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Relaxation Properties of Molecular Chains with Restricted Conformational Versatility of the Backbone

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ABSTRACT: This work deals with the study of the dielectric and mechanical behavior of polymers in which the conformational versatility of the backbone is severely restricted. The mechanical spectrum of the model, poly(dicyclohexylmethylene itaconate) (PDCMI), presents two absorptions in the glassy state that in increasing temperature order are called γ and β relaxations. Contrary to what occurs in most amorphous systems, the polymer only presents a weak glass–rubber relaxation, named α. By using deconvolution techniques to separate the peaks associated with the different absorptions, one finds that the strength of the β peak is nearly 6 and 3 times larger than the strength of the α and γ relaxations, respectively. The dielectric spectrum also presents two well-developed absorptions in the glassy state, one called γ, in the lower temperature side of the spectrum, that is much weaker than the β, located close to the glass–rubber relaxation; in addition, a shoulder at low frequencies in the spectrum is detected that presumably corresponds to a peak (β') that overlaps with the β process. Although conductivity processes overlapping with the dipolar contribution to the α absorption preclude the possibility of determining the strength of this latter relaxation, the analysis of the electric loss spectra permits us to conclude that both the dipolar α and β relaxations roughly have the same intensity. The values of the relaxation strength for the β and γ relaxations at 100 Hz are 0.88 and 0.07, respectively. The fact that both the mechanical and dielectric β relaxations are located in the same region of the spectrum, and also have the same activation energy ($\approx$42 kcal mol^{-1}), indicates that both relaxations are caused by the same molecular mechanisms. Thermally stimulated discharge current (TSDC) spectra exhibit a well-developed glass–rubber relaxation whose peak is centered at 50 °C, followed by two subglass relaxations, β and γ. The activation enthalpy for the peaks obtained by partial depolarization techniques in the β region is nearly half of that corresponding to the same zone of the spectrum obtained in a variable electric field. The analysis of the dipole moments of the chains suggests that as far as their polarity is concerned they behave as freely jointed chains. The dipolar correlation coefficient for the subglass region is calculated by assuming that the dielectric activity is only produced by reorientations of the side groups with respect to the frozen main chain. The fact that the value of the coefficient thus obtained is somewhat larger than the experimental one suggests that dipolar intermolecular interactions cannot be neglected in the dielectric behavior of these chains.

Introduction

The technological performance of polymeric materials is deeply connected to the motions of the chains which, in turn, are related to their structure. At the present time, however, the molecular mechanisms that produce rapid relaxation processes as manifested in dielectric relaxations, nuclear magnetic resonance, dynamic light scattering, etc., are poorly understood.[1-3] It is believed that conformational transitions from one conformational state to another, involving cooperativity of transitions of second neighbor bonds, would not produce excessive displacement of the molecular tails as required by the insensitivity to chain length shown by local relaxations. Computer simulations suggest that two pair transitions[4]

$$...g^{\pm}tt... \rightleftarrows ...ttg^{\pm}... \tag{1}$$

$$...ttt... \rightleftarrows ...g^{\pm}tg^{\mp}... \tag{2}$$

may account for most of the cooperativity involved in the relaxation behavior of symmetric simple systems. Therefore, transitions of this kind occurring in chains such as polyethylene, poly(ethylene oxide), etc., may be responsible for the dielectric and mechanical subglass absorptions detected in these polymers. However, conformational transitions taking place in flexible side groups seem to determine the secondary relaxations observed in asymmetric polymers. On the basis of this assumption, Boyd and co-workers[1] have developed a model that gives a good account of the dielectric strength of the subglass absorptions exhibited by poly(vinyl acetate) and poly(methyl acrylate). On the other hand, it is a widely admitted fact that the glass–rubber relaxation is produced by micro-Brownian generalized motions of the chains so that much more energy is dissipated in this process than in secondary absorptions.[5] For polymers in which conformational transitions in the main chain are severely restricted, the question related to the relative intensity of the secondary and glassy absorptions arises. It should be pointed out in this regard that both the loss modulus and the dielectric loss vs temperature plots reported for some itaconate polymers do not show a clear peak associated with the glass–rubber transition.[6-9]

The goal of this paper is 2-fold: On the one hand, the relaxation behavior of amorphous rigid polymers is studied by using as the model poly(dicyclohexylmethylene itaconate) (PDCMI). Sketches of the structure of this polymer are given in Figures 1 and 2. On the other hand, the mechanical and relaxation behaviors of the polymer in a wide interval of temperatures are reported, giving special emphasis to the analysis of the strengths of the

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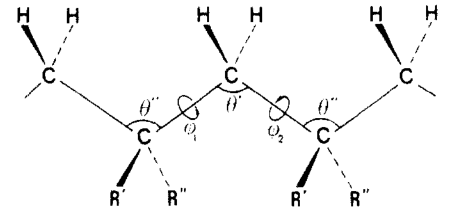

Figure 1. Isotactic diad of poly(dicyclohexylmethylene itaconate) in the *all-trans* conformation that was taken as the origin for the backbone rotational angles ($\phi_1 = \phi_2 = 0$). R′ and R″ represent the two ester side gorups, namely, $R' = -COOCH_2C_6H_{11}$ and $R'' = -CH_2COOCH_2C_6H_{11}$.

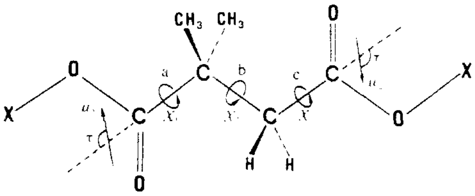

Figure 2. Structure of a diester of 2,2-dimethylsuccinic acid, used as the model compound for the repeating unit of poly(dicyclohexylmethylene itaconate), shown in the *all-trans* conformation that was used as the origin for the rotational angles χ_1, χ_2, and χ_3. X represents the alcoholic residue, i.e., $x = -CH_2C_6H_{11}$. The dipole moment of each ester group is indicated by an arrow pointing from negative to positive center of charges.

different absorptions appearing in the mechanical and dielectric spectra. Moreover, the conformational characteristics of the polymer are also investigated by critically analyzing the dipole moments of the chains.

Experimental Part

Monomer and Polymer Synthesis. Dicyclohexylmethylene itaconate (DCMI) was obtained by esterification of cyclohexylmethanol with itaconic acid using acetyl chloride as catalyst.[10,11] The monomer was purified at room temperature by crystallization from benzene. PDCMI was prepared by radical polymerization of the monomer at 67 °C for 24 h, using α,α′-azobis(isobutyronitrile) (AIBN: 0.3 mol %) as catalyst; the conversion amounted to 75%. Purification of the polymer was achieved by repeated dissolution in tetrahydrofuran and reprecipitation with diethyl ether and further drying in vacuum at 40 °C. ^{13}C NMR measurements[10,11] carried out on other itaconate polymers obtained by radical polymerization suggest that the isotactic content of these samples should be about 50%.

Dynamic Mechanical Measurements. Dynamic measurements were carried out on strips of PDCMI with a PL-DMTA apparatus in the temperature interval −100 to +70 °C and frequency range 0.1–10 Hz. The experiments were performed from low to high temperature at a heating rate of 1 °C/min.

Dielectric Experiments. Values of the dielectric constant ϵ of solutions of PDCMI in benzene were obtained at 10 kHz with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cylindrical cell. Increments of the indices of refraction of the solutions with respect to that of the solvent were measured at 632.8 nm with a differential refractometer (Chromatix Inc.). Values of the real ϵ' and loss ϵ'' components of the complex dielectric permittivity ϵ^* in the bulk were measured as a function of temperature with a plane condenser and a capacitance bridge TA DEA 2970 operating in the frequency range 0.001–30 kHz. The experiments proceeded from low (∼−120 °C) to high (∼60 °C) temperature at a heating rate of 1 °C/min.

Thermally Stimulated Discharge Currents (TSDC). TSDC experiments were carried out with a TSDC-RMA spectrometer (Solomat) on pills of PDCMI of thickness 1 mm and surface 64 mm², using spring electrodes. The spectrum covering the interval of temperature −140 to +60 °C was obtained by poling the sample at 80 °C under a potential of 500 V/mm, quenching it at −140 °C, and then recording the discharge current by warming the sample at a heating rate of 7 °C/min. Partial polarization discharge curves were also recorded by using poling windows of 10 °C; in all the cases the cooling temperature was 30 °C below the polarization temperature T_p, whereas the final temperature was 30 °C above T_p.

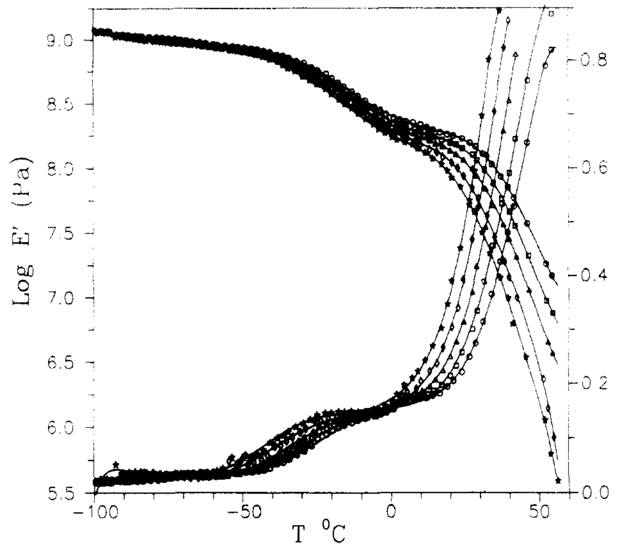

Figure 3. Dependence of both the storage relaxation modulus E' and tan δ on temperture for PDCMI at several frequencies: (☆) 0.1, (◇) 0.3, (△) 1, (□) 3, and (○) 10 Hz.

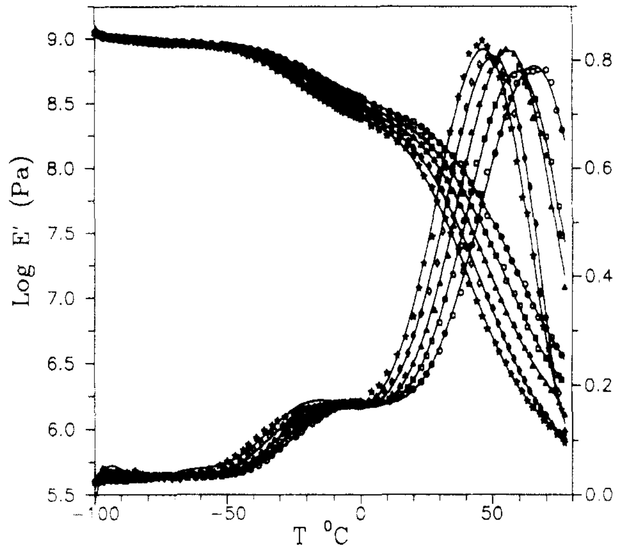

Figure 4. Variation of E' and tan δ with temperature for a PDCMI sample with a 0.07 weight fraction of tetrahydrofuran at several frequencies. (See Figure 3 for the values of the frequencies attached to the symbols indicated.)

Results

(A) Mechanical Relaxation Spectra. Values of both the storage relaxation modulus E' and the loss tan δ for PDCMI are plotted as a function of temperature in Figure 3. The modulus E' falls nearly 1 decade in the glassy region as a result of strong mechanical activity in this region, and then it decreases sharply in the glass–rubber transition. An inspection of the curve corresponding to tan δ suggests the presence of two absorptions in the subglass region, the strongest one overlapping with the glass–rubber relaxation. The loss steeply increases with temperature in the glass–rubber region, and the maximum of the absorption is not detected at the frequencies investigated. However, the maximum of the loss can be detected if a small amount of tetrahydrofuran (THF) is incorporated into the sample, as can be seen in Figure 4 where tan δ vs temperature is recorded for a sample containing a 0.07 weight fraction of THF.

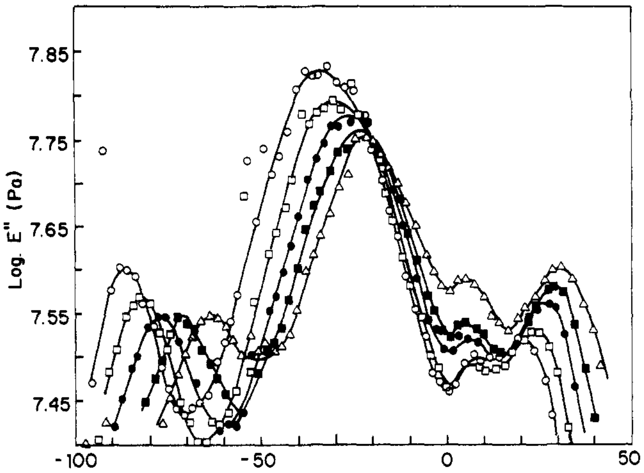

Figure 5. Mechanical relaxation spectrum for PDCMI expressed in terms of the loss modulus E'' vs temperature at several frequencies: (○) 0.1, (□) 0.3, (●) 1, (■) 3, and (△) 10 Hz.

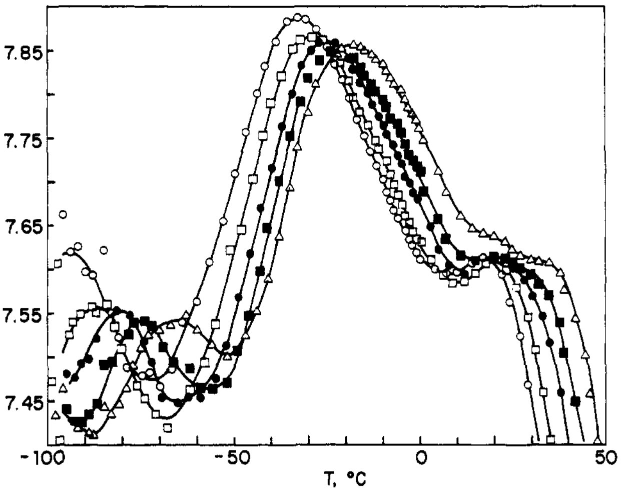

Figure 6. Mechanical relaxation spectrum expressed in terms of the loss modulus E'' vs temperature at several frequencies for a sample of PDCMI with a 0.07 content of THF. (See Figure 5 for the values of the frequencies attached to the symbols indicated.)

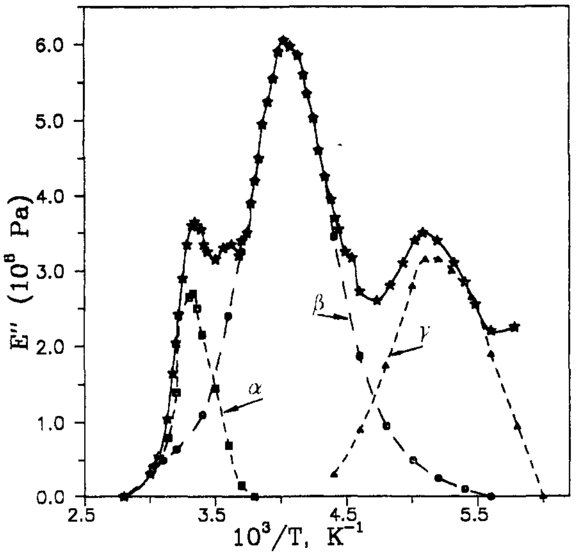

Figure 7. Deconvolution of the mechanical relaxation spectrum of PDCMI at 1 Hz.

The relaxation spectrum expressed in terms of the loss relaxation modulus is shown in Figure 5, where the relaxations corresponding to the subglass absorptions indicated above are clearly visible. Thus the relaxation that appears in the low-temperature zone of the spectrum, named γ, is centered at -78 °C at 1 Hz, whereas the maximum of the stronger relaxation, called β, is located at -27 °C at the same frequency. Contrary to what occurs for most amorphous polymers,[5] a clear peak associated with the glass–rubber relaxation is not detected. A weak peak corresponding to this absorption, named α, is centered at 28 °C at 1 Hz; the peaks appearing in the vicinity of the α relaxation are believed to be artifacts introduced during the measurements and therefore are not connected with molecular motions. In fact these peaks are attenuated in the curves corresponding to the samples containing THF (see Figure 6).

An important feature of poly(itaconates)[6] is that the mechanical β relaxation is the most prominent of all the relaxations appearing in the spectrum, and therefore it would be interesting to compare the relative strength of the different absorptions. The evaluation of the strength of the β relaxation was carried out by fitting the loss curve to the Fuoss–Kirkwood empirical expression[12]

$$E'' = E''_{\max} \operatorname{sech}\left[m \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\max}}\right)\right] \qquad (3)$$

where E_a is the activation energy that for the β process amounts to 42 kcal mol^{-1}, $E''_{\max}$ is the value of the loss modulus at the peak maximum, and m is an empirical parameter related to the width of the peak in such a way the wider the relaxation is, the lower m is; for a peak of the Debye type, $m = 1$. It should be pointed out that the activation energies associated with the α and γ processes were estimated to be 75 and 14 kcal mol^{-1}, respectively. By plotting $\cosh^{-1}(E''_{\max}/E'')$ vs $1/T$, one finds that m has a value of 0.162 at 1 Hz, so that the strength of the relaxation at this frequency can straightforwardly be obtained from the expression

$$\Delta E_\beta = 2(E_{\max}/m) \qquad (4)$$

By using this approach, $\Delta E_\beta = E_{\mu\beta} - E_{r\beta} = 7.40 \times 10^8$ Pa, where the subindices r and u refer to the relaxed and unrelaxed modulus in the β absorption. Computation of the strength of the relaxations also was carried out by considering that this quantity can be written as

$$\Delta E_i = \int_{T_1}^{T_2} \left(\frac{\partial E'}{\partial T}\right)_\omega \mathrm{d}T \qquad (5)$$

Here the subindex i refers to the α, β, and γ relaxations. By taking into account that

$$\left(\frac{\partial E'}{\partial T}\right)_\omega = -\left(\frac{\partial E'}{\partial \ln \omega}\right)_T \left(\frac{\partial \ln \omega}{\partial T}\right)_{E'} \simeq \frac{2}{\pi} E'' \frac{E_a}{RT^2} \qquad (6)$$

eq 5 becomes

$$\Delta E_i \simeq \frac{2E_a}{\pi R} \int_{T_1^{-1}}^{T_2^{-1}} E'' \, \mathrm{d}\left(\frac{1}{T}\right) \qquad (7)$$

The relaxation loss modulus plotted as a function of the reciprocal of the absolute temperature is shown in Figure 7. The evaluation of ΔE_i by means of eq 7 was performed by deconvoluting the overlapping curves corresponding to the different absorptions, as indicated in this figure, and the results obtained were $\Delta E_\gamma = 2.3 \times 10^8$ Pa, $\Delta E_\beta = 7.5 \times 10^8$ Pa, and $\Delta E_\alpha = 1.3 \times 10^8$ Pa. Accordingly, the intensity of the β relaxation is nearly 3 and 6 times larger than the intensities of the γ and α relaxations, respectively.

(B) Dielectric Relaxations. In Figure 8 the dependence of the dielectric loss ϵ'' on temperature at several frequencies is shown. The spectrum exhibits an ostensible

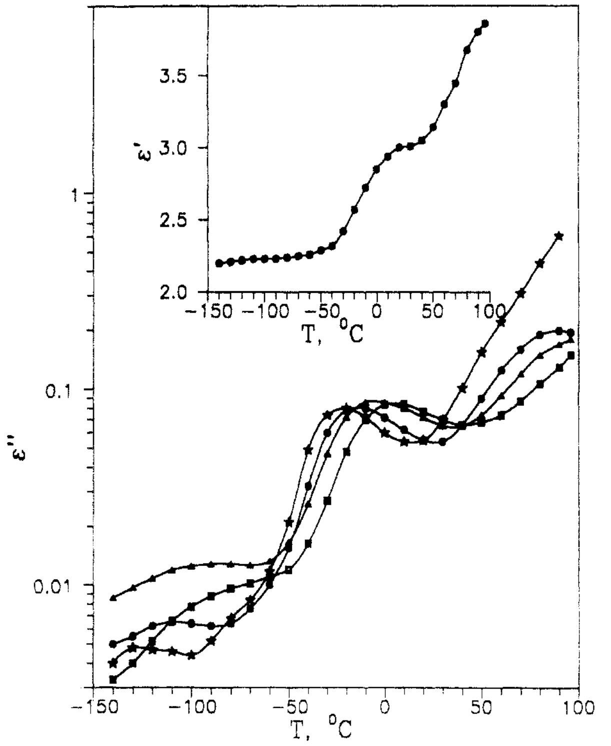

Figure 8. Temperature dependence of the dielectric loss on temperature for PDCMI at several frequencies: (☆) 0.01, (●) 0.1, (▲) 1, and (■) 10 kHz. In the inset is a plot of ϵ' vs temperature at 100 Hz.

subglass β absorption whose maximum, at 100 Hz, is located at −12 °C followed in decreasing temperature order by a comparatively weak absorption, named γ, centered at −110 °C. In addition, a shoulder in the vicinity of −80 °C (β' peak), is devised in the spectrum. The prominent β relaxation is also reflected in the dependence of the real component ϵ' of the complex dielectric permittivity on temperature. Thus, as can be seen in Figure 8, the plot ϵ' vs temperature exhibits a prominent plateau associated with the β absorption. The activation energies of the β and γ relaxations amount to 42 ± 1 and 6.0 ± 0.5 kcal mol^{-1}, respectively.

At low frequencies, conductivity processes associated with the glass–rubber relaxation give rise to a steep increase in the dielectric loss that precludes the possibility of detecting the dipolar relaxation in this zone of the spectrum. As a consequence, the dielectric results were analyzed in terms of the complex electric modulus, M^* $(=(\epsilon^*)^{-1})$. Values at 0.3 Hz of the real M' and loss M'' components of M^* are shown vs temperature in Figure 9. As expected, M' undergoes a significant decrease with temperature in the glassy region followed by a sharp decrease of this quantity in the glass–rubber zone; the loss presents a β peak, centered at −38 °C, followed by two overlapping peaks corresponding, in increasing temperature order, to dipolar and conductive processes associated with the glass–rubber relaxation.

By considering that the activation energies of the β and γ relaxations amount to 42 and 6 kcal mol^{-1}, respectively, fitting these peaks to the empirical Fuoss–Kirkwood equation can be achieved by using for the semiwidth of these relaxation values of m equal to 0.184 and 0.245, respectively. On the other hand, by plotting the dielectric loss against the reciprocal of temperature (see Figure 10) and using the procedures described before the mechanical loss modulus, the dielectric strengths at 100 Hz of the β and γ relaxations are found to be 0.88 and 0.07, respectively.

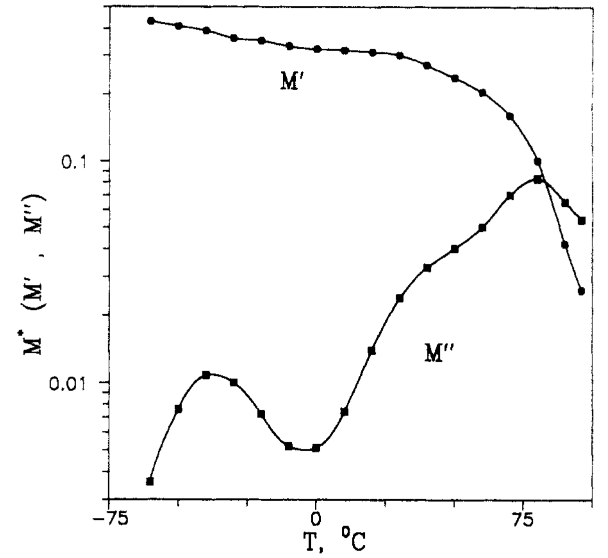

Figure 9. Variation of the components of the complex dielectric modulus on temperature for PDCMI at 0.3 Hz.

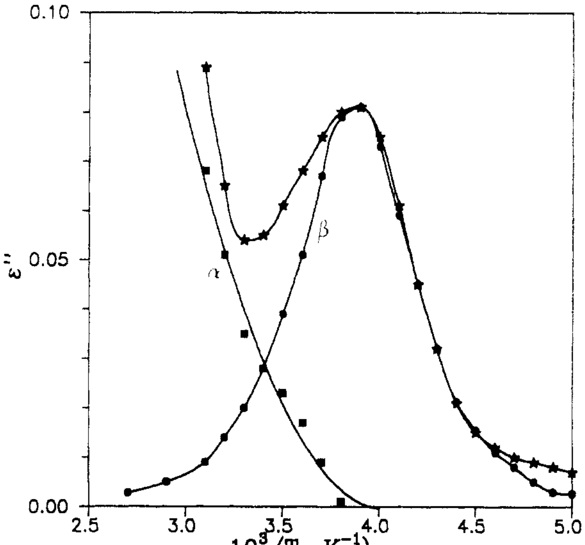

Figure 10. Deconvolution of the β dielectric relaxation for PDCMI at 100 Hz.

(C) Depolarization Discharge Currents. Values of the thermally stimulated discharge current for PDCMI are represented as a function of temperature in Figure 11. The relaxation spectrum presents a broad and weak γ relaxation, centered at −110 °C, followed by a comparatively strong β relaxation whose maximum is located at −30 °C. Contrary to what occurs in the mechanical and dielectric experiments under an alternating electric field, a well-developed glass–rubber relaxation centered at 50 °C appears in the TSDC experiments.

In order to determine the distribution of activation energies associated with the secondary TSDC processes, elementary peaks in the subglass region were obtained by partial depolarization of poled samples whose poling temperatures are given in Table I. The peaks obtained, shown in Figure 12, were assumed to be described by a single relaxation time τ whose temperature dependence was evaluated by means of the expression[13]

$$\tau(T) = \frac{\int_{T_{il}}^{T} I(T)\,\frac{dt}{dT}\,dT}{I(T)} \qquad (8)$$

where $I(T)$ is the discharge current intensity, dt/dT is the reciprocal of the heating rate, and T_{il} is the extreme

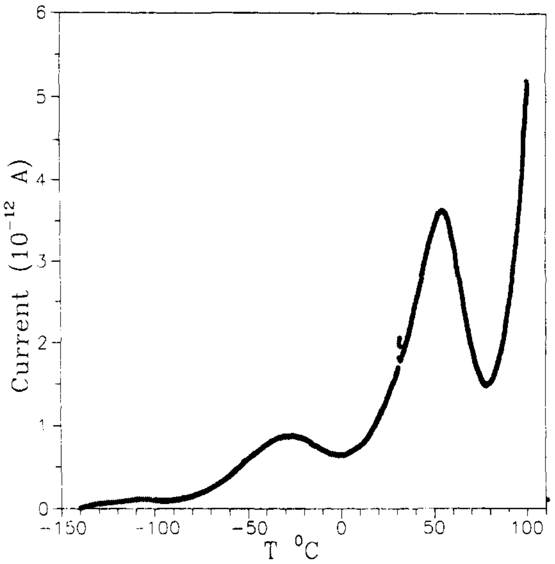

Figure 11. Thermostimulated discharge current vs temperature for PDCMI.

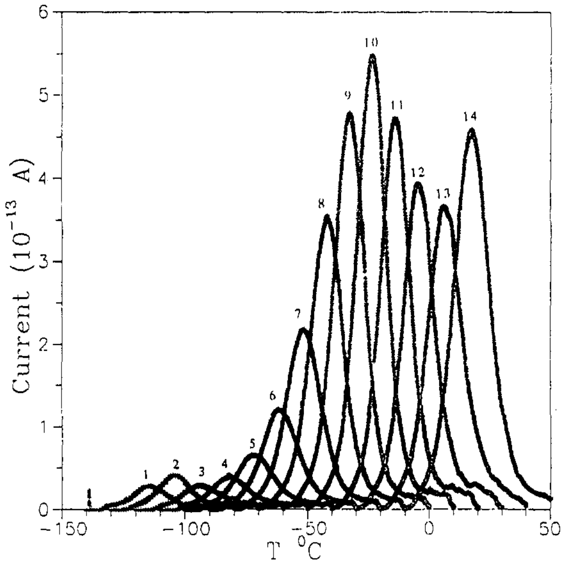

Figure 12. Elementary peaks obtained by partial depolarization of poled PDCMI samples. The poling temperatures are indicated in Table I.

Table I. Poling Temperatures, T_p, Activation Enthalpies, ΔH^{**}, Activation Entropies, ΔS^{**}, Relaxation Strength, $\Delta\epsilon_g$, and Temperatures, T_{max}, at the Maximum of the Curves Obtained by Partial Depolarization (Figure 10)

T_p, °C	T_{max}, °C	ΔS^{**}, cal/(mol K)	ΔH^{**}, kcal/mol	$10^3\Delta\epsilon_g$
-120.0	-114.2	-33	5	16.4
-110.0	-103.5	-21	8	20.2
-100.0	-93.2	-39	5	17.4
-90.0	-82.2	-28	7	24.1
-80.0	-72.8	-31	7	39.5
-70.0	-61.7	-23	9	63.6
-60.0	-51.5	-13	12	106.0
-50.0	-41.9	-1	15	159.0
-40.0	-32.6	6	17	197.6
-30.0	-23.6	20	22	224.6
-20.0	-13.7	2	18	194.7
-10.0	-4.7	14	22	176.4
0.0	5.9	9	21	179.3
10.0	17.3	-8	17	227.5

Table II. Summary of Dielectric Results for Poly(dicyclohexylmethylene itaconate)

T, °C	$2n_1\,dn/dw$	$d\epsilon/dw$	g_{intra}	$\langle\mu^2\rangle/x$, D^2	μ_{eff}, D
30	0.016	2.368	1.03	6.89	2.62
40	0.017	2.300	1.04	6.99	2.64
50	0.018	2.217	1.04	6.96	2.64
60	0.018	2.009	1.05	7.00	2.64

temperature in the lower temeprature side of each peak. By assuming that the elementary peaks are activated processes, the relaxation time associated with each peak can be expressed in terms of the absolute reaction rate theory by

$$\tau(T) = \frac{2\pi h}{\kappa T}\exp\left(\frac{\Delta G^{**}}{\kappa T}\right) \tag{9}$$

where ΔG^{**} is the activation free energy that is related to the activation enthalpy ΔH^{**} and activation entropy ΔS^{**} by the equation

$$\Delta G^{**} = \Delta H^{**} - T\Delta S^{**} \tag{10}$$

The values of the activation parameters for each elementary peak were calculated by means of eqs 9 and 10, and the results obtained are given in Table I. An inspection of the values of ΔH^{**} suggests a distribution of activation energies as was previously reported for poly(cyclohexyl acrylate).[14] The activation entropy is negative for the elementary peaks whose poling temperatures lie in the interval -120 to -50 °C as well as for the peak with T_p = 10 °C; for the other peaks it is positive.

In most cases the intensity of the partial depolarization peaks shown in Figure 12 increases with increasing poling temperature. The relaxation strength $\Delta\epsilon_g$ of each elementary peak was calculated by[13]

$$\Delta\epsilon_g = \epsilon_{rg} - \epsilon_{ug} = \frac{\int_{T_0}^{T_1} I(T)\,\frac{dT}{dT}\,dT}{e_0 A E} \tag{11}$$

where ϵ_{rg} and ϵ_{ug} represent respectivley the relaxed and unrelaxed dielectric permittivity for each peak, e_0 is the dielectric permittivity in vacuo (=8.854 pFm^{-1}), E is the electric field, A is the area of the sample, and T_0 and T_1 are respectively the extreme temperatures at the low and high temperature sides of the peaks. Values of the relaxation strength for the elementary peaks are given in Table I.

(D) Dipole Moments and Intramolecular Correlation Coefficient. Values of the mean-square dipole moment $\langle\mu^2\rangle$ per repeating unit for PDCMI were obtained by using the method of Guggenheim and Smith[15]

$$\frac{\langle\mu^2\rangle}{x} = \frac{27\kappa T M_0}{4\pi\rho N_A(\epsilon_1 + 2)^2}\left[\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right] \tag{12}$$

where κ is Boltzmann's constant, N_A is Avogadro's number, T is the absolute temperature, M_0 is the molecular weight of the repeating unit of the polymer, x is the degree of polymerization, ρ is the density of the solvent, and ϵ and n represent respectively the static permittivity and the index of refraction of the solution (those quantities with subindex 1 refer to the solvent). The plots of the increments of both dielectric permittivity ($\Delta\epsilon = \epsilon - \epsilon_1$) and the index of refractions ($\Delta n = n - n_1$) against the weight fraction of the polymer in solution, w, give straight lines from whose slopes the derivatives appearing on eq 12 were obtained. Values of these quantities for several temperatures are given in the second and third columns of Table II. In the fifth column of this table the results for $\langle\mu^2\rangle/x$, with an uncertainty of ±3%, are also given. These results can be expressed in terms of the effective dipole moment per repeating unit, $\mu_{eff} = (\langle\mu^2\rangle/x)^{1/2}$, and the dipolar

Table III. Preferred Orientation for the Side Groups of Each Repeating Unit of Poly(dicyclohexylmethylene itaconate)[a]

χ_1	χ_2	χ_3	E	μ_x	μ_y	μ_z
0	0	290	0	1.667	0.147	0.607
0	0	70	0	−0.709	−1.516	0.607
0	120	60	$E_2 = 0$	2.071	0.028	0.091
0	240	300	$E_2 = 0$	−0.735	−1.936	0.091
180	0	290	$E_1 = 1$	0.226	2.205	−1.185
180	0	70	$E_1 = 1$	−2.150	0.542	−1.185

[a] E represents the energy of each orientation in kcal mol^{-1}, while μ_x, μ_y, and μ_z (in D) indicate the components of the dipole moment of the repeating unit (obtained by addition of the dipoles of the two ester groups) written in the coordinate system affixed to skeletal bonds C–CH$_2$.

intramolecular correlation function g_{intra} by

$$g_{\text{intra}} = \frac{\langle \mu^2 \rangle}{2x\mu_0^{\,2}} = \frac{1}{2\mu_0^{\,2}}\mu_{\text{eff}}^{\,2} \qquad (13)$$

where the last part of eq 13 has been obtained by taking into account that each repeating unit contains two ester groups, each of them having a dipole moment of[16,17] $\mu_0 = 1.83$ D. Values of g_{intra} and μ_{eff} are represented respectively in the fourth and sixth columns of Table II.

Theoretical Results

(A) Intramolecular Dipolar Correlation Coefficient. The statistical model earlier developed[16] for the analysis of the unperturbed dimensions and dipole moments of itaconate polymers has been employed to calculate the intramolecular dipolar correlation. A two-state model, similar to that proposed by Sundararajan and Flory[18] for poly(methyl methacrylate) (PMMA), was used for the polymer backbone. Thus the statistical weight matrices are written as

$$\mathbf{U}' = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix};\ \mathbf{U}''_{\text{m}} = \begin{pmatrix} 1 & \alpha \\ \alpha & \alpha^2/\beta \end{pmatrix};\ \mathbf{U}''_{\text{r}} = \begin{pmatrix} \beta & \alpha \\ \alpha & \alpha^2/\beta \end{pmatrix} \qquad (14)$$

with the rotational isomers placed at $\phi = 0$ (trans) and 120° (*positive gauche*). Values of $\theta' = 112$ and $\theta'' = 110°$ were used for the bond angles of the chain backbone (see Figure 1). The side groups on each repeating unit contain three rotational angles that will be represented by χ_1, χ_2, and χ_3. Diesters of the 2,2-dimethylsuccinic acid, represented in Figure 2, are reasonable model compounds for the repeating unit. The conformational analysis of these kinds of diesters[17] and some itaconate polymers[16] allowed the evaluation of the conformational energies for the backbone as $E_\alpha = 1.4$ and $E_\beta = 0.6$ kcal mol^{-1}, as well as the determination of the preferred states for the side groups whose values are summarized in Table III.

The alcoholic residue in the ester groups (i.e., the X groups in Figure 2) are separated from the main chain for at least two bonds having rotational freedom. Therefore, these groups can orientate in such a way that their interactions with other groups of the chains are minimized, and, consequently, neither the conformational energies (E_α and E_β for the main chain and E_1 and E_2 for the side groups) nor the location of the rotational isomers (i.e., values of ϕ_1, ϕ_2, χ_1, χ_2, and χ_3 in the preferred orientations) is sensitive to the nature of these residues. The dipole moment of each one of the ester groups on the repeating unit was represented by a vector μ having a modulus[16,17] of 1.83 D and forming[19] an angle $\tau = 123°$ with respect to the C–CO bond.

Most of the calculations summarized in the present work were performed employing Monte Carlo procedures. The method used consisted of analyzing separately three characteristics of the chains, namely, the configuration, the conformation of the backbone, and the orientation of the side groups. A number N_{t} of chains, each one of them containing x repeating units, a predetermined fraction of *meso* diads w_{m}, and a Bernouillan distribution of *meso* and *racemic* centers were generated. Only one chain ($N_{\text{t}} = 1$) was used in the cases of pure isotactic or syndiotactic chains (i.e., $w_{\text{m}} = 1$ or $w_{\text{m}} = 0$), while $N_{\text{t}} = 20$ chains were generated for heterotactic polymers (i.e., $0 < w_{\text{m}} < 1$). All the results reported below were obtained with chains containing $x = 200$ repeating units. Some exploratory calculations performed with different chain lengths proved that the asymptotic limit of $\langle \mu^2 \rangle / x$ for $x \to \infty$ is reached with values of x smaller than 200; thus, for instance, differences in $\langle \mu^2 \rangle / x$ computed with $x = 200$ and $x = 250$ are within the limites of standard errors of the averages.

The statistical weight matrices indicated in eq 14 were used to compute a *priori* probabilities for all the allowed conformations of each pair of bonds in the polymer skeleton according to standard procedures.[20] The probability for the state r,s on the pair of skeletal bonds i−1, i is given by

$$p_{i-1,i}(\text{r,s}) = Z^{-1}U_1[\prod_{j=2}^{i-1} U_i]U_f^{\,0}[\prod_{j=i+1}^{n-1} U_j]U_n \qquad (15)$$

where $\mathbf{U}_i^{\,0}$ is a matrix obtained by replacing all the elements of $\mathbf{U}_i$ by zero except that of row r and column s. The probabilities computed with eq 15 were then used to generate N_{c} conformations of each chain.

Each side group of the polymer was assumed to be capable of adopting any of the six allowed orientations represented in Table III, according to their relative energies and without any kind of correlation with either orientation of the neighbor groups or conformation of the skeleton. Thus, once the configuration and conformation of the chain had been chosen, the orientation for each one of the side groups of the polymer was selected. The procedure was repeated N_0 times for each conformation of the skeleton; i.e., each conformation of the backbone was allowed to adopt N_0 different states, each one of them defined by a set of orientations of all the side groups.

Both the conformation of the skeleton and the orientation of the side groups of the chains in solution are continuously changing in such a way that they are able to visit all allowed states with the only restrictions imposed by their respective energies. This situation can be represented by taking $N_0 = 1$ which indicates that starting from any allowed state of the polymer described by a set of configurations of the quaternary carbons, a set of values of rotational angles ϕ_i for the skeleton and a set of rotations $(\chi_1, \chi_2, \chi_3)_i$ for the side groups, the next allowed state can be reached by changing ϕ, χ, or both kinds of angles.

Values of mean-square dipole moment $\langle \mu^2 \rangle$ were obtained by averaging the dipoles computed for all the $N_{\text{t}}N_{\text{c}}N_0$ states considered for each molecule with $N_0 = 1$ and $N_{\text{t}} = 20$ for heterotactic chains and $N_{\text{t}} = 1$ otherwise. Several tests performed with different values of N_{c} indicated that taking $N_{\text{c}} \approx 10^4$ standard errors amounted to ca. 0.5–1%, and, consequently, the results were indistinguishable from those computed with the standard methods of the matrix multiplication scheme.[20,21]

Values of μ_{eff} and g_{intra}, computed for three different tacticities of the sample at several temperatures and summarized in Table IV, indicate that these parameters are insensitive to the tacticity of the polymer. However, they are sensitive to the relative energies assigned to the allowed orientations of the side groups. Thus, for instance,

Table IV. Values of the Effective Dipole Moment, μ_{eff}, and the Intramolecular Correlation Function g_{intra} in the Amorphous State Computed with $N_0 = 1$, $N_c = 10^4$ and $N_t = 1$ for $w_m = 0, 1$ or $N_t = 20$ for $w_m = 0.5$

T (°C)	$w_m = 0.0$	$w_m = 0.5$	$w_m = 1.0$
	$\mu_{\text{eff}} = (\langle\mu^2\rangle/x)^{1/2}$		
60	2.40	2.40	2.29
50	2.42	2.42	2.30
40	2.47	2.45	2.35
30	2.48	2.48	2.35
	$g_{\text{intra}} = \langle\mu^2\rangle/2x\mu_0^2$		
60	0.863	0.858	0.786
50	0.875	0.874	0.791
40	0.909	0.894	0.824
30	0.919	0.919	0.826

the value of μ_{eff} is roughly doubled by allowing only one of the six orientations, due to the elimination of partial cancellations between dipole moments of consecutive diads that may have different orientations when more than one state is allowed for the side groups. Good agreement between the calculated and the experimental results is found using E_α and E_β, the values indicated before, together with the values of E_1 and E_2 indicated in Table III. The agreement between theory and experiment can be improved by small modifications of the parameters defining the allowed orientations of the side groups. Thus changes of ca. 0.5 kcal mol^{-1} in either E_1 or E_2 or ca. 10° in χ_3 (or any equivalent combination of modifications of more than one parameter at the same time) bring the theoretical result into exact coincidence with experiment.

(B) Intramolecular Dipolar Correlation Coefficient in the Glassy Region. In the glassy state, the polymer is supposed to have difficulties in changing the conformation of the skeleton, while some rotational freedom still remains in the side groups.[1,22] Therefore, whereas the evaluation of the intramolecular correlation coefficient in the liquid state implies averaging of μ^2 over conformational space that includes reorientations of the entire chains over all spatial directions together with internal reorientations, the evaluation of the correlation factor, $g_{\beta+\gamma}$, for asymmetric polymers with flexible side groups in the glassy region presumably only involves averaging of μ^2 over conformational space that includes reorientations of the side groups with respect to the frozen main chain. By using this approach, Boyd and Smith[1] developed a model, formally equivalent to that formerly described by Williams,[23] which predicts that $g_{\beta+\gamma}$ is given by

$$g_{\beta+\gamma} = \frac{1}{2x\mu_0^{\,2}}(\langle\mu^2\rangle - \langle\mu\rangle\cdot\langle\mu\rangle) \tag{16}$$

where $\mu = \sum\mu_i$ is the vector dipole moment associated with a chain in a given conformation. The mean-square dipole moment $\langle\mu^2\rangle$ appearing in eq 16 is computed with the some procedure described by eq 15. Thus, representing by μ_{ijk} the dipole moment of a chain having a configuration i (defined by a set of configurations for all the quaternary carbons of the skeleton), a conformation j (defined by a set of ϕ_i angles for the skeletal bonds), and orientation k (defined by a set of values of the χ rotational angles of the side groups), the value of $\langle\mu^2\rangle$ is obtained by

$$\langle\mu^2\rangle = \frac{1}{N_t N_c N_0}\sum_{i=1}^{N_t}\sum_{j=1}^{N_c}\sum_{k=1}^{N_0}(\mu_{ijk})^2 \tag{17}$$

However, the product $\langle\mu\rangle\cdot\langle\mu\rangle$ is computed by first averaging the components of the μ_{ijk} vector for all N_0 of the allowed orientations of the side groups and then averaging the square of the resulting modulus over the $N_t N_c$ configurations and conformations permitted to the polymer. Thus representing by $\mu^x{}_{ijk}$, $\mu^y{}_{ijk}$, and $\mu^z{}_{ijk}$ the components of the μ_{ijk} vector,

$$\langle\mu\rangle\cdot\langle\mu\rangle = \frac{1}{N_t}\sum_{i=1}^{N_t}\left[\frac{1}{N_c}\sum_{j=1}^{N_c}\left[\left(\frac{1}{N_0}\sum_{k=1}^{N_0}\mu^x{}_{ijk}\right)^2 + \left(\frac{1}{N_0}\sum_{k=1}^{N_0}\mu^y{}_{ijk}\right)^2 + \left(\frac{1}{N_0}\sum_{k=1}^{N_0}\mu^z{}_{ijk}\right)^2\right]\right] \tag{18}$$

As before, the average of eq 16 were calculated for chains containing 200 repeating units with $N_t = 1$ when either $w_m = 0$ or $w_m = 1$ and $N_t = 20$ otherwise. Some exploratory calculations performed with different combinations of values of N_c and N_0 proved that the results are rather insensitive to the exact values of these parameters provided that $N_0 \gg 1$. All the results presented below have been obtained with $N_c = N_0 = 100$ and typical values of the standard errors amounts to ca. 1%.

In the glassy state, the rotational angles utilized for the side groups were not, as usual, those corresponding to the average of the angles of the potential wells but the angles corresponding exactly to the minimum of energy. Thus angles of 300, 60° instead of 290, 70° were used for χ_3. Moreover, since the states for $\chi_1 = 180°$ have an energy significantly higher than the alternative states ($\chi_1 = 0°$), it is expected that bonds of type a (Figure 2) in the glassy state will be mostly in the state $\chi_1 = 0$. Calculations carried out at −20 °C, assuming $\chi_1 = 0°$, give $\langle\mu^2\rangle = 8.44$ and $\langle\mu\rangle\cdot\langle\mu\rangle = 5.85$ in D^2 units, so that $g_{\beta+\gamma} = 0.36$ for chains with $w_m = 0.5$. Increasing E_2 to 1 kcal mol^{-1}, values of $\langle\mu^2\rangle = 4.50$, $\langle\mu\rangle\cdot\langle\mu\rangle = 2.55$, and $g_{\beta+\gamma} = 0.29$ are obtained.

Discussion

An important issue in the study of the dielectric relaxation of polymer chains is the determination of the relative contributions of the intra- and intermolecular interactions to the secondary relaxations. Above the glass transition temperature, the intramolecular interactions expressed in terms of the dipolar intramolecular correlation coefficient g_{intra} should coincide with the value of this coefficient for isolated chains. The fact that the value of g_{intra} is ca. 1 suggests that the dipoles of the chains are nearly uncorrelated. Unfortunately, overlapping of the dipolar and conductivity contributions to the glass–rubber relaxation prevents the determination of the value of the correlation coefficient in the bulk, g, which involves both the inter- and intramolecular interactions.

Although at first sight the prominent β absorption exhibited by these chains would suggest relatively low dipolar intramolecular interactions in the glassy region, the fact that $g_{\beta+\gamma}$ is ca. 0.36 implies strong dipolar correlations in this zone. The experimental value of $g_{\beta+\gamma}$ can be evaluated from the experimental results by means of Osanger type equations such as the Fröhlich relation[24]

$$\epsilon_{r\beta} - \epsilon_{u\gamma} = \frac{3\epsilon_{r\beta}}{2\epsilon_{r\beta} + \epsilon_{u\gamma}}\left(\frac{\epsilon_{u\gamma} + 2}{3}\right)^2 \frac{4\pi N_A \rho g_{\beta+\gamma}(2\mu_0^{\,2})}{3M_0 \kappa T} \tag{19}$$

where the subindices r and u refer respectively to the relaxed and unrelaxed dielectric permittivities corresponding to the β and γ relaxations and μ_0 represents the dipole moment associated with an ester group. Overlapping of the β and α relaxation peaks makes it difficult to evaluate $\epsilon_{r\beta}$, so that the value of this quantity was obtained, as a first approximation, from the relation

$$\epsilon_{r\beta} = \epsilon_{u\gamma} + \Delta\epsilon_{\beta} + \Delta\epsilon_{\gamma} \tag{20}$$

where, as indicated before, $\Delta\epsilon_{\beta}$ (=0.88 at −20 °C) and $\Delta\epsilon_{\gamma}$ (=0.071) are the relaxation strengths of the β and γ relaxations, respectively. By assuming that $\epsilon_{u\gamma} = n^2 \approx 2.56$, $\epsilon_{r\beta}$ is found to have a value of 3.51 at −20 °C. These results substituted in eq 19 give $g_{\beta+\gamma} \approx 0.23$, a value that is somewhat lower than the value of this quantity ($\approx$0.36) obtained using eq 16. It seems therefore that moderate intermolecular interactions cannot be ruled out in the development of the secondary relaxations. The fact that both the mechanical and dielectric β absorptions have similar activation energies indicates that the same molecular motions give rise to both relaxations. Therefore, it is probable that conformational transitions occurring through χ_2 and χ_3 rotations, in combination with very restricted motions through bonds of type a in Figure 2, are mainly responsible for the great mechanical and dielectric activity observed in the glassy state in itaconate polymers.

A close inspection of the activation enthalpies involved in the partial thermodepolarization processes reveals that the peaks appearing in the γ region have a large negative activation entropy, indicating that low cooperativity occurs in the molecular motions that intervene in the processes. Contrary to what occurs in the ac experiments, the α peak exhibited by the TSDC spectrum is more prominent than the β relaxation as has been observed in conventional polymethacrylate.[13] Moreover, the intensity of the peaks in the region where the γ process occurs is low in comparison with that of the peaks registered in the β region. Both the positive activation entropy and the relatively high value of the relaxation strength of the thermodepolarization peaks occurring in the β zone suggest that a significant cooperativity takes place in the molecular motions that give rise to the β relaxation. The fact that the values of the activation enthalpy of the peaks occurring in this region lie in the vicinity of 20 kcal mol^{-1} suggests that simple molecular motions about C–CO bonds of type a in Figure 2 are involved in the depolarization processes. It should be pointed out in this regard that the energy barrier about C–CO bonds in the repeating unit of methyl methacrylate amounts to[25] 20 kcal mol^{-1}. The location and activation energy of the γ peak seems to suggest that it is caused by the same molecular motions that produce the mechanical γ relaxation (see below).

An important conclusion that arises from this work is that the strength of the β mechanical relaxation is nearly 6 times larger than that of the glass–rubber relaxation. This means that mechanical activity predominantly comes from molecular motions taking place in the side groups. Conformational changes in the skeleton bonds, which in most polymers are mainly responsible for the glass–rubber relaxation, are severely restricted in this polymer and, as a consequence, this absorption has a low intensity. As far as the dielectric glass–rubber relaxation is concerned, molecular motions arisen from generalized conformational changes about the C–CO bond directly linked to the backbone must intervene in the relaxation. The deconvolution of the dipolar and conductive overlapping electric loss peaks indicates that the dipolar glass–rubber relaxation is centered at ca. 37 °C with a value of $M'' \approx 10^{-2}$ at the peak maximum. This value is similar to that found for the β relaxation (see Figure 9), and, therefore, it can be concluded that both the dipolar α and β relaxations roughly have similar intensity.

As a consequence of the fact that the mechanical and dielectric γ relaxations are located at different temperatures in the respective spectra, both relaxations may be caused by different molecular motions. The position of the mechanical relaxation and, to a lesser extent, its activation energy seems to indicate that this absorption is caused by chair–chair flipping of the cyclohexyl ring as has been observed in other polymers with rings of this kind in the side chain.[26] The shoulder (β' peak) that appears at low frequencies in the dielectric spectrum, overlapping with the β relaxation, presumably is produced by the same molecular motions that gives rise to the mechanical γ process. Finally rotations about the low barrier energy bonds of type c in Figure 2 probably produce the ac dielectric γ relaxation.

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