitated three times with methanol, and dried in high vacuum at 60 °C for 72 h.

Characterization of the Polyesters. The number-average molecular weights of the polyesters PNG and PNFG, determined from the acid and hydroxyl indices, were 4500 and 3600 g mol^{-1}, respectively. The values of the glass transition temperatures of the polymers, measured with a DSC7 Perkin-Elmer calorimeter at a heating rate of 10 °C/min, were −40 °C for PNG and −33 °C for PNFG. The polyesters were characterized by IR and ^{1}H and ^{13}C NMR spectroscopies with a Varian XL 300 resonance apparatus, at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C, using tetramethylsilane as reference. The ^{1}H NMR spectra for the glycol residue present showed two singlets corresponding to methyl and methylenic protons which appeared at 0.75 and 3.80 ppm for PNG and slightly displaced to lower fields (1.1 and 4.15 ppm) for PNFG. The ^{13}C NMR spectrum of PNG exhibited six resonance signals corresponding to the different carbons of the structural unit of the polymer. The ^{13}C NMR spectrum of PNFG was somewhat more complex than that of PNG due to the coupling between the carbon and fluorine atoms. In addition to the signals associated with the glycol residue, the central carbon corresponding to the hexafluoroglutaric acid residue gives rise to nine resonance signals (divided in three triplets) centered at 110 ppm, with a one-bond coupling constant of 267.5 Hz, whereas that corresponding to two bonds was 32.2 Hz; these are typical values in fluorine compounds.[23] The other fluorinated carbons also present nine signals (divided in three triplets) centered at 108 ppm, with coupling constants similar to those indicated before. Three signals for the carbonyl carbon are observed with a two-bond coupling constant ^{13}C−^{19}F of 29.7 Hz, slightly lower than that of the other two carbons.

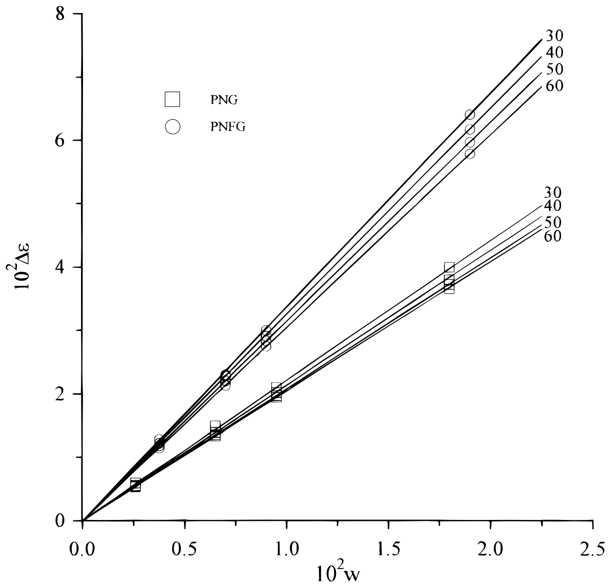

Figure 1. Dependence of the increments of the dielectric permittivity of the solutions ($\Delta\epsilon = \epsilon - \epsilon_1$) on the weight fraction of solute for poly(neopentyl glycol glutarate) (PNG) and poly(neopentyl glycol hexafluoroglutarate) (PNFG).

Dielectric Measurements. Values of the dielectric permittivity ϵ of solutions of the polyesters in benzene were measured at different temperatures with a capacitance bridge (General Radio, type 1620A). The measurements were performed with a three-terminal cell, at 10 kHz. At each temperature of interest, the term $d\epsilon/dw$, which is proportional to the total polarization of the molecular chains, was obtained from the slope of plots of the increments of the permittivity of the solutions with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) against the weight fraction w of solute in the solution, in the limit $w \to 0$. As an example, plots of this kind for PNG and PNFG are given in Figure 1. The electronic polarization arising from the distortion of the electronic clouds, caused by the electric field, is proportional to dn/dw. Values of this quantity were obtained from the slopes of plots of Δn ($= n - n_1$) against w, where the increments of the index of refraction of the solution, n, with respect to that of the solvent, n_1, were measured with a Brice-Phoenix differential refractometer. The atomic polarization was assumed to be negligible. Values of the mean-square dipole moment $\langle\mu^2\rangle$ were calculated by means of the method of Guggenheim and Smith:[24,25]

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

where k_B and N_A are, respectively, the Boltzmann constant and Avogadro's number, M is the molecular weight of the molecular chains, T is the absolute temperature, and ρ is the density of the solvent. The error involved in the determination of $\langle\mu^2\rangle$ was estimated to be ±3%.

Experimental Results

Values of $d\epsilon/dw$ and dn/dw for both PNG and PNFG are given at different temperatures in the third and fourth columns of Table 1, respectively. By comparing the values of $d\epsilon/dw$ for both polymers, one can see that the total polarization of PNFG is significantly higher than that of its hydrogenated counterpart. The polarity

Table 1. Summary of Dielectric Results for Poly(neopentyl glycol glutarate) (PNG) and Poly(neopentyl glycol hexafluoroglutarate) (PNFG) (Values at 30 °C of the Dipolar Correlation Coefficient g Are Given)

polyester	T, °C	$(\mathrm{d}\epsilon/\mathrm{d}w)^{\circ}$	$2n_1(\mathrm{d}n/\mathrm{d}w)^{\circ}$	$\langle\mu^2\rangle/x$, D^2	g	$\langle\mu^2\rangle$, D^2 [a]
PNG	30	2.20	0.02	4.20	0.65	5.25
	40	2.13	0.02	4.24		5.30
	50	2.07	0.02	4.36		5.48
	60	2.04	0.02	4.52		5.54
PNFG	30	3.37	0.19	9.57	0.99	12.1
	40	3.25	0.18	9.77		12.1
	50	3.14	0.18	9.98		12.2
	60	3.04	0.18	10.22		12.3

[a] The values of $\langle\mu^2\rangle$ represented in the seventh column, taken from ref 26, correspond to diethyl glutarate and diethyl hexafluoroglutarate, model compounds of PNG and PNFG, respectively.

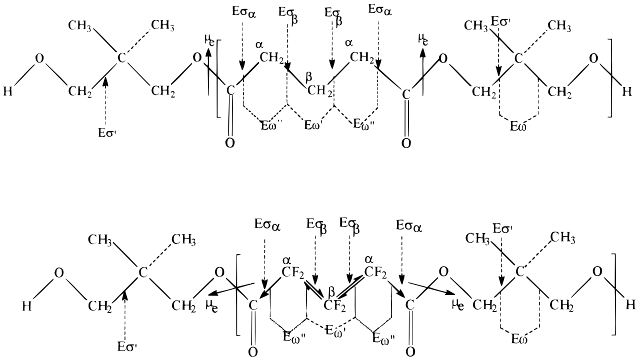

Figure 2. Scheme of the repeating units of PNG and PNFG in the all-trans conformation. Dipoles are indicated by arrows.

of the chains was expressed in terms of the mean-square dipole moment per structural unit, $\langle\mu^2\rangle/x$, where x is the number of structural units; the results obtained for this quantity are shown in the fourth column of Table 1. For comparative purposes, the values of $\langle\mu^2\rangle$ for diethyl glutarate and diethyl hexafluoroglutarate are also given.[26] It can be seen that the value of $\langle\mu^2\rangle$ for diethyl glutarate is nearly 23% larger than the value obtained for $\langle\mu^2\rangle/x$ of PNG, in spite of the fact that the terminal hydroxyl groups enhance the polarity of the chains. In the same way, the value of $\langle\mu\rangle^2$ for diethyl hexafluoroglutarate is also 32% larger than that of $\langle\mu^2\rangle/x$ for PNFG. These results suggest that correlations between the dipoles of consecutive repeating units are important in these polyesters.

The temperature coefficient of the mean-square dipole moment of PNG, expressed in terms of 10^3 d ln $\langle\mu^2\rangle/\mathrm{d}T$, amounts to 2.2 K^{-1}, somewhat lower than the value of 1.8 K^{-1} obtained for this quantity for diethyl glutarate. Because PNFG may undergo hydrolytic degradation at temperatures above 40 °C, a definite conclusion regarding the temperature coefficient of this polymer cannot be drawn from the results reported here.

Theoretical Results

Dipolar Correlation Coefficient for Poly(neopentyl glycol glutarate). The repeating unit of PNG in the all-trans conformation is shown in Figure 2. The dipolar correlation coefficient is expressed by

$$g = \frac{\langle\mu^2\rangle}{2(x{m_\mathrm{E}}^2 + {m_\mathrm{C\text{-}O}}^2 + {m_\mathrm{O\text{-}H}}^2)} \tag{2}$$

where x is the degree of polymerization. The dipole moment associated with the ester group, m_E, has a value[17] of 1.75 D and forms an angle[27,28] of 123° with the CH$_2$−C*(O*) bond, as indicated in Figure 2. The dipoles $m_\mathrm{C\text{-}O}$ and $m_\mathrm{O\text{-}H}$ corresponding to the terminal groups lie along the skeletal bonds, and their values[29] are 1.07 and 1.7 D, respectively. The values of g at 30 °C are given in the sixth column of Table 1.

The rotational angles about the skeletal bond of the acid residue were taken from the analysis of the dipole moment of dimethyl glutarate carried out by Abe and co-workers.[17] Thus the conformational states about the C$^\alpha$H$_2$−C*(O*) and C$^\alpha$H$_2$−C$^\beta$H$_2$ bonds were taken to be 0, ±123° and 0, ±113°, respectively. As for the energy $E\sigma_\alpha$ of gauche states about C$^\alpha$H$_2$−C*(O*), the results at hand are highly controversial.[15−22] From the analysis of the IR and ^{1}H NMR spectra of methyl propionate, values of this energy ranging from significantly larger than to lower than that of the alternative trans states have been reported. From an analysis of vicinal coupling constants, values of −0.6, 0.3, and 0.8 kcal mol^{-1}, respectively, have been obtained for the conformational energies, $E\sigma_\beta$, of gauche states about the C$^\alpha$H$_2$−C$^\beta$H$_2$ bonds relative to that of the corresponding trans state in methyl esters of succinic, glutaric, and adipic acids.[17] Second-order interactions arising from rotations of different sign about two consecutive skeletal bonds of the acid residue were considered to have energies $E_{\omega'} = E_{\omega''} = 1.4$ kcal mol^{-1} above that of the corresponding tt states.[17] Bonds of the type C*(O*)−O in the ester group are restricted to trans states. Gauche rotations about the O−CH$_2$ bonds of the glycol residue give rise to strong repulsive interactions between the methyl groups and the carbonyl group so that these bonds may also be considered to be restricted to trans states. The rotational states about the CH$_2$−C(CH$_3$)$_2$ bonds are located at 0, ±120°, the gauche states having an energy $E\sigma'$ ca. 0.6 kcal mol^{-1} below that of the alternative trans state. Second-order interactions arising from rotations of different sign about the consecutive CH$_2$−C(CH$_3$)$_2$−CH$_2$ bonds were assumed to have an energy $E_\omega = 1.4$ kcal mol^{-1} above that of the corresponding tt states.[21,22]

In the all-trans conformation, the dipoles associated with the ester groups of PNG chains are nearly parallel, giving for the dipolar correlation coefficient of this polymer a value of 19.26 at 30 °C. Departure from this conformation by rotations about the skeletal bonds will decrease the value of the dipolar correlation coefficient g. Values of g were calculated as a function of $E\sigma_\alpha$ using the following set of conformational energies: $E\sigma_\beta = 0.3$ kcal mol^{-1}, $E\sigma' = -0.6$ kcal mol^{-1}, $E\omega = E\omega' = E\omega'' =$ 1.4 kcal mol^{-1}. The results obtained, shown in Figure 3, indicate that the dipolar correlation coefficient increases as the gauche population about C$^\alpha$H$_2$−C*(O*) bonds increases. The theoretical value of g at 30 °C comes close to the experimental one for values of $E\sigma_\alpha <$ -1 kcal mol^{-1}. However, the value of this parameter for $E\sigma_\alpha = -1.0$ kcal mol^{-1} (0.73) is only in fair agreement with the experimental result (0.67 at the same temperature). The curve in Figure 3 showing the dependence of g on $E\sigma_\beta$ suggests that agreement between theoretical and experimental results requires an increase in the energy of gauche states about the C$^\alpha$H$_2$−C$^\beta$H$_2$ bonds. Thus for $E\sigma_\beta = 0.5$ kcal mol^{-1} and $E\sigma_\alpha =$ -1.0 kcal mol^{-1}, $g = 0.69$, in good agreement with experiment. For this set of conformational energies, 10^3 d ln $g/\mathrm{d}T = 0.62$ K^{-1}, in qualitative agreement with the experimental value of this quantity. It should be pointed out, however, that small errors involved in the experimental determination of g can produce significant

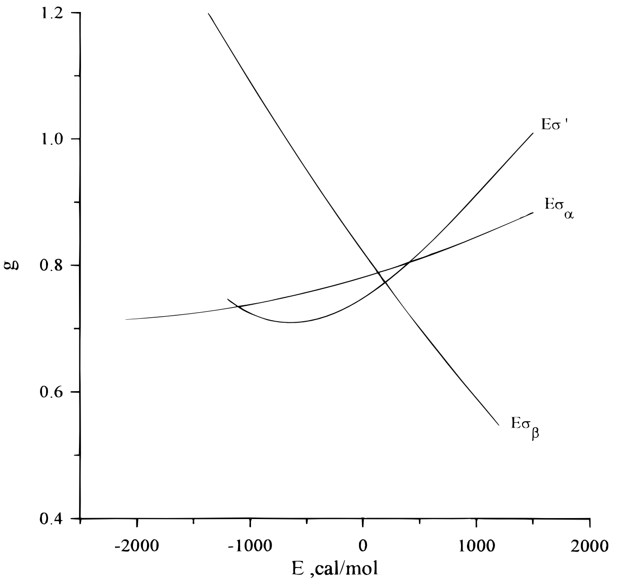

Figure 3. Curves showing the dependence of the dipolar correlation coefficient on $E\sigma_\alpha$, $E\sigma_\beta$, and $E\sigma'$ and relative energies of gauche states about the $C^{\alpha}H_2-C^*(O^*)$, $C^{\alpha}H_2-C^{\beta}H_2$, and $CH_2-C(CH_3)_2-CH_2$ bonds, respectively.

changes in the temperature coefficient. Consequently, g, rather than d ln g/dT, should be used in the determination of conformational energies.

The dipolar correlation coefficient is sensitive to the conformational population about the central $CH_2-C(CH_3)_2-CH_2$ bonds as a consequence of the fact that keeping these bonds in the tt conformation keeps the dipoles associated with the ester groups parallel, thus enhancing the value of g. As a result, rotations about these bonds will decrease the value of g as indicated in Figure 3, where it can be seen that for $E\sigma_\alpha = -1.0$ kcal mol^{-1} and $E\sigma_\beta = 0.3$ kcal mol^{-1}, g changes from 0.742 to 1.01 when $E\sigma'$ increases from -1.2 to 1.5 kcal mol^{-1}. The variation in g with the values of the second-order energies is, in comparison, rather small. In general, very good agreement between theoretical and experimental results is found for the following set of conformational energies: $E\sigma_\alpha = -0.7$ kcal mol^{-1}, $E\sigma_\beta = 0.7$ kcal mol^{-1}, $E\sigma' = -0.6$ kcal mol^{-1}, and $E\omega = E\omega' = E\omega'' = 1.4$ kcal mol^{-1}. With this set of conformational energies, the calculated values of g and 10^3 d ln g/dT amount to 0.65 and 0.78 K^{-1}, respectively, in good agreement with the experimental values $g = 0.67$ and 10^3 d ln g/d$T = 2.2$ K^{-1}.

Dipolar Correlation Coefficient for Poly(neopentyl glycol hexafluoroglutarate). There is no information concerning the effects of the fluorine atoms on the dipole moment associated with the $CF_2C^*(O^*)$-OCH_2 residue in the structural unit of PNFG whose structural unit in the all-trans conformation is shown in Figure 2. The dipoles associated with the structural unit of PNFG were obtained from the charge distribution for the model compound $CF_3-CF_2-COOCH_3$, computed with the Sybyl Molecular Modeling Package,[30] employing the MOPAC program and the AM1 procedure.[31,32] The usefulness of this approach to determine the dipole moments of fluorinated compounds was checked by calculating the dipole moments of trifluoroacetaldehyde and methyl fluoroformate and comparing them with experimental results. The calculated values are 1.90 and 2.54 D for the former and latter compounds, respectively, which are in reasonable agreement with the experimental dipole moments reported for these compounds in the literature:[33] 1.65−1.92 D for trifluoroacetaldehyde and 2.61 D for methyl fluoroformate. In view of the good agreement obtained between the calculated and experimental results for these fluorinated low molecular weight compounds, we proceeded to determine the distribution of charges in $CF_3-CF_2-COOCH_3$. From the distribution of residual charges for the CF_2 group, $F^{-0.118e}-C^{0.235e}-F^{-0.118e}$, and taking into account that $l_{C-F} = 1.36$ Å, one finds that the dipole moment associated with the C−F bond has a value of 0.77 D, and consequently, each of the two C−C skeletal bonds adjacent to a CF_2 group can be considered to have a dipole moment of 0.80 D. Moreover from the distribution of charges of the $COOCH_3$ moiety, one finds that the $C^{\alpha}F_2-C^*(O^*)-OCH_2$ residue has a dipole moment of 0.80 D, located along the $C^{\alpha}-C^*$ bond, and another dipole, m_E, located in the plane of the $C^*(O^*)-O-CH_2$ skeletal bonds, forming an angle of 15° with the $C^*(O^*)-O$ bond. As can be seen in Figure 2, the dipole moments of the central C−C bonds of the acid residue cancel out.

In contrast with the PNG case, the dipoles associated with the ester groups are nearly antiparallel for the all-trans conformation so that the value of g for this conformation amounts to only 0.19. Consequently, departure from this conformation by rotation about the skeletal bonds will increase g. Molecular mechanics calculations show that the rotational angles about the $C^{\beta}F_2-C^{\alpha}F_2-C^*(O^*)$ bonds of the acid residue are located at 0, ±120°. The calculations also predict that gauche states about $C^{\alpha}F_2-C^*(O^*)$ bonds have an energy $E\sigma_\alpha$ ca. 0.08 kcal mol^{-1} below that of the corresponding trans state. Gauche states about the $C^{\alpha}F_2-C^{\beta}F_2$ bonds of the acid residue have an energy 0.80 kcal mol^{-1} above that of the alternative trans states. Finally, gauche states of different sign about two consecutive bonds have an energy much larger than that of the corresponding tt state, and as a consequence, these states were considered to be forbidden. These results for the conformational energies associated with the skeletal bonds of the acid residue were taken as starting values in the theoretical calculation of g for PNFG. The energies for the glycol residue are the same as those used in the conformational analysis of PNG described above.

Values of g were calculated as a function of $E\sigma_\alpha$ using the following set of conformational energies: $E\sigma_\alpha = -0.1$ kcal mol^{-1}, $E\sigma_\beta = 0.80$ kcal mol^{-1}, $E\sigma' = -0.6$ kcal mol^{-1}, and $E\omega = 1.4$ kcal mol^{-1}. The results obtained, represented in Figure 4, show that the dipolar correlation coefficient decreases as the trans population about $C^{\alpha}F_2-C^*(O^*)$ bonds increases. Increasing $E\sigma_\alpha$ from -1.5 to 1.2 kcal mol^{-1} causes a reduction in g from 1.45 to 0.568. The results also show a significant dependence on the rotational population about $C^{\alpha}F_2-C^{\beta}F_2$ bonds. The value of g increases from 0.681 to 1.20 when $E\sigma_\beta$ increases from -1.2 to 1.0 kcal mol^{-1} (see Figure 4). Contrary to what occurs with the dipolar correlation coefficient of PNG, this parameter is rather insensitive to the gauche population about the central $CH_2-C(CH_3)_2-CH_2$ bonds of the glycol residue. For example, a variation of $E\sigma'$ from -1.2 to 1.2 kcal mol^{-1} only changes g from 1.16 to 1.20. Good agreement between theoretical and experimental results is obtained using the set of conformational energies indicated above. These give $g = 1.01$, very close to the experimental value of 0.99. The experimental mean-square dipole moment of diethyl glutarate (12.1 D^2) is also reproduced if $E\sigma_\alpha$ is considered to be somewhat smaller.[26] The theoretical

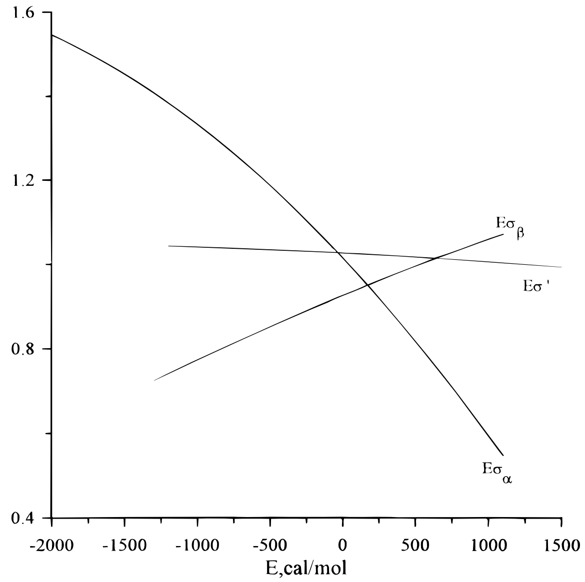

Figure 4. Variation of the dipolar correlation coefficient with $E\sigma_\alpha$, $E\sigma_\beta$, and $E\sigma'$ and the relative energies of gauche states about the $C^\alpha H_2-C^*(O^*)$, $C^\alpha H_2-C^\beta H_2$, and $CH_2-C(CH_3)_2-CH_2$ bonds, respectively.

value of $\langle\mu^2\rangle$ is 11.7 D^2 for $E\sigma_\alpha = -0.5$ kcal mol^{-1} and $E\sigma_\beta = 0.8$ kcal mol^{-1}.

The calculations suggest that the temperature coefficient of the dipolar correlation coefficient should be slightly negative for the set of conformational energies used above. The fact that the experimental value of this quantity is positive presumably is due to slight degradation which PNFG undergoes above 40 °C.

Discussion

In spite of the variety of work dealing with the evaluation of the conformational energies associated with gauche states about the skeletal bonds of the acid residue of aliphatic polyesters, some discrepancies concerning the energy of gauche states about $C^\alpha H_2-C^*(O^*)$ bonds still remain. Thus from the analysis of the IR and ^{1}H NMR spectra of methyl propionate, Dirlikov et al.[15] concluded that the most stable conformation is that in which the C=O group eclipses the $C^\alpha-H$ atom. However, an interpretation of the same type of spectra led Moravie et al.[16] to conclude that the trans conformation is more stable than the alternative gauche conformation by the enthalpy difference of $\Delta H(C^\alpha-C^*) = 1.1 \pm 0.3$ kcal mol^{-1}. An intermediate value of $\Delta H(C^\alpha-C^*) = 0.08$ kcal mol^{-1} has been reported from the analysis of infrared and Raman spectra of methyl propionate.[18,19]

More recently, the analysis of both the ^{1}H NMR spectra and the dipole moments of aliphatic diesters led Abe et al.[17] to suggest that gauche states are disfavored by nearly 1 kcal mol^{-1} over the alternative trans states. This is in clear disagreement with the values obtained for these energies from the critical interpretation of the temperature coefficient of the mean-square end-to-end distance, $d \ln \langle r^2\rangle_0/dT$, of poly(neopentyl glycol succinate),[22] poly(neopentyl glycol adipate),[21] and other polyesters prepared by polycondensation of adipic and sebacic acids with 2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane.[34] In order to reproduce the positive temperature coefficient exhibited by the dimensions of these polymers, it is necessary to postulate that $E\sigma_\alpha < 0$ and $E\sigma_\beta > 0$. In fact, values of $E\sigma_\alpha = -0.5$ kcal mol^{-1} and $E\sigma_\beta = 0.7$ kcal mol^{-1} reproduce the temperature coefficient of the unperturbed dimensions of the aliphatic polyesters. These results are confirmed by the theoretical analysis described above which shows that values of $E\sigma_\alpha$ and $E\sigma_\beta$ lying in the range, respectively, -0.5 to -1.0 and 0.3 to 0.8 kcal mol^{-1} give a good account of the dipolar correlation coefficient of PNG. To use $E\sigma_\alpha = 1.0$ kcal mol^{-1} and $E\sigma_\beta = 0.3$ kcal mol^{-1} as Abe et al.[17] suggest would give $g = 0.85$ and $d \ln g/dT = -0.6 \times 10^{-3}$ K^{-1}, in clear disagreement with the experimental values of 0.67 and 2.2×10^{-3} K^{-1}. What is more, the set of values $E\sigma_\alpha = 1.0$ kcal mol^{-1} and $E\sigma_\beta = 0.3$ kcal mol^{-1} would give for the mean-square dipole moment and its temperature coefficient of diethyl glutarate[26] the values of 6.35 D^2 and -5.6×10^{-4} K^{-1}, respectively, which differ significantly from the experimental results: 5.25 D^2 and 1.9×10^{-3} K^{-1}.

According to the results indicated above, inductive effects of the fluorine atoms produce a significant variation on the polarity of the partially fluorinated polyesters. However, the conformational statistics for PNG and PNFG are similar in the sense that in both polymers trans states about $C^\alpha-C^\beta$ bonds seem to be favored over the alternative gauche, whereas gauche states about $C^\alpha-C^*$ bonds are favored over the corresponding trans. In fact, the energies obtained for the rotational states about the skeletal bonds of the acid residue by comparing the experimental and calculated values of g ($E\sigma_\alpha = -0.1$ kcal mol^{-1} and $E\sigma_\beta = 0.7$ kcal mol^{-1}) are similar to those obtained by using semiempirical potential functions ($E\sigma_\alpha = -0.08$ kcal mol^{-1} and $E\sigma_\beta = 0.8$ kcal mol^{-1}). The values of these energies also reproduce satisfactorily the experimental dipolar correlation coefficient of diethyl hexafluoroglutarate.[26] An important difference between PNG and PNFG is that the dipolar correlation coefficient of the latter polymer is nearly insensitive to the rotational populations about the central $CH_2-C(CH_3)_2-CH_2$ bonds of the glycol residue. Whereas $g^\pm g^\pm$ states about these bonds in PNG decrease the parallel orientation of the ester groups flanking the glycol residue in the all-trans conformation, these changes in PNFG are nearly negligible. Unfortunately, the polymer is slightly unstable at temperatures above 40 °C, and consequently, the experimental value of the temperature coefficient is not reliable enough to be compared with the theoretical results. It should be pointed out, however, that the calculations indicate a negative temperature coefficient for the dipole moment in PNFG chains.

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