

Dielectric Relaxations in Poly(monocyclohexyl itaconate)

RICARDO DÍAZ-CALLEJA,^{1,*} LIGIA GARGALLO,² and DEODATO RADIĆ²

¹Laboratorio de Termodinámica y Fisicoquímica, E.T.S.I.I.V., Universidad Politécnica de Valencia, Apartado 22012, 46071 Valencia, Spain; ²Laboratorio de Fisicoquímica Molecular, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago, Chile

SYNOPSIS

A study of the dielectric relaxation spectrum of poly(monocyclohexyl itaconate) (PMCHI) is performed by means of two experimental techniques: first, at variable frequency in the audio zone and, second, by thermally stimulated depolarization currents. Because of the high conductivity of the samples, there is a hidden dielectric relaxation that can be detected by using the macroscopic dynamic polarizability α^* defined in terms of the dielectric complex permittivity ϵ^* by means of the equation $\alpha^* = (\epsilon^* - 1)/(\epsilon^* + 2)$. The transformation performed through this equation is discussed in order to obtain the dielectric relaxations in the zone of high temperatures and low frequencies of the spectrum.

INTRODUCTION

In previous papers^{1,2} we have remarked about the complexity of the dielectric relaxation spectrum of polymers derived from itaconic acid. Although there is information about the dynamic-mechanical properties of polydiesters derived from itaconic acid,³⁻⁵ references dealing with polymonoesters are scarce.⁶ Nevertheless, an intense dielectric activity is expected to be detected, especially due to the carboxyl groups by repeat unit, as in the case of polymonoesters with long side chains with 8-14 carbon atoms.¹ Glass transition temperature was not detected in this kind of polymer,⁷ as would be expected in amorphous polymers, nor was a dielectric relaxation, which, because of the characteristics of this polymer, could be associated to cooperative segmental motions related to the glass-rubber transition. On the other hand, the complex part of the loss dielectric permittivity increases markedly with the temperature, mainly at low frequencies, and no visible new relaxations could be detected at least in a reasonably high-temperature range.

The aim of this work was to study the dielectric relaxation behavior of a polymonoester derived from itaconic acid, containing a cyclohexyl ring as sub-

stituent in the side chain [poly(monocyclohexyl itaconate)]. Because of the presence of this substituent, it may be possible to observe a new relaxation associated with the chair-boat transition in the cyclohexyl group, as was observed in previous works.^{8,9} The chemical structure of this polymer together with the proposed absorption mechanisms, as will be discussed below, are shown in Scheme 1.

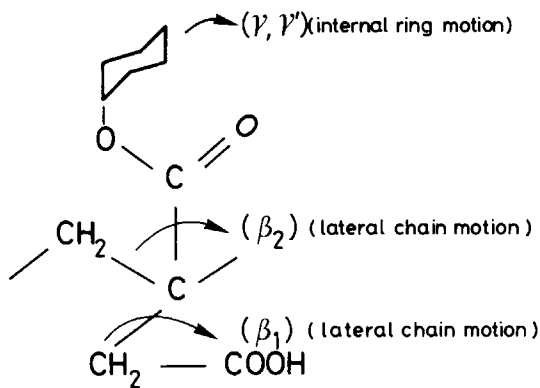
Another objective of this work was to emphasize the importance of the use of the complex polarizability [$\alpha^* = (\epsilon^* - 1)/(\epsilon^* + 2)$], considered as a macroscopic property of the polymer, although an intrinsic property, in order to detect the presence of hidden dielectric relaxations due to the increasing of the loss part of the complex permittivity, ϵ'' . As we will see, this procedure, which has been used in the study of other materials, reveals in our case, in terms of α'' and $\tan \delta_{\alpha''}$, a new dielectric relaxation whose presence is confirmed by thermodespolarization measurements.

EXPERIMENTAL

Monomer and Polymer Preparation

2-Cyclohexyloxycarbonylmethylacrylic acid (cyclohexyl hydrogen itaconate) was prepared by esterification of itaconic acid (1 mol) with cyclohexyl alcohol (3-4 mol) using acetyl chloride as catalyst¹⁰

* To whom correspondence should be addressed.



Scheme 1

according to the method previously described.^{11,12} Purification of the monomer was achieved by recrystallization from benzene.^{11,12} Radical polymerization of the monomer was carried out in bulk at 67°C under nitrogen using α, α' -azobisisobutyronitrile (AIBN) (0.1 mol) as initiator. Polymerization time was 24 h, and conversion of monomer to polymer was 75%. Purification of the polymer was achieved by repeated dissolution in THF and reprecipitation with diethyl ether before vacuum drying at 40°C.^{11,12}

Dielectric Measurements

The dielectric permittivity and loss tangent was measured between -150 and 100°C and 0.2 and 100 kHz by means of a Genrad 1620AP capacitance bridge over polymer samples previously dried at room temperature for a period of 1 month and was subsequently metallized by using gold electrodes. The corresponding films were obtained from THF polymer solutions. Films are very fragile as in the case of other polyitaconates.

Thermally stimulated depolarization current measurements (TSDC) were performed with a Solomat TSC/RMA at temperatures between -130°C and 70 or 90°C , with polarization temperatures at 20 and 50°C , respectively, at a heating rate of 7°C min^{-1} , and with fields of 150 and 200 V/mm, respectively. In this case, two copper filaments were soldered to a small piece of polymer of 18.5 mm^2 of surface metallized with colloidal silver. The moisture is controlled by submitting the experimental system to a vacuum of 10^{-4} mmHg, and the measurements were performed in the presence of an inert gas (He). By this experimental procedure, all the problems dealing with moisture, which are very important in TSDC due to the sensitivity of the measurement, are avoided.

RESULTS AND DISCUSSION

Figure 1 shows the real and imaginary part of the dielectric permittivity at three characteristic frequencies: 1, 10, and 100 KHz for poly(monocyclohexyl itaconate) (PMCHI). At least two relaxation processes can be clearly observed, one of them at low temperatures centered at -100°C and the other at slightly lower than room temperature. This second phenomenon is followed by an increasing of the loss due to conductivity, especially at low frequencies. Figure 2 shows the thermodepolarization spectra at the two measurement conditions mentioned in the Experimental section. In this case, the presence of at least four relaxation processes is clear. We are interested in establishing some correspondence between the observed relaxation processes by using both experimental techniques.

An exhaustive analysis of the alternative results in terms of $\tan \delta (= \epsilon''/\epsilon')$ (Fig. 3) reveals for the audio-frequency measurements a γ' relaxation process with an activation energy value about 9 kcal mol^{-1} calculated by means of the Arrhenius equation from $\text{Ln } \nu_m$ vs. T^{-1} , where ν_m is the frequency of the

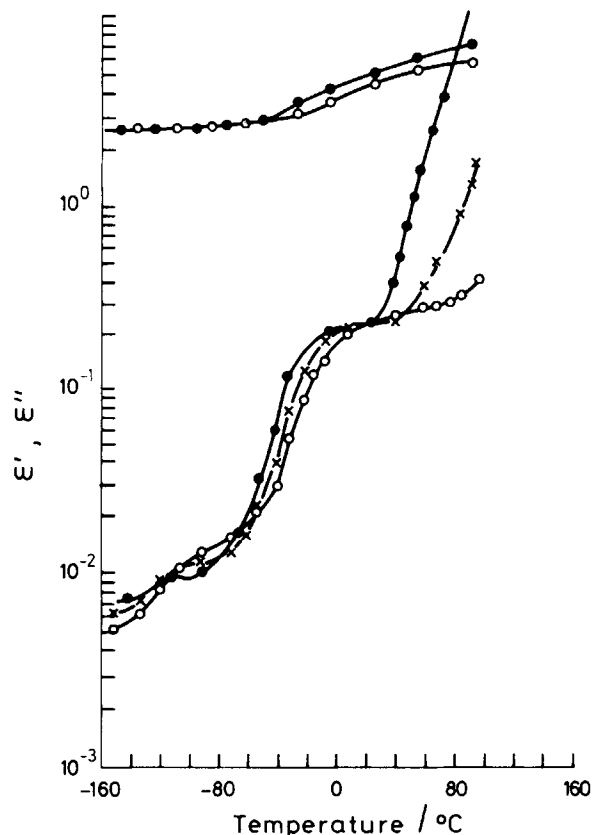


Figure 1 ϵ' (top) and ϵ'' (bottom) for PMCHI: (●) 1 kHz; (x) 10 kHz; (○) 100 kHz.

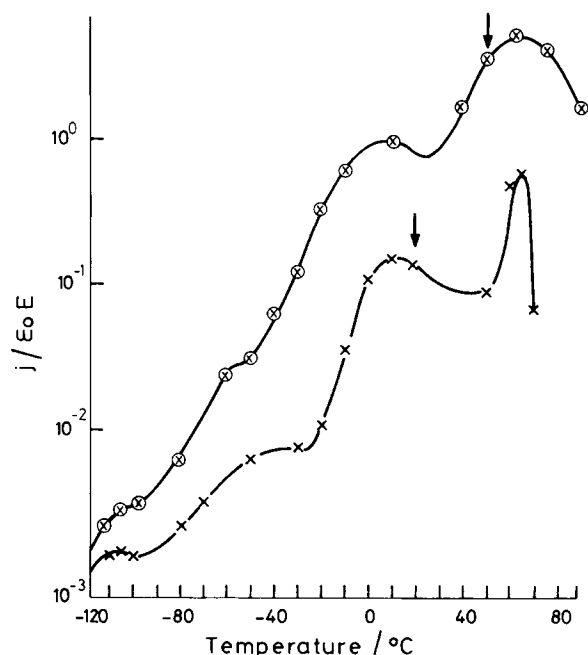


Figure 2 Thermally stimulated depolarization currents (TSDC). Top: (x): $T_{\max} = 90^{\circ}\text{C}$; $T_p = 50^{\circ}\text{C}$; $E = 200\text{ V/mm}$. Bottom (x): $T_{\max} = 70^{\circ}\text{C}$; $T_p = 20^{\circ}\text{C}$; $E = 150\text{ V/mm}$. Arrows denote the corresponding polarization temperatures.

maxima in $\tan \delta$. This relaxation is overlapped by the next relaxation at frequencies higher than 2 kHz. This second relaxation (β) is progressively broadening with increasing frequency. This behavior is similar to that found in other polymonoisitaconates.¹ At the same time, the activation energy calculated from the maxima in $\tan \delta$ increases from 28 to approximately 56 kcal mol⁻¹. This fact together with the asymmetric shape of the curves would indicate the presence of two subrelaxations, β_1 and β_2 , in the increasing temperature sense. A continuous increasing of the dielectric spectrum, in terms of $\tan \delta$ or ϵ'' , is observed. This behavior is probably due to an overlapping effect to the dielectric loss of one important component of the dc conductivity, which is produced mainly by the presence of the carboxylic group —COOH.

As was mentioned above, the dielectric spectrum in terms of thermally stimulated depolarization currents is more complex, showing peaks at -105 , -40 , 10 , and 65°C . The observed difference between the curves in Figure 2 is due to the different experimental conditions used in each case.

It is known¹³ that there is a correspondence between the maxima in ϵ'' and the peaks in the spectra of thermally stimulated depolarization currents,

with a splitting in the position of the maxima in the temperature axis. This fact is explained by the equivalent frequency for the peaks in the TSDC spectra given by

$$f = 0.113 E_a / SRT_m^2 \quad (1)$$

where E_a is the activation energy; S , the inverse of the scanning rate (8.57 s/ $^{\circ}\text{C}$); R , the gas constant; and T_m , the temperature at the maximum.

Values for f , the equivalent frequency in the ac dielectric spectrum, are of the order of 10^{-3} Hz. To test the validity of eq. (1) in order to compare TSDC and ac audio-frequency data, we would need to know the values of E_a , the activation energy, but it is difficult due to the complexity of the TSDC curve. Thus, we estimate E_a for the γ peaks as 12 kcal mol⁻¹. We have carried out the preceding estimation according to the procedure outlined in Ref. 15 on the assumption that all the secondary loss peaks meet together at about 10^{13} Hz at very high temperatures. On this ground and according to an Arrhenius equation, $\ln f_2/f_1 = E_a/R(T_m^{-1} - T_2^{-1})$, with $f_2 = 10^{13}$ Hz, $f_1 = 10^{-3}$ Hz, and $T_2 \rightarrow \infty$, we have $E_a = 0.0737 T_m$. Taking for T_m the observed value for the TSDC peak, a value of $E_a \approx 12$ kcal mol⁻¹ is obtained.

A value of 2.5×10^{-3} Hz for the equivalent frequency for the low-temperature peak in the ac spectrum is found. According to it, the observed peak in TSDC at -105°C cannot be due to the same mechanism causing the low-temperature peak in the ac measurements because the temperature for this last peak should be higher. In fact, a value of $T = -11^{\circ}\text{C}$ is obtained at 1 kHz by means of an Arrhenius equation with $E_a = 12$ kcal mol⁻¹ and, consequently, we think that the peak at -105°C corresponds to the chair-chair motion of the cyclohexyl ring with some contribution of the dipolar character of itself. This interpretation is in agreement with the results reported by Van Turnhout¹³ and Vanderschueren¹⁴ who observed this kind of relaxation in poly(cyclohexyl methacrylate) (PCHMA) in the same temperature range. This is in good agreement with the temperature of the peak obtained by mechanical measurements,¹⁵ -80°C at 1 Hz, and dielectric measurements,⁸ -20°C at 1 kHz. This type of molecular motion is fundamentally controlled by an intramolecular barrier and the position of the peak is slowly influenced by the environment; therefore, there is not a marked dependence with the type of polymer and the comparison of the results between PCHMA and PMCHI is appropriate.

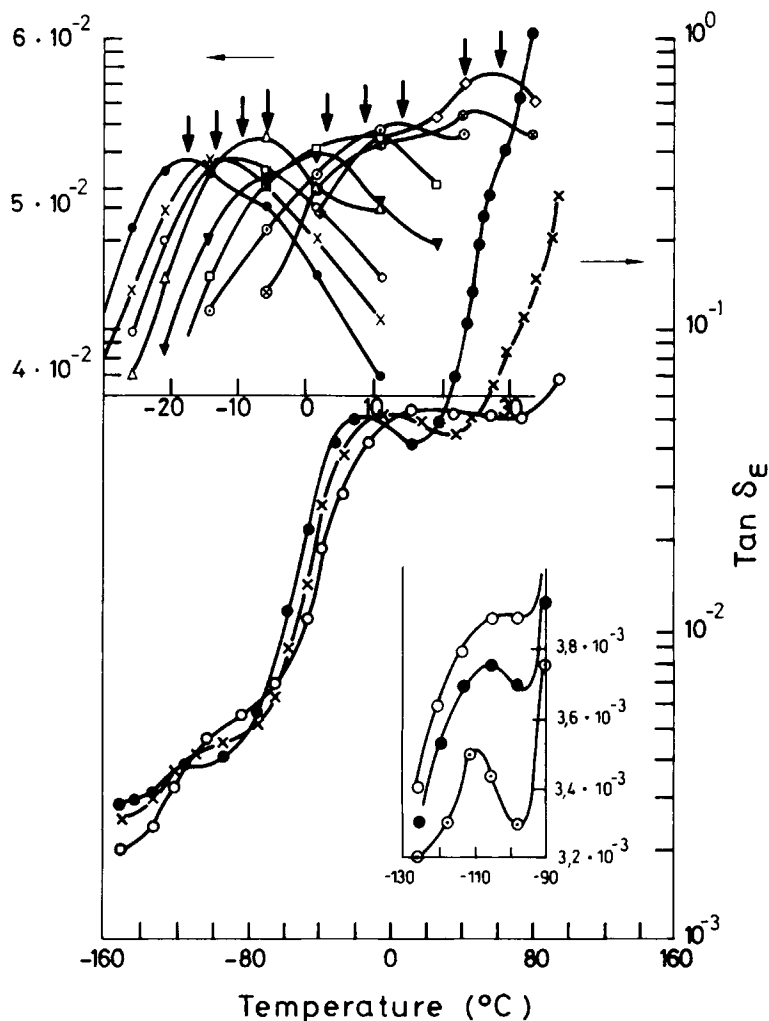


Figure 3 Variation of $\tan \delta_i$ as function of temperature for PMCHI. Top: Representation of the β relaxation: (●) 0.2 kHz; (x) 0.5 kHz; (○) 1 kHz; (△) 2 kHz; (▽) 5 kHz; (□) 10 kHz; (○) 20 kHz; (x) 50 kHz; (◇) 100 kHz. Middle: $\tan \delta_e$ for PMCHI at (●) 1, (X) 10, and (○) 100 kHz in the complete range of measurements. Bottom: Representation of the γ relaxation: (○) 0.5 kHz; (●) 1 kHz; (○) 2 kHz.

In alternative measurements (ranging from 0.2 to 100 kHz), this peak would appear overlapped to the low-temperature side of the β_1 peak, and for this reason, it cannot be distinguished in this kind of measurement. Presumably, ac measurements at 1 Hz or lower frequencies would show evidence of the γ peak.

The observed peak at -40°C has a more pronounced dipolar character and can correspond to a β dielectric relaxation. The molecular origin of this relaxation can be attributed to rotational motions of the ester groups and/or acid group of the side chains, which is in accord with the high value of the observed dielectric loss. This result is also in agreement with the behavior observed in other poly-

monoitaconates,^{1,2} where a very important dielectric relaxation is detected in the same temperature range. This relaxation can be due to lateral motions in the ester group, as well as in the acid group, with a strong dipolar effect due to the rotation of the $-\text{C}=\text{O}$ group in both cases. These motions could be coupled to the motions of the main chain. This result could explain our findings dealing with the low symmetry in the shape of the peak and the increasing of the activation energy with frequency. Therefore, there are two different motions but overlapped. In TSDC, both peaks could appear split: one of them would be the peak at -40°C , and the other, at 10°C . Nevertheless, the temperature for this second peak would indicate the presence of a dielectric absorption

in the audio-frequency range about 50 or 60°C, according to the observed splitting usually found between both series of relaxation peaks β_1 and β_2 . For example, if we adopt tentatively for the 10°C TSDC peak an activation energy of 50 kcal mol⁻¹, a value of 5×10^{-3} Hz for the equivalent frequency is obtained. Then, according to an Arrhenius equation, a value of $T = 55^\circ\text{C}$ is obtained for the ac peak at 1 kHz. For this reason, we prefer to assume that both molecular relaxation peaks appear overlapped in only one relaxation in ac as well as in TSDC measurements. There is another reason to attribute the peak at 10°C to a dielectric ac relaxation at higher temperatures that would be obscured because of conductivity effects. This problem is related to the apparent absence of a glass transition temperature, T_g , in polymonoitaconates. In fact, no mechanical or dielectric relaxation has been observed according to published results,^{1,2} which could be interpreted as a consequence of cooperative motions of the main chain, as is the case of a neat T_g . It is interesting to note that if there are relaxations associated to molecular motions, which involve almost all the elements of the structural units, including the motions of the main chain, there are few units that could give rise to enough mechanical or dielectric activity, in order to produce a new relaxation that could be attributed to a glass transition temperature.

On the other hand, the high conductivity observed, mainly at low frequencies, would overlap the existence of another new relaxation (Fig. 4). This situation is very similar to that found in charge-transfer complexes^{16,17} in which some of them have a pronounced semiconductor character. In this kind of compound, the observation of dielectric relaxations over room temperature is inhibited by the high conductivity observed. To avoid this problem and to detect the conductivity effect, it is possible to use the complex polarizability α^* defined as

$$\alpha^* = (\epsilon^* - 1)/(\epsilon^* + 2) \quad (2)$$

where ϵ^* is the complex permittivity. The transformation defined by the above equation has been applied^{16,17} with good results in the case of dielectric relaxation peaks in terms of α'' or $\tan \delta_\alpha$. This transformation implies a normalization of ϵ^* that is very useful especially for high values of ϵ' and ϵ'' . Therefore, α'_{max} tends to be unity. By this way, there is an interpretation of eq. (2) in terms of the scaling concept, because this formula reduces to a common basis the permittivity data.

Before following our analysis, it is convenient to make some comments about the physical meaning

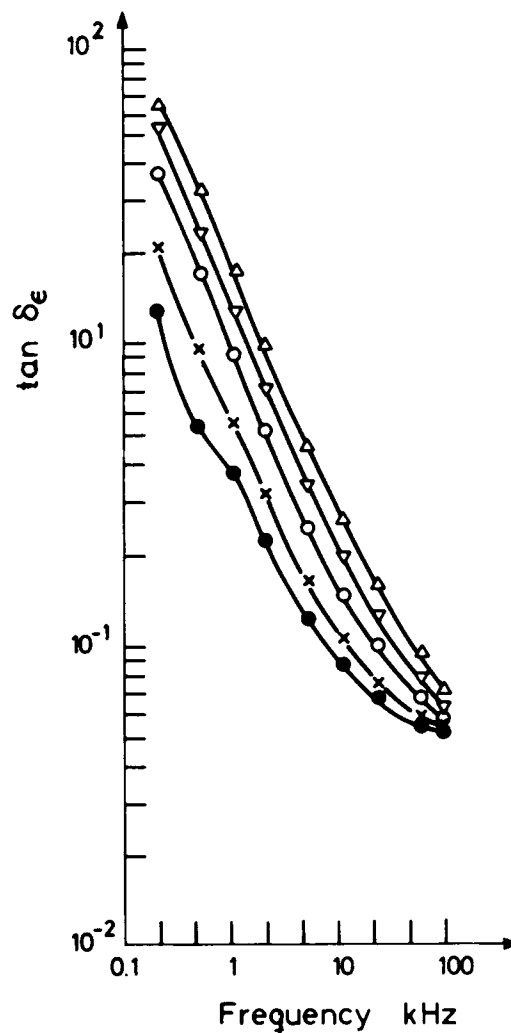


Figure 4 Variation of $\tan \delta_\epsilon$ as function of the frequency for PMCHI: (●) 71°C; (×) 80°C; (○) 88°C; (▽) 95°C; (△) 100°C.

of the dynamic polarizability: In a classic work,¹⁸ R. H. Cole analyzed the case of a dipole in a spheric cavity surrounded by a continuous fluid with constant dielectric permittivity and concluded that the macroscopic response in terms of time-dependent correlation of the electric moment of the specimen represents the polarization of the sphere. The analysis is carried out taking into account all the moments, i.e., the permanent and induced, and the result can be expressed by the following equation:

$$\begin{aligned} & [\epsilon^*(w) - 1]/[\epsilon^*(w) + 2] \\ &= (\epsilon_\infty - 1)/(\epsilon_\infty + 2) + (4\pi N/9KTV) \\ & \quad \langle \mu(0)M(0)f^0 \rangle L[-\dot{\psi}(t)] \quad (3) \end{aligned}$$

where $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$ represents the instantaneous polarizability of the sphere; $\psi(t) = \langle \mu(0)M(t)f^0 \rangle / \langle \mu(0)M(0)f^0 \rangle$ is the microscopic correlation function; $M = \sum_{i=1}^N \mu_i$ is the summation of all

the moments of the sphere; L represents the Laplace transform; and the term $L[-\psi(t)]$ is a decay function that represents the average momentum relative to the equilibrium value. Equation (3) gives the classical Debye equation where $\psi(t) = \exp(-t/\tau)$. The first member of eq. (3) represents the dynamic polarizability α^* of the sphere. This parameter is identical to that defined by Böttcher et al.¹⁹ in an analogous context. Because of this, Scaife²⁰ suggested that the dielectric data can be analyzed in terms of the polarizability $\alpha^* = \alpha' - j\alpha''$ of a sphere with a unity ratio, considering that in a dielectric

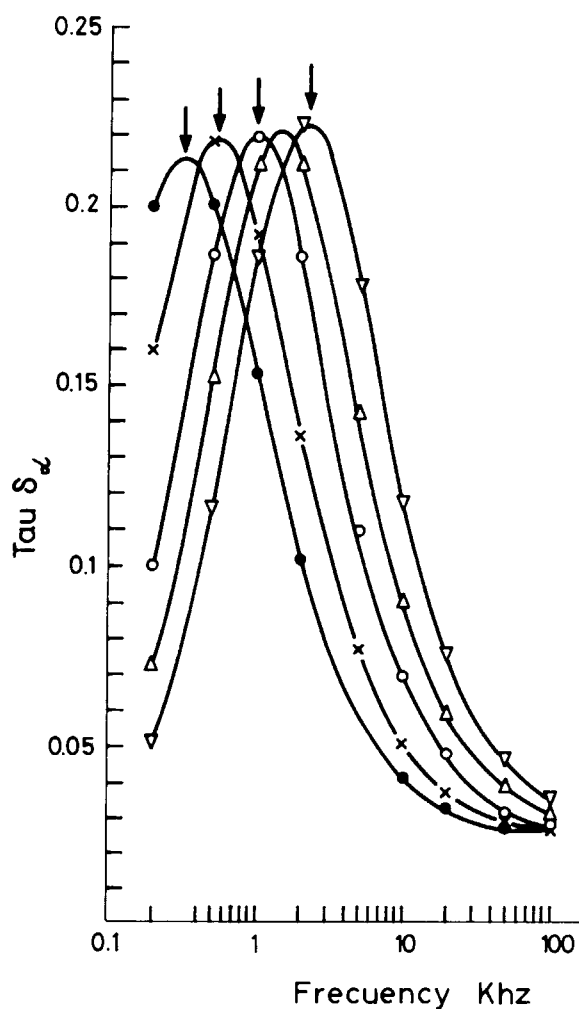


Figure 5 Variation of $\tan \delta_\alpha$ (referred to the polarizability α) as function of temperature: (●) 71°C; (x) 80°C; (○) 88°C; (△) 95°C; (▽) 100°C.

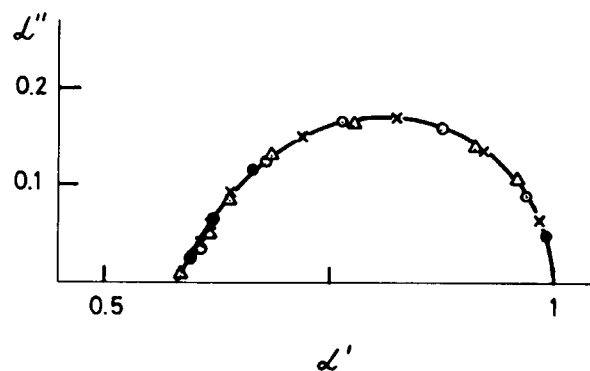


Figure 6 Cole-Cole arc α'' against α' : (△) 80°C; (○) 88°C; (x) 95°C; (●) 100°C.

sphere long-range dipole-dipole coupling vanishes when an alternating field is applied. Therefore, the only problem is to decide which of the functions ϵ^* or α^* are the most convenient in order to express the dielectric data. This subject has been analyzed by Havriliak and Negami.^{21,22} In our case, we will use α^* . From α^* , we can estimate α'' in order to describe the relaxation behavior of PMCHI over room temperature according to the procedure followed in charge-transfer complexes. Results are shown in Figure 5 for $\tan \delta_\alpha$, where

$$\tan \delta_\alpha = \alpha'' / \alpha' \quad (4)$$

where $\alpha' = [(\epsilon' - 1)(\epsilon' + 2) + \epsilon''^2] / [(\epsilon' + 2)^2 + \epsilon''^2]$ and $\alpha'' = 3\epsilon'' / [(\epsilon' + 2)^2 + \epsilon''^2]$.

The curves in Figure 5 correspond to temperatures between 71 and 100°C. The activation energy value for this relaxation, calculated according to an Arrhenius equation for the five maxima, is 16 kcal mol⁻¹. This is a small value for a glass transition, but not too much if we consider the above arguments about the small part of the macromolecule that remains to be activated, from the dielectric point of view, at higher temperatures than that of the β relaxation. A representation of α'' vs. α' in a Cole-Cole plot (Fig. 6) reveals that the results can be fitted irrespective of the temperature to a Cole-Davidson equation:

$$\alpha^* = \alpha_\infty + (\alpha_0 - \alpha_\infty)(1 + j\omega\tau_0)^{-\beta} \quad (5)$$

with the parameters $\alpha_\infty = 0.585$; $\alpha_0 = 1.0$; $\beta = 0.65$; $\tau_0 = 10^{-3}$ s. Because of the temperatures and frequency ranges, where the phenomenon is detected, we think that the corresponding peak in TSDC is that at 10°C. Therefore, the last maximum in the TSDC spectrum at about 60°C should correspond to space charge currents and is normally designated

as the ρ -peak. Many authors claim that this peak cannot be detected by conventional ac measurements. Only recently, Van Turnhout²³ showed that in the case of poly(ethyl methacrylate) (PEMA) dielectric permittivity measurements are also able to detect the ρ -peak.

CONCLUSIONS

In this work, we have studied the dielectric relaxation processes in poly(monocyclohexyl itaconate) in which we have compared the ac of audio-appearance measurements with those of thermally stimulated currents. By comparing both series of results, it is possible to conclude that the TSDC spectrum is notably more detailed, because it corresponds to lower frequencies due to the greater splitting of the relaxation peaks. However, both types of measurements can be considered as complementary. Summing up: The -110°C (γ') ac dielectric relaxation in this polymer has no counterpart in the TSDC spectrum; on the contrary, -105°C (γ) TSDC peaks correspond to an overlapped relaxation in the audio-frequency range by β_1 absorption. β_1 and β_2 peaks meet together at -40°C in TSDC and at room temperature in ac measurements. The appearance of a peak at 10°C in TSDC suggests the presence of a dielectric relaxation peak that would be hidden due to the higher conductivity in that temperature range. Finally, the 60°C TSDC peak would correspond to space charges. The transformation $\epsilon^* \rightarrow \alpha^*$ from permittivity to polarizability, being of the magnitude of macroscopic character, makes it possible to reveal a new relaxation as well as their characterization by conventional methods. The technique used in charge-transfer complexes has been shown to be useful also in the case of polymers with high conductivity at high temperatures.

R.D.-C. expresses his thanks to CICYT for partial financial support through Grant MAT/0555. D. R. and L. G. also express their thanks to the Dirección de Investigación (DIUC) Pontificia Universidad Católica de Chile and Fondecyt for financial help.

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Received October 3, 1991

Accepted November 19, 1991