PII: S0032-3861(96)00960-3

Dielectric and molecular mechanics study of the γ relaxations of poly(chloroethyl methacrylate) and poly(chloropropyl methacrylate)

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(Revised 9 October 1996)

Cryogenic dielectric measurements corresponding to the γ-relaxation zone have been made for poly(chloroethyl methacrylate) and poly(chloropropyl methacrylate). Molecular mechanics calculations using the Allinger MM2 force field have been carried out on monomer and trimer model compounds in an attempt to gain some insight into the possible origin of the γ-relaxation process which occurs in these polymers at low temperatures. In both cases, we found that the molecular mechanism of oxylcarbonyl side group rotation combined with reasonable constraints on movements of the neighbouring side groups gave theoretical activation energy requirements which were in good agreement with those determined from the experiment. © 1997 Elsevier Science Ltd.

(Keywords: molecular mechanics; poly(chloroethyl–methacrylate); poly(chloropropyl–methacrylate))

INTRODUCTION

Molecular mechanics can be considered as a useful tool for analysing the molecular motions causing secondary relaxations. However, in general, for each molecular group, there are many available molecular conformations consistent with the same value of energy. For this reason, in order to start with a systematic study, it is very convenient to analyse small molecular groups first, because they have less degrees of freedom and, therefore, the identification of the responsible molecular motions of the mechanism can be simplified. At the same time, the smaller the size of the group under study, the lower is the temperature at which the corresponding relaxation peak appears. That is, we are concerned with cryogenic relaxations in many cases, governed by barriers that are predominantly intramolecular.

The conformational calculations are useful in rationalizing the experimental data, but it is necessary to take into account that which only represents an approximation, a modelization, and therefore it cannot reproduce with perfect exactness the experimental results. The dielectric properties of polymethacrylates with long lateral chains have been extensively studied in the past by different authors[1–6]. In this paper we have carried out a molecular mechanics study of the motions of the lateral chains of poly(chloroethyl methacrylate) (PCEMA) and poly(chloropropyl methacrylate) (PCPMA), in order to relate them to the dielectric γ relaxation observed in the low temperature zone (about 125 K at 1 kHz) of the dielectric spectra of both polymers.

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The γ loss peak at approximately 120 K is also found in other related polymers with a side chain similar to the PCEMA and PCPMA, such as poly(propyl methacrylate) (PPMA)[6] and poly(n-butyl methacrylate) (PnBMA)[3] where the role of the chlorine atom is represented by a methyl group.

In our molecular mechanics study we have used a similar approach to the one employed by other authors[3,5–10], i.e. the use of model compounds (of one and three units) in order to interpret the responsible molecular motions of a determined transition of the corresponding polymer.

EXPERIMENTAL

Molecular mechanisms

The molecular mechanics calculations were performed using the force field method developed by Allinger and co-workers[11,12]. The energy is calculated using an empirical force field with potential functions for bond stretching, angle bending and Van der Waals', torsional and electrostatic interactions. The Allinger MM2 program can handle up to a maximum of 100 atoms, but for realistic computational times to be achieved, model compounds with between 40 and 50 atoms were used in this study. The calculations of theoretical energy requirements for a bond rotation were carried out with two model compounds of one and three units for each polymer, which simulates part of the polymer chains.

The first step in the calculations is to establish an initial geometry, then the program can be used to minimize the strain energy of this initial geometry by

making spatial readjustments of all the atoms. With this strain minimized geometry as a starting point, a bond is selected for rotation and is driven through 360° in 10° intervals. At each of these intervals the strain energy is again minimized until finally a potential energy curve for complete rotation is produced.

In spite of the fact that in secondary relaxations in polymers we probably deal with intra- and inter-molecular interactions[13], it should be noted that the present calculations neglect intermolecular inter-actions, because the calculation of the intermolecular contribution to secondary loss processes in glassy polymers is a difficult problem. Next, we will see that this assumption is consistent with our results.

Dielectric measurements

Dielectric relaxation measurements were carried out with a 1620 GENRAD bridge between 23 K and room temperature at frequencies of 0.5, 1, 2, 5, 10, 20, 50 and 100 kHz. Temperature control was carried out by means of an Oxford ITC4 unit by using a helium closed circuit and a home-made, guarded, three-terminal dielectric cell. Samples were pills of 10 mm diameter and 0.25 mm thickness.

The temperature interval between two consecutive measurements was 5 K, and a period of 1 h was used in order to stabilize the temperature.

RESULTS AND DISCUSSION

In *Figures 1* and *2* the dielectric permittivity ϵ' and loss ϵ'' are represented as a function of temperature at three frequencies for the PCEMA and PCPMA, respectively.
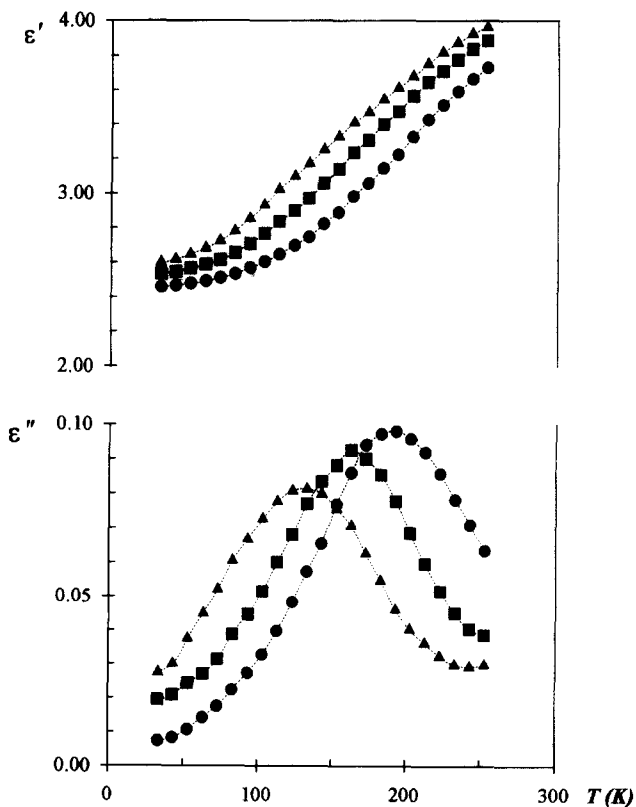
We can see clearly the existence of a relaxation peak which we will call γ relaxation. At 1 kHz the γ relaxation of PCEMA and PCPMA are centred around 125 and 133 K, respectively. The reported data, are consistent with the previous dielectric measurements of these polymers[5] in the common experimental range.

The dependence of the logarithm of the frequency of the maxima of $\epsilon''(\omega)$ to the inverse of temperature has been adjusted to an Arrhenius equation. The activation energies obtained for both polymers, PCEMA and PCPMA, are given in the first column of *Table 1*.

The position of the γ dielectric relaxation is in good agreement with the one obtained for the same com-pounds by Mikhailov and Borisova[2]. We will now compare the calculated conformational energy barriers with activation energies, E_a, obtained from dielectric relaxation measurements.
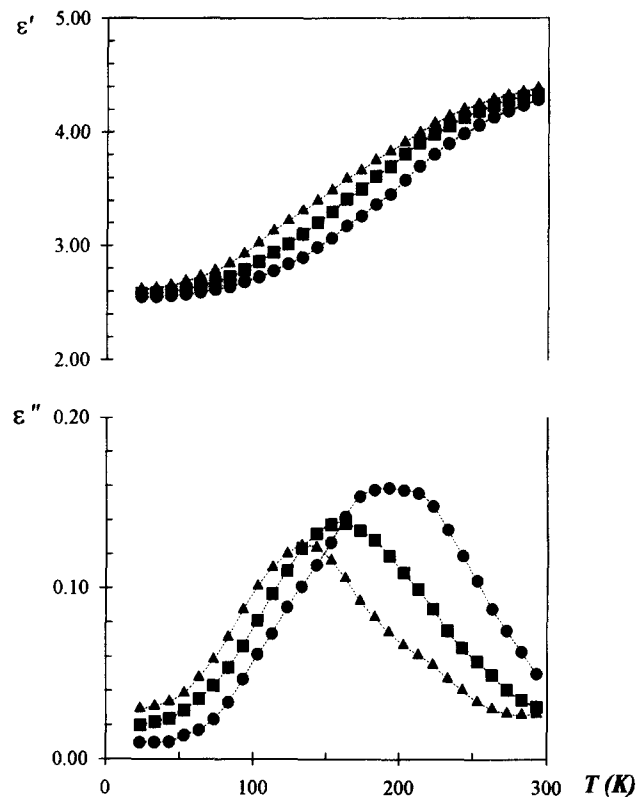
In order to interpret the molecular motions responsible

Figure 2 Temperature dependence of the dielectric permittivity ϵ' and loss ϵ'' of PCPMA at the same frequencies as in *Figure 1*

Table 1 Experimental activation energies, E_a, of the γ relaxation process compared with the energies obtained from the potential energy curves
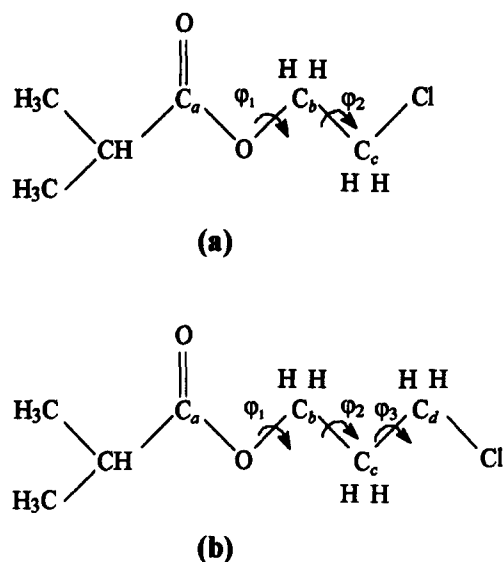
Polymer	E_a^a(kJ mol^{-1})	E_a^b(kJ mol^{-1})
PCEMA	22.09	20.97^c
		21.92^d
PCPMA	24.42	22.96^c
		24.00^d
PPMA[9]	21.92	16.39
PnBMA[10]	22.88	19.97

^{a} Arrhenius type
^{b} Molecular mechanics calculations
^{c} Monomer
^{d} Trimer model compounds

Figure 1 Temperature dependence of the dielectric permittivity ϵ' and loss ϵ'' of PCEMA at three frequencies (●, 100 kHz; ■, 10 kHz; ▲, 1 kHz)

Figure 3 Schematic drawing of the one-unit model compounds of (a) PCEMA and (b) PCPMA

for this transition, the molecular mechanics calculations were carried out on two model compounds of one and three units. A diagram of the one-unit model compound used is shown in *Figure 3*.

The calculations were confined to the rotation around the C_b–C_c bond, because previous calculations showed that the rotation barriers of other bonds are too high to be related to the γ relaxation, which is the subject of the present study.

The one-unit model (monomer) compounds were used to study the behaviour of side groups without interference from other side groups. *Figure 4a* shows the contour map of the conformational energy of the monomer model compound of PCEMA polymer at 298 K as a function of the rotation angles around the O–C_b bond (ϕ_1) and the C_b–C_c bond (ϕ_2). The region around (0°, 120°) and (0°, 240°) is probably inaccessible because of severe steric hindrance between the carbonyl oxygen and the terminal chlorine of the ethyl group. The contour map shows 12 potential maxima and nine potential minima indicated by capital letters; E (180°, 180°) is a centre of symmetry, and A and J, B and H, C and G, and D and F are mirror images.

This polymer was also approached by a three-unit model. We used a main chain of seven carbon atoms with side chains placed in the syndiotactic configuration on positions 2, 4 and 6. We chose the syndiotactic configuration, since in polymers on which relaxation measurements have been carried out, syndiotactic sequences are predominant. Because of this reason, the contour map was constructed with rotation angles around the C_b–C_c bond of the central ester group in order to enter into account the interactions between different side groups and to obtain more realistic results. In *Figure 4b* the contour map of the conformational energy of the three-unit model as a function of the rotation angle ϕ_1 and ϕ_2 is represented. On this occasion, the centre of symmetry is not presented on the contour maps, but the positions of maxima and minima are very similar, though the global minimum is changed from E to F. The differences between the coordinates of the one-unit and three-unit model compounds are most pronounced for A and G, but the difference for the
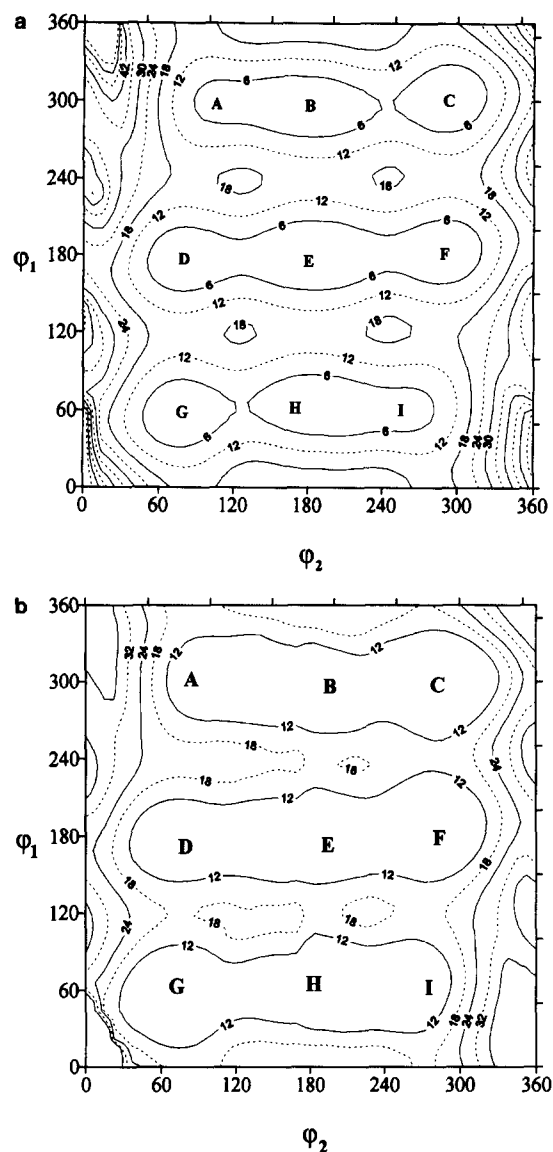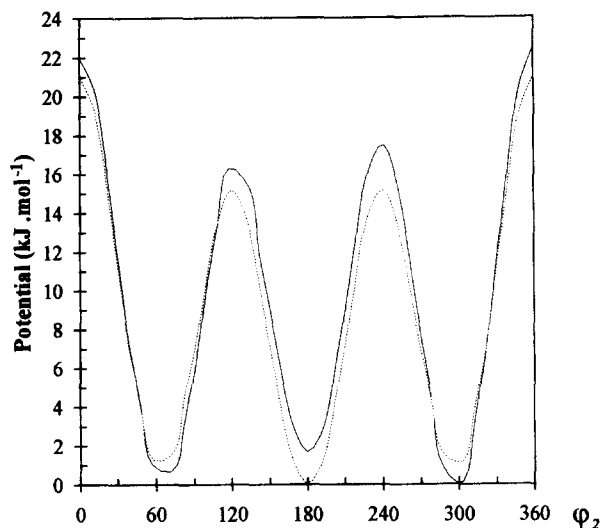

Figure 4 Contour map of the conformational energy (kJ mol^{-1}) of (a) monomer and (b) trimer model compounds of PCEMA

transition states is, in general, not important (8° or less). Probably, the former difference is caused by the interaction between the terminal chloromethyl group of the ester side chain and the methyl group attached directly to the main chain in the case of the three-unit model compound.

The most probable path of rotation is D ↔ E ↔ F ↔ D in which ϕ_1 is kept almost constant (rotation of the chloroethyl group around the ϕ_2 axis). The energy barriers for D ↔ E, E ↔ F and F ↔ D transitions are 20.97, 15.18 and 21.09 kJ mol^{-1} for the monomer, and 21.92, 16.31 and 22.42 kJ mol^{-1} for the trimer model compound. The potential along this path is drawn in *Figure 5* in which the top curve represents the potential path for the three-unit model compound and the bottom curve represents the potential path for the one-unit model compound. Because of the effect of the chain backbone and of the neighbouring one-unit model compound, the minimum E in the bottom curve is lowered with respect to those in the top curve, but the difference is not important.

In the same way, a contour map of conformational energy at 298 K, for the one-unit model compound of the

Figure 5 Potential energy (kJ mol^{-1}) profile for rotation of C_b–C_c bond (ϕ_2, with $\phi_1 = 180°$) for PCEMA model compounds
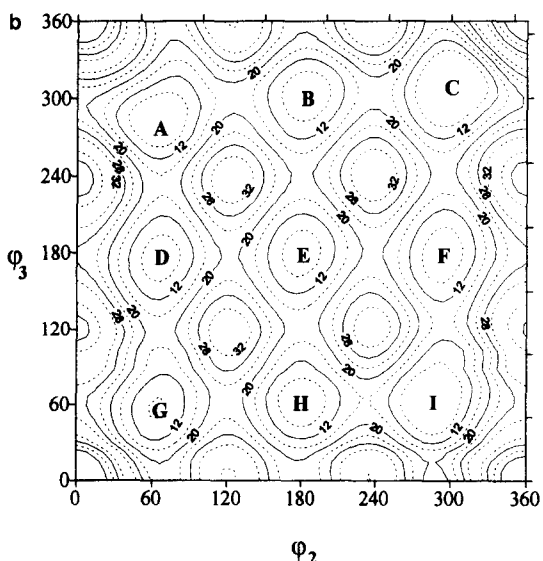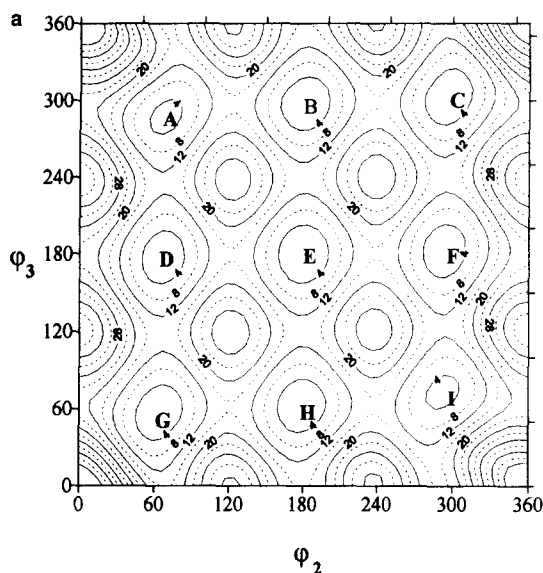

Figure 6 Contour map of the conformational energy (kJ mol^{-1}) of (a) monomer and (b) trimer model compounds of PCPMA

PCPMA polymer, was constructed with rotation angles around the C_b–C_c bonds (ϕ_2) and C_c–C_d bond (ϕ_3) as coordinates. The rotation around the O–C_b bond (ϕ_1) leads to energy minima which are too high and should be ignored. The contour map of the conformational energy obtained is drawn in *Figure 6a*, where nine potential minima and 12 potential maxima (also indicated by capital letters) are found. We could observe that the regions around (0°, 0°), (0°, 360°), (360°, 0°) and (360°, 360°) are also inaccessible on this occasion because of steric hindrance between the carbonyl oxygen and the terminal chlorine of the propyl group. This figure shows also a centre of symmetry in E (180°, 180°); A and J, B and H, C and G, and D and F are mirror images. This polymer was also approached with a three-unit model, a main chain of seven carbon atoms with side chains placed in the syndiotactic configuration on positions 2, 4 and 6. On this occasion also, in order to enter into account the interactions between different side groups, the contour map was constructed with rotation angles around the C_b–C_c bond of the central ester group. *Figure 6b* represents the contour map of the conformational energy of the trimer model compound as a function of the rotation ϕ_2 and ϕ_3. As in the previous case, the centre of symmetry is not presented on the contour map. Though the positions of the maxima and minima are very similar, the global minimum is changed from E to F, and the differences between the coordinates of the monomer and the trimer model compounds, probably caused by the interaction between the terminal chloromethyl group of the ester side chain and the methyl group attached directly to the main chain in the case of the three-unit model compound, are most pronounced for A and G (6° or less).

Figure 7 shows the conformational energies ΔH_{298} *versus* the C_b–C_c rotation angles (with $\phi_3 = 180°$) for the two model compounds. The lowest minima are D, E and F and the most probable path of rotation is D ↔ E ↔ F ↔ D, in which ϕ_3 is constant ($\phi_3 = 180°$) and ϕ_2 is the variable. The energy barriers for this transition, calculated with monomer and trimer model compounds, are 22.96 and 24.00 kJ mol^{-1}, respectively.

We can observe in *Table 1* that the values of activation
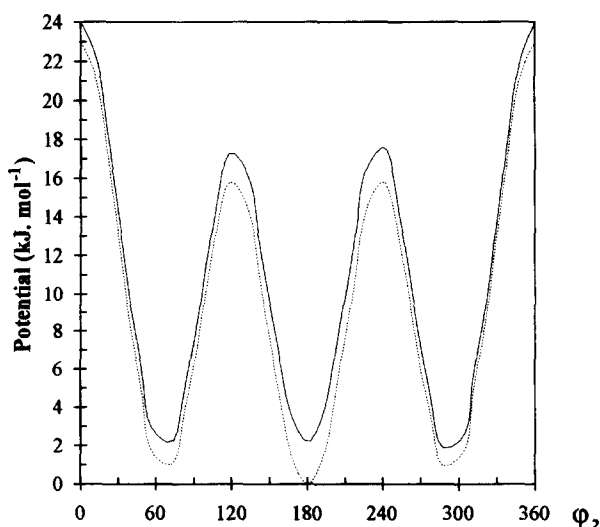
Figure 7 Potential energy (kJ mol^{-1}) profile for rotation of C_b–C_c bond (ϕ_2, with $\phi_3 = 180°$) for PCPMA model compounds

energies obtained from molecular mechanics calculations compare well with the experimental values. This indicates that the intermolecular interactions are negligible. Moreover, the values obtained employing one-unit and three-unit model compounds are very similar, indicating that the length of the chain is not a determining factor in the activation energy associated with the relaxations under study.

In *Table 1* the conformational energies for related polymers are also summarized. The value of the activation energy obtained for PCEMA ($22.05\,\mathrm{kJ\,mol^{-1}}$) is similar to the one obtained for PPMA[6] ($22.05\,\mathrm{kJ\,mol^{-1}}$). In the same way, the value of the activation energy obtained for PCPMA ($24.13\,\mathrm{kJ\,mol^{-1}}$) is similar to that obtained for PnBMA[3] ($22.88\,\mathrm{kJ\,mol^{-1}}$). The similarity of the values obtained is in accordance with the fact that the single difference between these polymers is the substitution of the terminal chlorine group in the side chain for a methyl group.

Detailed study of the γ peaks

In order to obtain more detailed information about this relaxation we have applied the Eyring equation:

$$f = \frac{kT}{2\pi h} \exp\left(\frac{\Delta G}{RT}\right) \tag{1}$$

where k, h and R are the Boltzmann, Planck and gas constants, respectively, and ΔG is the Gibbs free energy of the barrier to the relaxation process, which is related to the activation enthalpy ΔH and activation entropy ΔS by $\Delta G = \Delta H - T\Delta S$. This leads to

$$\ln \frac{f}{T} = \ln \frac{k}{2\pi h} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{2}$$

where the ΔH and the activation energy E_a given by the Arrhenius equation are related by $E_a = \Delta H + RT$. The values of ΔH and ΔS were directly determined from $\ln(f/T)$ *versus* $1/T$ plots and the results obtained are summarized in *Table 2*. The low value of the activation entropy suggests, according to Starkweather[13-16], that the dielectric γ process is a simple secondary relaxation.

In order to fit the observed absorption to an empirical model, the Fuoss-Kirkwood equation[14] was used to fit the experimental data according to

$$\epsilon'' = \epsilon''_{max} \cdot \mathrm{sech}\, mx \tag{3}$$

where m is a parameter dealing with the broadening of the relaxation and

$$x = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{max}}\right) \tag{4}$$

where E_a is the activation energy, T_{max} is the temperature at the peak maximum, and m is an empirical parameter that increases as the broadening of the relaxation increases, in such a way that its value is 1 for a Debye

Table 2 Eyring's equation parameters

Polymer	ΔH ($\mathrm{kJ\,mol^{-1}}$)	ΔS ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
PCEMA	20.787	0.3985
PCPMA	23.171	0.3761

Table 3 Values of the parameter m of the Fuoss-Kirkwood equation and relaxation strength, $\Delta\epsilon$, of the relaxation process for both compounds

f(kHz)	m	$\Delta\epsilon$	m	$\Delta\epsilon$
100	0.146	1.225	0.162	1.951
50	0.137	1.328	0.161	1.867
20	0.149	1.204	0.170	1.722
10	0.147	1.239	0.165	1.667
5	0.143	1.141	0.162	1.613
2	0.150	1.063	0.165	1.522
1	0.143	1.075	0.164	1.523
0.5	0.137	1.093	0.169	1.389

type peak. Since the γ relaxation obeys Arrhenius behaviour with an activation energy presented in *Table 1*, the plot of $\cosh^{-1}(\epsilon''_{max}/\epsilon'')$ *versus* $1/T$ permits us to obtain m for the different isochrones.

The values of m parameter given in *Table 3* do not show a noticeable dependence on the frequency of the isochrone. The low value of this parameter, in both cases, seems to be an indication of the distributed and cooperative character of the process.

The strength of the γ relaxation $\Delta\epsilon_\gamma$, commonly determined from Cole-Cole plots, was evaluated in our case by means of the relation[18]:

$$\Delta\epsilon_\gamma = 2\frac{\epsilon''_{max}}{m} \tag{5}$$

obtained from equations (3) and (4). Values of this quantity obtained using values of m obtained from isochrones are also summarized in *Table 3*.

CONCLUSIONS

The molecular mechanics calculations strongly support the idea that the molecular mechanism of the γ relaxation is a limited rotation around the C_b–C_c bond.

The small difference in the value of activation energy obtained from molecular mechanics calculations and from dielectric experimental data indicate that the intermolecular interactions are negligible.

The barriers calculated by molecular mechanics calculations are very similar to those obtained by molecular mechanics calculations for other polymers structurally related to PCEMA and PCPMA, such as PPMA[6] and PnBMA[3], respectively. However, it is interesting to emphasize that the calculated barriers for PCEMA and PCPMA are somewhat higher than those corresponding to PPMA and PnBMA polymers. Probably, that originates from the fact that, in our compounds, we have instead of methyl groups the more voluminous chlorine atoms, and for this reason, we can expect that, in our case, the hindrance to the movement is higher.

The low value obtained for the m parameter, related to the broadening of the relaxation, in the Fuoss-Kirkwood equation[17], is an indication of the distributed and cooperative character of the process. In this sense, Shimizu *et al.*[3] were suggesting that in the case of PnBMA (related to PCPMA) there are two coupled γ and γ' peaks assigned to the rotation of the n-propyl group and the terminal ethyl group. In this sense, we could

explain the low value of the *m* parameter obtained as a consequence of two coupled relaxations.

ACKNOWLEDGEMENTS

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