Synthesis and Polarity of Acrylate Polymers with Long Hydrophilic Side Groups

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ABSTRACT: The kinetic aspects of the radical polymerization of triethylene glycol monoacrylate are studied finding that the values of $k_p/k_t^{1/2}$ are in the range 0.17−0.40 $L^{1/2}/mol^{1/2}\ s^{1/2}$ at temperatures between 50 and 65 °C. The values of the activation enthalpy, ΔH^{**}, and activation entropy, ΔS^{**}, of the global process amount of 11.0 kcal mol^{-1} and −28.3 cal mol^{-1} K^{-1}, within the range reported for other acrylate polymers. Mean-square dipole moments per repeating unit, $\langle\mu^2\rangle/x$, were determined from measurements of dielectric permittivities in dilute dioxane solutions. The results at 30 °C were $\langle\mu^2\rangle/x = 7.97$ D^2 and 10^3 d ln $\langle\mu^2\rangle/dT = 0.85$ K^{-1}. Values of dipole moments associated with the conformations of the side groups range from 0.2 to 5 D, and hence a combination of standard matricial products and Monte Carlo techniques were used to evaluate by the rotational isomeric state model the dipolar correlation coefficient of the chains. Good agreement between theoretical and experimental results was found using the set of statistical weights utilized for other acrylate polymers with short side groups.

Introduction

The polarity of molecular chains with polar groups rigidly attached to the main chain shows a strong dependence on the statistics of the chains whenever the polar groups occupy neighboring positions in the main chain.[1] This dependence decreases as the distance between polar groups increases so that dipoles become nearly uncorrelated when they are separated by five or more skeletal bonds.[2] For most polymers, the dipoles associated to the polar groups are perpendicular to the chain contour (type B dipoles[3]), so that the dipole moment, μ, for each conformation of the chain is uncorrelated to the end-to-end distance, r; consequently, the dielectric relaxation spectra of the chains only present absorptions associated with segmental and local motions, both relaxation processes being independent on molecular weight. The relaxation spectra of polymers with dipoles having a component perpendicular and another parallel to the chain contour (type A + B dipoles) present an additional absorption,[3] associated with the disentanglement of molecular chains, called normal mode relaxation, whose average relaxation time scales with the 3.4 power of molecular weight.[4]

The dielectric relaxation spectra of polymers with polar flexible side groups (type C dipoles) like those of the chains with type B dipoles only exhibit relaxation processes associated with segmental and local motions.[5] However, the equilibrium dielectric properties of these chains do not depend only on the statistics of the skeletal bonds, as occurs in chains with type B dipoles, but they also depend on the statistics of the side groups.[6,7] The statistics of these chains thus become more complex because the contribution of each side group to the polarity of the chain cannot be singled out owing to the fact that it is dependent on its conformation. It is then an aim of this work to calculate the polarity of chains whose side groups exhibit a wide distribution of dipole moments.

In our laboratories attention is being paid to the synthesis of polymers with hydrophilic character. Pursuing in the objective of preparing hydrophilic polymers that may have biomedical applications as hydrogels, efforts are currently being devoted to the synthesis and characterization of different monomers with either OH or NH_2 groups in their structure. In this way, the chemical and kinetics aspects of the synthesis of polymers containing hydroxyl groups in their structure have been reported elsewhere.[8−11] These studies are extended in this paper to the synthesis of polymers with long polar side groups which may give rise to the formation of hydrogels. The strategy used was to prepare acrylate chains containing triethylene glycol as alcoholic residue in the ester group.

This work reports the synthesis and kinetics of polymerization of triethylene glycol acrylate and the main characteristics concerning the structure and thermal properties of the polymer obtained, poly(triethylene glycol acrylate) (PTEGA). The effect of the long side groups on the polarity of PTEGA chains is analyzed by measuring their mean-square dipole moment and further interpreting the experimental results in terms of the rotational isomeric state model.

Experimental Section

Materials. Triethylene glycol was dried by azeotropic distillation of the water content from a mixture of the glycol with benzene. Benzene and dioxane (Merck) were purified by conventional methods, whereas acryloyl chloride (Fluka) and triethylamine were used as received. 2,2′-Azobis[isobutyronitrile] was purified by crystallization from methanol and dried under high vacuum at room temperature.

Synthesis of Triethylene Glycol Acrylate. The monomer was obtained under nitrogen atmosphere by reaction, at 20 °C, of triethylene glycol with acryloyl chloride in benzene solution, using triethylamine as absorbent of the hydrogen chloride evolved during the reaction. The mole ratio of glycol to acid chloride was 7/3 in order to obtain a better yield of the monoester. Acryloyl chloride was slowly added to the mixture for 2 h, and the reaction was permitted to proceed for 10 h more. The triethylammonium chloride was removed by filtration. The mixture of mono- and diester monomers was washed several times with distilled water to remove unreacted triethylene glycol, and the aqueous phase was in turn extracted with chloroform to separate the acrylate monomers and added to the benzene solution of monomers initially obtained. Finally, the solvent was eliminated by freeze-drying.

Separation of the Mixture of Monomers. Owing to the difficulty involved in the separation of monomers by distillation, flash chromatography was used for their purification. The separation was carried out in a column of silica gel 60 (230−400 mesh ASTM) using a mixture of 70/30 n-hexane/ethyl acetate as eluent. The monoester was extracted from the

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column by successive separations of the diacrylate monomer and final elution with pure ethyl acetate. The mole fraction of the monoester monomer obtained was ca. 0.80, in quite good agreement with the results obtained for other monomers synthesized under similar conditions.

Characterization of the Monomers. The two acrylate esters were characterized by ^{1}H and ^{13}C NMR spectroscopy. The resonance spectra were registered with a Varian XL-300 apparatus operating at 300 MHz for ^{1}H NMR and at 75.4 MHz for ^{13}C NMR, using deuterated chloroform as solvent and tetramethylsilane as internal reference. A close inspection of the ^{13}C NMR spectra of both monomers showed the absence of the resonance signals corresponding to the diacrylate in the monoester, thus indicating the purity of the latter monomer.

Polymerization Reactions. Homopolymerization reactions of triethylene glycol monoacrylate (TEGA) were carried out in dioxane solution at temperatures between 50 and 65 °C, using AIBN as initiator. The progress of the reactions was measured with a double-branch dilatometer, with 6 cc capacity and 1.036 mm capillary diameter. The polymer formed, PTEGA, was isolated from the reaction medium by several precipitations in *n*-hexane and finally was dried in high vacuum at 60 °C.

Characterization of the Polymer. The characterization and the stereochemical composition of PTEGA were determined by ^{13}C NMR spectroscopy using a Varian XL-300 spectrometer, deuterated chloroform as solvent, and tetramethylsilane as internal standard.

In acrylic polymers, the stereoregularity of the chains is more difficult to measure than in methacrylic ones due to the fact that the chemical shifts of the carbons and protons are less influenced by the stereochemical configuration of nearby units. In this sense, only the carbonyl carbons of the side chain and the methine carbons of the main chain give different signals that suggest a tacticity effect. Particularly, the peaks corresponding to the C=O carbons show a complicated spectral pattern with overlapping of almost all the signals. Nevertheless, by deconvolution of the different peaks, the signals were separated, and the isotactic replacement was estimated to be 0.30 ± 0.05.

The glass transition temperature of PTEGA was determined calorimetrically with a Perkin Elmer DSC8 calorimeter at a heating rate of 10 °C/min and was found to be −48 °C. As a consequence of the high flexibility of the pendent chain, PTEGA is much softer at room temperature than other polyacrylates containing hydroxyl groups in the side chains such as poly(3-hydroxyneopentyl acrylate)[9] ($T_g = 8$ °C).

Dielectric Measurements. The static dielectric permittivity of solutions of the polymer in dioxane were obtained as a function of both the weight fraction of solute, w, and temperature with a capacitance bridge (General Radio; type 1620 A) coupled with a three-terminal cell. The experiments were performed at 10 kHz, a frequency at which the real component, ϵ', of the complex dielectric permittivity, ϵ^*, coincides with the static dielectric permittivity. Increments of the dielectric permittivity of the solutions with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) were plotted at the temperatures of interest against w, giving straight lines from whose slopes the derivatives $\mathrm{d}\epsilon/\mathrm{d}w$ in the limit $w \to 0$ necessary to determine the mean-square dipole moments of the chains were obtained. Increments in the value of the index of refraction of the solutions with respect to that of the solvent ($\Delta n = n - n_1$) were measured with a differential refractometer (Chromatix Inc.). In the same way, values of Δn at each temperature of interest were also plotted against w, and the value of derivative $\mathrm{d}n/\mathrm{d}w$ was determined. Values of the mean-square dipole moment per repeating unit, $\langle\mu^2\rangle/x$, were obtained from these quantities by means of the equation of Guggenheim[12] and Smith[13]

$$\frac{\langle\mu^2\rangle}{x} = \frac{27k_BTM_o}{4\pi\rho N_A(\epsilon_1+2)^2}\left(\frac{\mathrm{d}\epsilon}{\mathrm{d}w} - 2n_1\frac{\mathrm{d}n}{\mathrm{d}w}\right) \tag{1}$$

where M_o is the molecular weight of the repeating unit, k_B and N_A are, respectively, the Boltzmann constant and Avogadro's number, T is the absolute temperature, and ρ is the density of the solvent. The results obtained from $\langle\mu^2\rangle/x$ at several temperatures are given in the sixth column of Table 1. The error involved in the evaluation of $\langle\mu^2\rangle/x$ was estimated to be ±3%. The temperature coefficient expressed in terms of 10^3 d ln $\langle\mu^2\rangle/\mathrm{d}T$ amounted to 0.85.

Table 1. Values at Different Temperatures of $\mathrm{d}\epsilon/\mathrm{d}w$ and $2n_1\mathrm{d}n/\mathrm{d}w$ Obtained, Respectively, from Dielectric and Refractive Index Measurements on Solutions of Poly(triethylene glycol acrylate) in Dioxane Together with the Results for the Dipolar Intramolecular Correlation Coefficient, g_{intra}, and the Mean-Square Dipole Moment per Repeating Unit, $\langle\mu^2\rangle/x$

T, °C	$\mathrm{d}\epsilon/\mathrm{d}w$	$2n_1\mathrm{d}n/\mathrm{d}w$	g_{intra}[a]	$\langle\mu^2\rangle/x$, D^2
30	4.902	0.152	0.677	7.97
40	4.702	0.165	0.677	7.98
50	4.558	0.168	0.687	8.10
60	4.390	0.173	0.692	8.16

[a] A value of $g_{\mathrm{intra}} = 0.58$ was theoretically calculated for the side group.

Owing to the insolubility of PTEGA in other nonpolar solvents (benzene, toluene, cyclohexane, carbon tetrachloride, etc.), potential solvent effects on the polarity of the chains arising from dioxane ability to H-bond with the hydroxyl group of the polymer could not be investigated. However, these effects were studied in poly(neopentyl glycol acrylate),[14] finding that the differences between the values of the dipole moments of the polymer measured in dioxane and benzene lie within the estimated experimental error (±3%).

Results and Discussion

Kinetics of Polymerization. By assuming that the decomposition of the initiator is a first-order reaction, the rate of radical-initiated polymerization can be written as

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_p\left(\frac{2fk_d[\mathrm{I_o}]}{k_t}\right)^{1/2}[\mathrm{M}]\exp\left(\frac{-k_dt}{2}\right) \tag{2}$$

where k_d, k_p, and k_t are the rate constants for initiator decomposition, propagation, and termination reactions, respectively, [M] is the instantaneous concentration of monomer, [I$_o$] is the initial concentration of initiator, and f is the efficiency of the initiator. Moreover, in the development of eq 2, it is assumed that depropagation reactions do not take place and the thermal polymerization is negligible. The integration of eq 2 gives

$$\ln\frac{[\mathrm{M_o}]}{[\mathrm{M}]} = 2k_p\left(\frac{2f[\mathrm{I_o}]}{k_tk_d}\right)^{1/2}\left[1 - \exp\left(\frac{-k_dt}{2}\right)\right] \tag{3}$$

In dilatometric experiments, it is useful to transform eq 3 in the following one

$$-\ln\left[\left(1 - \frac{\Delta h}{\Delta h_{100}}\right)\frac{V_o}{V_o - \Delta V}\right] = 2k_p\left(\frac{2f[\mathrm{I_o}]}{k_tk_d}\right)^{1/2}\left[1 - \exp\left(\frac{-k_dt}{2}\right)\right] \tag{4}$$

that can be written in the alternative form

$$\Delta h = \Delta h_{100}\left\{1 - \frac{V_o - \Delta V}{V_o}\exp\left\{-2k_p\left(\frac{2f[\mathrm{I_o}]}{k_tk_d}\right)^{1/2} \times \left[1 - \exp\left(\frac{-k_dt}{2}\right)\right]\right\}\right\} \tag{5}$$

where Δh and Δh_{100} are the changes of dilatometric height at time t and at 100% of conversion, V_o is the

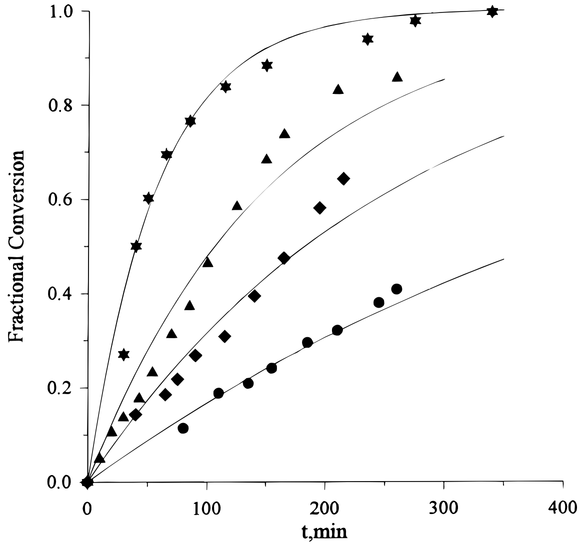

Figure 1. Fractional conversion of monomer as a function of time for the polymerization of TEGA in 1,4-dioxane at different temperatures.

initial volume of monomer and solvent in the dilatometer, and ΔV is the change of volume at a given time.

The analysis of the kinetic data carried out by a nonlinear least-squares procedure[9] allows the evaluation of the kinetic constants that intervene in the chemical reactions. This method permits the determination of $fk_p/k_t^{1/2}$, k_d, and Δh_{100}, avoiding the evaluation of the last magnitude by other procedures such as measurements of densities of both polymer and monomer at different temperatures. In this work, k_d has been considered to be a nonadjustable parameter at each temperature owing to the fact that it is almost independent of the solvent.

With the experimental results of Δh, the values of Δh_{100} and $fk_p/k_t^{1/2}$ were determined. The values of k_d at different temperatures were taken from the literature.[15,16] Once Δh_{100} is known, the values of the fractional conversions were found directly from both Δh and the changes of volume during the polymerization reactions. Figure 1 shows the time dependence of the fractional conversion for the polymerization of TEGA in dioxane.

The application of eq 4 to the data obtained by nonlinear least squares allows the linearization of the results. By considering the efficiency of the initiator $f = 0.6$, straight lines intercepting the origin of coordinates are obtained with slopes equal to $k_p/k_t^{1/2}$ as can be seen in Figure 2. Values of $k_p/k_t^{1/2}$ are shown in Table 2 for the polymerization of TEGA at different temperatures.

It is difficult to compare the values of $k_p/k_t^{1/2}$ obtained in the kinetics of polymerization of TEGA with the corresponding results for other acrylic monomers. In some cases, similar values are indicated for acrylates with unsubstituted alkyl[17] groups (methyl, ethyl, propyl, or butyl), whereas acrylates with a branched alkyl group[9,17] present higher values of $k_p/k_t^{1/2}$ due probably to lower termination rate constants.

The temperature dependence of the ratio $k_p/k_t^{1/2}$ may be written as an Arrhenius equation

$$\frac{k_p}{k_t^{1/2}} = A \exp -\left(\frac{\Delta E^{**}}{RT}\right) \tag{6}$$

where A is a combination of the frequency factors for the two rate constants, $\Delta E^{**} = \Delta E_p^{**} - \Delta E_t^{**}/2$, ΔE_p^{**} and ΔE_t^{**} being, respectively, the activation energies of propagation and termination, T is the absolute temperature, and R is the gas constant. According to the transition state theory, the rate constants may also be expressed by

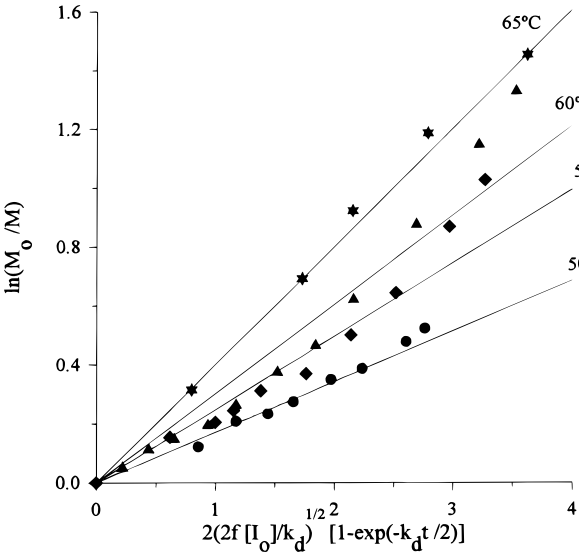

Figure 2. Kinetic plots for the polymerization of 3-hydroxyneopentyl methacrylate in 1,4-dioxane at several temperatures.

Table 2. Kinetic Constants for the Polymerization of TEGA in 1,4-Dioxane[a]

T, °C	$k_p/k_t^{1/2}$, L$^{1/2}$/mol$^{1/2}$ s$^{1/2}$
50	0.17
55	0.25
60	0.30
65	0.40

[a] $[M_o] = 1$ mol/L. $[I_o] = 1.22 \times 10^{-2}$ mol/L.

$$\frac{k_p}{k_t^{1/2}} = \left(\frac{kT}{h}\right)^{1/2} \exp\left(-\frac{\Delta H^{**}}{RT}\right) \exp\left(\frac{\Delta S^{**}}{RT}\right) \tag{7}$$

where k and h are the Boltzmann and Planck constants and where ΔH^{**} and ΔS^{**} are given by

$$\begin{aligned} \Delta H^{**} &= \Delta H_p^{**} - \Delta H_t^{**}/2 \\ \Delta S^{**} &= \Delta S_p^{**} - \Delta S_p^{**}/2 \end{aligned} \tag{8}$$

ΔH_i^{**} and ΔS_i^{**} (i = p or t) being, respectively, activation enthalpies and activation entropies for both propagation and termination reactions.

An Arrhenius fit for the polymerization TEGA in dioxane is obtained (Figure 3) with the values of $k_p/k_t^{1/2}$ shown in Table 2. The straight line allows the determination of the activation parameters for the polymerization of this monomer under the conditions described in the experimental part, and the results obtained were 1.35×10^7 L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$, 11.7 kcal mol^{-1}, 11.0 kcal mol^{-1}, and -28.3 cal mol^{-1} K^{-1} for A_p, ΔE^{**}, ΔH^{**}, and ΔS^{**}, respectively. The value of ΔE^{**} is within the range reported in the polymerization of other acrylic monomers.[9]

Dipole Moments. Earlier studies carried out on the polarity of several acrylic polymers including phenyl[7] and cyclohexyl esters of polyacrylic acid[18] show that the

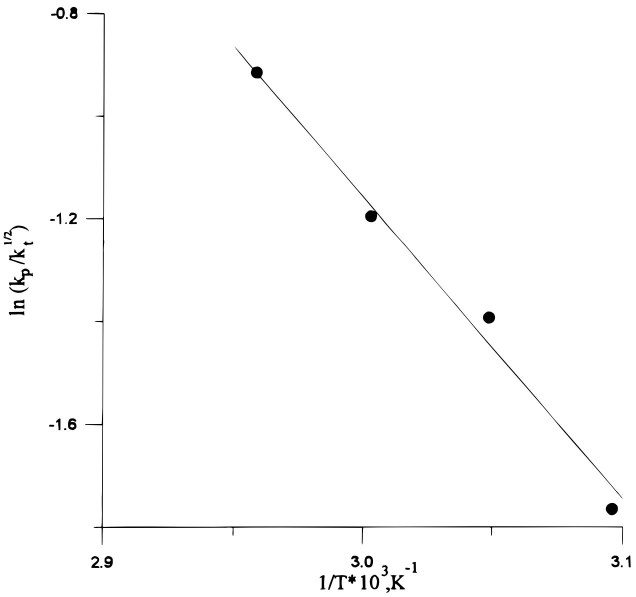

Figure 3. Arrhenius plot for the polymerization of 3-hydroxyneopentyl methacrylate in 1,4-dioxane.

mean-square dipole moments of the chains can be evaluated by using a statistics that assumes that each skeletal bond is restricted to trans (t) and gauche (g) states. Each of these states splits into two: $\chi = 0$ and $\chi = \pi$ conformations in which the carbonyl group is, respectively, in cis and trans conformation to the methine bond. Thus the model describing the statistics of these chains is a four-rotational states model [(t, $\chi = 0$), (t, $\chi = \pi$), (g, $\chi = 0$), and (g, $\chi = \pi$)] whose statistical weight matrices are[6,7]

$$\mathbf{U}' = \begin{bmatrix} 1 & 0 & \rho & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{bmatrix} \qquad (9)$$

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

$$\mathbf{U}''_r = \begin{bmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix};\ \mathbf{U}''_m = \begin{bmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{bmatrix} \qquad (10)$$

for racemic and meso configurations of the $C^{\alpha}-CH_2-C^{\alpha}$ of the bond pair. The average rotational angles about the skeletal bonds of meso diads are $\langle\phi_1,\phi_2\rangle_{tt}$ = 16°, 16°, $\langle\phi_1,\phi_2\rangle_{tg}$ = 3°, 114°, and $\langle\phi_1,\phi_2\rangle_{gt}$ = 114°, 3°. For racemic diads $\langle\phi_1,\phi_2\rangle_{tt}$ = 3°, 3°.

The mean-square dipole moment per repeating unit may be written as[19]

$$\frac{\langle\mu^2\rangle}{x} = \frac{\mathbf{P}_1\left[\prod_{k=1}^{x}(\mathbf{U}'_k\otimes\mathbf{E}_5)\mathbf{G}'_k(\mathbf{U}''_k\otimes\mathbf{E}_5)\mathbf{G}''_k\right]\mathbf{P}_n}{Zx} \qquad (11)$$

where Z is the rotational partition function, the symbol $\otimes$ denotes the direct product, $\mathbf{E}_5$ is the identity matrix of order 5, and $\mathbf{G}'_k$ and $\mathbf{G}''_k$ are pseudodiagonal matrices given by

$$\begin{aligned}\mathbf{G}'_k = \mathrm{diag}[&\mathbf{M}'_k(t, \chi = 0), \mathbf{M}'_k(t, \chi = \pi), \\ &\mathbf{M}'_k(g, \chi = 0), \mathbf{M}'_k(g, \chi = \pi)] \\ \mathbf{G}''_k = \mathrm{diag}[&\mathbf{M}''_k(t, \chi = 0), \mathbf{M}''_k(t, \chi = \pi), \\ &\mathbf{M}''_k(g, \chi = 0), \mathbf{M}''_k(g, \chi = \pi)]\end{aligned} \qquad (12)$$

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

$$\mathbf{M}_k = \begin{bmatrix} 1 & 2\mathbf{m}^T\mathbf{T} & m^2 \\ 0 & \mathbf{T} & \mathbf{m} \\ 0 & 0 & 1 \end{bmatrix}_k \qquad (13)$$

where $\mathbf{T}$ is the transformation matrix that projects a vector from reference frame $i + 1$ to its representation in the reference frame i 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[$M_n(\chi = 0)$, $M_n(\chi = \pi)$, $M_n(\chi = 0)$, $M_n(\chi = \pi)$], 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.

The evaluation of the mean-square dipole moments of the chains by the standard matricial method described above requires the knowledge of the conformational statistics of the side groups. In Figure 4 the repeating unit of PTEGA is shown. In brief, gauche states about CH_2-CH_2 bonds that give rise to first-order interactions between two oxygen atoms are located at ±120°, having an energy 0.4 kcal mol^{-1} below that of the alternative trans states (0°), whereas gauche states about CH_2-O ether bonds are located at ±110° and their energy is 0.9 kcal mol^{-1} above that of the corresponding trans states (0°).[1,2,20] Moreover, the CO–O bond of the ester group is restricted to trans state, whereas gauche states about the CH_2-O bond of this group are disfavored by ca. 0.4 kcal mol^{-1} with respect to the alternative trans states;[1,2] the rotational angles of these bonds are located at 0° and ±104°. Rotations of different sign about two consecutive bonds are only permitted for a pair of bonds which give rise to second-order interactions between $CH_2\cdots O$ and $CH_2\cdots CO$ bonds whose energies are 0.6 and 1.4 kcal mol^{-1} above that of the alternative tt states.[1,2] It should be indicated that the penultimate bond of Figure 4 can be considered freely rotating. The dipole moments corresponding to the ether ($O-CH_2$) and CH_2-CH_2 bonds were considered to be[2] 1.07 and 0.00 D, respectively, whereas the dipole associated to the ester group amounts to 1.78 D, its direction forming an angle of 123° with the CH–C*O* bond.[21] Moreover, the skeletal bond angles of the side groups were taken to be 68.5°.

The conformational versatility of the glycol residue entails a distribution of dipole moments associated with the side chain. The distribution was obtained by generating all available conformations and assigning the statistical weight of each conformation using the statistics described before; then the dipole moment and energy were evaluated for each conformation. The distribution of μ was determined in the form of a histogram for each value of μ ± 0.25, starting in μ = 0.25, by summing all the statistical weights for all the

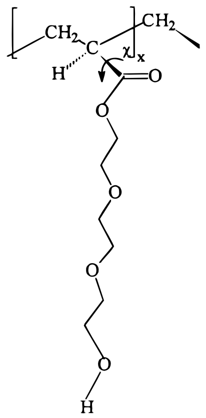

Figure 4. Structural unit of PTEGA.

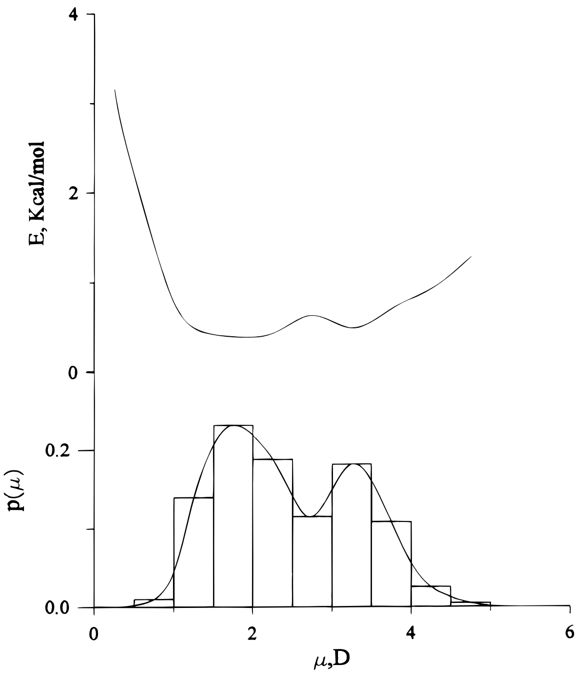

Figure 5. Average conformational energies (top) and distribution of dipole moments (bottom) of the side group as a function of the dipole moments of the corresponding conformations.

conformations whose dipole moments lie in the interval $\mu \pm 0.25$ and further normalization with respect to the total. In the same way, the average of the conformational energy was calculated for each interval of $\mu \pm 0.25$. The histogram, represented in Figure 5, shows that the distribution of dipole moments of the side groups is of bimodal type, the modes of the distribution being located at 1.75 and 3.25 D, respectively. It should also be noted that the dipole moments of the conformations of the side groups lie in the range 0.25−5 D. Values of the average conformational energy corresponding to the conformations whose dipole moments lie in the interval $\mu \pm 0.25$, represented in the top of Figure 5, suggest that the conformations with the largest and lowest polarity are those with higher energy, that is, those involving gauche states about ether bonds and rotations of different sign about consecutive bonds that give rise to second-order interactions between a carbonyl and a methylene group.

At first sight, the rather wide distribution of dipole moments of the side groups would lead one to conclude that the approach described above for the evaluation of the mean-square dipole moment of simple polyacrylates would not be feasible to calculate the conformational dependent properties of PTEGA. In fact a rigorous approach would require to formulate statistical weight matrices whose dimensions were equal to 2 times the number of conformations available to the side groups, a task that obviously could not be carried out even with the most sophisticated computers. In order to determine the contribution of each repeating unit to the polarity of the chain, the probability of the rotational states of each bond was obtained by means of the expression[1]

$$p(\zeta)_i = Z^{-1}\left[\prod_{h=1}^{i-1}\mathbf{U}_h\right]\mathbf{U}'_i\left[\prod_{j=i+1}^{N}\mathbf{U}_j\right] \qquad (14)$$

where Z is the partition function of the side group, $\mathbf{U}'_i$ is a matrix in which all the elements are zero except those corresponding to the state ζ, and $\mathbf{U}_1$ and $\mathbf{U}_n$ are, respectively, row and column vectors that convert the matricial product of eq 14 into a scalar. A Monte Carlo routine that provide the variable contribution of the side group to the polarity of the chain was used. In brief, the contribution of the side groups to the polarity of the chain was determined by generating for each side group nine random numbers lying in the range between 0 and 1 from which and using the probabilities obtained for the rotational states of each skeletal bond of the side group the dipole moment associated with the conformation generated is calculated in the reference frame in which the x axis coincides with the C*O*−O bond, whereas the y axis is in the plane formed by the C$^{\alpha}$H−C*O*−O bonds. Finally, the contribution of the side group in the reference frame of the C$^{\alpha}$H−CH$_2$ skeletal bond of the main chain is obtained for each of the two rotational states of the C$^{\alpha}$H−C*O* bond ($\chi = 0, \pi$).

The calculation of the mean-square dipole moment for chains containing 200 units was performed following the procedures described above. Thus 20 chains with Bernouillian placement of meso and racemic diads were obtained in which the isotactic replacement fraction was 0.30. For each of these chains, 200 chains were generated and the values of $\langle\mu^2\rangle$ were calculated by using eq 11. The values of $\langle\mu^2\rangle$ were computed using as first approximation the set of statistical weights utilized for other polyacrylates, specifically, $\rho = 1.1$, $\gamma_1 = 1.40$, $\gamma_2 = 1.89$, $\gamma = 1.39$, and $\beta = 1.80$. The values computed for $\langle\mu^2\rangle$ were expressed in terms of the dipolar intramolecular correlation coefficient

$$g_{\text{intra}} = \frac{\langle\mu^2\rangle}{x\sum_{i=1}^{n} m_i^{\,2}} \qquad (15)$$

where m_i represents the dipole moment associated with the bond i of the side group. Experimental values of this quantity are given in the fourth column of Table 1. By using the values of the bond dipole moments given above, one finds that $\sum_i m_i^2 = 11.78$ D^2. In general the mean-square dipole moment of the chains was found to be very sensitive to the population of both tπ,t0 and tπ,tπ conformations as expressed by γ_1 and γ_2. As shown in Figure 6, g_{intra} decreases as γ_2 increases, reaching a minimum in the vicinity of $\gamma_2 = 2$, and then increases as the population in which the carbonyl group is in trans conformation with respect to the methine bond goes up. The curve showing the dependence of g_{intra} on γ_1 (Figure 6) drops as this parameter increases,

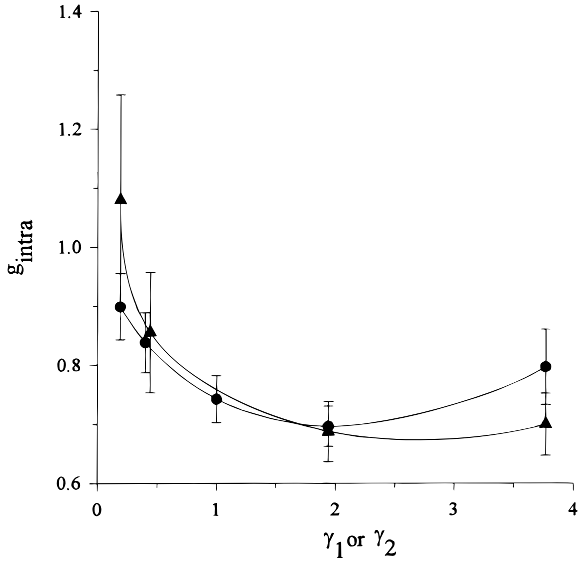

Figure 6. Influence of γ_1 and γ_2 on the dipolar intramolecular correlation coefficient (g_{intra}).

even more rapidly than that corresponding to γ_2, until the statistical parameter reaches a value of ca. 2 and then the value of g_{intra} remains nearly constant with increasing values of γ_1. Thus the calculations indicate that g_{intra} diminishes from 0.90 to 0.69. When γ_2 increases from 0.19 to 1.91. In the same way, the intramolecular correlation coefficient diminishes from 1.08 to 0.69 when γ_1 increases from 0.19 up to 1.94. The dependence of the intramolecular correlation coefficient on both β and γ is nearly insignificant. With the set of statistical weights $\beta = 2.29$, $\gamma = 1.1$, $\gamma = 1.39$, $\gamma_1 = 1.43$, and $\gamma_2 = 1.90$, the intramolecular correlation coefficient is calculated to be 0.70 ± 0.06, in pretty good agreement with the experimental result, 0.67 ± 0.03, at 30 °C. It should be pointed out that this set of statistical weights also describes the dipolar intramolecular correlation coefficient of poly(cyclohexyl acrylate),[18] poly(*o*-chlorocyclohexyl acrylate),[22] and poly(benzoylphenyl acrylate).[23]

Summing up, the conformational characteristics of the main chain seem to play a minor role on the polarity of PTEGA. Instead, as occurs with polyacrylates with short side groups, the energy governing the orientations of the carbonyl groups of two consecutive C═O bonds in racemic diads has a major incidence on the polarity of chains with long flexible side groups.

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