Dipolar Correlations in Poly(cyclohexyl acrylate)

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ABSTRACT: The experimental intramolecular correlation coefficient for poly(cyclohexyl acrylate) (PCA), $g_{intra} = 1 + \sum_{i,j} \langle \cos \gamma_{ij} \rangle$, where γ_{ij} is the angle between the i and j relaxing dipoles, increases from 0.752 at 30 °C to 0.813 at 60 °C. A rotational states scheme that assumes that each C^α–C^*O^* bond has accessibility to two states gives a very good account of the experimental results. The dipolar correlation coefficient g that includes the intra- and intermolecular interactions between the relaxing dipoles was determined from dielectric measurements carried out on the polymer in the bulk. By assuming that the Maxwell relationship $\epsilon_\infty = n^2$ holds, where n is the index of refraction and ϵ_∞ the dielectric permittivity at infinite frequency, the value of g at 30 °C was found to be 0.68. The closeness between g and g_{intra} indicates that dipolar intermolecular interactions do not greatly influence the dielectric behavior of this polymer. The analysis of the dielectric and mechanical spectra of PCA seems to suggest that both the dielectric and mechanical subglass absorptions are caused by the same molecular motions. Attempts to quantify the dielectric subglass absorption are made. On the other hand, the study of the temperature dependence of the α relaxation suggests that the critical volume necessary for either a dielectric or a mechanical relaxation process to take place is lower in poly(cyclohexyl acrylate) than in most polymers.

Introduction

It is a well-admitted fact that the glass–rubber relaxation, labeled α, is the result of long-range generalized motions involving rotations about skeletal bonds. However, the elucidation of the mechanism that gives rise to the subglass or β relaxation is somewhat difficult.[1-8] On the one hand, it is believed[5-8] that the secondary relaxations are mainly associated with motions of a flexible side group attached to the main chain and/or with local motions of the main chain. According to this assumption the β relaxation is the result of hindered molecular modes of motions that take place well below the glass transition temperature where general segmental motion is frozen. It should be pointed out in this regard that a molecular model, recently developed by Smith and Boyd,[8] seems to give a good account of the dielectric strength of the β subglass relaxation in polymers with dipolar flexible side groups, in terms of the intramolecular interactions of these groups. On the other hand, it is postulated[2-4] that intermolecular interactions alone can produce the energy barriers for a secondary relaxation peak, so that only specific intramolecular interactions are not required for the development of subglass absorptions. In support of this assumption there are arguments such as the presence of β relaxations in small molecular liquids lacking any intramolecular degree of freedom capable of producing dielectric activity.

In a recent work[9] the dynamic dielectric properties of cyclohexyl isobutyrate (CI) and cyclohexyl 2,4-dimethylglutarate (CG), model compounds of the repeating unit and the dimer of poly(cyclohexyl acrylate) (PCA), respectively, were investigated. A surprising result of this work is that CI exhibits a strong subglass β relaxation, in comparison with that of the compound with a higher conformational versatility, CG. Other esters with internal degrees of freedom capable of producing dielectric activity, such as phenyl 2,4-dimethylglutarate (PG) and m-chlorophenyl 2,4-dimethylglutarate (MCPG), also present a weak subglass absorption.[9] It is the purpose of this paper to measure the dielectric relaxation spectrum of PCA and to compare it with the respective spectra of CI and CG.

An important aspect in the description of the dielectric relaxation spectrum of amorphous polymers is the prediction of the overall relaxation strength of the combined $\alpha + \beta$ processes. In general, this strength can be predicted by means of Onsager[10] type expressions, such as the Fröhlich[11] equation, in which intermolecular and intramolecular dipolar correlation factors intervene.[1] The latter factor is the same as the dipole moment ratio which in turn can be defined as the mean-square dipole moment normalized by an effective group dipole moment. However, a still unresolved issue is whether intermolecular dipolar interactions play an only marginal role in the relaxation behavior owing to the fact that dipolar interaction dies away fairly quickly as the distance between dipoles increases. Therefore, it is also the purpose of this paper to calculate both theoretically and experimentally the intramolecular correlation factor for PCA and to compare it with that calculated from dielectric measurements carried out in the bulk.

Experimental Section

Cyclohexyl acrylate was synthesized by the addition of 20% dioxane to an aqueous reaction medium containing cyclohexanol and 5% NaOH. Freshly distilled acryloyl chloride was added dropwise to the solution cooled below 0 °C. Crude cyclohexyl acrylate was extracted 2-fold with ether, washed with distilled water, dried overnight with calcium chloride and then with calcium hydride, and finally distilled at a reduced pressure.

Poly(cyclohexyl acrylate) was obtained at 50 °C by radical polymerization of cyclohexyl acrylate in benzene, using benzoyl peroxide as catalyst and keeping the conversion below 12%. The polymer was isolated by precipitation, filtered, and dried at vacuum until a constant weight was attained.

The stereochemical composition was determined from the analysis of the ^{13}C NMR spectrum of the polymer recorded in a chloroform solution with a Varian XL-300, at 75 MHz. The molar fraction of iso-, syndio-, and heterotactic triads, determined from the CH and C=O signals amounted to 0.21, 0.30, and 0.49, respectively. The number-average molecular weight of the polymer measured with a Knauer high-speed membrane osmometer was found to be 150 000. The glass transition temperature, determined by dilatometry, has a value of 25 °C.

Values of the dielectric constant ϵ of solutions of PCA in benzene were obtained at 10 kHz with a capacitance bridge (General Radio Type 1620 A) and a three-terminal cylindrical

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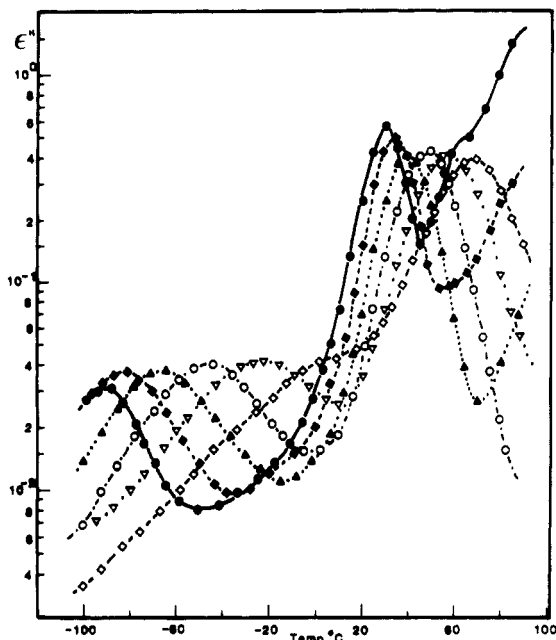‡ Instituto de Ciencia y Tecnología de Polímeros.

Figure 1. Dependence of the dielectric loss ϵ'' on temperature for poly(cyclohexyl acrylate) (PCA) at several frequencies: (●) 0.1, (♦) 1, (▲) 10, (○) 10^2, (▽) 10^3, and (◇) 10^4 Hz.

Figure 2. Details of the dielectric β relaxation, expressed in terms of the loss tan δ, for poly(cyclohexyl acrylate) (PCA), cyclohexyl 2,4-dimethylglutarate (CG), and cyclohexyl isobutyrate (CI). Results are taken from ref 9.

cell. Increments in the refractive index Δn of the solutions with respect to the solvent were measured at 632.8 nm with a differential refractometer (Chromatix Inc.). Both ϵ and Δn were determined at 30, 40, 50, and 60 °C. Values of the components of the complex dielectric constant in the bulk were measured as a function of temperature and frequency with a three-terminal plane condenser and a capacitance bridge Du Pont DEA 2970 that operates in the frequency range 0.001–30 kHz. The measurements proceeded from low to high temperature. Dynamic mechanical measurements were carried out on strips of PCA with a PL-DMTA apparatus at a heating rate of 1 °C/min, the range of frequencies being 0.1–10 Hz.

General Results

Dielectric and Mechanical Results in the Bulk. Values at several frequencies of the dielectric loss ϵ'' are represented as a function of temperature in Figure 1. The relaxation spectrum at each frequency presents a prominent peak in the high-temperature region associated with the glass–rubber relaxation. It is worthy to point out that the temperature of the maximum of the peak at 0.1 Hz is only 4 °C above the dilatometric glass transition temperature. Another well-defined peak, labeled β, is detected in the subglass region with a maximum located in the vicinity of –90 °C at 1 Hz. As can be seen in Figure 2, the intensity of the β peak is similar to that of the model compound of the repeating unit, CI, but is much larger than that of the dimer, CG.

For comparative purposes the components at several frequencies of the complex relaxation modulus are plotted as a function of temperature in Figure 3. The spectra displays the features reported earlier by Heijboer[12] for acrylic polymers with cyclohexyl side groups. An important drop in the value of the storage relaxation modulus with increasing temperature occurs in the subglass region, reflected by a strong β mechanical relaxation observed in the loss relaxation modulus versus temperature plots. It is important to stress that the β dielectric loss peak lies nearly at the same temperature as the mechanical peak; for example, the maxima of the dielectric and mechanical β absorptions at 0.1 Hz are located at –90 and –89 °C, respectively. Both relaxations are activated processes
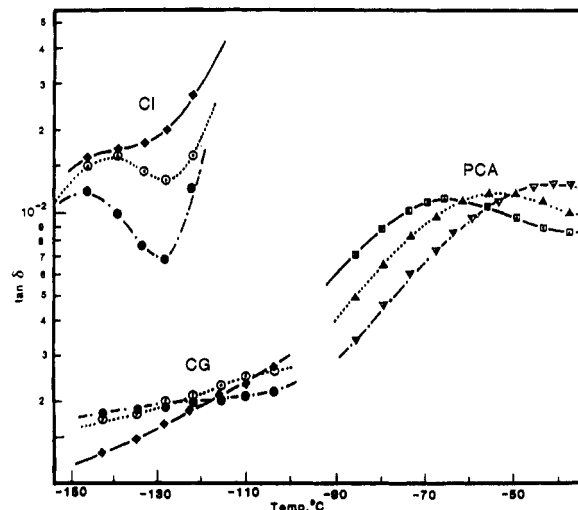
described by the Arrhenius equation

$$\log \nu = \log \nu_0 - E_a/2.3003RT_m \qquad (1)$$

where ν is the frequency, E_a is the activation energy, and T_m is the temperature at the maximum of the peak. The plots log ν versus $1/T_m$ give straight lines with values of 11.9 (49.79) and 14.2 kcal mol^{-1} (59.41 kJ mol^{-1}) for the activation energies of the dielectric and mechanical absorptions, respectively; the respective values of the intercepts, 13.3 and 15.2, nearly lie within the interval 13–15 reported for the secondary absorption of most amorphous systems.[5]

The total dielectric relaxation strength is related to the relaxing dipoles of magnitude μ_0 by the familiar Fröhlich equation[11]

$$\epsilon_r - \epsilon_u = \frac{3\epsilon_r}{2\epsilon_r + \epsilon_u}\left(\frac{\epsilon_u + 2}{3}\right)^2\frac{4\pi N_p g\mu_0^2}{3\kappa T} \qquad (2)$$

where ϵ_r and ϵ_u denote, respectively, relaxed and unrelaxed dielectric constants, N_p is the number of relaxing species per unit of volume, T is the absolute temperature, and κ is Boltzmann's constant. The parameter g is given by[1]

$$g = 1 + \sum_{i<j}\langle\cos\gamma_{ij}\rangle + \sum_{k<l}\langle\cos\gamma_{kl}\rangle \qquad (3)$$

where the second and third terms of the second member of this equation represent the intramolecular and intermolecular dipolar correlations, respectively. The experimental values of ϵ_r and ϵ_u were obtained by analyzing the dielectric results using the Cole–Cole formalism. Plots of the real ϵ' and loss ϵ'' components of the complex dielectric constant ϵ^* for the α relaxation at 30 °C are shown in Figure 4. As usual, the plot corresponding to the glass–rubber absorption is a skewed arc that approaches the abscissa in the high-frequency region along a straight line. The curve is described by the Havriliak–Negami equation[13]

$$\epsilon_\alpha^* = \epsilon_{u\alpha} + \frac{\epsilon_{r\alpha} - \epsilon_{u\alpha}}{[1 + (i\omega\tau_0)^{1-\bar{\alpha}}]^{\bar{\beta}}} \qquad (4)$$

where $\epsilon_{r\alpha}$ and $\epsilon_{u\alpha}$ are the relaxed and unrelaxed dielectric permittivities of the α process and τ_0 is the corresponding central relaxation time. Values of these parameters are shown in Table I. Usually, the complex dielectric plot for
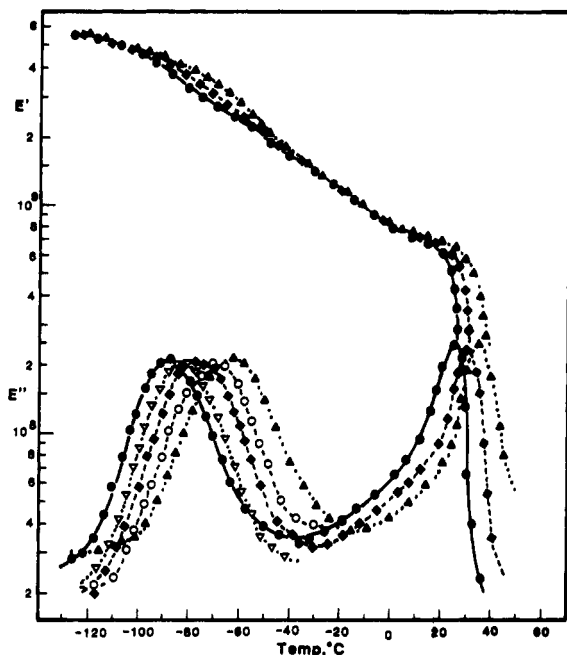
Figure 3. Variation of the storage E' and loss E'' relaxation moduli with temperature for poly(cyclohexyl acrylate) (PCA) at several frequencies: The symbols ●, ▽, ◆, O, and ▲ represent results at 0.1, 0.3, 1, 3, and 10 Hz, respectively. For the sake of clarity E' is only represented at three frequencies in the whole temperature range, and the same occurs for E'' in the glass–rubber zone.
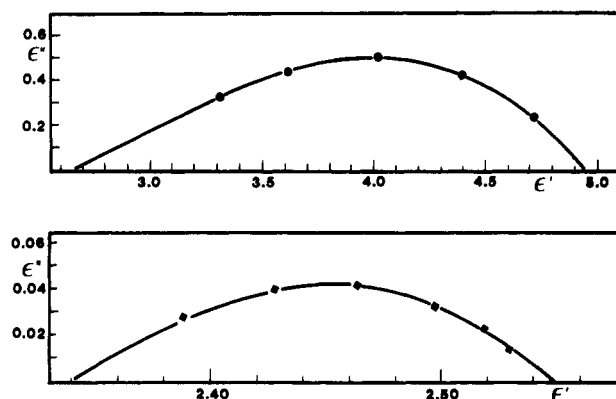

Figure 4. Cole–Cole plots for the dielectric glass–rubber (upper curve) and β (lower curve) relaxations of poly(cyclohexyl acrylate) (PCA) at +30 and –20 °C, respectively.

Table I
Havriliak–Negami Parameters for the α and β Relaxations

T, °C	ϵ_r	ϵ_u	τ_0, s	$\bar{\alpha}$	$\bar{\beta}$
			α Relaxation		
30	4.94	2.66	1.77	0.285	0.41
			β Relaxation		
–80	2.56	2.36	1.59×10^{-1}	0.53	0.86
–60	2.56	2.35	1.13×10^{-2}	0.52	0.835
–40	2.55	2.35	1.32×10^{-3}	0.49	0.78
–20	2.55	2.34	1.87×10^{-4}	0.45	0.69

the β absorption is an arc that is fitted by the familiar Cole–Cole equation[14]

$$\epsilon_\beta^* = \epsilon_{u\beta} + \frac{\epsilon_{r\beta} - \epsilon_{u\beta}}{1 + (i\omega\tau_0)^{\bar{\beta}}} \qquad (5)$$

where the assumption is usually made that the unrelaxed dielectric constant of the α absorption corresponds to the relaxed dielectric constant of the β relaxation. However, the β relaxation of PCA is a slightly skewed arc that fits
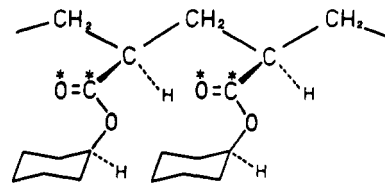

Figure 5. Schematic representation of a meso diad of poly(cyclohexyl acrylate) (PCA) in the all-trans conformation.

Table II
Summary of Dielectric Results and Values of the Intramolecular Correlation Factor, g_{intra}, for Poly(cyclohexyl acrylate)

T, °C	$2n_q\,dn/dw$	$d\epsilon/dw$	g_{intra}
30	0.20	2.13	0.752
40	0.15	1.98	0.756
50	0.09	1.90	0.786
60	0.04	1.81	0.813

the Havriliak–Negami expression (Figure 4). The values of $\bar{\alpha}$, $\bar{\beta}$, and τ_0 for the β relaxation at different temperatures are also given in Table I.

If the assumption is made that the magnitude of the dipole moment of the side group is similar to that of cyclohexyl isobutyrate (1.93 D)[9] and the values of $\epsilon_{r\alpha}$ and $\epsilon_{u\beta}$ given in Figure 4 are used in eq 2, g is found to be 0.64. The value of this quantity is slightly higher if $\epsilon_{u\beta}$ is assumed to be equal to the square of the refractive index of the polymer ($n = 1.5002$ at 30 °C); in this case $g = 0.68$.

Experimental Intramolecular Dipolar Correlations. The intramolecular correlation coefficient g_{intra} can be obtained from dielectric measurements in solution by using the Guggenheim and Smith method[15]

$$g_{intra} = \frac{27\kappa T M_0}{4\pi\rho\mu_0^2 N_A(\epsilon_1 + 2)^2}\left[\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right] \qquad (6)$$

where κ and N_A are, respectively, Boltzmann's constant and Avogadro's number, M_0 is the molecular weight of the repeat unit of the polymer, T is the absolute temperature, ρ and n_1 are the density and refractive index of the solvent, respectively. The parameters ϵ and n denote the dielectric constant and index of refraction of the solutions, respectively, whereas w represents the weight fraction of polymer in the solution. The derivatives $d\epsilon/dw$ and dn/dw at the temperatures of interest were obtained from the slopes of the plots ϵ and $n - n_1$ versus w in the limit $w \rightarrow 0$. Values of these quantities as a function of temperature are given in the second and third columns of Table II. In the fourth column of this table are also given the results for g_{intra}, where it can be seen that the value of this quantity slightly increases as the temperature increases. The uncertainty of these values was estimated to be ±5%. The temperature coefficient, expressed in terms of $10^{-3}\,d\ln g_{intra}/dT$, has a value of 2.13 K^{-1}.

Theoretical Calculations

Total Intramolecular Correlation Factor. In the theoretical evaluation of g_{intra}, the four rotational states scheme developed by Yarim-Agaev et al.[16] for the description of the conformational properties of oligomers of poly(methyl acrylate) (PMA) was used. Conformational calculations carried out on cyclohexyl isobutyrate,[9] using semiempirical potential functions, show that the rotational minima about O–C$_{ey}$ and C–C* bonds in Figure 5 are located at $\psi = \pm140°$ and $0, \pi$, respectively. Therefore, the scheme assumes that each bond is restricted to two rotational states t and g, but each of these states is split

into two: $\chi = 0$ and π corresponding to the conformations in which the carbonyl bond is cis and trans to the methine bond, respectively. The statistical weight matrices used with the states in the order $(t,\chi=0)$, $(t,\chi=\pi)$, $(g,\chi=0)$ and $(g,\chi=\pi)$ were[16,17]

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

for the CH_2–C^α–CH_2 bond pair, and

$$\mathbf{U}_r'' = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad \mathbf{U}_m'' = \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix} \qquad (8)$$

for racemic and meso configurations of the C^α–CH_2–C^α bond pair. The skeletal bond angles were assumed to be $112.5°$ in all cases. The 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 dipole moment μ_0 associated with the side group was assumed to have a value of 1.93 D, similar to that recently reported[9] for cyclohexyl isobutyrate, and it forms an angle of 123° with the C^α–C^*O^* bond.[18]

The intramolecular correlation factor for PCA chains was evaluated following the procedures described by Flory and co-workers.[19,20] According to these methods, g_{intra} is given by

$$g_{\text{intra}} = Z^{-1}\mathbf{P}_1 \prod_{k=2}^{x-1} (\mathbf{S}'\mathbf{P}_k)\mathbf{P}_x / x\mu_0^2 \qquad (9)$$

where Z is the rotational partition function and $\mathbf{P}_k$ can be written as

$$\mathbf{P}_k =$$

$$\begin{pmatrix} \mathbf{G}_k'(t,\chi=\pi) & & & \\ & \mathbf{G}_k'(t,\chi=\pi) & & \\ & & \mathbf{G}_k'(g,\chi=0) & \\ & & & \mathbf{G}_k'(g,\chi=\pi) \end{pmatrix} \times$$

$$(\mathbf{U}_k'' \otimes \mathbf{E}_5) \times$$

$$\begin{pmatrix} \mathbf{G}_k''(t,\chi=0) & & & \\ & \mathbf{G}_k''(t,\chi=\pi) & & \\ & & \mathbf{G}_k''(g,\chi=0) & \\ & & & \mathbf{G}_k''(g,\chi=\pi) \end{pmatrix} \qquad (10)$$

$\mathbf{P}_1$ and $\mathbf{P}_x$ are respectively row and column vectors to convert eq 9 in a scalar; specifically, $\mathbf{P}_1 = \text{row} (G_{11},0,0...0)$ and $\mathbf{P}_x = \text{column} (G_x(\chi=0), G_x(\chi=\pi), G_x(\chi=0), G_x(\chi=\pi))$, where G_{11} and G_x represent the first row and last column of the generator matrix $\mathbf{G}$.

On the other hand, $\mathbf{S}' = \mathbf{U}' \otimes \mathbf{E}_5$, where the symbol $\otimes$ denotes the direct product and $\mathbf{E}_5$ is the identity matrix of order 5. The elements of the diagonal of $\mathbf{P}_k$ are the familiar generator matrices $\mathbf{G}$ that are given by[21]

$$\mathbf{G}_k = \begin{pmatrix} 1 & 2\mu^T\mathbf{T} & \mu^2 \\ 0 & \mathbf{T} & \mu \\ 0 & 0 & 1 \end{pmatrix}_k \qquad (11)$$

In this equation μ is the contribution of the bond to the polarity of the chains, $\mathbf{T}$ is the transformation matrix that
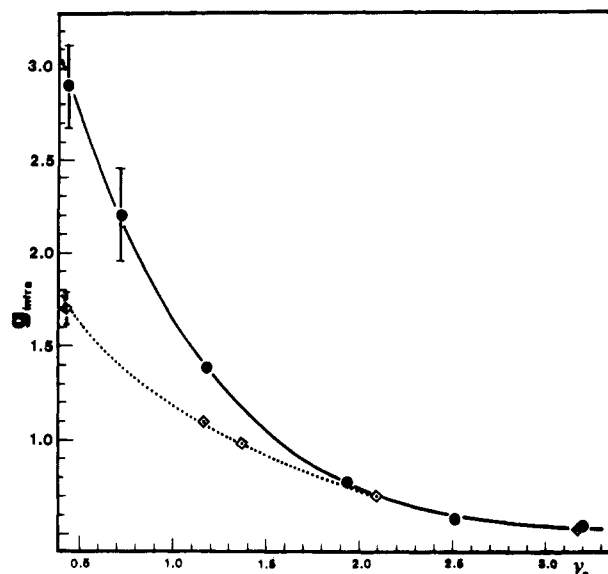

Figure 6. Dependence of the correlation coefficient g_{intra} on the statistical weight parameter γ_2. Continuous and dotted curves correspond to probabilities of isotactic replacements of 0.40 and 0.25, respectively.

by premultiplication converts the representation of a dipole moment in reference frame $k + 1$ to its representation in the reference frame k. The components of the dipole moment in the reference frame C^α–CH_2 are $\mu_x = 1.141$, $\mu_y = -1.555$, and $\mu_z = -0.027$ D for $\chi = 0$ and $\mu_x = -0.320$, $\mu_y = 0.513$, and $\mu_z = 1.844$ D for $\chi = \pi$. For CH_2–C^α bonds the components of μ are nil.

Ten representative chains of 100 repeat units each, in which the probability of isotactic replacement was assumed to be 0.40, were generated by Monte Carlo techniques, and the respective values at 30° of g_{intra} were calculated by using the set of statistical weights $\rho = 1.1$, $\beta = 1.8$, $\gamma_1 = 1.3$, $\gamma = 4$, and $\gamma_2 = 2.5$ that describe the conformation-dependent properties of poly(phenyl acrylate) (PPA).[17] The calculations indicated in Figure 6 show that g_{intra} drops from 1.71 ± 0.05 to 0.528 ± 0.005 when the value of γ_2 increases from 0.44 to 3.20. In this interval of values of γ_2 the temperature coefficient 10^3 d ln $g_{\text{intra}}/\mathrm{d}T$ increases from -0.59 ± 0.02 to 2.52 ± 0.2. An inspection of the figure suggests that the experimental values can be reproduced for $\gamma_2 = 1.91$. In this case g_{intra} and 10^3 d ln $g_{\text{intra}}/\mathrm{d}T$ amount to 0.748 and 2.3 ± 0.3 in good concordance with the respective experimental values, 0.752 and 2.1, respectively. The influence of the stereochemical composition on the polarity of PCA chains is also indicated in Figure 6 where g_{intra} is plotted versus γ_2 for chains in which the probability of isotactic replacement is 0.25. It can be seen that the intramolecular correlation coefficient is only sensitive to the stereochemical composition for low values of the statistical weight that governs the fraction of consecutive dipoles with the same orientation in a racemic diad.

Intramolecular Correlation Factor in the Subglass Relaxation. Whereas the determination of g_{intra} by eq 9 implies averaging over conformational space that includes reorientation of the entire chains over all spatial directions together with internal reorientations, the subglass relaxation of molecular chains with polar flexible side groups presumably involves motions of the side groups with respect to the frozen main chain coupled with cooperative local motions of the skeletal bonds of the main chain. By considering that the dielectric secondary relaxation of asymmetric polymers is only produced by motions of the

side groups, Smith and Boyd[8] have devised a model that predicts that the internal correlation factor for the β absorption is given by

$$g_\beta = (N/N_p\mu_0^2)[\langle \mathbf{m}_i(\zeta)^2\rangle - \langle \mathbf{m}_i(\zeta)\rangle\cdot\langle \mathbf{m}_i(\zeta)\rangle] \quad (12)$$

where N is the number of molecular chains per unit of volume, N_p is the number of relaxing species, $\mathbf{m}_i(\zeta)$ is the dipole moment of the chain i associated with the conformation ζ, and μ_0 is the modulus of the dipole moment of the side group. Since $\mathbf{m}_i(\zeta) = \Sigma_k\mu_k$, eq 12 can be written as[8]

$$g_\beta = (N/N_p\mu_0^2)(\sum_k \mu_k^2 - \sum_k \langle \mu_k\rangle^2 + \sum_k\sum_{j\neq k} \langle \mu_k\cdot\mu_j\rangle - \sum_k\sum_{j\neq k} \langle \mu_k\rangle\cdot\langle \mu_j\rangle) \quad (13)$$

As indicated before, each side group has accessibility to two rotational states located at $\chi = 0$ and π corresponding respectively to the conformations in which the carbonyl group is cis and trans with respect to the methine bond. At low temperatures the dipoles tend to be located in the lowest energy rotational states, and, consequently, the dipole–dipole correlation term $\langle \mu_j\cdot\mu_k\rangle - \langle \mu_j\rangle\cdot\langle \mu_k\rangle$ becomes relatively small.[8] Therefore, eq 13 can be expressed in an approximate way as

$$g_\beta \approx (N/N_p\mu_0^2)(\sum_k \mu_k^2 - \sum_k \langle \mu_k\rangle^2) = (N/N_p\mu_0^2)[\sum_k \mu_k^2 - \sum_k(p_k(1)^2 + p_k(2)^2)\mu_k^2 + 2p_k(1)\ p_k(2)\ \mu_k(1)\cdot\mu_k(2)] \quad (14)$$

where $p_k(1)$ and $p_k(2) = 1 - p_k(1)$ represent the probability of finding the dipoles associated with the rotational states $\chi = 0$ and π, respectively. Conformational calculations predict that the rotational state $\chi = \pi$ has an energy nearly 0.6 kcal mol⁻¹ below that of the alternative conformational state,[9] so that the values of $p_k(1)$ and $p_k(2)$ would be 0.27 and 0.73, respectively. With these values eq 14 gives g_β = 0.520, a result significantly larger than the experimental one (0.114), calculated by eq 2 by considering that $\epsilon_{r\beta} = \epsilon_{u\alpha}$ and $\epsilon_{u\beta} = n^2$. Better agreement between the predictions of the model and experiment could be obtained by increasing the value of $p_k(2)$. Thus, by assuming $p_k(2)$ = 0.95, one obtains g_β = 0.126, a value close to the experimental result (0.113 at 20 °C).

With the aim of analyzing the effects of the cross-correlation factors of eq 13 on the value of g_β, 100 representative chains of the whole system were generated by using Monte Carlo methods. From each of these chains, 100 new chains in which different distributions of rotational states about the C^α–C^*O^* bonds exist were generated. By assuming that $p_k(2)$ = 0.73, one obtains $g \approx$ 0.72, indicating that the sampling is good. For each of the new chains m^2 and $\mathbf{m}$ were obtained respectively by means of eq 11 and the generator matrix

$$\mathbf{A}_k = \begin{pmatrix} \mathbf{T} & \mu \\ 0 & 1 \end{pmatrix}_k \quad (15)$$

For these new 100 chains the values of $\langle m^2\rangle$ and $\langle \mathbf{m}\rangle^2$ were determined. The same procedure was repeated with each of the primitive chains, and the values of $\langle m^2\rangle$ and $\langle \mathbf{m}\rangle^2$ were averaged over all of the primitive chains. If $p_k(2)$ = 0.73, the result obtained for g_β from eq 12 is 0.484 (0.520 from eq 14), a value that is far from the experimental result. For $p_k(2)$ = 0.95, the values of g_β obtained by eqs 12 and 14 are respectively 0.124 and 126. Therefore, these calculations confirm the previous assumption that $\langle \mu_j\cdot\mu_k\rangle \approx \langle \mu_j\rangle\cdot\langle \mu_k\rangle$ for chains in which $p_k(2)$ is large.
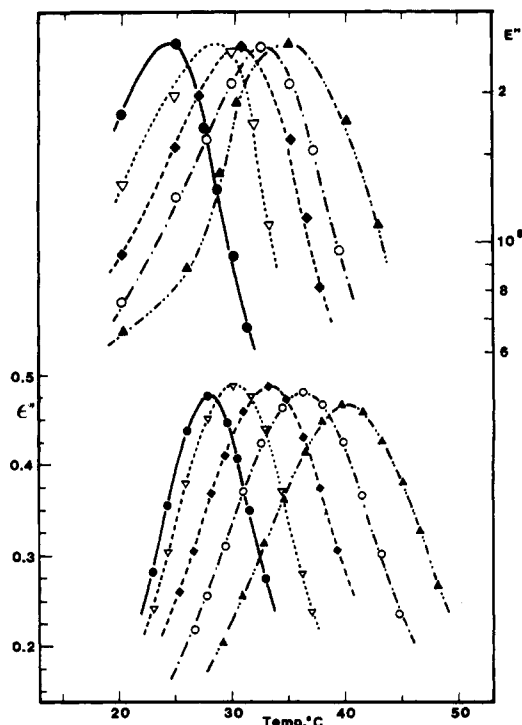

Figure 7. Details of the mechanical (upper curves) and dielectric (lower curves) glass–rubber relaxations for poly(cyclohexyl acrylate) (PCA) at (●) 0.1, (▼) 0.3, (◆) 1, (○) 3, and (▲) 10 Hz.

According to this model, the dielectric β relaxation of PCA could be produced by conformational changes taking place in less than 5% of the side groups occupying the lowest energy states. Finally, it should be pointed out that the treatment described above is formally equivalent to the model of partial relaxation of dipoles for the β process described by Williams[2] except now the conformations are specified.

Glass–Rubber Relaxation. At each frequency the maximum of the dielectric α relaxation is nearly 3 °C above that of the corresponding mechanical absorption. This can be seen in Figure 7 where both relaxations are represented in detail for frequencies lying in the range 0.1–10 Hz. For amorphous polymers the glass–rubber relaxation is governed by the free volume so that the relaxation time τ^* can be expressed by the Doolittle[22] equation

$$\tau^* = A \exp(B/\Phi) \quad (16)$$

where Φ is the relative free volume and B is a parameter close to unity. The assumption that the free volume is a linear function of temperature leads eq 16 to the expression proposed earlier by Vogel[23]

$$\ln \tau^* = A' + m/(T - T_\infty) \quad (17)$$

where T_∞ is a parameter nearly 50 °C below the glass transition temperature, B is a parameter close to unity related with the critical volume v^* necessary for a relaxation process to take place, and m is the ratio of B to the expansion coefficient α. The relaxation times interpreted in terms of eq 16 give straight lines for T_∞ = –25 °C (see Figure 8). The slopes of these lines obtained by least-squares analysis have values of 1270 K (ρ = –0.9999) and 1300 K (ρ = –0.9891) for the dielectric and mechanical relaxations, respectively. Therefore, both the dielectric and mechanical relaxation times show the same temperature dependence. Similar analysis carried out earlier[9] on the dielectric α relaxation of CI and CG gives for m the values of 2750 and 2140 K, respectively; in other
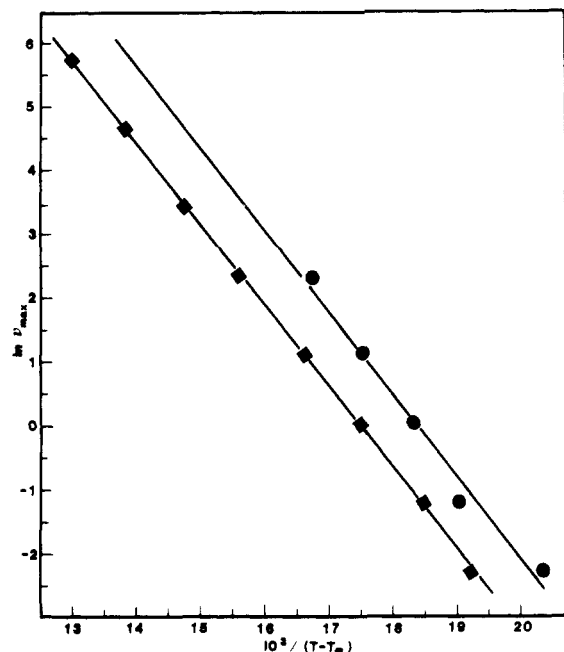
Figure 8. Temperature dependence of the maximum of the frequency for the glass–rubber relaxation of poly(cyclohexyl acrylate) (PCA).

Figure 9. Master curves for the α relaxation of cyclohexyl isobutyrate (CI)[9] (- - -), cyclohexyl-2,4-dimethyl glutarate) (CG)[9] (—), and poly(cyclohexyl acrylate) (PCA) (···). The experimental results are fit by curves calculated by the KWW equation.

words, the α process of these low molecular weight compounds shows a stronger temperature dependence than that of the polymer.

The ratio of the relative free volume to B, at T_g, can be obtained by the relationship

$$\Phi_g/B = (T_g - T_\infty)/m \qquad (18)$$

From the analysis of either the mechanical or the dielectric data Φ_g/B is found to be 0.038, a result that is significantly larger than the standard value of 0.025 ± 0.005 obtained for most systems,[24] presumably as a consequence of the fact that the parameter v^* for PCA may be much lower than those for many other polymers.

The linear phenomenological theory of dielectrics relates the complex permittivity to the normalized decay function $\phi(t)$ of the α process by the familiar expression[25]

$$\frac{\epsilon_\alpha^* - \epsilon_{u\alpha}}{\epsilon_{r\alpha} - \epsilon_{u\alpha}} = \int_0^\infty \left[-\frac{d\phi(t)}{dt} \right] e^{-i\omega t} \qquad (19)$$

where $\phi(t)$ is commonly given by the Kohlrausch–Williams–Watts (KWW) equation[26,27]

$$\phi(t) = \exp(-t/\tau)^{\bar\gamma} \qquad (20)$$

The master curve for the dielectric loss of the α process of PCA chains, shown in Figure 9, was obtained by horizontal shifting of the normalized isotherms obtained in the vicinity of the glass transition temperature. This curve fits to the KWW equation for $\bar\gamma = 0.42 \pm 0.02$. In the same figure and for comparative purposes the normalized master curves for CG and CI are also shown. As expected the complexity of the α process seems to be higher for the polymer than for the low molecular weight compounds CI and CG.

Discussion

In general, polymers with flexible side groups exhibit a strong subglass mechanical relaxation that was attributed by Heijboer[12] to flip–flop motions of the cyclohexyl ring. The fact that a decrease of nearly half a decade occurs in the storage relaxation modulus of PCA chains suggests a
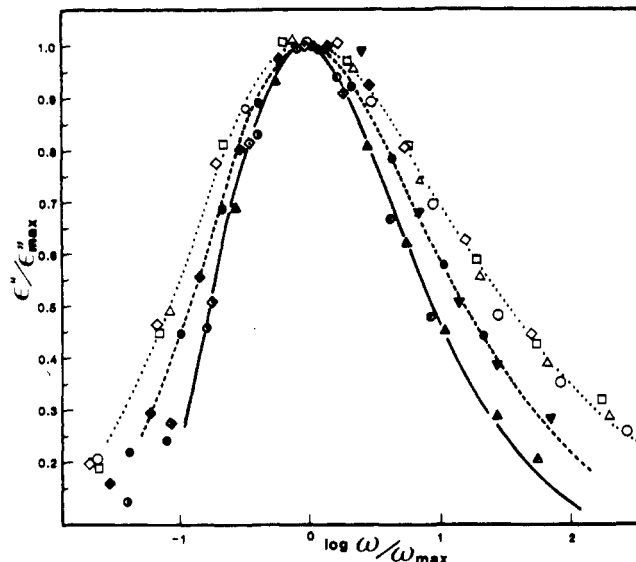
significant mechanical activity in the β process of this polymer. A prominent β absorption also appears in the dielectric spectrum of PCA whose maximum, at each frequency, is located very close to the temperature associated with the maximum of the mechanical peak. Moreover, both relaxations are activated processes with activation energies of similar value. Therefore, these facts suggest that similar molecular motions should produce both the mechanical and dielectric secondary relaxations of PCA chains.

Dielectric activity in PCA could be produced by conformational changes of the side groups without intervening local motions of the skeletal bonds of the main chain. As was discussed before, the model devised by Smith and Boyd[8] based on motions of the side groups apparently gives a good account of the dielectric relaxation strength of the β process. However, since mechanical activity in the subglass region could also involve cooperative local motions[28] of the main chain, it is unlikely that motions of the flexible side groups alone will produce the mechanical β relaxation. It is more likely that motions of the side groups control the local motions of the main chain and therefore both the mechanical and dielectric β relaxations would arise from coupling of these two kinds of motion.

Dielectric measurements carried out on solutions and extrapolated to zero concentration give values for the correlation factor g_{intra} that can be reproduced by a rotational isomeric states scheme that considers that each of these states is associated with two rotational states of the C–C*O* bonds of the side group. The term g that involves inter- and intramolecular correlation factors has a value similar to that of g_{intra}, suggesting therefore that the total dielectric relaxation strength $\epsilon_{r\alpha} - \epsilon_{u\beta}$ of PCA in the bulk can be accounted for by considering only intramolecular interactions between the relaxing dipoles. However, it should be considered that strong intermolecular interactions have been detected in acrylic polymers with chlorophenyl side groups,[29] presumably as a consequence of the high critical volume necessary for a relaxation process to take place in these polymers.

The total dielectric relaxation process of PCA chains in the bulk can be interpreted exclusively in terms of intramolecular interactions, though it is not possible to discriminate the molecular motions that produce the

secondary relaxation. This, however, is not the case for CI and CG, the low molecular analogues of PCA. Thus the curves of Figure 9 suggest that the α relaxation of CI is more complex than that of CG in spite of the larger internal degrees of freedom of the latter compound. Moreover, the intensity of the secondary relaxation of CI is similar to that of PCA whereas CG presents in comparison a weak relaxation (see Figure 2). The anomalous secondary relaxations exhibited by CG cannot be explained by simple intramolecular interactions. In this case the possibility that intermolecular interactions contribute to the subglass absorption cannot be ruled out. In this context, it has been emphasized that only specific intramolecular mechanisms are not required for the development of subglass absorptions.[2-4] In fact intermolecular interactions can also provide the energy barriers for the β relaxations. Unfortunately, it does not seem feasible to resolve by any available experimental method the relative contributions of the intra- and intermolecular interactions to the secondary relaxations.

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