7324 *J. Phys. Chem. A* **1997,** *101,* 7324−7329

MD Simulation of the α Dielectric Relaxation of 2-Chlorocyclohexyl Isobutyrate

Enrique Saiz,[†] Evaristo Riande,*[,‡] and Ricardo Díaz-Calleja[§]

Departamento de Química-Física, Universidad de Alcalá, 28871 Alcalá de Henares, Spain, Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006 Madrid, Spain, and Departamento de Termodinámica Aplicada, ETSII, Universidad Politécnica de Valencia, 46022 Valencia, Spain

Received: February 12, 1997; In Final Form: May 2, 1997[⊗]

The temperature dependence of the real ϵ' and loss ϵ'' components of the complex dielectric permittivity ϵ^* of 2-chlorcyclohexyl isobutyrate, obtained in nonisothermal conditions at several frequencies, is reported. The calorimetric glass−liquid transition of the compound is −89 °C. The α relaxation in the frequency domain was obtained at the temperatures of interest, indirectly from these isochrones, and directly from measurements carried out in isothermal conditions. The exponent of the stretch KWW function that describes the relaxation is significantly lower in the former case (≈0.40) than in the latter (≈0.58). The MD trajectory of the rotational angle χ_1, defined as the rotation over the ClC−CO bond of the cyclohexane ring, does not show chair-to-inverse-chair conformation transitions at 300 K within a reasonable computing time, high temperatures being necessary to detect them. The time dependent dipolar autocorrelation coefficient, $\phi(t)$, was obtained from the trajectories of the dipole moment at 300 and 750 K. The autocorrelation function obtained at 300 K predicts an α relaxation that is rather narrow in comparison with that determined with the autocorrelation coefficient evaluated at 750 K. The experimental values of the components of the complex dielectric permittivity are in good agreement with those calculated using the autocorrelation function evaluated at 750 K.

Introduction

As a noncrystallizable liquid approaches the glass transition in the cooling process, molecular mobility is slowed in such a way that the mechanisms that keep the liquid structure in equilibrium do not take place on the time scale of the experiment. Consequently, degrees of freedom of the system appear to be lost. A characteristic of the glass transition is that relaxation mechanisms associated with the responses to perturbations caused by external force fields (mechanical, electric, etc.) exhibit a temperature dependent activation energy for an appreciable range above T_g. The relaxation times are related to the temperature by the empirical Vogel−Tammer−Hess−Fulcher (VTHF) equation[1−3]

$$\tau = \tau_0 \exp\left(\frac{m}{T - T_0}\right) \tag{1}$$

In this expression m, T_0, and τ_0 are adjustable parameters. There are, however, some common features related with the values of m and T_0 for different glassy systems. For example, the value of T_0 is for most systems about 50 K below that of T_g. In liquids that become glassy when supercooled but also can develop crystalline order if cooled slowly, the specific heat of the glass and the crystal has the same value at T_0 . For this reason, T_0 is currently assumed to be the Kauzmann temperature;[4,5] that is, the temperature at which the conformational entropy of the system is zero. On the other hand, comparison of the VTHF and Doolittle[6] equations predicts that the relative free volume at T_g is given by

$$\frac{\Phi_g}{B} = \frac{T_g - T_0}{m} \tag{2}$$

Here B can be viewed as a parameter depending on the ratio v^*/v_m, where v^* is the critical volume necessary for a relaxation process to take place and v_m is the volume of the segments intervening in the relaxation.[7] In many glass-forming systems the value of Φ_g/B lies in the range[8] 0.025 ± 0.005.

The glass transition relaxation process depends on the energy barriers opposing conformational transitions in such a way that the lower the barriers, the lower/larger the temperature/frequency at which the process appears. This is especially observed in polymers where the introduction of bulky substituents in the chains decreases the molecular flexibility and shifts the glass−rubber relaxation or α process to lower frequencies. The glass−rubber relaxation in polymers has traditionally been associated with generalized micro-Brownian motions of the chains. The fact that the location of the glass−rubber process of these systems, either in the loss-temperature plane or in the frequency domain, only shows a small dependence on molecular weight suggests that some sort of cooperativity in the conformational transitions occurs.[9] Otherwise the volume swept by the chains would largely increase with increasing molecular weight so that, at a given temperature, the relaxation would shift to lower frequencies in the frequency domain. The enormous internal degrees of freedom of molecular chains together with the molecular cooperativity render difficult the simulation of the glass−liquid process by means of realistic methods. However, this analysis may be amenable for low molecular weight glass-forming systems if intermolecular interactions are neglected.

In our laboratories, efforts have successfully been devoted to simulate equilibrium conformational dielectric properties of low molecular weight compounds that could be used as molecular models of flexible side groups of asymmetric polymer chains, specifically acrylic and methacrylic polymers. Thus MD simulation methods were used to calculate the mean-square dipole moments from the integral of the trajectories of the dipole moments in the conformational space.[10−12] These studies are extended in this work to simulate the time dependent dipolar autocorrelation coefficient of 2-chlorocyclohexyl isobutyrate

---

[†] Universidad de Alcalá.

[‡] CSIC.

[§] Universidad Politecnica de Valencia.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S1089-5639(97)00541-0 CCC: $14.00

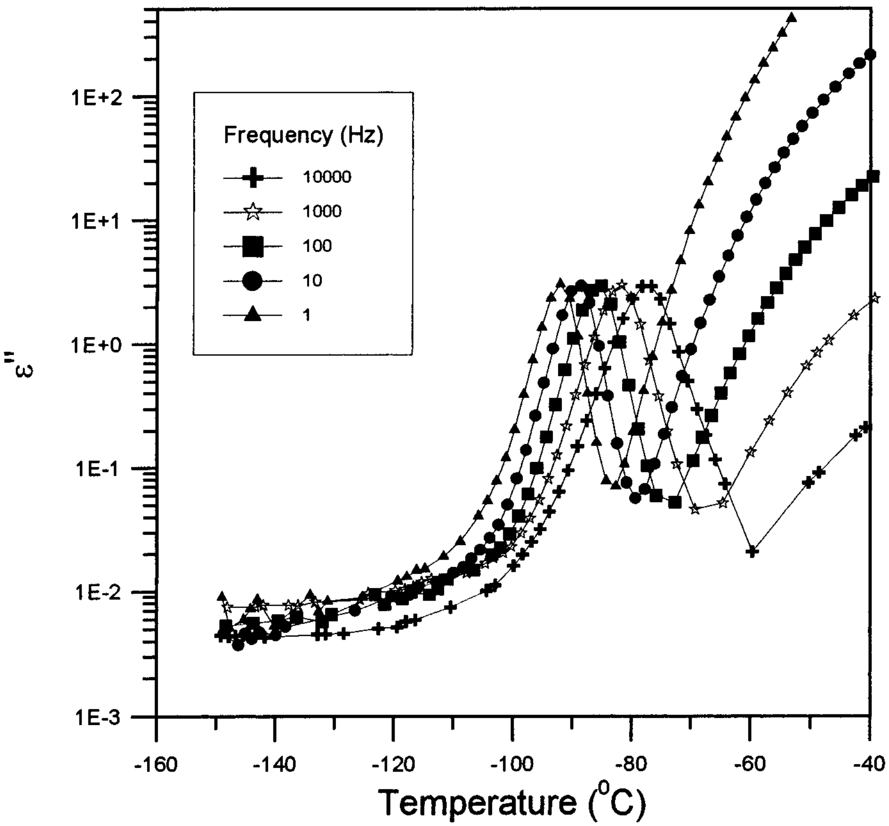

Figure 1. Temperature dependence of the dielectric loss for 2-chlorocyclohexyl isobutyrate at the frequencies indicated.

(CCHI) and to further determine by standard methods the frequency dependence of both the real ε′ and loss ε″ components of the complex dielectric permittivity ε* of this compound. The values of these quantities thus determined are compared with those experimentally obtained.

Experimental Part

2-Chlorocyclohexyl isobutyrate (CCHI), model compound for the repeating unit of poly(2-chlorocyclohexyl acrylate), was obtained by condensation of 2-chlorocyclohexanol and isobutyric acid in a solution of refluxing toluene, using an equimolecular amount of *p*-toluenesulfonic acid and boric acid (2%) as catalyst. The solvent was evaporated and the product was isolated from the reaction medium by column chromatography (Kiesel-gel 60, Merck) using a mixture of chloroform/ethane (75/25, v/v) as eluent.

The ^{1}H NMR spectrum of CCHI was registered in chloroform solution with a Varian XL-300 at 300 MHz. The hydrogen bound to the C_2 atom of the cyclohexyl ring gives eight signals in the interval 3.786−3.865 δ, while the hydrogen bound to the C_1 atom gives six signals in the range 4.729−4.806 δ. The position of these signals in the spectrum indicates that these hydrogens are in an axial position in the cyclohexyl ring with a chair conformation, and consequently, the O and Cl atoms are equatorial. This arrangement is also supported by the values of the H,H vicinal coupling constants between the hydrogens of the C_1, C_2, and C_3 carbons as well as of the C_1, C_2, and C_6 carbons. The values of the coupling constants are $J(H_{2a},H_{1a}) = 9.0$ Hz, $J(H_{2a},H_{3a}) = 10.4$ Hz, and $J(H_{2a},H_{3e}) = 4.2$ Hz for the hydrogen at the C_2, and $J(H_{1a},H_{2a}) = 9.2$ Hz, $J(H_{1a},H_{6a}) = 9.4$ Hz, and $J(H_{1a},H_{6e}) = 4.6$ Hz for the hydrogen at C_1. Accordingly, the configuration with conformations in which the location of the O/Cl atoms is eq/ax or ax/eq is not detected in the spectrum.

The glass transition temperature of the compound was measured with a Perkin-Elmer DSC-4 calorimeter at a heating rate of 10 °C/min. The value of this quantity, taken at the onset of the low-temperature side of the thermogram, was −89 °C.

Experimental values of the loss ε″ and real ε′ components of the dielectric permittivity of CCHI were obtained with a three terminal plane condenser and a capacitance apparatus TA-DEA operating in the frequency range 10^{-4}−30 kHz.

Experimental Results

Isochrones showing the temperature dependence of the dielectric loss on temperature are shown in Figure 1. These results were obtained from low to high temperature at a heating rate of 1 °C/min. The curves only exhibit a prominent absorption associated with the glass−rubber relaxation, called the α process, with maxima located at −92, −88, −82, and −78 °C at 1, 10, 10^3, and 10^4 Hz, respectively. Interfacial and conductive effects that preclude the possibility of obtaining the maxima of the peaks at low frequencies in poly(2-chlorocyclohexyl acrylate) are not important in the CCHI molecule studied in this work. It is worthy to note that subglass relaxations were not detected in the interval of temperature in which the measurements were performed.

The α relaxation in the frequency domain was obtained from the isochrones. An example of the α relaxation thus obtained at −80 °C is shown in Figure 2. With the aim of investigating the effect of nonthermal equilibrium conditions on the shape of the curve of this relaxation, this process was further measured in thermal equilibrium. For comparative purposes these results are also plotted in Figure 2. It can be seen that the curves obtained in thermal equilibrium are narrower than those determined from the isochrones, and consequently, the dielectric measurements should be performed in isothermal conditions. Otherwise curves are obtained that may lead to the wrong conclusion that the process has a wider distribution of relaxation times (or a lower value of the stretch exponent when the results are analyzed in terms of the KWW equation) than it really has.

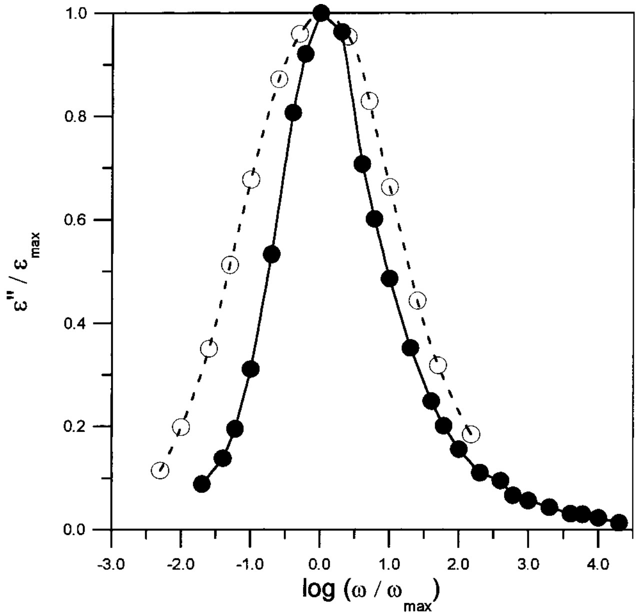

Figure 2. The α relaxation at −80 °C in the frequency domain for 2-chlorocyclohexyl isobutyrate. Empty and filled symbols represent, respectively, results obtained from isochrones measured in nonthermal equilibrium and from data measured at −80 °C at several frequencies.

Theoretical Calculations

The phenomenological theory of linear relaxation processes predicts that the complex dielectric permittivity ϵ^* is given by[13−15]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = 1 - \int_0^\infty \phi(t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \qquad (3)$$

where ω is the frequency of the perturbation field, ϵ_0 and ϵ_∞ are the dielectric permittivities at frequencies zero and infinite, respectively, and $\phi(t)$ is the dipolar correlation coefficient whose extreme values are 1 at time $t = 0$ and zero at $t \to \infty$, respectively. The dipolar correlation coefficient is expressed by the stretch KWW function:[16,17]

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \qquad (4)$$

where τ_0 is a mean relaxation time and β lies in the interval $0 < \beta \leq 1$. The value of β increases as the complexity of the relaxation process decreases. For a process of Debye type, that is, a process with a single relaxation time, the value of β is 1.

In molecular terms, the normalized time dependent dipolar correlation coefficient $\phi(t)$ can be expressed by

$$\phi(t) = g(t) = \frac{\langle \sum_{i,j} \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(t)\rangle}{\langle \sum_{i,j} \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(0)\rangle} = \frac{\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle + \sum_{i\neq j}\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(t)\rangle}{\langle \mu^2\rangle_i + \sum_{i\neq j}\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(0)\rangle} \qquad (5)$$

where brackets mean averages; $\langle \mu^2\rangle_i$ is the mean-square dipole moment of the molecule i; $\mu_i(t)$ and $\mu_j(t)$ represent, respectively, the evolution with time of the dipole moment of the molecules i and j. Because dipolar correlations sharply decrease with distance between dipoles, intermolecular cross-correlation contributions may be considered negligible and $\phi(t)$ is customarily written as

$$\phi(t) = g(t) = \frac{\langle \mu_i(0)\,\mu_i(t)\rangle}{\langle \mu^2\rangle} \qquad (6)$$

where $\phi(t)$ (or $g(t)$) is called the time dependent dipolar autocorrelation coefficient.

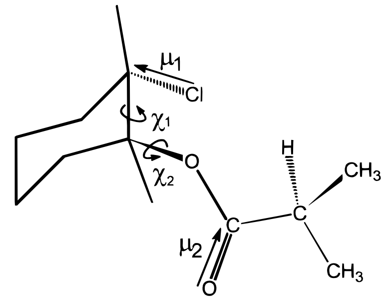

Figure 3. The molecule of 2-chlorocyclohexyl isobutyrate (CCHI) shown in the conformation that places both the chlorine atom and the ester residue at the equatorial positions of the cyclohexane ring.

A rough sketch of the CCHI molecule with both the chlorine atom and the ester residue located at the equatorial positions of the cyclohexane ring is represented in Figure 3. The rotational angle χ_1 is defined as the rotation over the ClC−CO bond of the cyclohexane ring and therefore monitors the conformation of the cycle. The rotation over the CC−OC* bond that governs the orientation of the ester residue with respect to the ring is represented by χ_2. Values of 180° were assigned to the trans orientation of both rotational angles. In the former rotation, the trans orientation, $\chi_1 = 180°$, corresponds to the conformation in which both substituents are located at axial positions, while the conformation represented in Figure 3 that has both groups in equatorial positions corresponds to $\chi_1 \approx 60°$.

The arrows in Figure 3 indicate the approximate direction (pointing from negative to positive centers of charge) of the main contributions to the total dipole moment of the molecule that come from the C−Cl bond and the ester residue. However, these contributions are indicated only for illustrative purposes to facilitate intuitive interpretations. The actual computation of the molecular dipole moment along the MD trajectory in the phase space was performed by assigning partial charges to all the atoms of the molecule of CCHI and computing the center of gravity of positive and negative charges for each conformation adopted by the molecule during the simulation. The partial charges were calculated using the AMPAC[18] program and the AM1 procedure. MD simulations were performed with the Sybyl molecular modeling[19] package, utilizing the Tripos force field,[20] for an isolated molecule. Coulombic contributions to the potential energy were obtained assigning a value of 4 to the static dielectric permittivity. The geometry of the molecule was optimized with respect to bond lengths, bond angles, and rotations, and the resulting conformation was used as the starting point for the MD trajectory. The leapfrog algorithm[21] was used to integrate the Newton equation of motion for each atom with a time step of 1 fs, i.e. 10^{-15} s. The molecule was first warmed from 0 K to the working temperature with increments of 20 K, allowing a relaxation period of 500 time steps at each intermediate temperature. The simulation was continued for 2×10^6 time steps at constant temperature, and the data of interest (i.e., geometry, energy, dipole moment, and rotations) were recorded at regular time intervals.

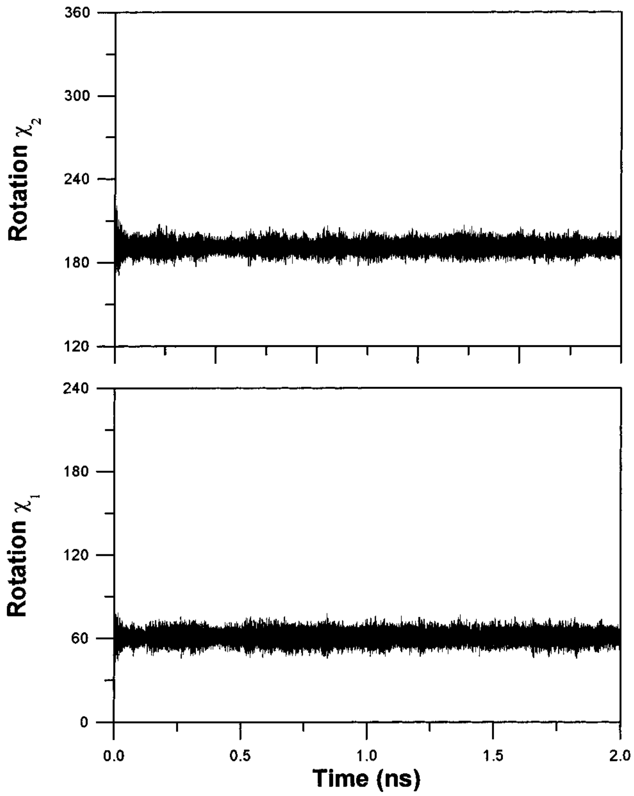

Figure 4. Time dependence of the rotational angles χ_1 (governing the conformation of the ring) and χ_2 (determining the orientation of the ester residue) for a MD trajectory of the CCHI molecule performed at 300 K taking the conformation shown in Figure 3 as a starting point.

MD simulations performed at 300 K showed that the evolution of the dipole moment with time was dependent on the conformation (equatorial or axial) used as the starting point of the trajectory. Rather fast changes occur in the value of the dipole moment along the trajectory, the value of this quantity oscillating between ca. 2.4 and 2.8 D for the equatorial conformation and 2.8 and 3.2 D for the axial. The evolution with time of the rotational angles χ_1 (responsible for the chair-to-inverse-chair transition) and χ_2 (which determines the orientation of the ester residue with respect to the cyclohexane ring) is shown in Figure 4 for a MD trajectory performed at 300 K and started with the ester residue placed in the equatorial position. It can be seen that the value of this quantity oscillates roughly between 50° and 70°, far below the fluctuation that would be necessary for the chair-to-chair conformational transition to take place. In the same way, the oscillations of χ_2 take place within the approximate range of 190° ± 10°. Something similar occurs when the MD trajectory is started from the axial conformation of the molecule. These results suggest that either much more time or a much higher temperature would be necessary to detect these transitions. To circumvent this problem using a reasonable computing time, MD simulations were performed at 750 K, and the results obtained are shown in Figure 5. Here one can observe that χ_1 varies between ca. 20° and 200°; that is, chair-to-chair conformational transitions occur in the cyclohexane ring. The oscillations of χ_2 cover the full range 0−360°, with special incidence of trans (i.e. $\chi_2 = 180°$) and gauche (i.e. $\chi_2 = \pm 60°$) orientations.

For the reasons outlined above, to detect all the relaxation mechanisms requires the calculation of the dipolar correlation coefficients at high temperature. However, with the aim of studying the effects of the conformational transitions of the cyclohexane ring on the dielectric relaxation of CCHI the dipolar correlation coefficient was calculated at 300 and 750 K. The evaluation of $\phi(t)$ was carried out by the procedure briefly described below.

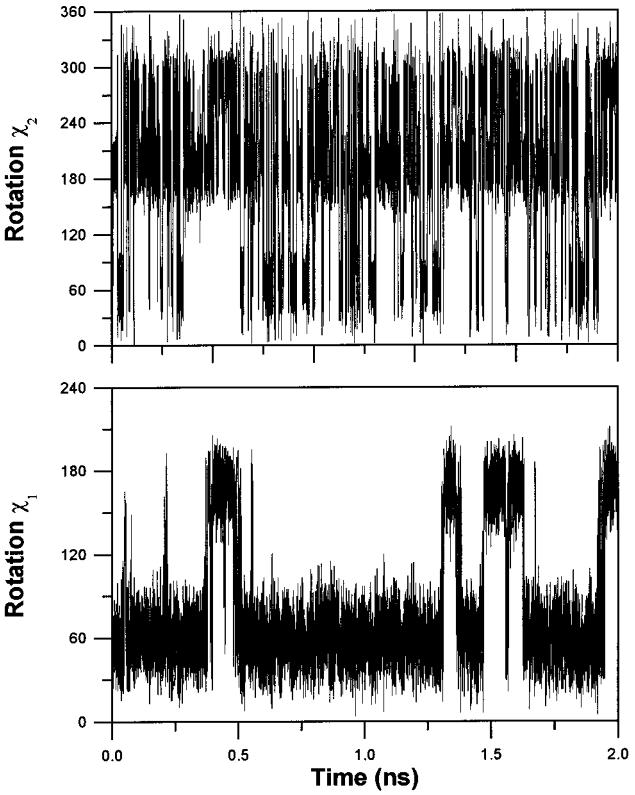

Figure 5. The same as Figure 4 with calculations performed at 750 K.

Conformations generated along the MD trajectories were recorded, and their dipole moment calculated, every 100 steps for $T = 300$ K and every 20 steps for $T = 750$ K, thus providing a total number of conformations of $N = 3 \times 10^4$ and 1.5×10^5, respectively, for $T = 300$ and 750 K, respectively, each one of them separated by $\Delta = 100$ fs for 300 K and $\Delta = 20$ fs for 750 K. The normalized dipolar autocorrelation coefficient was computed as a function of time by the following equation:

$$\phi(n\Delta) = \frac{1}{\langle \mu^2 \rangle (N-n)} \sum_{i=1}^{N-n} \boldsymbol{\mu}[i\Delta]\cdot\boldsymbol{\mu}[(i+n)\Delta] \tag{7}$$

This equation represents an average over the $(N - n)$ values of ϕ obtained with all the pairs of conformations that are separated by a time increment equal to $n\Delta$. The value of the autocorrelation function decreases rather fast with increasing time; thus $\phi(n\Delta) \approx 0$ for values of n that are much smaller than the total number of studied conformations N, and therefore $N - n$ is very large (higher than 20 000 in all the results presented below), which ensures a good sampling of ϕ over all the conformational space.

The variation of $\phi(t)$ with time for the two temperatures (300 and 750 K) is shown in Figure 6. These curves in conjunction with eq 3 should allow the determination of ϵ' and ϵ'' at the temperatures of interest. However, preliminary calculations showed that the treatment of the data is more efficiently done if the noise that appears in the autocorrelation curves is eliminated. For that purpose, the curves were fitted to the KWW relationship (eq 4), and the best values of β and τ_0 were obtained. The sum of the squared deviations are given in Table 1. The quality of the fitting can also be observed in Figure 6, where the dotted lines representing the fitting function are nearly coincident with the solid lines that represent the values of $\phi(t)$.

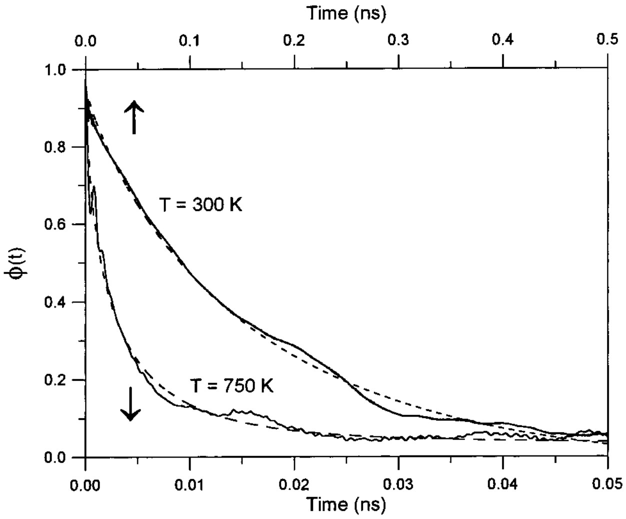

Figure 6. Dipole correlation function $\phi(t)$ as function of time for the CCHI molecule obtained at temperatures of 300 and 750 K. Solid lines were computed from MD trajectories according to eq 7. Dotted lines represent least-squares fittings to the KWW function (eq 4).

TABLE 1: Values for the τ_0 and β Parameters of the KWW Equation (Eq 4) Obtained through Least-Squares Fitting of the Dipolar Correlation Function $\phi(t)$ Computed from MD Trajectories of the CCHI Molecules Performed at Two Temperatures. The σ^2 Parameter Indicates the Sum of the Squared Deviations on the Fitting

$$\phi(t) = \exp[-(t/\tau_0)^\beta]$$

T (K)	τ_0 (ns)	β	$10^4\,\sigma^2$
300	0.162 50	0.850	2.6
750	0.002 34	0.577	2.5

According to eq 3, ϵ' and ϵ'' can be written in terms of $\epsilon'/(\epsilon_0 - \epsilon_\infty)$ and $\epsilon''/\epsilon''_{\max}$, where $\epsilon''_{\max}$ is the loss at the maximum of the peak, by means of the following equations:[15]

$$\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = 1 - \int_0^\infty \phi(t) \cos \omega t \, \mathrm{d}t$$

$$\frac{\epsilon''(\omega)}{\epsilon''_{\max}} = \frac{1}{\epsilon''_{\max}} \int_0^\infty \phi(t) \sin \omega t \, \mathrm{d}t \qquad (8)$$

Values of these integrals were obtained by the method outlined by Williams et al.,[22]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(\omega\tau_0)^{n\beta}} \frac{\Gamma(n\beta + 1)}{\Gamma(n + 1)} \left[\cos\left(\frac{n\beta\pi}{2}\right) - \mathrm{i}\sin\left(\frac{n\beta\pi}{2}\right)\right] \qquad (9)$$

for high frequencies (i.e., $-1 \le \log(\omega\tau_0) \le +4$ when $\beta > 0.25$), and

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{(\omega\tau_0)^{n-1}}{\Gamma(n)} \Gamma\left(\frac{n + \beta - 1}{\beta}\right) \left[\cos\left(\frac{(n-1)\pi}{2}\right) + \mathrm{i}\sin\left(\frac{(n-1)\pi}{2}\right)\right] \qquad (10)$$

for low frequencies.

The results obtained from the values of the autocorrelation function evaluated at 300 and 750 K are plotted as a function of $\omega/\omega_{\max}$ in Figures 7 and 8. In the same figure and for comparative purposes, the experimental results obtained at −85 °C are also plotted. Significant discrepancies between the experimental results and those evaluated with the autocorrelation function calculated at 300 K can be observed. The reason for these discrepancies lies in that at this temperature chair-to-inverse-chair conformational transitions do not occur in the cyclohexane ring in the real time of 2 ns used in the calculations. Actually, contributions to $\phi(t)$ from these transitions are not accounted for in the evaluation of the components of the dielectric permittivity, and consequently the relaxation presents a rather narrow distribution of relaxation times. However, a reasonably good agreement between the theoretical and experimental results is found by using the function $\phi(t)$ determined at 750 K in eqs 8. As was discussed above, rather fast conformational transitions occur in the cyclohexane ring at this

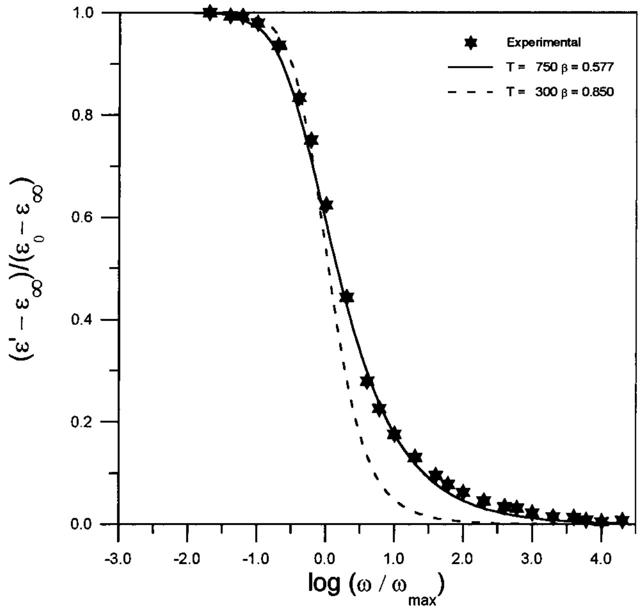

Figure 7. Normalized values of the real component ϵ' of the complex electrical permittivity ϵ^* as a function of frequency. The lines represent values computed from MD trajectories performed at 300 and 750 K, while the points indicate experimental results obtained at −85 °C.

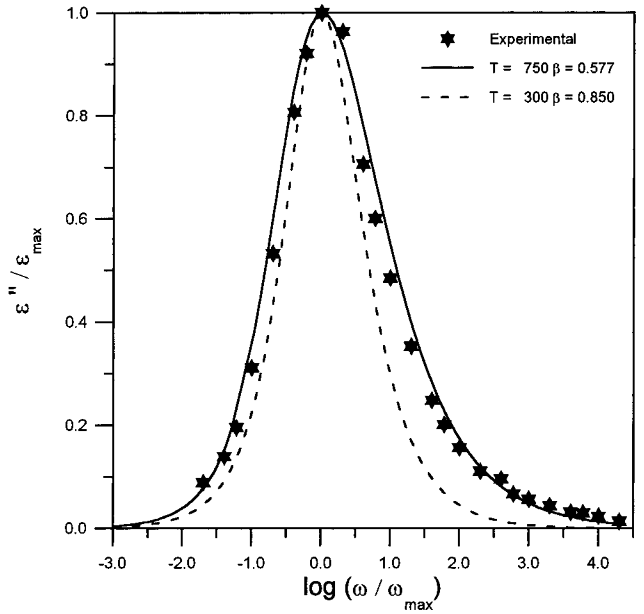

Figure 8. The same as Figure 7 for the loss component ϵ''.

temperature, and as a result, the calculated quantities resemble the experimental ones.

These results show that the intramolecular motions occurring in CCHI give a good account of the α relaxation of this compound. Interactions with the surroundings shift the frequencies of the relaxation to lower values without apparently changing the width of the distribution of relaxation times. It should be pointed out that despite the relatively low complexity of CCHI, the exponent of the KWW stretch function (≈0.58) is surprisingly close to the value of 0.40−0.56 reported for this quantity in poly(2-cholorocyclohexyl acrylate). The similarity of both values indicates that the intramolecular motions of the side groups play a pivotal role in the development of the glass−rubber relaxation of this polymer.

Acknowledgment. This work was supported by the DGICYT through Grants PB94-0364 and PB 95-0134-C02-01.

References and Notes

(1) Vogel, H. *Z. Phys.* **1921**, *22*, 645.
(2) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(3) Tamman, G.; Hese, W. Z. *Anorg. Allg. Chem.* **1926**, *156*, 245.
(4) Kauzmann, K. *Chem. Rev.* **1948**, *43*, 219.
(5) Stillinger, F. H. *Science* **1995**, *267*, 1935.
(6) Dolittle, A. K; Doolittle, D. B. *J. Appl. Phys.* **1957**, *28*, 901.
(7) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1958**, *29*, 1049.
(8) Ferry, J. D. *Viscoelastic Properties of Polymers*; Interscience: New York, 1980.
(9) Ediger, M. D.; Adolf, D. B. *Adv. Polym. Sci.* **1994**, *116*, 73.
(10) Saiz, E.; Riande, E. *J. Chem. Phys.* **1995**, *103*, 3832.
(11) Saiz, E. ; Riande, E.; Guzmán, J.; Iglesias, M. T. *J. Phys. Chem.* **1996**, *100*, 3832.
(12) Saiz, E.; Guzmán, R.; Iglesias, M. T.; Riande, E. *J. Phys. Chem.* **1996**, *100*, 18345.
(13) Hill, N.; Vaughan, W.; Price, A. H.; Davies, M. *Dielectric Properties and Molecular Behavior*; Van Nostrand: New York, 1969.
(14) Williams, G. *Adv. Polym. Sci.* **1979**, *33*, 59.
(15) Riande, E.; Saiz, E.; *Dipole Moments and Birefringence of Polymers*; Prentice Hall, Englewood Cliffs, NJ, 1992.
(16) Kohlrausch, R. *Ann. Phys.* **1847**, *12* (3), 3931
(17) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
(18) *AMPAC, Quantum Chemistry Program Exchange*; Department of Chemistry, Indiana University, Bloomington, IN 47405
(19) Tripos Associates Inc., St. Louis, MO 63144.
(20) Clark, M.; Cramer, R. D., III; van Opdembosch, N. *J. Comput. Chem.* **1989**, *10*, 983.
(21) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
(22) Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Trans. Faraday Soc.* **1971**, *67*, 1323.
(23) Díaz-Calleja, R.; Riande, E.; San Román, J.; Compañ, V. *Macromolecules* **1995**, *28*, 614.