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Relaxational Study of Poly(2-chlorocyclohexyl methacrylate) by Thermally Stimulated Current, Dielectric, and Dynamic Mechanical Spectroscopy

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ABSTRACT: A comparative study of the mechanical and dielectric relaxation spectra of poly(2-chlorocyclohexyl methacrylate) (P2CCM) is reported. Two clear relaxational zones are found. The spectra present a moderate subglass γ absorption, followed in increasing temperature order by a prominent α glass−rubber relaxation process. The last peak is not clearly observed in dielectric measurements due to conductivity effects which overlap the loss permittivity spectrum. Moreover, evidence of remnant mechanical as well as dielectric activity is observed near room temperature. This phenomenon has already been observed in poly(2-chlorocyclohexyl acrylate) (P2CCA). To describe in a suitable way these results, a deconvolution method has been proposed to get information about the relaxational behavior of this polymer. A more detailed analysis about the third relaxation called β, between α and γ relaxations, has been achieved by using the thermally stimulated depolarization current technique (TSDC). Special attention was devoted to the analysis of the molecular motion that produces dielectric and mechanical activity in glassy P2CCM as well as to link the elementary TSDC to the ac dielectric spectra. A comparative study of P2CCM and P2CCA is also reported.

Introduction

In the glassy state and under mechanical/electric perturbative force fields, polymers with polar side groups exhibit considerable mechanical as well as dielectric activity.[1−5] Acrylic polymers with cyclohexyl or chlorocyclohexyl groups in the side chain present a strong subglass mechanical/dielectric dispersion. This behavior has been attributed to chair-to-chair inverse conformational transitions of the rings.[6] However, molecular dynamic (MD) studies[5,7] show that the relaxational activity in the spectra of the polymers cyclohexyl or chorocyclohexyl rings cannot be exclusively attributed to the simple chair-to-chair conformational transitions as it is usually done.

To gain a better understanding of the mechanisms causing the high relaxational activity mentioned above, it is advisable to combine dielectric and mechanical studies on polymers containing these groups. Moreover, because of the high resolution of the thermally stimulated depolarization current (TSDC) technique, TSDC experiments may be useful to obtain aditional information, particulary in this kind of systems where it is interesting to analyze the fine structure of the relaxational processes.[8−10] In a recent work,[5] TSDC experiments of P2CCA reveal the existence of a new relaxational process.

The aim of the present work is to report the study of the relaxational behavior of poly(2-chlorocyclohexyl methacrylate) (P2CCM) using different methods (mechanical, ac dielectric, and TSDC techniques) and the comparison with the results found for poly(2-chlorocyclohexyl acrylate) (P2CCA) recently published.[4,5]

Experimental Section

Monomer and Polymer Preparation. 2-Chlorocyclohexyl methacrylate was prepared by reaction of methacryloyl chloride with 2-chlorocyclohexyl alcohol in toluene solution and *N*,*N*-dimethylaniline at reflux temperature for 12 h, according to the procedures reported previously.[11−13] Monomer was polymerized at 50 °C in vacuo, in the presence of α,α'-azobis(isobutyronitrile) (AIBN), 2×10^{-3} to 7×10^{-2} mol L^{-1}.

Dielectric Measurements. The real ϵ' and loss ϵ'' components of the complex dielectric permittivity ϵ^* were determined as a function of both temperature and frequency with a DEA 2970 apparatus from TA Instruments operating at 19 differents frequencies, in the frequency range 10^{-1}−10^5 Hz.

Dynamic Mechanical Measurements. The real E' and loss E'' components of the complex relaxation modulus E^* were measured at five frequencies (30, 10, 3, l, and 0.3 Hz) with a Rheometrics DMTA Mark II apparatus in double-cantilever flection.

For both the dielectric and mechanical measurements, the experiments proceeded from low to high temperature at a heating rate of 1 °C min^{-1}, except near the glass-transition temperature where a step method (5 °C) to measure was used in order to reproduce quasi-equilibrium conditions.

Thermally Stimulated Depolarization Current (TSDC) Experiments. TSDC experiments were carried out with a TSC-RMA (Solomat) spectrometer on polymer pills of 1 mm of thickness and 60 mm^2 of surface. The global spectrum was obtained by poling the sample at 130 °C for 5 min under a potential of 500 V mm^{-1} and quenching at −140 °C. Then the field was removed and the electrodes short-circuited, and after keeping the sample at the quenching temperature for about 2 min, it was warmed at the constant rate of 7 °C min^{-1}. From the time derivative of the depolarization ($J = -dP/dt$), the global spectrum was obtained. Partial polarization discharge current experiment were also performed by using poling windows of 5 °C. In all the cases, the limits of the depolarization curves were 20 °C below and 40 °C above the polarization temperatures T_p.

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Table l. $E''_{\max_\gamma}$ (Pa), $m_\gamma E_{a\gamma}/R$ (K), $T_{\max_\gamma}$ (K), m_γ, $E''_{\max_\beta}$ (Pa), $m_\beta E_{a\beta}/R(K)$, $T_{\max_\beta}$ (K), and m_β Parameters Appearing in Eq 2 at the Five Experimental Frequencies Studied

f, Hz	$E''_{\max_\gamma}$, Pa	$m_\gamma E_{a\gamma}$/R, K	$T_{\max_\gamma}$, K	m_γ	$E''_{\max_\beta}$, Pa	$m_\beta E_{a\beta}/R$, K	$T_{\max_\beta}$, K	m_β
0.3	1.77×10^8	2184	191.7	0.372	1.16×10^8	1592	292.6	0.140
1.0	1.80×10^8	2019	199.9	0.344	1.17×10^8	2008	302.1	0.176
3.0	1.80×10^8	1992	207.8	0.339	1.16×10^8	2081	313.0	0.182
10.0	1.85×10^8	2008	216.9	0.342	1.13×10^8	2340	327.0	0.205
30.0	1.88×10^8	2200	225.6	0.375	9.84×10^7	2046	341.0	0.179

Results and Discussion

The loss relaxation moduli are represented as a function of temperature, at several frequencies, in Figure l. The loss curves exhibit at 0.3 Hz a subglass absorption centered at −81 °C (γ process), a broad and non-well-defined absorption centered around 30−35 °C (β process), and a prominent glass−rubber relaxation (α process) centered at 87 °C. In any case, both the position and the intensity of the maximum of the γ and α peaks shift to higher temperature, and their height increases when the frequency increases.

For the analysis of the mechanical and dielectric spectra it is convenient to deconvolute the observed relaxations into their components. Furthermore, if an objective method of decomposing the overlaped relaxations is applied, a previous knowledge of the peak shape is also required. Subglass relaxations are usually nearly symmetric peaks, and therefore both isochrons and isotherms can be characterized by means of the Fuoss−Kirkwood equation.[14] This semiempirical model has been extensively used with good results in the representation of the mechanical and dielectric relaxations according to

$$\Gamma'' = \Gamma''_{\max} \operatorname{sech} mx \tag{1}$$

where Γ'' represents the mechanical/dielectric loss and $\Gamma''_{\max}$ is the value of these quantities at the maximum of the peak, $x = (E_a/R)(1/T - 1/T_{\max}) = \ln f/f_{\max}$, $T_{\max}$ and $f_{\max}$ are respectively the temperature and frequency where Γ'' have a maximum value ($\Gamma''_{\max}$), E_a is the apparent activation energy, R is the gas constant, and m is a parameter ($0 < m < 1$) related to the broadness of the relaxation in the sense that the larger m, the wider the distribution is. The value of $m = 1$ corresponds to a single relaxation time (Debye peak). The strength of the mechanical and dielectric relaxation peak can be calculated from the relationship[15] $\Delta\Gamma = 2\Gamma''_{\max}/m$, where $\Delta\Gamma$ represents ΔE and $\Delta\epsilon$ for the mechanical and dielectric relaxations, respectively.

Usually the additivity of each one of the contributions to the relaxations is assumed.[16] According to this procedure, the following equation to represent the empirical data is proposed:

$$\Gamma'' = \sum_i \Gamma''_{\max_i} \operatorname{sech}\left[m_i \frac{E_{a_i}}{R}\left(\frac{1}{T_{m_i}} - \frac{1}{T}\right)\right] \tag{2}$$

The function was determined from a multiple nonlinear regression analysis of the experimental data, allowing the three characterizing peak parameters (i.e., $\Gamma''_{\max_i}$, $m_i E_{a_i}/R$, $T_{\max_i}$) to vary. By this way, the fitting strategy considers, as a first approximation, only two contributions to eq 2: one for γ relaxation and other for the β (α relaxation is previously separated assuming a symmetric shape for this relaxation). Table 1 compiles the mechanical ($\Gamma'' \equiv E''$) calculated data. In this table the calculated parameters corresponding to eq 2 at all the experimental frequencies studied and the corresponding values of m_i are summarized. In this case, the activation energy values of 49 ± 1 and 77 ± 1 kJ mol^{-1} obtained previously by the Arrhenius plot were taken into account. Figure 2 shows the most probable γ and β relaxations which result from the application of the least-squares resolution method to the experimental E'' versus temperature at 0.3 Hz. The sum of the two calculated relaxations is very close to the experimental curve. Despite the complexity of the experimental spectra, the proposed deconvolution method seems to

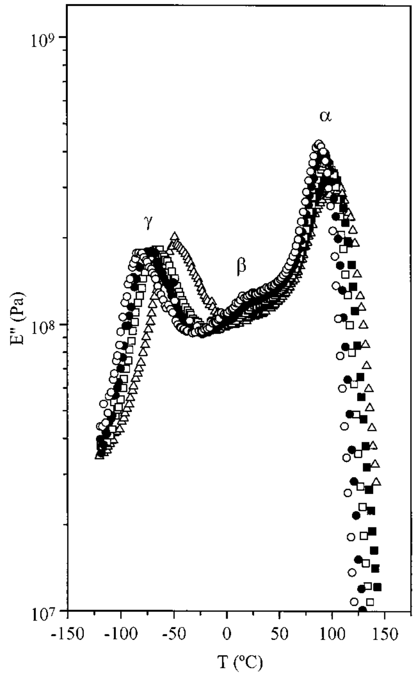

Figure 1. Temperature dependence of loss (E'') relaxation moduli of P2CCM at several frequencies: (○) 3×10^{-1} Hz, (●) 10^0 Hz, (□) 3×10^0 Hz, (■) 10^1 Hz, and (△) 3×10^1 Hz.

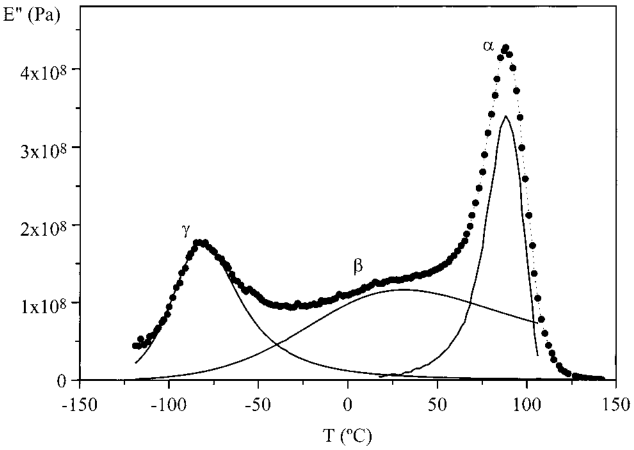

Figure 2. Deconvoluted mechanical loss curves at 0.3 Hz showing the different relaxation zone. Black circles correspond to the experimental data and lines the result of fit.

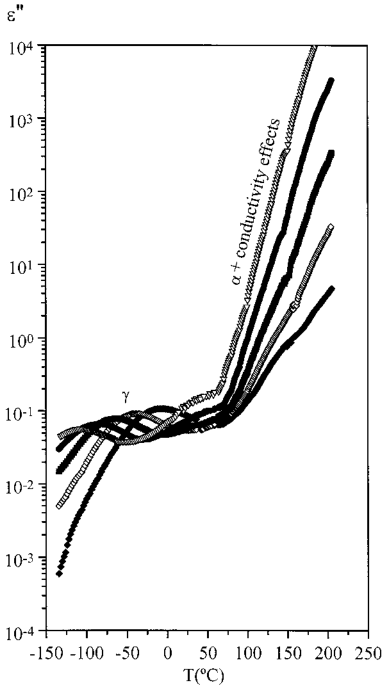

Figure 3. Loss permittivity (ϵ'') of P2CCM at several frequencies as a function of temperature: (▽) 10^{-1} Hz, (●)10^0 Hz, (■)-10^1 Hz, (◇)10^2 Hz, and (◆)10^3 Hz.

be a convenient approach to interpret the relaxational behavior of this polymer.

The dielectric spectrum, expressed in terms of the dielectric loss in Figure 3, also presents a subglass γ relaxation whose location is shifted to lower temperatures (about 15 °C) relative to the mechanical γ absorption. As for the mechanical spectra, the relaxation peaks shift to higher temperature with the frequency, and their height also increases. In this case, it is interesting to note that the α relaxation cannot be easily observed due to the continuous increasing of the loss permittivity. This phenomenon, involving a continuous increasing of the loss permittivity when the temperature rises, suggests that the conductivity contributions (combination of the bulk conduction and interfacial polarizations effects) are dominant in the dielectric response.[4,17] When the electric modulus formalism is used for the representation of the data, it could be possible to gain confidence about this fact, because a better visualization of both effects is obtained. The electric modulus is defined as

$$M^* = \frac{1}{\epsilon^*} \tag{3}$$

and consequently

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad \text{and} \quad M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \tag{4}$$

where M' and M'' are the storage and loss dielectric modulus, respectively. In Figure 4 M'' against temperature at several frequencies is represented. The advantages of this kind of representation are evident due to the better resolution observed for γ, β, α, and conductive relaxations (see curve corresponding to 0.1 Hz). In the curve corresponding to 100 Hz it is possible to observe the dipolar and conductive effects overlapped.

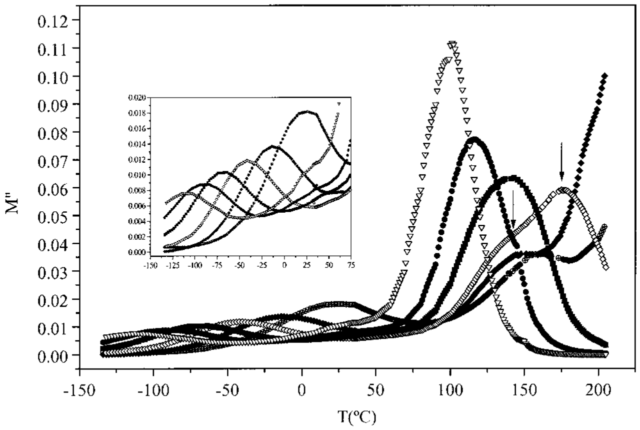

Figure 4. Electric modulus (M'') of P2CCM at several frequencies as a function of temperature: (▽) 10^{-1} Hz, (●) 10^0 Hz, (■) 10^1 Hz, (◇) 10^2 Hz, (◆) 10^3 Hz, and (⊕) 10^4 Hz. The arrows indicate the position of the α and conductive relaxations.

Table 2. $M''_{\max_\gamma}$, $m_\gamma E_{a\gamma}/R$ (K), $T_{\max_\gamma}$ (K), and m_γ Parameters Appearing in Eq 4 at Different Experimental Frequencies Studied

f, Hz	$M''_{\max_\gamma}$	$m_\gamma E_{a\gamma}/R$, K	$T_{\max_\gamma}$, K	m_γ
0.1	0.007 64	730.12	161.6	0.2
0.2	0.008 29	800.92	167.2	0.21
0.3	0.008 39	834.9	170.9	0.21
0.5	0.008 37	840.39	174.4	0.22
1	0.008 76	872.57	179.6	0.22
2	0.009 12	942.62	185.7	0.24
3	0.009 24	931.32	190.2	0.24
5	0.009 61	971.54	195.7	0.25
10	0.010 12	1063.7	204.1	0.27
20	0.009 56	1299.13	211.1	0.33
30	0.010 43	1330.6	215.4	0.34
50	0.011 00	1384.73	220.4	0.35
100	0.011 62	1466.24	228.9	0.38
200	0.012 09	1511.15	238.3	0.39
300	0.012 68	1545.82	243.5	0.40
500	0.012 77	1785.9	250.2	0.46
1000	0.014 00	1955.34	261.1	0.50

In the dielectric case, the Γ'' of eq 1 has been remplaced by M'', which corresponds to the electric loss modulus. The best calculated parameters and the corresponding values of m_i obtained using the activation energy value from the Arrhenius plot (40 ± 1 kJ mol^{-1}) are summarized in Table 2. In this case, only the γ relaxation is taken into account because β relaxation is not clearly observed due to the continuous increasing of the loss permittivity (combination of the α relaxation, bulk conduction, and interfacial polarization effects).

To perform a more detailed analysis of the complex relaxation processes in this material, TSDC experiments were carried out. The global TSDC spectrum for P2CCM, represented in Figure 5, presents a prominent α peak, associated with the glass transition temperature, whose maximum is located at 120 °C. In the glassy region a weak peak centered at 0 °C is detected, which corresponds to a not well-developed β process. Decreasing in temperature, an apparent γ peak whose maximum is located at −100 °C can be observed. The shape of this curve, showing the temperature dependence of the depolarization process, vaguely reminds one of the experimental ac isochrone at low frequency. In Figure 4, it can be observed that the glass−rubber relaxation, or α peak, is dominated by conductive phenomena and interfacial conductivity at low frequencies. On the other hand, the β peak becomes hardly detectable even at low

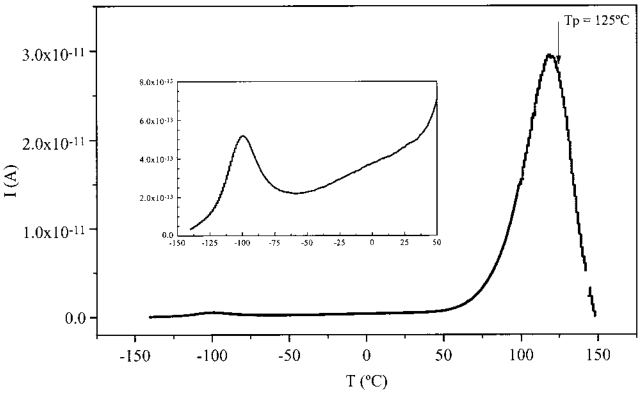

Figure 5. Global TSDC spectrum of P2CCM over the glassy and glass−rubber regions. In the inset is the TSDC spectrum for the polymer in the glassy state.

frequencies, whereas the γ peak is relatively strong. To get a deeper insight into relaxational behavior of P2CCM, especially on the elusive β relaxation, several methods can be used.

One of them is to polarize at a temperature between β and α relaxations, but in this study we prefer to follow the more resolute partial windowing technique.

Concerning TSDC data, the equivalent frequency at which ac experiments should be performed, to obtain a loss peak at the same temperature as the γ TSDC peak, can be obtained from the current density $J(T)$ measured during a TSDC experiment. $J(T)$ is given by[9]

$$J(T) = \frac{P_e(T_p)}{\tau_0} \exp\left(-\frac{E_a}{kT}\right) \exp\left[\frac{-1}{h\tau_0}\int_{T_0}^{T} \exp\left(-\frac{E_a}{kT'}\right) \mathrm{d}T'\right] \tag{5}$$

where $P_e(T_p)$ is the equilibrium or steady-state polarization at the polarizing temperature T_p, k is Boltzmann's constant, and h is the heating rate, which is constant in the experimental conditions used. In this equation an Arrhenius dependence of the relaxation times on temperature was postulated. When TSDC reaches the maximun temperature T_{max} of the peak, $(\mathrm{d}J/\mathrm{d}T)_{T=T_{max}}$ leads to zero. The equivalent frequency f_{eq} can be obtained by differentiating eq 5,

$$f_{eq} = \frac{hE_a}{2\pi k T_{max}^{\ 2}} \tag{6}$$

According to this equation, and taking into account that $E_a \sim 40$ kJ mol^{-1}, the value of f_{eq} is approximately, 3×10^{-3} Hz. This result indicates that the location of the γ absorption in the dielectric ac isochrone, measured in the vicinity of this frequency, should be in fairly good agreement with that of the same relaxation in the TSDC global spectrum. However, this frequency is out of the experimental range of frequencies available with our experimental equipment. Therefore, it is not possible for a direct comparison between TSDC peaks and ac experimental data. It can only be decided if the position of the current peak is compatible with a given dielectric relaxation by extrapolating the dielectric function ln f vs $1/T_{max}$ to the equivalent frequency. T_{max} is the maximum temperature of the loss curve at frequency f.

As mentioned above, to get a deeper insight into the relaxational behavior of P2CCM, partial TSDC experiments were carried out. Experiments were performed in the glassy state using poling temperatures T_p lying in the range −100 to 0 °C. The elementary relaxation processes thus obtained, shown in Figure 6, present a T_{max} of the peak that are a linear function of T_p. The elementary relaxation processes were assumed to be described by a single relaxation time whose temperature dependence is given by[18]

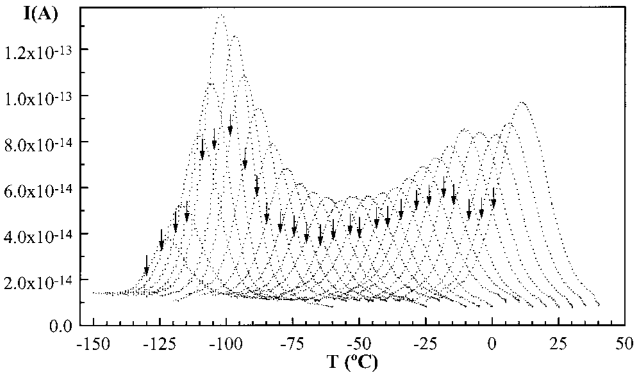

Figure 6. Elementary subglass TSDC spectra obtained at the following poling temperatures: −130, −125, −120, −115, −110, −105, −100, −95, −90, −85, −80, 75, −70, −65, −60, −SS, −50, −45, −40, −35, −30, −25, −20, −15, −10, −5, and 0 °C.

$$\tau^{-1}(T) = \frac{hJ(T)}{\int_{T_0}^{T} J(T)\, \mathrm{d}T} \tag{7}$$

where h is the constant heating rate and T_0 is the extreme temperature at the lower side of each peak. The temperature evolution of the relaxation times is expressed by the Arrhenius equation

$$\tau(T) = \tau_0(T) \exp\left(\frac{E_a}{kT}\right) \tag{8}$$

where τ_0 is a preexponential factor and E_a is the activation energy for the process. The plot of log τ against $1/T$ is linear, at least up to the half-width temperature. By this way the preexponential factor and the activation energy can be obtained from the linear part of the curves. The values of τ_0 and E_a are summarized in Table 3. It can be seen in this table that the values of the activation energy seem to increase with T_p, while the values of the preexponential factor do not follow a defined trend. Nevertheless, according to the theory of TSDC,[19] τ_0 is a decreasing function of T_p. Moreover, the results show that the E_a is distributed in the ranges ~41−42 and 70−76 kJ mol^{-1} for the γ and β relaxations, respectively, in good agreement with the obtained values from mechanical and ac dielectric data.

The relaxation strength of each elementary peak was calculated by means of the expression[20]

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty = \frac{\int_{T_0}^{T_\infty} J(T)\, \mathrm{d}T}{\in_0 hAE} \tag{9}$$

where ϵ_∞ and ϵ_0 represent respectively the relaxed and unrelaxed dielectric relative permittivity for each peak, $\in_0$ is the dielectric permittivity in vacuo (=8.854 pF m^{-1}), A is the area of the sample, E is the electric field, and T_0 and T_∞ are the extreme temperatures at the low- and high-temperature side of the peaks, respectively. The values of the calculated relaxation strength for the elementary peaks, represented as a function of T_p, give

Table 3. Temperature Dependence of the Preexponential Factors (τ_0) and the Activation Energies (E_a) of the Relaxation Times and the Relaxation Strengths Associated with the Elementary Peaks Represented in Figure 8

T_p (°C)	log τ_0	E_a (kJ mol^{-1})	$\Delta\epsilon$
−130	−8.395	24.7753	0.0223
−125	−8.414	25.3040	0.0406
−120	−10.981	34.3412	0.0695
−115	−11.259	35.9564	0.0878
−110	−11.780	38.2157	0.1086
−105	−12.033	40.4942	0.0999
−100	−12.331	42.2160	0.0960
−95	−11.948	42.2920	0.0784
−90	−11.766	42.7948	0.0695
−85	−11.046	41.3017	0.0565
−80	−10.873	41.5719	0.0527
−75	−10.654	41.9747	0.0470
−70	−10.470	42.2064	0.0477
−65	−10.497	43.1957	0.0483
−60	−10.415	43.8975	0.0518
−55	−10.490	45.3685	0.0492
−50	−10.682	46.9644	0.0555
−45	−10.889	48.9449	0.0580
−40	−11.081	50.8004	0.063 7
−35	−11.283	52.9828	0.0665
−30	−11.383	54.4152	0.0750
−25	−11.896	57.9051	0.0808
−20	−12.948	64.5580	0.0892
−15	−13.032	66.1059	0.0915
−10	−13.437	69.7688	0.0910
−5	−13.270	70.0861	0.0970
0	−14.104	75.9891	0.1098

a curve whose shape reminds one of that of the global TSDC spectrum in the glassy region. Thus, in the region in which the γ peak is located, the curve presents a well-defined maximum, and a small shoulder overlaped with the α process can also be observed in the temperature interval corresponding to the β process.

As, we have mentioned above, the results at low frequencies for the components of the complex dielectric permittivity of the polymer in the glassy state show the presence of a well-defined absorption centered at ∼−110 °C (for 0.1 Hz). This absorption is followed, on the order of higher temperatures, by a poorly defined β relaxation process. At higher frequencies, the latter process is not detected (see Figure 3). Due to the fact that the overlapping of the relaxation processes in the glassy state is less pronounced as frequency decrease, it is interesting to analyze the components of the complex dielectric permittivity at very low frequencies. For this reason, the values of ϵ' and ϵ'' from the elementary TSDC spectra were calculated. These quantities are related to the TSDC results by the expressions[20,21]

$$\epsilon' = \epsilon_\infty + \sum_{i=1}^{n} \frac{\Delta\epsilon_i}{1 + \omega^2\tau_i^{\,2}(T)}$$

$$\epsilon'' = \sum_{i=1}^{n} \frac{\Delta\epsilon_i \omega\tau_i(T)}{1 + \omega^2\tau_i^{\,2}(T)} \tag{10}$$

where $\Delta\epsilon_i$ is the relaxation strength, ϵ_∞ is the infinite-frequency dielectric constant, ω is the angular frequency, and $\tau_i(T)$ is the Debye relaxation time for the system i in which its temperature dependence is determined by eq 8. The number n of the sum in eqs 10 denotes numbers of a series of elementary spectra isolated by TSDC experiments (Figure 6). Activation energies (E_{ai}) and preexponential factors (τ_{0i}), shown in Table 3, corresponding to the ith elementary spectrum were used. In the present calculation of ϵ', the value 2.55 was considered as value of ϵ_∞ referring to the experimental data.

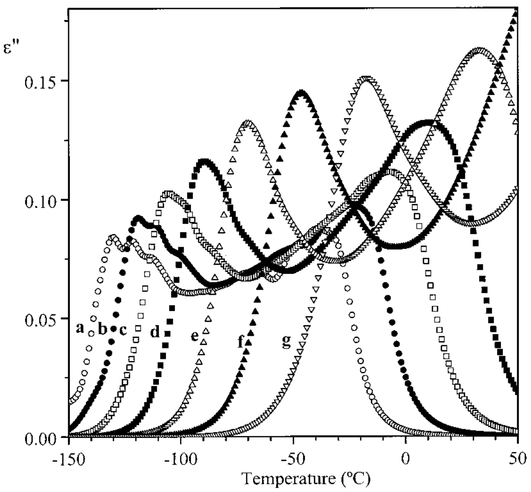

Figure 7. Isochrones representing at low frequencies the temperature dependence of the loss factor of ϵ^*, obtained from eq 10 for P2CCM in the glassy state. The curves a, b, c, d, e, f, and g correspond respectively to 10^{-3}, 10^{-2}, 10^{-1}, 10^{0}, 10^{1}, 10^{2}, and 10^{3} Hz.

The temperature dependence of the components of ϵ^* obtained from eqs 10 is shown at several frequencies in Figure 7. The isochrones present a complex pattern, showing several relaxational processes. Notice that the position of the main peaks agrees with that observed in ac experiments. On the other hand, the intensity of the low-temperature peak at 0.1 Hz is slightly larger (0.1) than that corresponding to dynamic dielectric measurements (0.06). The small discrepancies observed between the simulated and the experimental frequencies can be interpreted in terms of the sensitivity of the calculated equivalent frequency with the parameters appearing in eq 6.[8,9,22]

Conclusions

The values of the activation energy associated with the mechanical and dielectric γ relaxation for P2CCM, i.e., 49 and 40 kJ mol^{-1}, respectively, are very similar to those obtained for P2CCA, i.e., 58 and 42 kJ mol^{-1}. The position and the height of this relaxation are also similar in both polymers (see Figure 8a,b). The similar relaxational behavior observed for both polymers is in good agreement with their chemical structures. In fact, these polymers only differ in the methyl group in the α position, which influences greatly the value of the glass transition. This is an indication that the main chain does not play a significant role in the motions responsible for the γ relaxation. The origin of the considerable subglass mechanical and dielectric activity found in these polymers can be probably the same and due to the cyclohexyl groups in the side chain. Nevertheless, according to recent molecular dynamic calculations,[4,5,7] the mechanical and dielectric activity cannot be exclusively attributed to chair-to-chair conformational transitions in the cyclohexyl ring.[1,2] Probably, molecular motions associated with the side groups, such as conformational transitions through O−C_y and CH−C*O* bond, are involved in the subglass absorptions.

Measurements carried out show the existence of activity between γ and α relaxations. Moreover, the

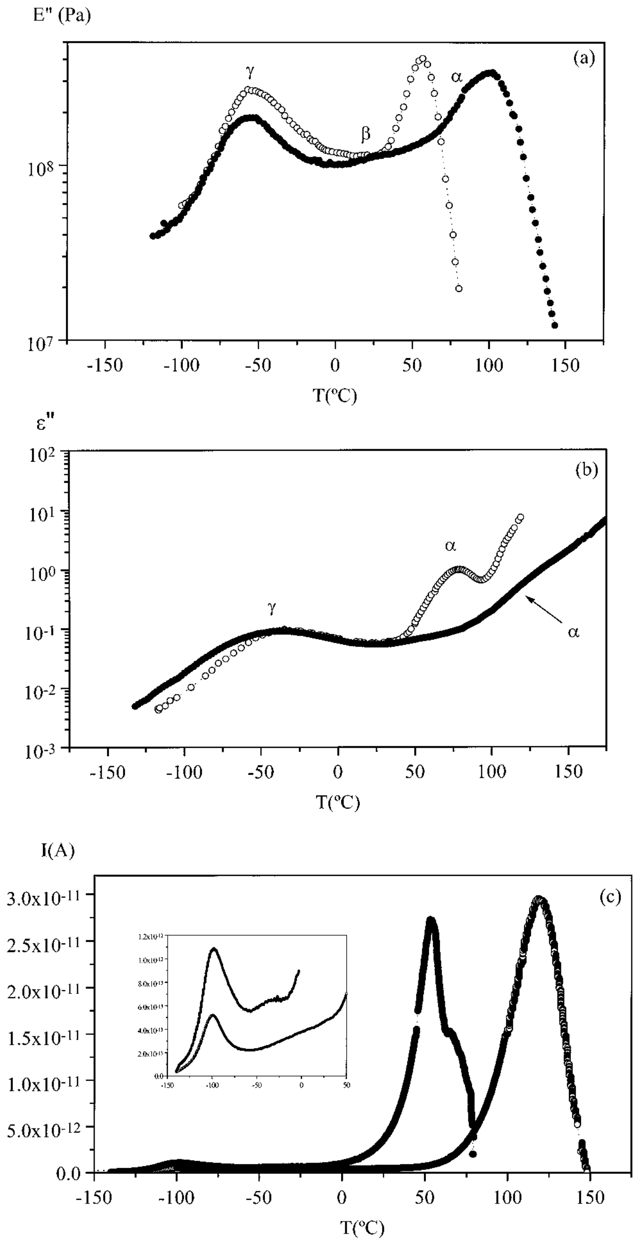

Figure 8. (a) Temperature dependence of the loss permittivity (E'') of P2CCA (○) and P2CCM (●) at 100 Hz. (b) Temperature dependence of the loss (ϵ'') relaxation moduli of P2CCA (○) and P2CCM (●) at 10 Hz. (c) Global TSDC spectrum of P2CCA (○) and P2CCM (●) over the glassy and glass–rubber regions. (Discrepancies between the intensity of the global thermograms are due to the different experimental conditions used in each case.)

calculated ac data in the β zone show the existence of structure in the observed process. The value of the activation energy associated with the processes responsible for the β relaxation calculated using the mechanical and TSDC spectra for P2CCM is ~77 kJ mol^{-1}. The molecular origin of this relaxation can be attributed to the rotations of the whole side chain. However, the participation of the main chain could not be disregarded. A similar relaxation have been observed in poly(n-alkyl methacrylate)s.[6]

According to the TSDC results, the β process is a combined process and probably is more complex in P2CCM polymer than in the analogous P2CCA. This explains that the ac calculated data (from TSDC, eqs 10) in the case of P2CCA[5] show only one elementary peak in the β zone, whereas in the case of P2CCM the presence of at least two peaks is observed (Figure 8c).

To analyze these differences, a deconvolution method described previously for the decomposition of the overlaped relaxation in P2CCA at 0.3 Hz was used. The results show that the value of the m_β parameter is 0.45 whereas at the same frequency this parameter is 0.14 in the case of P2CCM. The minor value of m_β (broad process) suggests that the β relaxation in P2CCM involves a weighted sum of elementary processes occurring in a variety of local environments.

The analysis of the subglass relaxations in the simulated ac data shows that the γ peak is weaker than the β one. The opposite behavior is found in both the ac and TSDC global spectra. The origin of this disagreement may be attributed to the simulations of the ac spectra by means of eqs 10. In fact, some contributions obtained from depolarization curves at relatively high poling temperatures were used, in which the contribution of glass–rubber relaxation is not negligible. It is difficult to split the last relaxation from the β relaxation because of the narrow range of temperatures where they appear in the TSDC spectra. This phenomenon was observed previously in a similar study carried out with P2CCA.[5]

On the other hand, as can be seen in Figure 8b, the resolution of the α relaxation in dielectric measurements for P2CCM is not clear. This fact is associated with the presence of important conductive effects, probably overlapped to electrode blocking phenomena. The conductive effects could be attributed to the presence of the ions due to low molecular weight substances remaining in the polymeric matrix from the polymerization process. The second phenomenon is probably related to the contact of the sample with the electrodes, which involves microscopic defects.[23]

The α relaxation temperature in mechanical measurements is about 60 °C lower in P2CCA than in P2CCM (Figure 8a). Since acrylate polymers differ from the methacrylates in the substitution of a hydrogen atom for the methyl group on the α carbon atom, this result probably reflects a decrease in steric hindrance to main-chain motions effected by the replacement of the α $-CH_3$ group by a hydrogen atom.

According to the results found in this work, it is possible to conclude that the substitution in the main chain of one hydrogen by a methyl group affects not only the position of the α relaxation but also the complexity of the β process which is more complicated in the case of methacrylate derivatives.

Finally, it can be concluded that TSDC partial depolarization measurements together with the simulation of dielectric data are a powerful tool to elucidate the mechanism of the relaxation processes—especially in the case of polymers where these processes are complicated and/or in the case that these processes are detectable only at very low frequencies where it is difficult to obtain resolute dielectric experimental data.

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