Dynamic Mechanical and Dielectric Relaxational Behavior of Poly(cyclohexylalkyl methacrylate)s

Ricardo Díaz Calleja,[†] Abel García-Bernabé,[†] Enrique Sánchez-Martínez,[‡] Andrea Hormazábal,[§] Ligia Gargallo,[§] Fernando González-Nilo,[§] and Deodato Radić*,[§]

Departamento de Termodinámica Aplicada, Universidad Politécnica de Valencia, Apartado 22012, E-46071, Valencia, Spain; Departamento de Ingenieria Electrónica, Universidad Politécnica de Valencia, Apartado 22012, E-46071, Valencia, Spain; and Departamento de Química Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

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ABSTRACT: The dynamic mechanical and dielectric behavior of three poly(cyclohexylalkyl methacrylate)s with different spacer groups has been studied. The study was performed by determining the components of the complex relaxation modulus E^* and the complex dielectric permittivity ϵ^*. Results are discussed in terms of the effect of the side chain structure and the insertion of flexible spacer groups. Molecular dynamic calculations for the repeating unit of the polymers under study are analyzed. Close to room temperature the interconversion between axial and equatorial conformations is not observed whitin the total time of 5 ns. The analysis was then performed from 1000 to 1500 K, and the results were extrapolated to lower temperatures. By this way the fraction of axial and equatorial conformations was calculated. The free energy change against the number of carbon atoms in the side chain is in excellent agreement with the experimental data. This means that the γ relaxation associated with the chair-to-chair conformational change in the cyclohexyl group is also influenced by the length of the spacer group. The molecular dynamics approach allows to observe the relative incidence of the two conformations of the cyclohexyl group which can be related to the motions responsible for the γ relaxation.

Introduction

Polymers containing long side chains with cyclohexyl rings are able to show several conformational states.[1−6] The chains have a large number of degrees of freedom which can produce several molecular motions. This structural fact produces a great variety of transitions and relaxations when the material is affected by mechanical or dielectric force fields. Moreover, the flexibility of the saturated ring also allows to flipping (chair-to-chair) motions of the cyclohexyl group. These motions have been attributed as the responsible of the molecular origin that produce rapid relaxation processes in dynamic mechanical as well as dielectric measurements. From this interpretation, Heijboer[1,7] suggests that the ostensible subglass absorption exhibited by the mechanical spectra of polymers with cyclohexyl groups is produced by flipping motion of the ring. It is well-known that the chair-to-chair motions in the cyclohexyl ring produces a mechanical relaxation at −80 °C at 1 Hz as reported by Heijboer.[1] A mechanism of this type was also suggested to explain the subglass absorption appearing in the dielectric relaxation spectrum of poly(2-chlorocyclohexyl acrylate) (P2ClCHA).[8] However, NMR studies[9] and molecular dynamics calculations[10] performed on poly(2-chlorocyclohexyl isobutyrate), a model compound of P2ClCHA, show that chair-to-chair transitions on the cyclohexyl group could not be held the only responsible for the subglass absorption observed in the dielectric relaxation spectra of the polymer at −80 °C (1 Hz).

Recently we have reported the dielectric and mechanical behavior of poly(cyclohexylmethyl methacrylate) (PCHMM).[2,3] This polymer shows a variety of absorptions due to the versatility of its structural moiety. The effect of the flexible spacer groups on the dynamic mechanical and dielectric behavior of polymers should be taken into account in order to gain confidence about the molecular origin of the relaxations in this kind of material. By this way it seems interesting and necessary to compare the results mentioned above with a polymer containing the cyclohexyl group with a longer spacer. Molecular dynamics procedures should be a powerful tool in order to elucidate the molecular origin of the motions responsible for the observed relaxations and on the effect of the chemical structure over the conformational changes of these polymers.

The aim of the present work is to analyze the relaxational behavior of poly(cyclohexylethyl methacrylate) (PCHEM), poly(cyclohexylpropyl methacrylate) (PCHPM), and poly(cyclohexylbutyl methacrylate) (PCHBM) and to compare their behavior with the two first members of the series poly(cyclohexyl methacrylate) (PCHM)[1] and poly(cyclohexylmethyl methacrylate) (PCHMM).[2] By using an appropriate molecular dynamics package, it should be possible to simulate the experimental results obtained by classical relaxational techniques.

Experimental Section

Monomer and Polymer Preparation. Cyclohexylethyl methacrylate (CHEM), cyclohexylpropyl methacrylate (CHPM), and cyclohexylbutyl methacrylate (CHBM) were obtained by reaction of methacryloyl chloride with the corresponding cyclohexyl alcohol using triethylamine as acid acceptor at reflux temperature in toluene solution following a procedure previously reported for related monomers.[2,11] Radical polym-

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[†] Departamento de Termodinámica Aplicada, Universidad Politécnica de Valencia.

[‡] Departamento de Ingenieria Electrónica, Universidad Politécnica de Valencia.

[§] Pontificia Universidad Católica de Chile.

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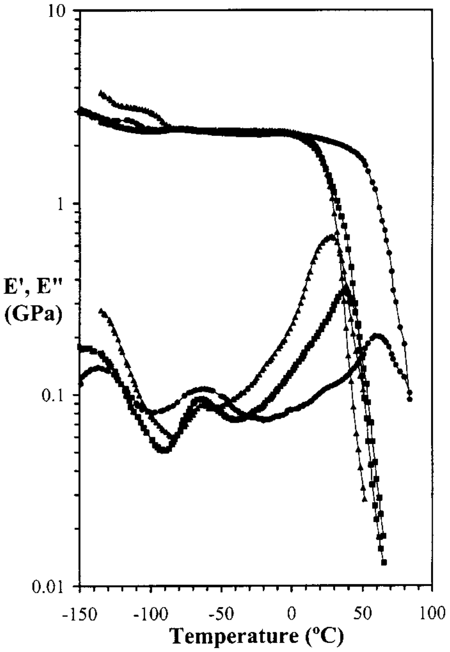

Figure 1. Storage modulus and loss modulus for PCHEM (●), PCHPM (■), and PCHBM (▲) at 10 Hz.

erization was achieved in toluene solution under vacuum using α,α′-azobis(isobutyronitrile) as initiator at 50 °C for 48, 36, and 24 h for CHEM, CHPM, and CHBM, respectively. Polymers were purified by successively reprecipitation in THF with methanol. The calorimetric glass transition temperature (T_g) measured at 10 °C/min are 332, 302, and 293 K, respectively.

Dynamic Mechanical Measurements. The storage and loss components of the complex relaxation modulus E^* were obtained with a Rheometric DMTA MarkII in double cantilever flexural mode. The experiments were carried out on molded samples of 1 × 10 × 8.5 mm^3 at a heating rate of 1 °C/min at 0.3, 1, 3, 10, and 30 Hz from −150 °C up to a temperature close to the glass transition. In the vicinity of T_g, the measurements were made in isothermal conditions at 5 °C steps.

Dielectric Measurements. The real and imaginary parts of the complex dielectric permittivity ϵ^* were measured in a dry nitrogen atmosphere with a DEA 2970 apparatus from TA Instruments. The heating history was similar to that used in the mechanical measurements. Twenty-six frequencies in the range 10^{-1}−10^5 Hz were used.

Molecular Dynamics Calculations. The programs Cerius 2 (MSI) were used on an O2 (R10000) SGI workstation to build three-dimensional models for the repeating unit of the polymer in study, and dynamics modules (MSI) were employed for energy minimization and molecular dynamics calculations. All calculations were done with force field PCFF (MSI), and a cutoff for van der Waals and Coulombic interaction was 10 and 12 Å, respectively. The structures were minimized (steepest descent and conjugate gradient algorithm) and followed by a molecular dynamics simulation of 5 ns at different temperatures (1000−1500 K).

Results and Discussion

Dynamic Mechanical Measurements. Figure 1 shows the storage and loss tensile moduli for poly(cyclohexylethyl methacrylate) (PCHEM), poly(cyclohexylpropyl methacrylate) (PCHPM), and poly(cyclohexylbutyl methacrylate) (PCHBM) at 10 Hz. In this figure can be observed four relaxation peaks. At low temperature two relaxations are observed labeled as δ and γ, respectively. Another two relaxations are observed at high temperature (β and α), the last one corresponding to the glass transition temperature. The β relaxation is observed as a shoulder of the α relaxation. This fact precludes the analysis of the β relaxation.

Table 1. Parameters of Fuoss−Kirkwood Equation for δ and γ Relaxations of PCHEM

f (Hz)	$E''_{\max\delta}$ (GPa)	m_δ	$T_{\max\delta}$ (K)	ΔE_δ (GPa)	$E''_{\max\gamma}$ (GPa)	m_γ	$T_{\max\gamma}$ (K)	ΔE_γ (GPa)
30	0.142	0.20	139	1.42	0.080	0.37	221	0.43
10	0.139	0.20	135	1.39	0.083	0.33	213	0.51
3	0.132	0.20	134	1.31	0.081	0.44	198	0.37
1	0.128	0.18	131	1.44	0.082	0.50	192	0.33
0.3	0.127	0.17	128	1.52	0.087	0.48	186	0.37

Table 2. Parameters of Fuoss−Kirkwood Equation for δ and γ Relaxations of PCHPM

f (Hz)	$E''_{\max\delta}$ (GPa)	m_δ	$T_{\max\delta}$ (K)	ΔE_δ (GPa)	$E''_{\max\gamma}$ (GPa)	m_γ	$T_{\max\gamma}$ (K)	ΔE_γ (GPa)
30	0.444	0.29	134	3.03	0.185	0.67	220	0.67
10	0.444	0.30	131	3.00	0.188	0.67	210	0.67
3	0.424	0.30	128	2.80	0.192	0.64	202	0.64
1	0.418	0.31	126	2.72	0.199	0.57	196	0.57
0.3	0.401	0.29	123	2.75	0.209	0.52	198	0.52

Table 3. Activation Energy and tan $\delta_{\max}$ (10 Hz) for δ and γ Relaxations

polymer	$E_{a\delta}$ (kcal mol^{-1})	$E_{a\gamma}$ (kcal mol^{-1})	tan $\delta_{\max\delta}$	tan $\delta_{\max\gamma}$
PCHM[1]		11.3		0.081
PCHMM[3]		12.5		0.051
PCHEM	9.06	11.19	0.05	0.045
PCHPM	6.46	10.93	0.063	0.040
PCHBM		9.61		0.037

The δ and γ relaxations have been deconvoluted for the Fuoss−Kirkwood[12] empirical expression (eq 1) for PCHEM and PCHPM. The parameters obtained at different frequencies are given in Table 1.

$$E = \sum_{i=\delta,\gamma} E''_{\max_i} \operatorname{sech}\left(m_i \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\max_i}}\right)\right) \qquad (1)$$

where E_a is the activation energy, R is the gas constant, $T_{\max}$ is the temperature where E'' has a maximum value ($E''_{\max}$), and m is a parameter ($0 < m \leq 1$) that is related to the broadness of the peak. The strength of the two relaxations (ΔE) was calculated using the expression

$$\Delta E = \frac{2E''_{\max}}{m} \qquad (2)$$

The values of the m parameter in Tables 1 and 2 show that the γ relaxation is broader than the δ relaxation. This indicates that γ relaxation probably involves a more complex molecular motion than δ relaxation. The activation energies for δ and γ relaxations of the three polymers obtained from an Arrhenius plot are summarized in Table 3. A decreasing of the activation energy with increasing of the length of the spacer group is observed. Comparison of tan δ values at 10 Hz of the five members of this family of polymers (Figure 2a,b) shows that the maximum of the tan δ value for the γ relaxation decreases as the length of the spacer group increases. Instead, the maximum of the loss tangent of the δ relaxation increases as the length of the spacer group increases. δ relaxation is not observed in the polymer spacer group, i.e., poly(cyclohexyl methacrylate).[1] This relaxation is attributed to another kind of motion of the cyclohexyl ring like small rotations of the

Table 4. Parameters of Fuoss–Kirkwood Equation in Frequency Domain for α Relaxation

	T (°C)	$E''_{\max}$ (GPa)	m	$f_{\max}$ (Hz)	ΔE (GPa)
PCHEM	65	0.22	0.22	0.68	1.98
	70	0.207	0.30	4.15	1.40
	75	0.205	0.30	16.63	1.35
PCHPM	30	0.928	0.23	1.70	8.16
	35	0.947	0.32	6.43	5.84
	40	0.954	0.42	16.64	4.57
PCHBM	25	0.465	0.40	11.13	2.31

Table 5. Parameters of Havriliak–Negami Eq 4 for α Relaxation at Temperature Indicated

polymer	T (°C)	ΔE (GPa)	$\bar{\alpha}$	$\bar{\beta}$	τ (s)
PCHEM	70	1.29	0.26	22	4450
PCHPM	35	5.76	0.29	84	32
PCHBM	25	2.30	0.38	2.8	0.70

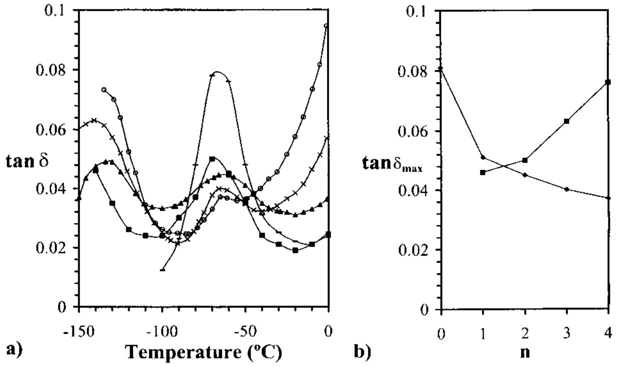

Figure 2. (a) Temperature dependence of the tan δ at 10 Hz for (—) PCHM (from ref 1), (■) PCHMM (from ref 3), (▲) PCHEM, (×) PCHPM, and (○) PCHBM. (b) Variation of the intensity of the maximum of tan δ with the number carbon atoms of the spacer group for the γ (◆) and δ (■) relaxations.

group as a whole around the bond containing the connecting link. If the spacer (connecting link) is absent, those motions would be restrained. This result indicates that the spacer group participate in both the δ and γ relaxations.

The α relaxation was analyzed using the Fuoss–Kirkwood equation (eq 3) in the frequency domain at constant temperature.

$$E'' = E''_{\max}\,\mathrm{sech}\left[m \ln\left(\frac{f}{f_{\max}}\right)\right] \tag{3}$$

where $f_{\max}$ is the frequency for which the loss modulus E'' attains a maximum value $E''_{\max}$. The results are summarized in Table 4. Alternatively, we can use the skew Havriliak–Negami[13] equation for the analysis of the α mechanical relaxation. The new equation[14] (eq 4) takes into account the asymmetric character of the α relaxation.

$$E^* = E_0 + \frac{E_\infty - E_0}{(1 + (j\omega\tau)^{-\bar{\alpha}})^{\bar{\beta}}} \tag{4}$$

where E_0 and E_∞ are the relaxed and unrelaxed modulus, respectively, and τ is the relaxation time where $\bar{\alpha}$ and $\bar{\beta}$ are two parameters related to the shape and skewness of the Argrand plot. As $E_0 \ll E_\infty$, E_0 may be neglected and $\Delta E = E_\infty - E_0 \approx E_\infty$. The values of E_∞ and the parameters $\bar{\alpha}$, $\bar{\beta}$, and the relaxation time (τ) are compiled in Table 5. Figure 3 shows the Argand plot for PCHPM at 35 °C. The results show that the value of ΔE for Fuoss–Kirkwood and Havriliak–Negami models are similar.

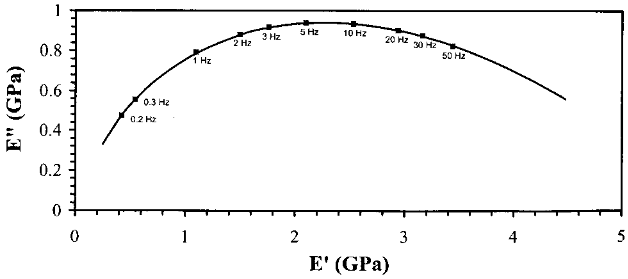

Figure 3. Argrand plot of PCHPM at 35 °C. The solid lines are the HN equation, and symbols (■) are the experimental data with its frequency.

The temperature dependence of the α relaxation in the frequency domain can be conveniently analyzed by means of the Vogel–Fulcher–Tamman–Hesse (VFTH) theory[15–17] according to

$$\ln(f_{\max}) = A - \frac{m}{T - T_\infty} \tag{5}$$

where A and m are constant, and T_∞ in this equation is an empirical parameter related to the Kauzmann temperature or the temperature at which the conformational entropy is zero. The T_∞'s obtained are 210, 225, and 187 K for PCHEM, PCHPM, and PCHBM, respectively.

Comparison of VFTH equation with Doolittle equation yields

$$\frac{\phi}{B} = \frac{T - T_\infty}{m} \tag{6}$$

which relates the free volume that appears in the Doolittle equation with the value of m in the VFTH relationship. The relative free volumes at T_g are 3.5, 3.6, and 3.6% for PCHEM, PCHPM, and PCHBM, respectively, which is in relatively good agreement with the free volume theory.

To get a more compact source of information about the mechanical properties, the so-called reduced frequency nomograph[18] for the three polymers was performed. First, it is necessary to generate a master curve using the time–temperature superposition. This procedure first suggested by Leaderman[19] indicates that the experimental data can be shifted on the horizontal time scale (or frequency) in order to extrapolate it beyond the experimentally measured time frame. The shift factor (a_T) was related with the temperature by Williams–Landel–Ferry (WLF) equation[20] (eq 7).

$$\log(a_T) = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \tag{7}$$

where C_1 and C_2 are constants and T_0 is an arbitrary reference temperature. If T_0 is replaced by T_g (the glass transition temperature) in WLF equation, the constants C_1 and C_2 are "universal" and have the value 17.44 and 51.60, respectively. The T_0 and the constants C_1 and C_2 obtained are shown in Table 5.

The nomographs[21] for PCHEM, PCHPM, and PCHBM are depicted starting by plotting the viscoelastic master curve as a function of reduced frequency ($a_T f$). An auxiliary frequency scale is then constructed as the

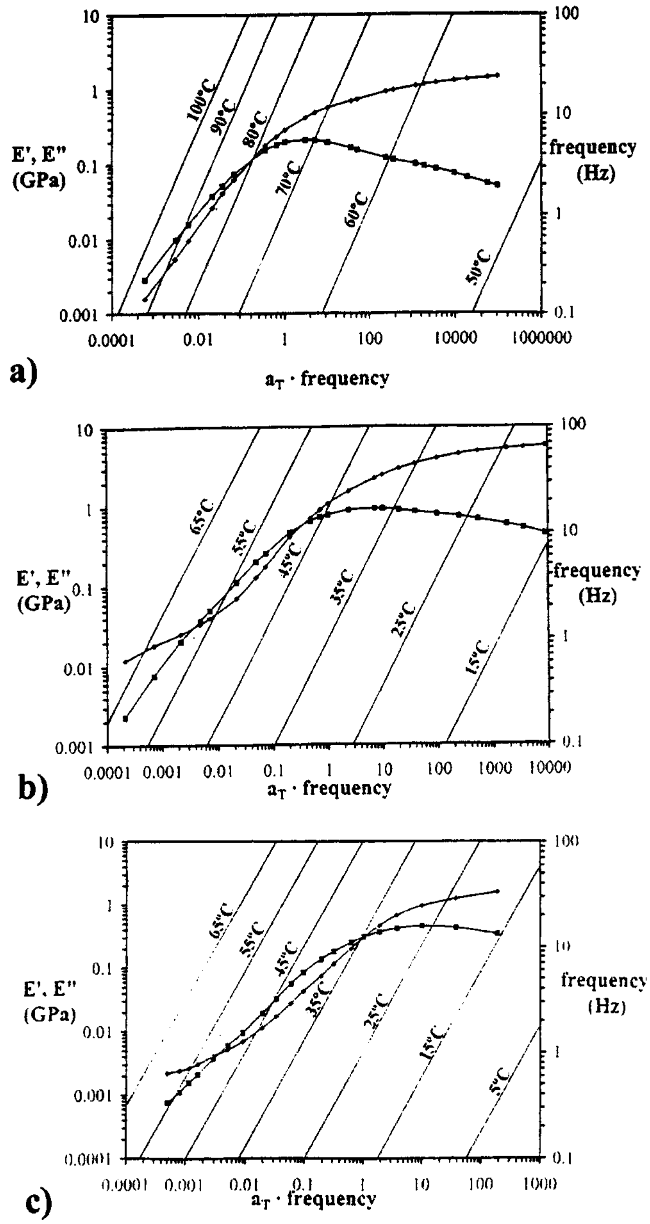

Figure 4. Master curve represented on reduced frequency nomographs of (a) PCHEM, (b) PCHPM, and (c) PCHBM. Symbols are (◆) for storage modulus and (■) for loss modulus. The oblique line represent isotherms with its corresponding temperature.

ordinate on the right-hand side of the graph and the values of the reduced frequency ($a_{Ti}f_j$). f gives rise to a set of corresponding oblique lines representing the temperatures.

Parts a, b, and c of Figure 4 are the nomographs for PCHEM, PCHPM, and PCHBM, respectively. To use the nomographs, we trace a horizontal line (isochrone) at one frequency in the auxiliary frequency scale. The intersection with the isothermal line defines a value of reduced frequency (a_Tf). At this reduced frequency the storage (E') and loss modulus (E'') are found. These nomographs are used very often in the analysis of polymeric materials with technological applications and give information about the mechanical data at temperatures and frequencies out of the experimental range of measurements.

Dielectric Measurements. Dielectric permittivity and loss for the three polymers are shown in Figure 5 at only one frequency for sake of clarity. In this Figure, it can be observed one peak corresponding to the dynamic glass transition. The sub-glass relaxations are very small, and its value lies near the limit of the measurement of the apparatus.

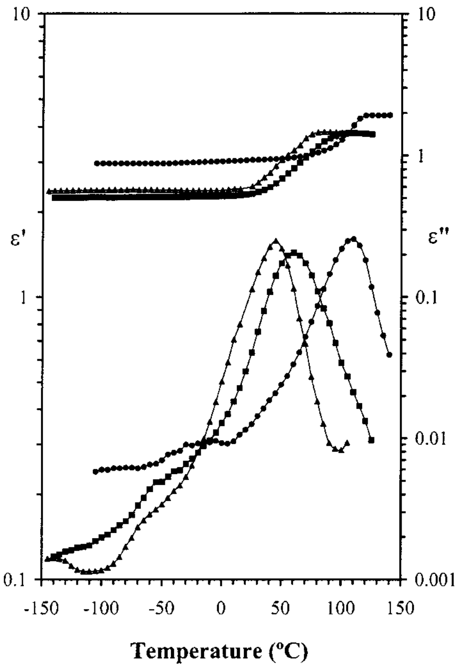

Figure 5. Dielectric permittivity and loss for PCHEM (●), PCHPM (■), and PCHBM (▲) at 100 Hz.

The conductive contribution (ϵ''_c) is separate from the loss permittivity, using a hopping model.[22]

$$\epsilon''_c = \frac{\sigma}{\epsilon\omega^s} \tag{8}$$

where ω is the angular frequency, ϵ the permittivity of the vacuum, σ the conductivity, and s a parameter to determine. The value of s is 0.75 for PCHEM, 0.85 for PCHPM, and 1 for PCHBM. In the case of the PCHBM, the conductivity is described by the Maxwell–Wagner–Sillars[23–25] equation. In the case of PCHEM and PCHPM the observed values of s indicate that together with pure ionic conductivity, new spurious phenomena appear due to partial blocking of the charges near the electrodes. This phenomenon has been systematically observed.[26] Figure 6 represents log ϵ'' vs log ω. Here a different tendency for the slope in the conductive contribution is observed. The activation energy of the conductivity is calculated for the Arrhenius plot of ln σ against T^{-1} (Figure 7). The values of the activation energy are 24.6, 18.1, and 25.8 kcal mol^{-1} for PCHEM, PCHPM, and PCHBM, respectively.

The α relaxation without the conductive contribution was analyzed by Havriliak–Negami[13] (HN) equation.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + (j\omega\tau)^{-\bar{\alpha}})^{\bar{\beta}}} \tag{9}$$

where ϵ_0 and ϵ_∞ are the relaxed and unrelaxed permittivity, respectively, and $\bar{\alpha}$ and $\bar{\beta}$ are two parameters related to the shape and skewness of the Cole–Cole plot. The Havriliak–Negami[13] parameters are summarized in Table 7.

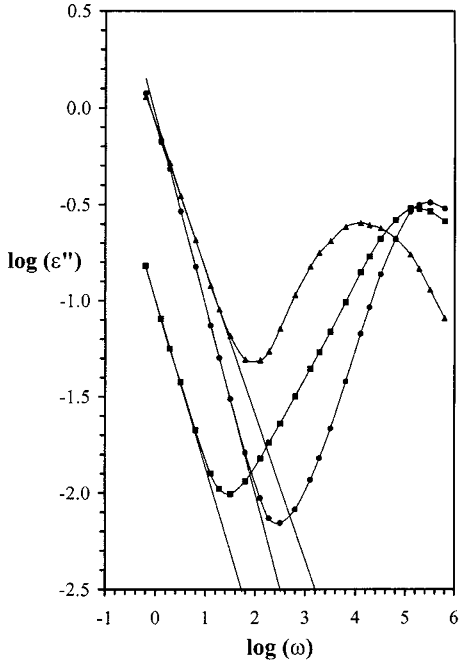

Figure 6. Frequency dependence of the dielectric loss ϵ'' for (▲) PCHEM at 125 °C, (■) PCHPM at 100 °C, and (●) PCHBM at 90 °C. The solid line indicate the conductive contribution with different slopes.

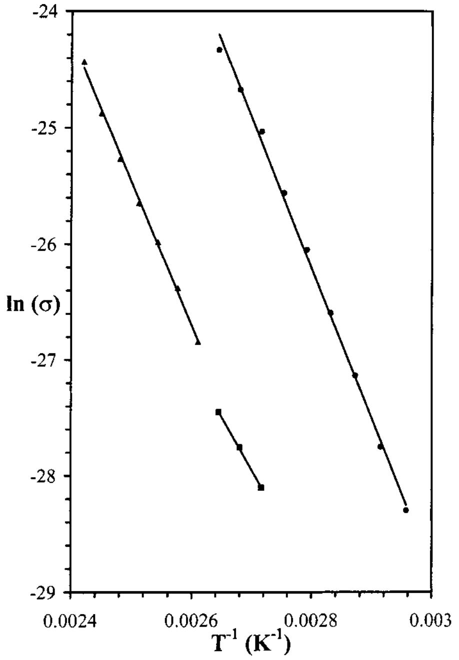

Figure 7. Arrhenius plot for the conductivity of (▲) PCHEM, (■) PCHPM, and (●) PCHBM.

Table 6. Reference Temperature T_0 and Constants C_1 and C_2

polymer	T_0 (°C)	C_1	C_2
PCHEM	70	7.07	46.38
PCHPM	35	17.39	131.63
PCHBM	25	13.94	119.99

Table 7. Parameters of Havriliak–Negami Eq 8 for α Relaxation at Indicated Temperature

polymer	T (°C)	ϵ_∞	ϵ_0	$\bar{\alpha}$	$\bar{\beta}$	τ (s)
PCHEM	90	3.02	4.59	0.42	0.70	0.18
PCHEM	95	3.00	4.51	0.44	0.65	0.058
PCHPM	45	2.13	3.46	0.36	0.78	0.040
PCHBM	45	2.14	3.21	0.60	0.64	2.32×10^{-3}
PCHBM	50	2.16	3.17	0.69	0.60	1.05×10^{-3}

The temperature dependence of dielectric relaxation by Vogel–Fulcher–Tamman–Hesse (VFTH) theory[15–17] was also analyzed. The T_∞ values obtained are 253, 225, and 200 K for PCHEM, PCHPM, and PCHBM, respectively, and the relative free volumes at T_g are 2.6, 3.6, and 3.6% for PCHEM, PCHPM, and PCHBM, respectively, in good agreement with the free volume theory.

Molecular Dynamics Calculations. To get information about the origin of the secondary γ relaxation, molecular dynamics (MD) calculations over the repeating unit were performed. Dynamics at 5 ns for all the systems ($6 \times 5 = 30$ ns of total simulation) were carried out. Close to room temperature (ca. 300 K) the interconversion between axial and equatorial orientations is not observed within the total time of 5 ns allowed to the MD trajectories. The system was then stabilized for 5 ns at six different temperatures, i.e., 1000, 1100, 1200, 1300, 1400, and 1500 K, using PCFF field force. From these data it is possible to calculate the ratio of the fractions of axial and equatorial conformations (f_{eq}/f_{ax}) by using the Boltzmann equation

$$\Delta G = -RT \ln \frac{f_{eq}}{f_{ax}} \tag{10}$$

The $\Delta G/R$ value between these two conformations can be obtained by plotting ln f_{ax}/f_{eq} against T^{-1}.

Exploratory calculations proved that keeping the length of the MD simulations in 5 ns, temperatures as high as 1000 K have to be used to increase the conformational mobility to the point of observing a large number of transitions, thus allowing the evolution of averaged values that are independent of the starting point of the trajectory.[10] Consequently, we have performed simulations at several temperatures from 1000 to 1500 K for each system ($R' = 0$, 1, 2, 3, and 4, R being the number of carbon atoms of the spacer group). Figure 8a shows the variation of $\Delta G/R$ for the conformational chair-to-chair flipping against the number of carbon atoms calculated for the γ relaxation. Comparison of this plot with the experimental one (Figure 2b) is in good agreement. This comparison can be achieved through the analysis of the variation of the intensity of the maximum of tan δ for the γ relaxation (taken from Figure 2b) vs $\Delta G/R$. A linear correlation between actual values of $\Delta G/R$ and the experimental intensity of tan δ was performed. A straight line with a correlation coefficient of 0.982 is obtained. Therefore, free energy change against the number of carbon atoms in the side chain is in excellent agreement with the experimental data which means that the number of carbon atoms of the spacer has an influence on the γ relaxation associated with the chair-to-chair conformational change in the cyclohexyl group. Figure 8b shows the results of the probability distribution for the torsional angle ϕ (see scheme in Figure 8b) obtained at 1000 K for PCHMA and PCHBMA in order to stress the differences in the conformational behavior of the polymers due to the presence of a spacer group. The areas under the peaks of each curve represent the relative incidence of the two conformations allowed to the molecule and thus permit the evaluation of the fractions f_{ax} and f_{eq}. According to these results, when the side group does not have a spacer group, i.e., the cyclohexyl group is directly joined to the ester group, axial conformations are preferred,

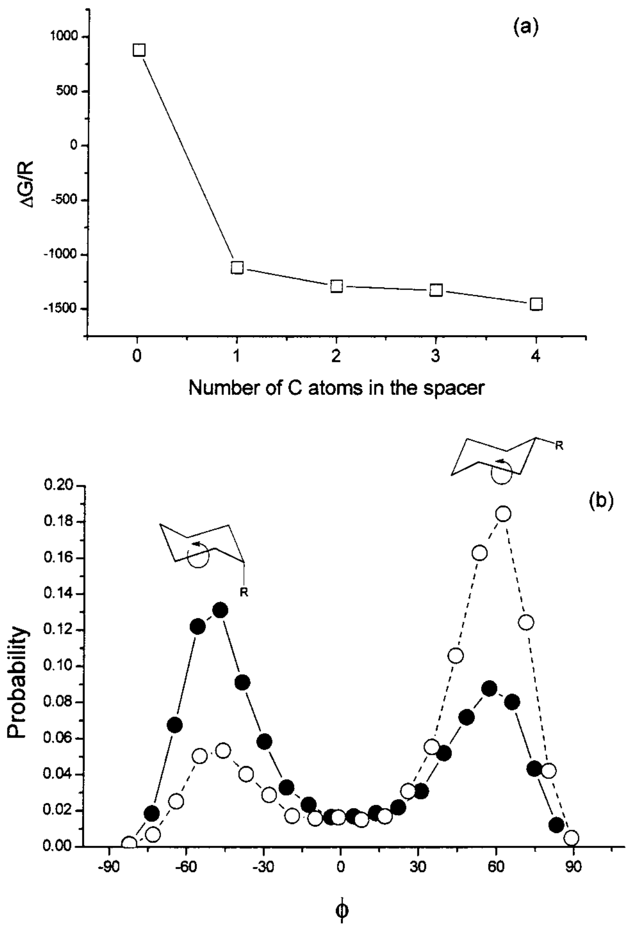

Figure 8. (a) Molecular dynamics simulation results of the variation of free energy change ($\Delta G/R$) of the chair-to-chair conformational change against of the number of the carbon atoms of the spacer group. (b) Probability distribution of the torsional angle ϕ obtained at 1000 K for PCHMA (●) and PCHBMA (○).

but when the spacer group exists, equatorial conformations are preferred. This molecular dynamics approach seems to be useful to explain in part the experimental differences observed in tan $\delta_{\max}$ for the γ relaxation in poly(cyclohexylalkyl methacrylate)s.

Conclusions

This study shows the presence of four distinct mechanical relaxations for the three polymers analyzed, namely δ, γ, β, and α in the temperature range from −150 to 100 °C. The behavior of the α relaxation is similar to that reported for polymers with analogous structures.[26] The δ and γ relaxations of PCHEM and PCHPM have been characterized by Fuoss−Kirkwood equations. The maximum of the loss factor in δ relaxation is lower and the relaxation is broader than the γ relaxation. Therefore, the intensity of the δ relaxation is larger than the γ relaxation. Nevertheless, the height of the loss factor depends on the length of the spacer group what would indicate that the spacer group takes part on both the δ and γ relaxations.

The α relaxation was analyzed by the symmetric equation of Fuoss−Kirkwood and a new model which is very similar to the asymmetric Havriliak−Negami equation used in the analysis of dielectric spectroscopy. According to the T_g values calculated, the free volume can be appropriately described by the free volume theory. Nomographs for the three polymers, i.e., PCHEM, PCHPM, and PCHBM, were obtained.

The dielectric α relaxations were analyzed by using the Havriliak−Negami equation. The sub-T_g relaxations γ and δ are small due probably to the absence of polar groups in the side chain. For this reason γ and δ relaxation are more important in dynamic mechanical than in dielectric force fields.

Molecular dynamics calculations of the free energy for the chair-to-chair conformational change of the cyclohexyl group for the polymers under study are in good agreement with the experimental relaxation data. These results allow us to conclude that the effect of the length of the spacer group also influences the barrier opposite the motion causing the γ absorption associated with the chair-to-chair conformational change. The effect of the spacer on the relaxational behavior can be explained by a conformational analysis of the relative incidence of the two conformations of the cyclohexyl group.

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