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Conformational and Experimental Studies on the Dipole Moments of Models of Comblike Polymers

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ABSTRACT: The synthesis and radical polymerization of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate are described. The values found at 50 and 60 °C for the rate constants ratio, $k_p/k_t^{1/2}$, are similar to those reported for some acrylic polymers with short side groups at the same temperatures although conflicting results are obtained by comparison with the kinetic constants reported for other similar acrylic monomers. The experimental value of the mean-square dipole moment per repeating unit of the resulting polymer, poly{2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} was 7.24 D^2 at 30 °C. This result is very close to the value of 7.83 D^2 found, at the same temperature, for the model compound of the side group of the polymer, 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacetate. Owing to the wide distribution of dipole moments associated with the side groups, the dipolar correlation coefficient of the chains was calculated by combining matricial products of the rotational isomeric state model and Monte Carlo techniques. The calculations suggest that the statistics of long side groups rather than the statistics of the main chain govern the dipolar correlation coefficient of atactic comblike polymers.

Introduction

Owing to the fact that skeletal bonds change much more in polarity than they do in length, the mean-square dipole moment of molecular chains, $\langle \mu^2 \rangle$, is more sensitive to the chemical structure than other more traditional conformational properties such as the mean-square end-to-end distance, $\langle r^2 \rangle_0$.[1,2] However, contrary to what occurs with the molecular dimensions, the polarity of simple bonds in isolated chains may be strongly affected by their environment and, consequently, dipoles associated with groups of bonds rather than dipoles of simple bonds should be used in the theoretical evaluation of the mean-square dipole moment of polymer chains.[3,4]

Whenever the dipoles contributing to the polarity of molecular chains are rigidly attached to the backbone, the mean-square dipole moment can be obtained by standard matricial methods similar to those used in the theoretical calculation of the molecular dimensions. The situation is different when the polar contributions are associated with flexible side groups, as occurs, for example, in acrylic polymers.[5,6] In this case, the dipolar contribution is not a definite one since it depends on the conformation of the side group which, in turn, is continuously changing. Consequently, the theoretical calculation of $\langle \mu^2 \rangle$ by statistical mechanics procedures will require us to combine matricial and Monte-Carlo methods.

This work addresses the experimental and theoretical calculations of the dipolar correlation coefficient, g_{intra} ($=\langle \mu^2 \rangle / x\sum m_i^2$, where $\langle \mu^2 \rangle$ and $x\sum m_i^2$ represent, respectively, the unperturbed mean-square dipole moment of the chains and of the freely jointed chains), of polymers with flexible long side groups. For this purpose, poly{2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} (PD22A), the repeating unit of which is shown in Figure 1, was chosen. In order to investigate how the backbone may influence the polarity of comblike polymer chains, a parallel study was carried out on the dipolar correlation coefficient of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacetate (D22AC), the model compound of the side group of PD22A. The evaluation of g_{intra} is important to predict the dielectric relaxation strength, $\Delta\epsilon$, of polymers in the bulk, which depends on $g\sum_i m_i^2$, where g involves both intra- and intermolecular dipolar correlations. Since dipolar correlations sharply decay as the distance between dipole entities increases, it is expected[7−9] that $g \approx g_{\text{intra}}$ and, consequently, the knowledge of g_{intra} would allow us to predict the dielectric relaxation strength of polymers in the bulk from their chemical structure.

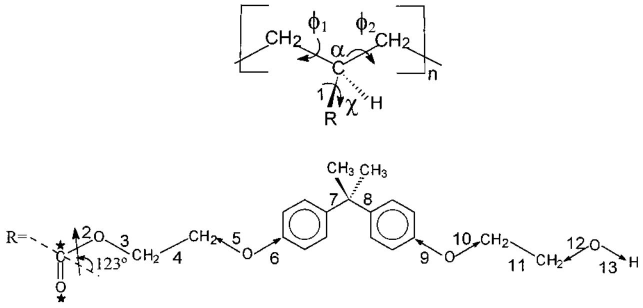

Figure 1. Sketch of the repeating unit of poly{2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} (PD22A). For 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacetate (D22AC), model compound of the side group of the polymer, R = CH_3. The dipoles associated with the side group are indicated by arrows.

This work forms part of a more general one in which the relaxation behavior of both molecular chains with long side groups in their structure and the corresponding model compounds of their side groups are comparatively studied. Attention was also paid to the polymerization kinetics of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate (D22A) with the aim of obtaining information on the effect of long side groups on the rate polymerization constants of acrylic monomers.

Experimental Section

Materials. The glycol 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane, 90% purity, supplied to us by Glasurit SA, was

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purified by successive crystallizations in toluene (Panreac) and further dried with molecular sieves (Merck) (mp 115−116 °C; lit.[10] 110.5 °C). Chloroform was dried with calcium chloride. Benzene and 1,4-dioxane were purified by conventional methods, while triethylamine (Fluka), acetyl chloride, and acryloyl chloride were used as received.

Synthesis of 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl Monoacrylate and 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl Monoacetate. 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate was obtained at 20 °C, under a nitrogen atmosphere, by reaction of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl with acryloyl chloride in chloroform, using triethylamine as absorbent of the hydrogen chloride evolved during the reaction. Previous studies[11,12] showed that an optimum yield of the monoester component in the monoester/diester mixture formed during the reaction is obtained when the mole ratio of glycol to acid chloride is about 7/3. The esterification was carried out by adding dropwise acryloyl chloride to the reaction medium for 2 h, and then the reaction was permitted to proceed for 10 additional hours. The triethylammonium chloride formed and the solvent were successively removed by filtration and rotoevaporation in vacuum, respectively. The reaction products were extracted with benzene and the solution was washed several times with distilled water to remove the unreacted 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane, dried with calcium chloride, and finally, the benzene was rotoevaporated in vacuum. The monofunctional monomer, 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate, was separated from the difunctional one, 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl diacrylate, by chromatography (Kiesel-gel 60, Merck) using a mixture of benzene/ethyl acetate (75/25, v/v) as eluent. The molar fraction of monoester in the mixture was 0.79.

2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl monoacetate, model compound of the side group of the polymer, was obtained from 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane and acetyl chloride using the procedures described in the synthesis and isolation of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate.

Characterization of the Esters. ^{1}H and ^{13}C NMR spectra of the esters were obtained with a Bruker-200 apparatus operating at 200 MHz for ^{1}H and 75.4 MHz for ^{13}C NMR, using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. The quantitative analysis of the ^{13}C NMR spectra proved the purity of both the monoacrylate monomer and the model compound of the side group of the polymer.

Polymerization Reactions. 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate was polymerized in dioxane solution using 2,2′-azobis(isobutyrontrile) (AIBN) as initiator. The conversion of the monomer at two temperatures, 50 and 60 °C, was determined with a double-branched dilatometer having 6 cm^3 of capacity and 1.06 mm capillary diameter. The polymer formed in the radical polymerization was isolated from the reaction medium by precipitation with *n*-hexane and dried in vacuum at 60 °C. The solubility of the polymer proves the absence of cross-linking reactions and, consequently, it is an additional indication on the purity of the monomer.

Characterization of the Polymer. The stereochemical composition of the polymer was determined by ^{13}C NMR spectroscopy using a Varian XL-300 spectrometer, deuterated chloroform as the solvent, and tetramethylsilane as the standard reference. In these polymers only the carbonyl carbons of the side chain and the methine carbons of the main chain give signals associated with tacticity effects. The peak corresponding to the carbonyl carbon shows a complicated spectral pattern as resulting from several overlapping signals. The separation of the different signals by deconvolution allowed us to determine the probability of the isotactic replacement, whose value was 0.30 ± 0.05.

The glass transition temperature of PD22A was measured with a Perkin-Elmer DSC calorimeter at a heating rate of 10 °C/min. The value of this quantity, taken as the temperature at which the low-temperature side of the endotherm deviates from the baseline, was 22 °C. The glass transition temperature of the model compound of the side group of the polymer, measured in the same experimental conditions, was −27 °C.

Table 1. Summary of Dielectric Results for 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl Monoacetate (D22AC) and Poly{2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} (PD22A)

material	T, °C	dϵ/dw	$2n_1$ dn/dw	$\langle\mu^2\rangle/x$, D^2 [a]	g_{intra}
D22Ac	20	2.51	0.10	7.71	0.66
	30	2.42	0.10	7.83	0.67
	40	2.33	0.10	7.96	0.68
	50	2.26	0.10	8.14	0.70
PD22A	20	2.83	0.35	7.19	0.61
	30	2.72	0.36	7.24	0.62
	40	2.62	0.37	7.26	0.62
	50	2.54	0.38	7.33	0.63

[a] For D22Ac, $x = 1$.

Dielectric Measurements. The dielectric permittivity ϵ of solutions of both PD22A and D22A in 1,4-dioxane were measured at 10 kHz with a capacitance bridge (General Radio, type 1620) coupled with a three terminal cell. The increments in the dielectric permittivity of the solutions with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) were plotted at each temperature of interest against the weight fraction of polymer in the solution, w. From the slopes of the straight lines, the values of dϵ/dw in the limit $w \rightarrow 0$, were obtained. In order to determine the orientation polarization, P_o, it is necessary to subtract from the total polarization P (=k dϵ/dw, where k is a proportionality constant), the electronic polarization P_e (=k dn/dw, where n is the index of refraction of the solution). Values of dn/dw were obtained from plots of the increments of the index of refraction of the solutions with respect to that of the solvent ($\Delta n = n - n_1$) against w. The atomic polarization, P_a, was considered to be negligible. The results for dϵ/dw and $2n_1$ dn/dw are given in the second and third columns of Table 1.

Values of the mean-square dipole moment, $\langle\mu^2\rangle$, were obtained by the method of Guggenheim and Smith[13,14]

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

where M is the molecular weight of the solute, T is the absolute temperature, ρ is the density of the solvent, and k_B and N_A are, respectively, the Boltzmann constant and Avogadro's number. The results obtained for both the mean-square dipole moment per repeating unit of PD22A, $\langle\mu^2\rangle/x$, and the mean-square dipole moment of D22AC are given at several temperatures in the fourth column of Table 1. The errors involved in the determination of $\langle\mu^2\rangle$ in both cases was ±3%. The values of the temperature coefficient of the polymer and the model compound of the side group, expressed in terms of 10^3 d ln $\langle\mu^2\rangle$/dT, were 0.6 and 1.8 K^{-1}, respectively.

Results and Discussion

Polymerization Kinetics. By assuming that neither depropagation reactions nor thermal polymerization occur in the radical polymerization of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate, the evolution of the concentration of monomer [M] with time can be written as

$$[M] = [M_0]\ \exp\left[-2k_p\left(\frac{2f[I_0]}{k_tk_d}\right)^{1/2}\left(1 - \exp\frac{-k_dt}{2}\right)\right] \qquad (2)$$

where [M$_0$] and [I$_0$] are, respectively, the initial concentrations of monomer and initiator, f is the efficiency of the initiator, and k_d, k_p, and k_t are the rate constants for initiator decomposition, propagation, and termination reactions, respectively. In dilatometric experiments as those carried out in this work, it is convenient to write eq 2 in the following alternative form[11,12]

$$\Delta h = \Delta h_{100}\left\{1 - \frac{V_0 - \Delta V}{V_0}\exp\left\{-2k_p\left(\frac{2f[\mathrm{I}_0]}{k_t k_d}\right)^{1/2}\left[1 - \exp\left(-\frac{k_d t}{2}\right)\right]\right\}\right\} \quad (3)$$

where Δh and Δh_{100} are respectively the changes of dilatometric height by the effect of the polymerization at time t and at 100% conversion, V_0 is the initial volume of solvent and monomer in the dilatometer, and ΔV ($=\pi r^2 \Delta h$) is the change of volume at t. The evaluation of $k_p/(k_t k_d)^{1/2}$ and Δh_{100} was carried out by a nonlinear least-squares procedure.[10] It is noteworthy that the method allows the determination of Δh_{100} without needing the densities of both the polymer and the monomer at different temperatures. Since k_d is nearly independent of the nature of the solvent, this rate constant was considered to be a nonadjustable parameter at each temperature, and its value was directly taken from the literature.[15,16] On the other hand, by considering the efficiency of the initiator $f = 0.6$, the value of $k_p/k_t^{1/2}$ can be obtained from the least-squares analysis.

Values of the experimental fractional conversion, $1 - [\mathrm{M}/\mathrm{M}_0]$ ($=\Delta h/\Delta h_{100}$), are shown as a function of time in Figure 2. The experimental results were linearized by plotting them as a function of $1 - \exp(-k_d t/2)$, as suggested by eq 3, using the values of Δh_{100} and $k_p/k_t^{1/2}$ obtained by simulation methods. The relatively good fit observed in Figure 3 between the experimental results and those predicted by eq 3 is rather remarkable if one considers the relatively low decrease in volume that takes place in the total conversion as a consequence of the small difference between the density of the polymer and that of the monomer. The values of $k_p/k_t^{1/2}$ obtained at 50 and 60 °C are shown in Table 2. These values are similar to those reported for acrylates with unsubstituted alkyl groups[17] (methyl, ethyl, propyl, or butyl), but significantly lower than those reported for the acrylates with a branched alkyl group in their structure.[18] In the latter case, the relatively high values of $k_p/k_t^{1/2}$ presumably arise from the hindering effect that branching causes in the termination process. In the same table and for comparative purposes, the values of this ratio at the temperatures of interest are shown for three acrylic monomers also containing hydroxyl groups in their structure: triethylene glycol acrylate (TEGA),[18] tetraethylene glycol acrylate (TTEGA),[19] and 3-hydroxyneopentyl acrylate[11] (HNPA). From the results shown in Table 2, a definite dependence on the bulkiness of the pendent chain is not observed. For example, the values of $k_p/k_t^{1/2}$ obtained for the polymerization of tetraethyleneglycol acrylate (TTEGA) are much higher than those reported for other acrylates,[17,20] including the acrylates with branched side groups indicated before. All that shows the difficulties involved in the comparison of these kinetic constants, and at present we cannot explain the reason why an additional oxyethylene unit in TTEGA can modify in such a manner the reactivity of this monomer in comparison to that of TEGA by either increasing k_p or decreasing k_t. To establish the effect of the pendent chains on the reactivity of unsaturated monomers would require us to measure the absolute values of both the propagation and termination rate constants.

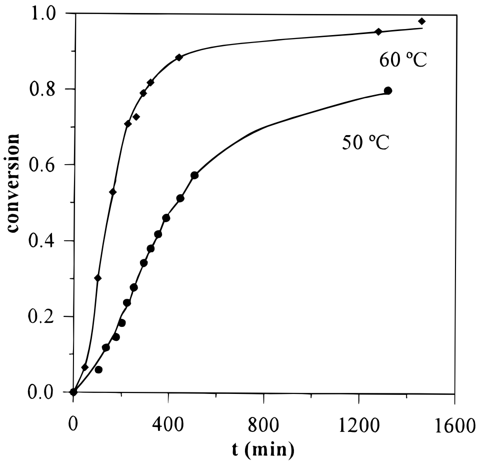

Figure 2. Time dependence of the fractional conversion for the polymerization of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate (D22A) in dioxane at 50 and 60 °C.

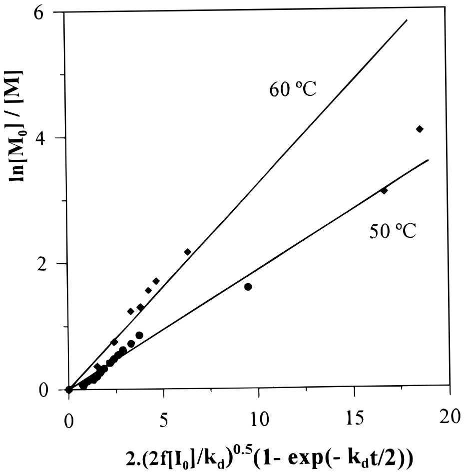

Figure 3. Kinetics plots for the polymerization of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate (D22A) in dioxane at 50 and 60 °C.

Table 2. Kinetic Rate Constants for the Polymerization of 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl Monoacrylate (D22A), Triethylene Glycol Acrylate (TEGA), Tetraethylene Glycol Acrylate (TTEGA), and 3-Hydroxyneopentyl Acrylate (HNPA)

monomer	T, °C	$k_p/k_t^{1/2}$, L$^{1/2}$ mol$^{1/2}$ s$^{1/2}$
D22A	50	0.19
	60	0.32
TEGA	50	0.17
	60	0.30
TTEGA	50	1.10
	60	1.24
HNPA	50	0.52
	60	0.72

Theoretical Analysis of the Polarity of the Chains and the Model Compound of the Side Groups

Dipole Moments of 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propyl Monoacetate. A sketch of this model compound can easily be derived from the side group of PD22A shown in Figure 1. Owing to the conformational versatility of this molecule, the distribution of dipole moments was calculated by using the conformational energies briefly described below. The C*(O*)−O bond of the ester group is restricted to the trans state[21] whereas the O−CH$_2$ bond of the ester moiety presents three minima located at 0 and ±104°, the gauche states having an energy ca. 0.4 kcal mol^{-1} above that of the alternative trans states.[1,21] The rotational states about the CH_2-CH_2 bonds are located at 0 and ±120°. When rotational states about these bonds give rise to first-order interaction between an oxygen atom of an ester group and the oxygen atoms of an ether group, gauche states have an energy of ca. -0.8 kcal mol^{-1} with respect to that of the corresponding trans states.[22] This energy increases to -0.5 kcal mol^{-1} when the interactions take place between the oxygen atoms of two ether groups.[23] The rotational states of ether bonds are located at 0 and ±110° with gauche states having an energy ca. 0.9 kcal mol^{-1} above that of the corresponding trans states.[21,23] As for bonds 6−9 in Figure 1, the rotational minima are located at 45, 135, 225, and 315°. The corresponding statistical weight matrices are[24−26]

$$\mathbf{U}_6 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix} \qquad \mathbf{U}_7 = \mathbf{U}_9 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

$$\mathbf{U}_8 = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix} \tag{4}$$

For consistency, the statistical weight matrix corresponding to the skeletal bond 10 is

$$\mathbf{U}_{10} = \begin{pmatrix} 1 & 0 & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \\ 1 & \sigma & 0 \end{pmatrix} \tag{5}$$

where σ is the statistical weight of gauche states about CH_2-O ether bonds. Rotations of different sign about two consecutive skeletal bonds were considered negligible with the exception of those about the 3,4 and 11,12 bonds of Figure 1. In the first case the secondary energy was assumed to be 1.4 kcal mol^{-1} above that of the corresponding tt states whereas in the second one the energy was considered to be similar to that of the tt state.

The dipole moment associated with the ester group has a value of 1.77 D, and it forms an angle of 123° with the $CH_3-C^*(O^*)$ bond.[3] The dipole moments corresponding to the ether ($O-CH_2$) and the hydroxyl ($O-H$) bonds lie along the O−C and O−H bonds, and their values are 1.07 and 1.7 D, respectively.[23] The distribution of dipole moments in the model compound of the side chains was determined in the form of a histogram by means of the expression

$$p(\mu_k) = \frac{\Omega(\mu_k - \delta < \mu_k < \mu_k + \delta)}{Z} \tag{6}$$

where Ω is the sum of the statistical weights of the conformations with dipole moments lying in the range $\mu_k \pm \delta$ and Z is the rotational partition function. In the evaluation of the histogram the value of $\delta = 0.25$ D was used. The histogram obtained, represented in Figure 4, shows a bimodal distribution with modes located in the vicinity of 2 and 3.5 D. In the same figure, the average values of both the end-to-end distance $\langle r \rangle$ of the conformations compatible with $\mu_k \pm \delta$ and their energies are shown. It can be seen that while the energy does not follow a definite trend, $\langle r \rangle$ increases with μ, suggesting that the most extended conformations exhibit the higher polarity.

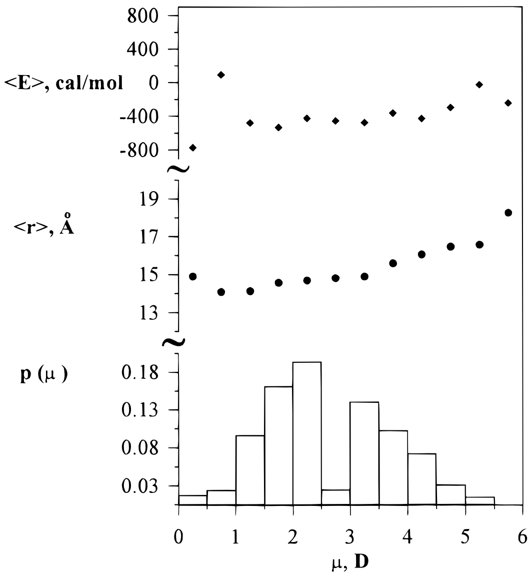

Figure 4. Average conformational energies (top), end-to-end distance (middle), and distribution of dipole moments of the side groups (bottom).

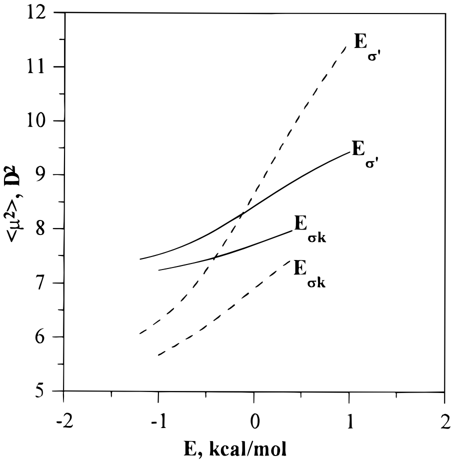

Figure 5. Variation of the mean-square dipole moment of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacetate (D22AC) (continuous line) and 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl diacetate (D22DAC) (broken line) with the energies associated with gauche states about $O-CH_2$ bonds of the ester residue, $E_{\sigma k}$, and about CH_2-CH_2 bonds, $E_{\sigma'}$.

The calculations suggest that the polarity of the side groups is especially sensitive to the energy of gauche states about the ester CH_2-O bonds, $E_{\sigma k}$, and CH_2-CH_2 bonds, $E_{\sigma'}$. The results in Figure 5 show that as these energies increase, the fraction of high-polarity extended conformations increases and, consequently, the value of $\langle \mu^2 \rangle$ goes up. For comparative purposes, the dependence of $\langle \mu^2 \rangle$ for 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl diacetate (D22DAC) on the values of these energies is also shown in this figure. An inspection of the curves suggests that the polarity of D22DAC is significantly more sensitive to both $E_{\sigma k}$ and $E_{\sigma'}$ than that of D22AC, presumably as a consequence of the freely rotating character of the terminal CH_2-OH bond in this latter molecule. In general, using the values of the conformational energies indicated above, the calculated result for the mean-square dipole moment of D22AC is 7.9 D^2 at 30 °C, in very good agreement with the experimental value, 7.8 D^2, at the same temperature. Similar treatment applied to D22DAC gives $\langle \mu^2 \rangle = 7.4$ D^2 at 30 °C, also in good agreement with the experimental result,[25] 7.6 D^2.

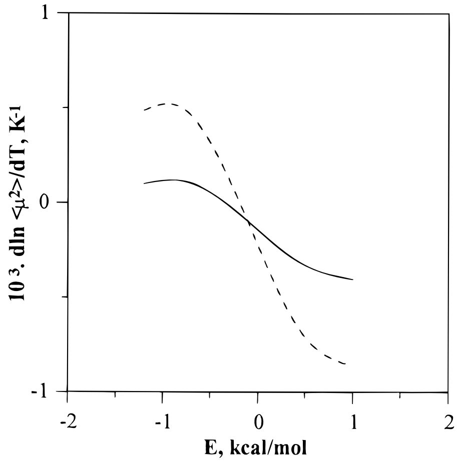

Figure 6. Dependence of the temperature coefficient of the mean-square dipole on $E_{\sigma'}$ for 2,2-bis[4-(2-hydroxyethoxy)-phenyl]propyl monoacetate (D22AC) (continuous line) and 2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl diacetate (D22DAC) (broken line).

The dipole moment of D22AC increases with temperature. The temperature dependence of the dipole moment, expressed in terms of d ln $\langle\mu^2\rangle/\mathrm{d}T$, is very sensitive to the conformational energy associated with gauche states about CH_2-CH_2 bonds. The results shown in Figure 6 indicate that to obtain values of d ln $\langle\mu^2\rangle/\mathrm{d}T > 0$, as the experimental results suggest, requires values of $E_{\sigma'} < 0$. It is noteworthy that as a result of the freely rotating nature of the penultimate CH_2-OH bond, the temperature coefficient of the dipole moment of D22AC is less sensitive to $E_{\sigma'}$ than its acetylated counterpart.

In the evaluation of the mean-square dipole moment per repeating unit of the molecular chains of PD22A, use was made of the statistics utilized for other acrylate polymers with short side groups such as poly(methyl acrylate) (PA). Thus the skeletal bonds were assumed to be restricted to trans and gauche states. Each of these states splits into two to account for the conformations in which by rotation about the side C−C*(O*) bond the carbonyl group is cis ($\chi = 0$) and trans ($\chi = \pi$) to the methine bond. The statistical weight matrices for the resulting four states model [(t, $\chi = 0$), (t, $\chi = \pi$), (g, $\chi = 0$), (g, $\chi = \pi$)] are the following[5,6]

$$\mathbf{U}' = \begin{pmatrix} 1 & 0 & \rho & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{pmatrix} \qquad (7)$$

for the $CH_2-C^{\alpha}-CH_2$ bond pair and

$$\mathbf{U}''_{\mathrm{r}} = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{U}''_{\mathrm{m}} = \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix} \qquad (8)$$

for racemic and meso configurations of the bonds pair. The skeletal bond angles were assumed to be 112°, and the average rotational angles for the meso diads were $\langle\phi_1, \phi_2\rangle_{\mathrm{tt}} = 16°, 16°$, $\langle\phi_1, \phi_2\rangle_{\mathrm{tg}} = 3°, 114°$ and $\langle\phi_1, \phi_2\rangle_{\mathrm{gt}} = 114°, 3°$. For racemic diads $\langle\phi_1, \phi_2\rangle_{\mathrm{tt}} = 3°, 3°$.

The mean-square dipole moment per repeating unit of PD22A chains, $\langle\mu^2\rangle/x$, was obtained by means of the following expression[21,27,28]

$$\frac{\langle\mu^2\rangle}{x} = \frac{\mathbf{P}_1\prod_{k=1}^{x}[(\mathbf{U}'\otimes\mathbf{E}_5)\mathbf{G}'_k(\mathbf{U}''_k\otimes\mathbf{E}_5)\mathbf{G}''_k]\mathbf{P}_n}{Zx} \qquad (9)$$

where the rotational partition function Z is given by

$$Z = \mathbf{U}_1\prod_{k=1}^{x}(\mathbf{U}'\mathbf{U}''_k)\mathbf{U}_n \qquad (10)$$

$\mathbf{U}_1$ = row (1 0 0 0) and $\mathbf{U}_n$ = column (1 1 1 1) convert the matricial product of eq 11 into a scalar. In eq 10, the symbol ⊗ denotes the direct product, $\mathbf{E}_5$ is the identity matrix of order 5 and $\mathbf{G}'_k$ and $\mathbf{G}''_k$ are pseudo-diagonal matrices given by

$$\begin{aligned} \mathbf{G}'_k &= \mathrm{diag}[\mathbf{M}'_k(t, \chi = 0),\ \ \mathbf{M}'_k(t, \chi = \pi), \\ &\qquad \mathbf{M}'_k(g, \chi = 0),\ \ \mathbf{M}'_k(g, \chi = \pi)] \\ \mathbf{G}''_k &= \mathrm{diag}[\mathbf{M}''_k(t, \chi = 0),\ \ \mathbf{M}''_k(t, \chi = \pi), \\ &\qquad \mathbf{M}''_k(g, \chi = 0),\ \ \mathbf{M}''(g, \chi = \pi)] \end{aligned} \qquad (11)$$

the elements of the pseudodiagonal matrices being the generator matrix $\mathbf{M}_k$ defined as

$$\mathbf{M}_k = \begin{pmatrix} 1 & 2\mathrm{m}^{\mathrm{T}}\mathbf{T} & \mathbf{m}^2 \\ \mathbf{0} & \mathbf{T} & \mathbf{m} \\ 0 & \mathbf{0} & 1 \end{pmatrix}_k \qquad (12)$$

where $\mathbf{T}$ is the transformation matrix that projects a vector from reference frame $k + 1$ to its representation in the reference frame k and $\mathbf{m}$ is the contribution of the bond to the polarity of the chain. $\mathbf{P}_1$ and $\mathbf{P}_n$ are, respectively, row and column vectors to convert eq 11 in a scalar; specifically, $\mathbf{P}_1$ = row [M_{11} 0 0...0] and $\mathbf{P}_n$ = column [$M_{\mathrm{n}}(\chi = 0)$ $M_{\mathrm{n}}(\chi = \pi)$ $M_{\mathrm{n}}(\chi = 0)$ $M_{\mathrm{n}}(\chi = \pi)$], where M_{11} and M_{n} represent, respectively, the first row and last column of the generator matrix $\mathbf{M}$ in which $m = 0$. The contribution of the side group to the polarity is associated with a reference frame located at the $C^{\alpha}-CH_2$ bond, and consequently, the dipole moment corresponding to the CH_2-C^{α} bonds is nil.

In the calculations, the dipole moment associated with CH_2-C^{α} was assumed to be zero and the dipolar contribution of the side group was attached to the $C^{\alpha}-CH_2$ bond. Owing to the wide distribution of dipole moments of the side groups, a rigorous treatment would require us to formulate statistical weight matrices with dimensions $2(N - 1) \times 2(N - 1)$, where N is the number of skeletal bonds of the side groups. Of course this is an unfeasible approach, and the determination of the contribution of the side group to the polarity of the chain was decided using the method briefly described below. First, the probability of the rotational states of each bond of the side group was obtained by the following equation[21]

$$p(\zeta)_i = Z^{-1}[\prod_{h=1}^{i=1}\mathbf{U}_h]\mathbf{U}'_i[\prod_{j=i+1}^{N}\mathbf{U}_j] \qquad (13)$$

where $\mathbf{U}_1$ = row (1 0 0 0) and $\mathbf{U}_n$ = column (1 1 1 1), $\mathbf{U}_i'$ is the statistical weight matrix in which all the elements are zero except those corresponding to the state ζ and Z is the rotational partition function of the side group. Then the contribution of the side groups to the polarity of the chains was obtained by generating for each

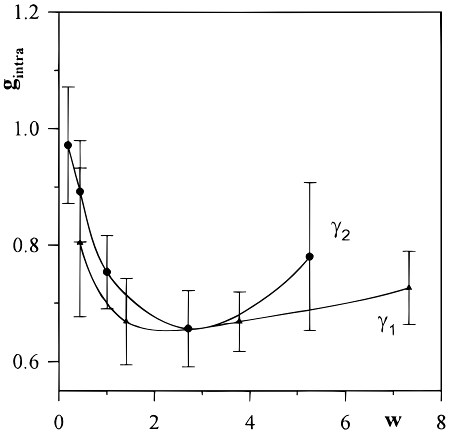

Figure 7. Variation of the intramolecular dipolar correlation coefficient with the statistical weight parameters associated with the conformations about $C^{\alpha}-C^*(O^*)$ bonds in racemic dyads for poly{[2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} (PD22A).

repeating unit 10 random numbers lying in the range between 0 and 1. From these numbers and the probabilities of each rotational state of the backbone of the side group, the dipole moment associated with the conformation was obtained in the reference frame in which the x axis lies along the $C^*(O^*)-O$ bond, the y axis is in the plane defined by the $C^{\alpha}H-C^*(O^*)-O$ bonds, and the z is in such a direction that it completes a right-handed coordinate axis. The final contribution of the dipole moment of the side group in the reference frame of the $C^{\alpha}-CH_2$ bonds of the main chain was obtained for the two rotational angles of the $C^{\alpha}-C^*(O^*)$ bond ($\chi = 0°, 180°$).

The calculation of the mean-square dipole moment of PD22A proceeded by generating 10 representative chains of 200 repeating units each, in which the isotactic replacement fraction was 0.30. The evaluation of the mean-square dipole moment of each of these chains was repeated 200 times, the dipole moment contribution of each repeating unit each time being obtained by the method outlined above. The starting set of statistical weights used in eqs 7 and 8 were the same as those utilized for other acrylate polymers,[28,29] specifically, $\rho = 1.1$, $\gamma_1 = 1.40$, $\gamma_2 = 1.89$, $\gamma = 1.39$, and $\beta = 1.80$. Preliminary calculations showed that the value of $\langle \mu^2 \rangle$ is very sensitive to the statistical weights governing the cis and trans conformations of the $C^{\alpha}-C^*(O^*)$ bonds with respect to the methine bond in racemic diads. The evolution of $\langle \mu^2 \rangle$ with γ_1 and γ_2 was expressed in terms of the intramolecular dipolar correlation coefficient, g_{intra}, given by

$$g_{\text{intra}} = \frac{\langle \mu^2 \rangle}{x(m_{E}{}^2 + 4m_{CO}{}^2 + m_{OH}{}^2)} \qquad (14)$$

where x is the number of repeating units in the chains and m_E, m_{CO}, and m_{OH} are, respectively, the dipole moments associated with the ester, ether, and hydroxyl groups. An inspection of the results plotted in Figure 7 shows that g_{intra} strongly decreases as the probability of unfavorable orientations (nearly antiparallel orientation) of consecutive dipoles in racemic diads, expressed by γ_2, increases. As occurs with other acrylate polymers,[27,28] the sensitivity of the dipolar correlation coefficient to the statistical weights embodied in the meso diads is rather small. The set of statistical weights, $\rho = 1.1$, $\beta = 1.80$, $\gamma = 1.39$, $\gamma_1 = 1.40$, and $\gamma_2 = 2.6$, gives a good account of the experimental results. With this set of statistical weights, the calculated value of g_{intra} is 0.66, in satisfactory agreement with the experimental result, 0.62. In Figure 8, the effect of the stereoregularity of the chains on g_{intra} is shown. The curve of this figure, calculated using $\gamma_2 = 1.89$, suggests that the dipolar correlation coefficient is strongly dependent on the stereochemical structure for chains in which the isotactic replacement, w_{iso}, is below 0.20. However, for $w_{\text{iso}} > 0.20$ the effect of the stereochemical composition on g_{intra} is nearly negligible.

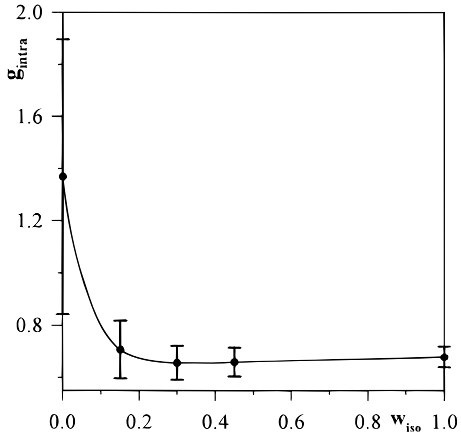

Figure 8. Dependence of the intramolecular correlation coefficient on the isotactic replacement fraction for poly{2,2-bis[4-(2-hydroxyethoxy)phenyl]propyl monoacrylate} (PD22A).

Conclusions

The value of the experimental dipolar correlation coefficient for the model compound of the side group (0.67) is only slightly larger than that of the molecular chains (0.62). This result indicates that the statistics of the backbone plays a relatively minor role in the polarity of comblike polymers. For chains in which the isotactic replacement is larger than 0.20, the polarity of comblike polymers is largely governed by the statistics of the side groups. Consequently, the theoretical calculation of the mean-square dipole moment of the side chains can be used, as a first approximation, to predict the polarity of atactic comblike polymers.

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