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Correlations of Relaxing Dipole Entities and Conductivity Effects on Model Compounds and Molecular Chains with 2-Chlorocyclohexyl Esters in Their Structure

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ABSTRACT: The temperature and frequency dependence of the complex dielectric permittivity ϵ^* for both 2-chlorocyclohexyl isobutyrate (CCHI) and poly(2-chlorocyclohexyl acrylate) (PCCHA) is reported. The polymer exhibits an ostensible β relaxation, centered at -60 °C at 5 Hz, whose activation energy at constant frequency seems to increase with temperature followed by a glass-rubber relaxation or α process, centered at 70 °C at 5 Hz, in which conductive processes become dominant at low frequencies. The model compound only exhibits a glass-liquid relaxation whose maximum is located at -92 °C at 1 Hz. The analysis of the dielectric results in terms of the electric modulus suggests that whereas the conductive processes in CCHI are produced only by free charges, the conductivity observed in PCCHA involves both free charges and interfacial phenomena. The experimental intramolecular dipolar correlation g_{intra} is somewhat larger than 1 for both CCHI and PCCHA, suggesting that correlations of orientation enhance the polarity of these systems. A 4 × 4 rotational states scheme which accounts for two rotational states about the CH-CO bonds of the side group reproduces very satisfactorily the intramolecular correlation coefficient of the polymer. Finally, the critical interpretation of the dielectric results obtained in the bulk indicates that intermolecular dipolar interactions do not play a significant role in the dielectric behavior of these systems.

Introduction

The physical performance of polymer chains is straightforwardly connected with the chain mobility which in turn is determined by the chemical structure. The less hindered the conformational changes about the skeletal bonds of the main chain are, the lower is the glass transition temperature.[1] The chemical structure also strongly influences the molecular motions that give rise to secondary relaxation below T_g.[2] Subglass absorptions in polymers without flexible side groups are believed to arise from local motions of the main chain without involving significant changes in the position of the chain tails. In support of this assumption is the fact that the relaxation times associated with these absorptions do not show a noticeable molecular weight dependence. Computer simulations carried out by Helfand[3] and co-workers on poly(ethylene) chains suggests that second-neighbor pair conformational transitions of type $..g^{\pm}tt.. \rightleftarrows ..ttg^{\pm}...$ and $....ttt... \rightleftarrows ...g^{\pm}tg^{\pm}...$ are mainly responsible of the subglass absorptions taking place in these chains.

Secondary absorptions in polymer chains with flexible side groups seem to be the result of conformational changes either on the side groups alone or coupled with local conformational transitions in the main chain.[2,4,5] In order to study the influence of the side groups on the dynamics of molecular chains, it is advisable to carry out dynamic experiments on chains with side groups in which a variety of conformational transitions about these groups can occur. Earlier dielectric experimental work[6] performed on poly(cyclohexyl acrylate) showed that its relaxation spectrum presents a well developed β absorption, centered at -80 °C at 10 Hz, presumably caused by the same molecular motions that produce the β mechanical absorption. It is worthy to point out in this regard not only the similar location of the β absorption in the mechanical and dielectric relaxation spectra but also the roughly similar values of the activation energies observed for both relaxations.

In this work the dielectric relaxation behavior of poly(2-chlorocyclohexyl acrylate) (PCCHA) is studied, and the results are compared with those previously reported for poly(cyclohexyl acrylate) (PCHA). In order to obtain a better understanding of the dielectric response of PCCHA, attention is also paid to the analysis of the response of 2-chlorocyclohexyl isobutyrate (CCHI), a molecule whose structure is closely related to that of the repeating unit of PCCHA. The relaxation spectrum of cyclohexyl isobutyrate (CHI) exhibits a well developed β absorption and therefore it might also be expected that a similar subglass relaxation can be detected in CCHI. The presence of β processes in small molecules such as bromobenzene, 1-chloronaphthalene, etc., in which conformational transitions should not produce dielectric activity, give support to models that assume that intermolecular interactions play an important role in the development of secondary relaxations.[7-9] Therefore, a goal of this study is to determine the intra- and intermolecular dipolar correlations of orientation for both the molecular compound CCHI and the polymer PCCHI.

Experimental Section

Synthesis and Characterization of 2-Chlorocyclohexyl Isobutyrate (CCHI) and Poly(2-chlorocyclohexyl) (PCCHA). 2-Chlorocyclohexyl isobutyrate, model compound for the repeating unit of poly(2-chlorocyclohexyl acrylate), was obtained by condensation of isobutyric acid and 2-chlorocyclohexanol in a solution of refluxing dry toluene, using an equimolecular mixture of p-toluenesulfonic acid and boric acid (1%) as catalyst. The solvent was separated by evaporation, and the product was further isolated from the reaction medium by column chromatography

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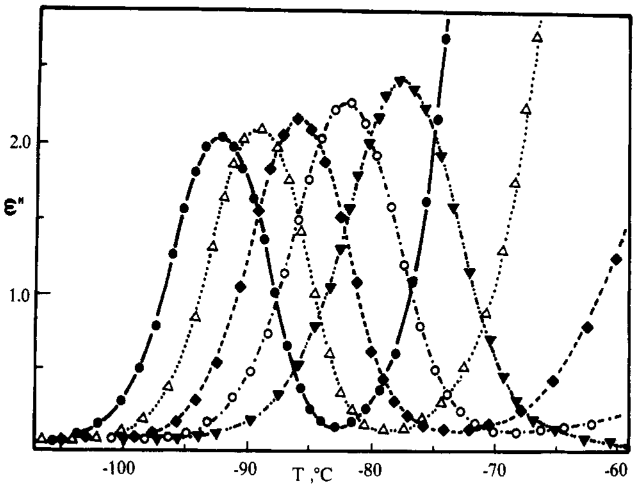

Figure 1. Dependence of the dielectric loss on temperature for 2-chlorocyclohexyl isobutyrate (CCHI) at several frequencies: (●) 1, (△) 10, (◆) 10^2, (○) 10^3, and (▼) 10^4 Hz.

(Kiesel-gel 60, Merck), using a mixture of chloroform/heptane (75/25, v/v) as eluent.

2-Chlorocyclohexyl acrylate was synthesized by dropwise addition of freshly distilled acryloyl chloride to a solution of 2-chlorocyclohexanol in an aqueous medium containing 2% dioxane and 5% sodium hydroxide. The monomer was extracted with ether, washed with water, dried successively with calcium chloride and calcium hydride, and finally distilled at reduced pressure.

Poly(2-chlorocyclohexyl acrylate) was obtained at 50 °C by radical polymerization of 2-chlorocyclohexyl acrylate in benzene, using AIBN as initiator. The polymer was precipitated with methanol, dissolved in benzene, precipitated again with methanol, and finally dried in vacuo at 70 °C. The number-average molecular weight of the sample used in this study was found to be 117 500 g/mol. The ^{13}C NMR spectrum of PCCHA was registered in chloroform solution with a Varian XL-300 at 75 MHz. The values of the molar fractions of the iso-, syndio and heterotactic triads, determined from the C–H signals (40.68, 41.30 and 41.85 δ) were 0.22, 0.50, and 0.28, respectively.

The values of the glass transition temperatures of CCHI and PCCHA, taken at the onset of the thermogram obtained with a DSC-4 calorimeter at a heating rate of 10 °C/min, were found to be −89 and 59 °C, respectively.

Dielectric Measurements. The real ϵ' and loss ϵ'' components of the complex dielectric permittivity ϵ^* for CCHI and PCCHA in the bulk were measured as a function of temperature with a three terminal plane condenser and a capacitance apparatus TA DEA 2970 operating in the frequency range 10^{-4}–30 kHz. The experiments proceeded from low to high temperature at a heating rate of 1 °C/min. Values of the dielectric permittivity of solutions of CCHI and PCCHA in benzene were measured at 10 kHz with a three terminal cylindrical cell coupled with a capacitance bridge (General Radio, 1620 A). At this frequency ϵ' and the static permittivity ϵ have similar value. Increments of the index of refraction of the solutions with respect to that of the solvent were measured at 632.8 nm with a differential refractometer (Chromatix Inc.).

Results

A. Dielectric Relaxation Spectra. The curves depicting at several frequencies the dependence of the loss dielectric permittivity on temperature for CCHI are shown in Figure 1. Though the experiments were performed from −140 °C up, only a single relaxation centered at ca. −92 °C at 1 Hz, was observed. The location and intensity of this relaxation indicates that this absorption corresponds to the glass-liquid relaxation or α process; secondary relaxations are not detected down to −140 °C. The dependence of ϵ' on temperature for the low molecular weight compound is shown in Figure 2 where it can be seen that this quantity, as usual, steeply increases in the glass-liquid process. The strength of the glass-liquid relaxation was obtained at different temperatures from complex dielectric plots, as that one shown as an example in Figure 3. The Cole plots are slightly skewed arcs which can be described by the Havriliak–Negami equation[9]

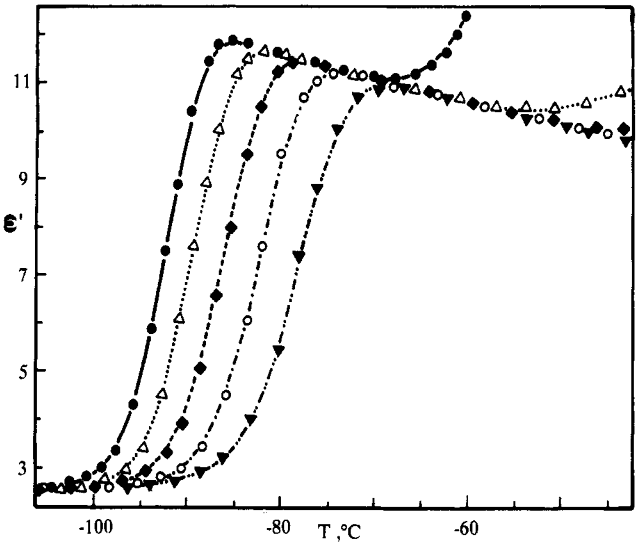

Figure 2. Variation of the real permittivity with temperature for 2-chlorocyclohexylisobutyrate (CCHI) at the frequencies indicated in Figure 1.

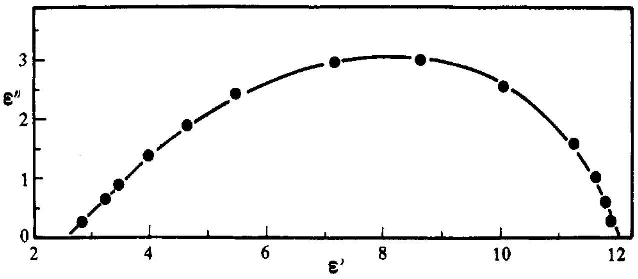

Figure 3. Complex dielectric plot for 2-chlorocyclohexyl acrylate (CCHI) at −85 °C.

Table 1. Relaxation Strength for the Dielectric Glass-Rubber Process of 2-Chlorocyclohexyl Isobutyrate (CCHI) at Several Temperatures

T, °C	$\Delta\epsilon_\alpha$	T, °C	$\Delta\epsilon_\alpha$
−85	9.20	−70	8.40
−80	8.95	−65	8.20
−75	8.65		

$$\epsilon^*(\omega) = \epsilon_{\alpha u} + \frac{\epsilon_{\alpha r} - \epsilon_{\alpha u}}{[1 + (i\omega\tau)^{\bar{\alpha}}]^{\beta}} \qquad (1)$$

where the subindices r and u refer, respectively, to the relaxed and unrelaxed dielectric permittivities and τ is the average relaxation time. The values of the α, β, and τ parameters at −89 °C amount to 0.87, 0.575, and 2.1×10^{-3} s, respectively. As usual, the values of $\Delta\epsilon_\alpha = \epsilon_{\alpha r} - \epsilon_{\alpha u}$, given in Table 1, show a decreasing dependence on temperature.

The temperature dependence of the dielectric loss for PCCHA, at several frequencies, is shown in Figure 4. The relaxation spectrum exhibits an ostensible peak, centered at 70 °C at 5 Hz, clearly associated with the glass-rubber relaxation; this α process is followed in decreasing temperature order by a β subglass relaxation peak whose maximum is located at ca. −60 °C, at the same frequency, nearly 20 °C above that of the β peak of PCHA.[6] An important feature of the α relaxation is that conductive processes become dominant at low frequencies so that the maximum of the peak cannot be detected at frequencies below 5 Hz. It should be pointed out that even at relatively

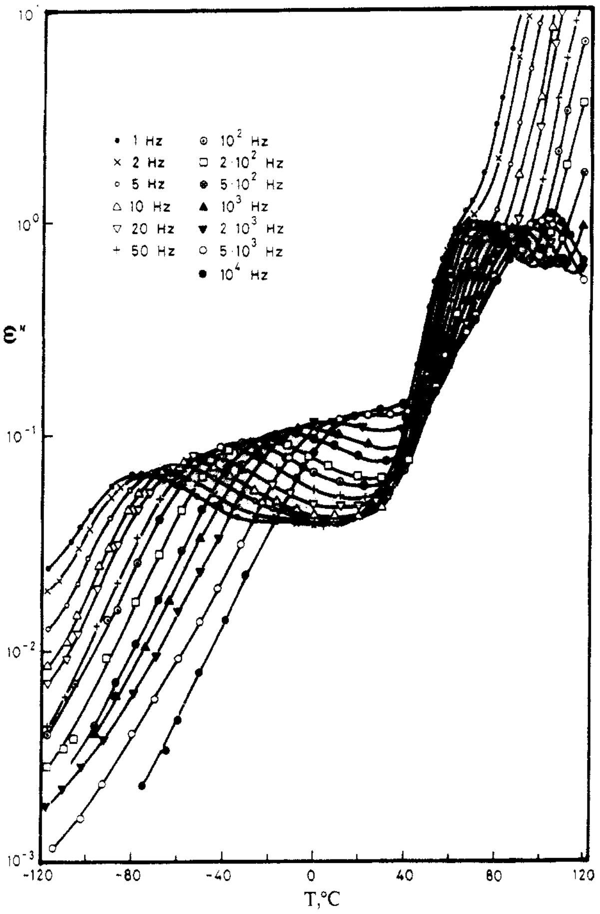

Figure 4. Changes in the dielectric loss with temperature for poly(2-chlorocyclohexyl acrylate) (PCCHA) at the frequencies indicated.

high frequencies, conductive effects become dominant at temperatures slightly above that corresponding to the peak maximum.

As usual, the intensity of the β relaxation increases with temperature (Figure 5). In order to determine the strength of the subglass relaxation, the peaks were analyzed in terms of the empirical Fuoss–Kirkwood expression[10]

$$\epsilon''(\omega) = \epsilon''_{\max}(\omega)\ \mathrm{sech}\ m \ln\frac{\omega_{\max}}{\omega} \qquad (2)$$

where $\omega = \exp(-E_a/RT)$, E_a being the activation energy whose value obtained from the isochromal temperature scans amounts to 11.0 kcal mol^{-1}. The term $\ln(\omega_{\max}/\omega)$ is given by[2]

$$\ln\frac{\omega_{\max}}{\omega} = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\max}}\right) \qquad (3)$$

$\omega''_{\max}$ and $T_{\max}$ referring, respectively, to the angular frequency and the temperature at the peaks maxima. By plotting $\cos h^{-1}(\epsilon''_{\max}/\epsilon'')$ *vs* $1/T$ one finds the values of m given in Table 2 for different temperatures. The relaxation strength, $\Delta\epsilon_\beta$, can be calculated by means of the relationship

$$\Delta\epsilon_\beta = \epsilon_{r\beta} - \epsilon_{u\beta} = 2\frac{\epsilon''}{m} \qquad (4)$$

where, as before, the subindices r and u refer, respectively, to the relaxed and unrelaxed dielectric permittivities in the β region. Values of the relaxation strength as a function of temperature are given in Table 2 where it can be seen that, as usual, the relaxation strength increases with temperature.

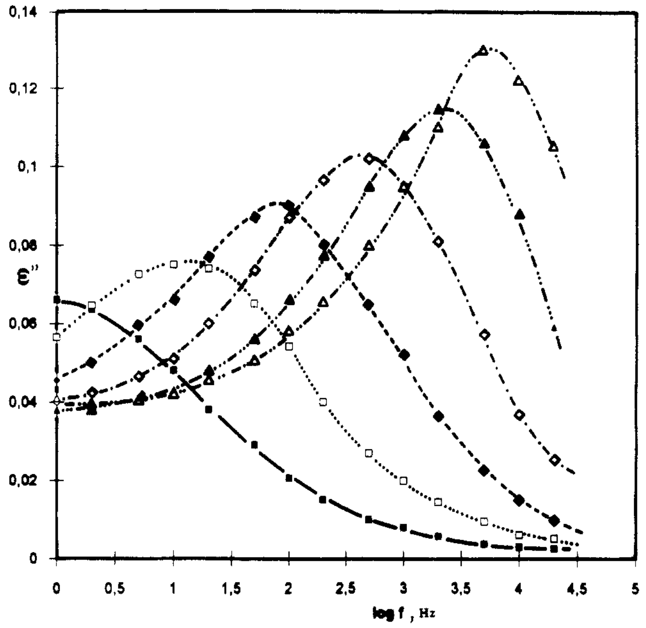

Figure 5. Detailed description of the dependence of the dielectric loss on frequency for the β region of the dielectric spectrum of poly(2-chlorocyclohexyl acrylate) (PCCHA), at several temperatures: (■) -80, (□) -60, (◆) -40, (◇) -20, (▲) 0, and (△) 20 °C.

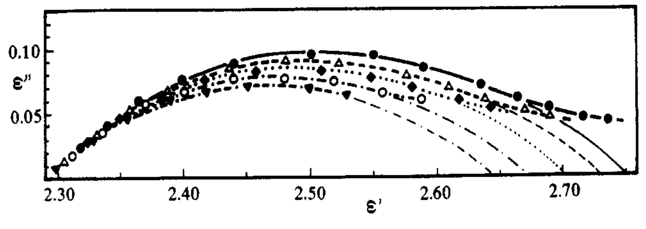

Figure 6. Complex dielectric plots for the β region of poly(2-chlorocyclohexyl acrylate) (PCCHA) at several temperatures: (▼) -70, (○) -60, (◆) -50, (△) -40, and (●) -30 °C.

Table 2. Values, at Different Temperatures, of the Relaxation Strength of the β Process of Poly(2-chlorocyclohexyl acrylate) (PCCHA) Obtained from Eqs 4 and 5 and the Values of m in Eq 4

T, °C	m	$\Delta\epsilon_\beta$ (eq 4)	$\Delta\epsilon_\beta$ (eq 5)
−70	0.418	0.33_0	0.35_0
−60	0.442	0.34_2	0.37_6
−50	0.477	0.36_5	0.40_3
−40	0.490	0.36_7	0.43_9
−30	0.500	0.38_2	0.45_5

Alternatively to this model, the dielectric results for the polymer in the β region were fit to the Cole–Cole expression[11]

$$\epsilon^*(\omega) = \epsilon_{u\beta} + \frac{\epsilon_{r\beta} - \epsilon_{u\beta}}{1 + (i\omega\tau)^{\bar{\alpha}}} \qquad (5)$$

The complex dielectric plots are arcs (Figure 6) from whose intercepts with the abscissa axis the values of $\Delta\epsilon_\beta$ indicated in Table 2 are obtained. In general the changes in the relaxation strength with temperature follow the same trend that the results calculated for this quantity from eq 4. It should be pointed out, however, that the values of $\Delta\epsilon_\beta$ determined from the Cole–Cole plots are slightly higher than the values obtained from eq 4.

The β relaxation follows Arrhenius behavior with an average activation energy of 11.0 kcal mol^{-1}. In an earlier work[12] carried out on PCHA the activation energy was found to be a distributed function around the average value obtained by the classical Arrhenius treatment. For comparative purposes the temperature dependence of the

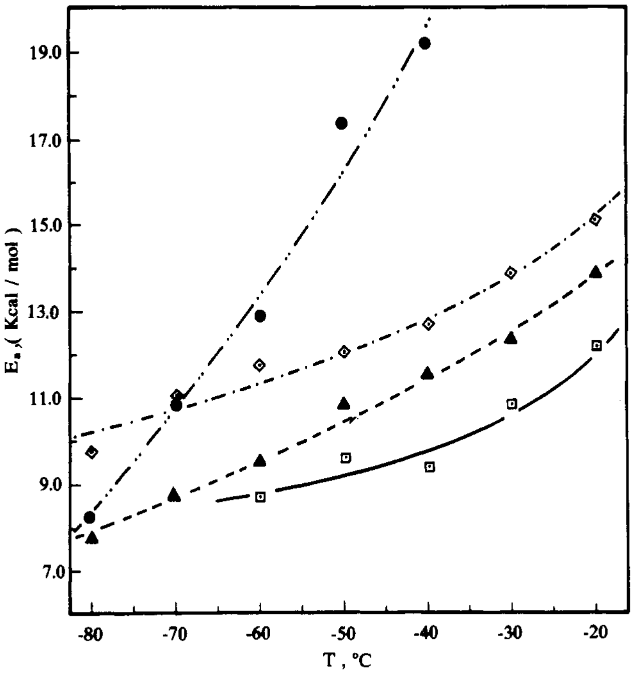

Figure 7. Temperature dependence of the activation energy associated with the β region of poly(2-chlorocyclohexyl acrylate) (PCCHA) at several frequencies: (●) 1, (◇) 10, (▲) 100, and (▣) 1000 Hz.

activation energy, E_a, associated with the β relaxation process of PCCHA was determined by expressing E_a along the path ϵ' = constant as

$$E_a = R\left(\frac{\partial \ln \omega}{\partial(1/T)}\right)_{\epsilon'} = RT^2\left(\frac{\partial \ln \omega}{\partial T}\right)_{\epsilon'} \qquad (6)$$

This relation in conjunction with the relationship

$$\left(\frac{\partial \epsilon'}{\partial \ln \omega}\right)_{T^{-1}}\left(\frac{\partial \ln \omega}{\partial T^{-1}}\right)_{\epsilon'}\left(\frac{\partial T^{-1}}{\partial \epsilon'}\right)_{\ln\omega} = -1 \qquad (7)$$

gives

$$E_a = RT^2\frac{d\epsilon'/dT}{d\epsilon'/d\ln \omega} \qquad (8)$$

The evaluation of $d\epsilon'/dT$ was carried out directly by using the Software of the DEA 2970 apparatus whereas the derivative $d\epsilon'/d \ln \omega$ was obtained by the approximate relation[13]

$$\frac{d\epsilon'}{d\ln \omega} = \frac{2}{\pi}\epsilon'' \qquad (9)$$

Values of E_a are represented as a function of temperature in Figure 7 where it can be seen that the activation energy at constant frequency increases with temperature. Here the activation energy is not a distributed function presumably as a consequence of the fact that the β process overlaps with the α-glass rubber relaxation and, consequently, more complicated motions become involved in the relaxation process as the temperature goes up.

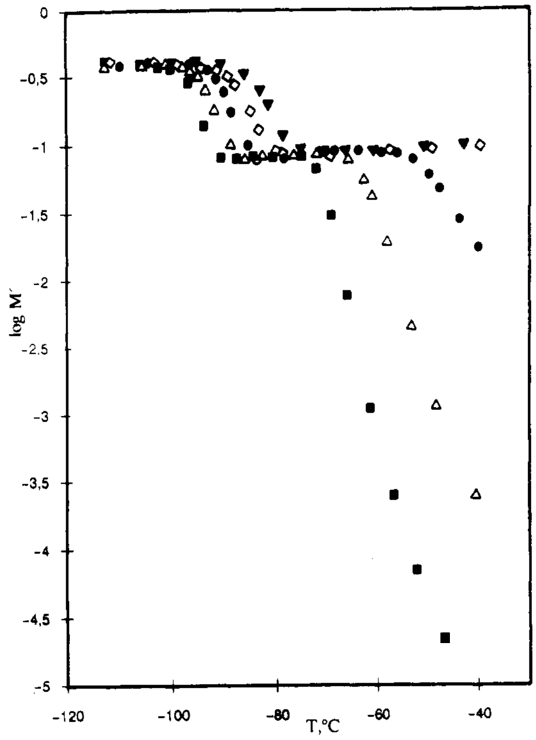

Figure 8. Variation of the real electric modulus with temperature for 2-chlorocyclohexyl isobutyrate (CCHI) at several frequencies: (■) 1, (△) 10, (●) 10^2, (◇) 10^3, and (▼) 10^4 Hz.

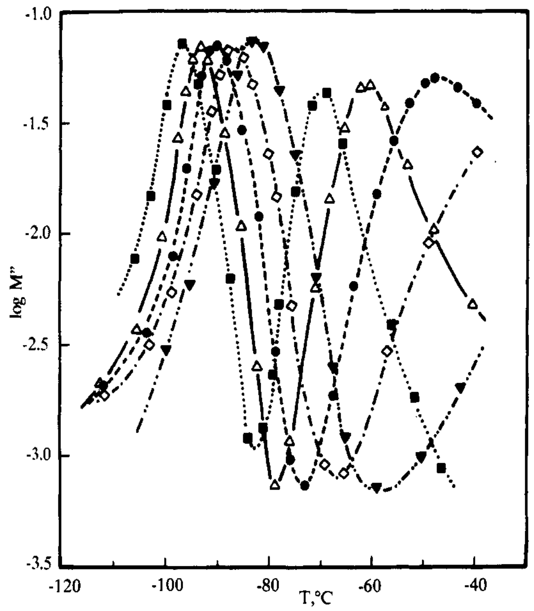

Figure 9. Changes on the electric loss modulus with temperature for 2-chlorocyclohexyl isobutyrate at the frequencies indicated in Figure 8.

B. Dipolar and Conductive Contributiions to the Glass-Rubber Process: Interpretation of the Results in Terms of the Complex Electric Modulus. Owing to the large conductive effects detected in the glass-rubber relaxation of PCCHA and the glass-liquid process of CCHI at moderately low frequencies, it seems advisable to investigate the conductive and dipolar contributions to the α peak of both the polymer and the model compound of its repeating unit, by expressing the dielectric results in terms of the complex electric modulus $M^* = (\epsilon^*)^{-1}$. The values of the components of the complex permittivity were converted to the components of M^* by the relations

$$M^* = M' + iM'' \qquad (10)$$

$$M' = \epsilon'/(\epsilon'^2 + \epsilon''^2); \qquad M'' = \epsilon''/(\epsilon'^2 + \epsilon''^2) \qquad (11)$$

The curves depicting the temperature dependence of M' and M'' for CCHI, represented in Figures 8 and 9, respectively, exhibit two well differentiated regions. On the one hand, M' presents a plateau separating the first part of the curve, associated with the dipolar process, from the second one, associated with the conductivity. On the other hand, M'' shows two well developed peaks which in increasing temperature order are caused by dipolar and conductive processes.

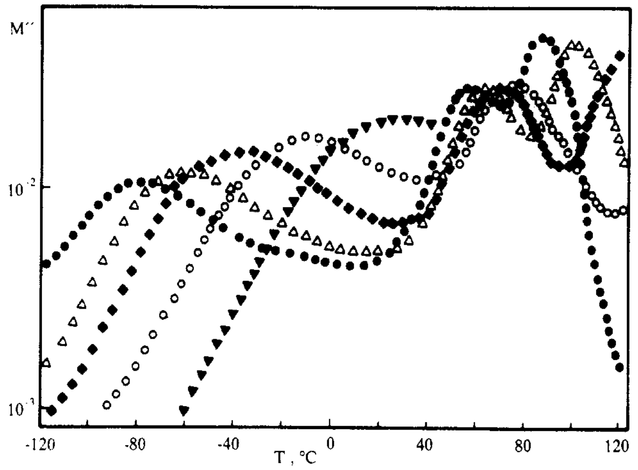

Figure 10. Temperature dependence of the loss electric modulus for poly(2-chlorocyclohexyl acrylate) (PCCHA) at several frequencies: (●) 1, (△) 10, (◆) 10^2, (○) 10^3, and (▼) 10^4 Hz.

The relaxation spectrum for PCCHA, expressed in terms of the electric loss modulus in Figure 10, shows a well developed β absorption in the glassy region followed by two relaxations in the glass-rubber zone produced in increasing temperature order by dipolar and conductive processes. It is worthy to note that the separation of the dipolar and conductive α peaks in the polymer is not so well defined as in the spectrum of the model compound CCHI. The same trends can be seen in the temperature dependence of the real electric modulus (Figure 11) where the well developed plateau separating the dipolar and conductive contributions in the glass-rubber relaxation of CCHI becomes less and less well defined in the polymer, as frequency decreases.

The fact that the value of the half width for the conductive peaks of CCHI is 1.14 (Figure 12) suggests that they are produced by a single Debye process in which the complex permittivity can be written as

$$\epsilon^*_c = \epsilon_{\infty c}[1 + (i\omega\tau_c)^{-1}] \qquad (12)$$

so that the equivalent circuit is simply a parallel RC combination. In eq 12 the conductivity relaxation time τ_c is defined as

$$\epsilon''_c = \epsilon_{\infty c}(\omega\tau_c)^{-1} = \frac{\sigma}{\omega\epsilon_0} \qquad (13)$$

where ϵ_0 is the permittivity of free space (=8.8542 pF/m), and σ is the conductivity. The free charge contribution can also be expressed in terms of the electric modulus by

$$M^*_c = M_{\infty c}\left(\frac{1}{1 + (i\omega\tau_c)^{-1}}\right) = M_{\infty c}\left(1 - \frac{1}{1 + i\omega\tau_c}\right) \qquad (14)$$

At low frequencies, where free charge conduction governs the glass-rubber relaxation process, eq 12 suggests that $\epsilon''_c \sim \omega^{-1}$. Therefore the dipolar contribution to the total dielectric loss can be separated by subtracting from ϵ'' the values of ϵ''_c given in the straight line of slope −1 of the double logarithmic plot ϵ''_c *vs* ω shown for CCHI in Figure 13. In this way, the dipolar α peaks shown in the lower part of this figure were obtained. it is worthy to point out that only free space charges and dipolar processes contribute to the glass rubber relaxation of the low molecular weight compound, and, as a consequence, the M'' *vs* M' complex plot in the low-frequency region is a semicircle from whose intercept with the abscissa axis in the high-frequency region the value of $M_{\infty c} = \epsilon_{\infty c}^{-1}$ is determined.

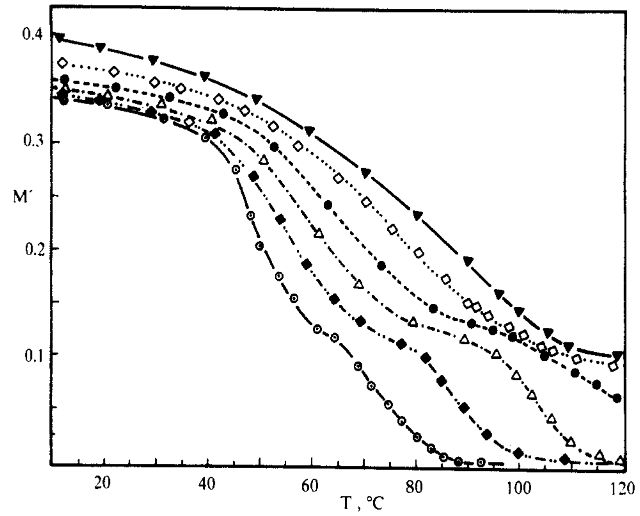

Figure 11. Dependence of the real electric modulus on temperature for poly(2-chlorocyclohexyl acrylate) in the glass-rubber region: (◎) 0.1, (◆) 1, (△) 10, (●) 10^2, (◇) 10^3, and (▼) 10^4 Hz.

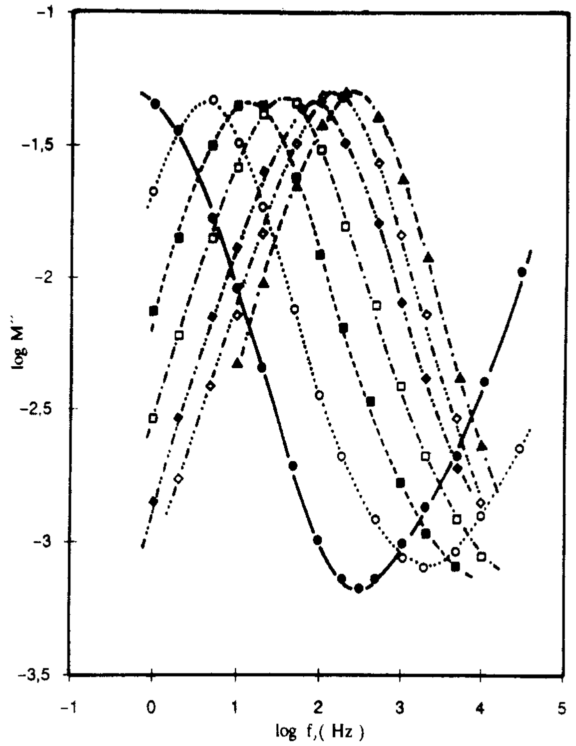

Figure 12. Free charge conductive peaks of 2-chlorocyclohexyl isobutyrate at several temperatures: (●) −70, (○) −65, (■) −60, (□) −55, (◆) −50, (◇) −45, and (▲) −40 °C.

The lack of a well defined separation between the conductive and dipolar processes in the glass-rubber relaxation of PCCHA (Figure 4), prompted us to analyze in detail all the presumable contributions to this process. In the low-frequency region, the double logarithmic plot of the dielectric loss *vs* frequency is a straight line with slope −1, as would be expected from a process caused by free space charges. By subtracting the values of conductivity loss ϵ''_c from the experimental results one fines $\epsilon'' \sim \omega^{-h}$ in the low-frequency region of the spectrum, where the values of h is ca. 0.5. This contribution has been attributed to interfacial phenomena as will be discussed below.

Interfacial phenomena observed in dielectrics have usually been considered as resulting from space charge buildup near electrodes which partially or wholly blocks charge transport.[14] These effects have been represented by an equivalent circuit which includes a Warburg-like impedance[15] for diffusion effects, $Z_i^* = z_i(i\omega)^{-\alpha}$, in series

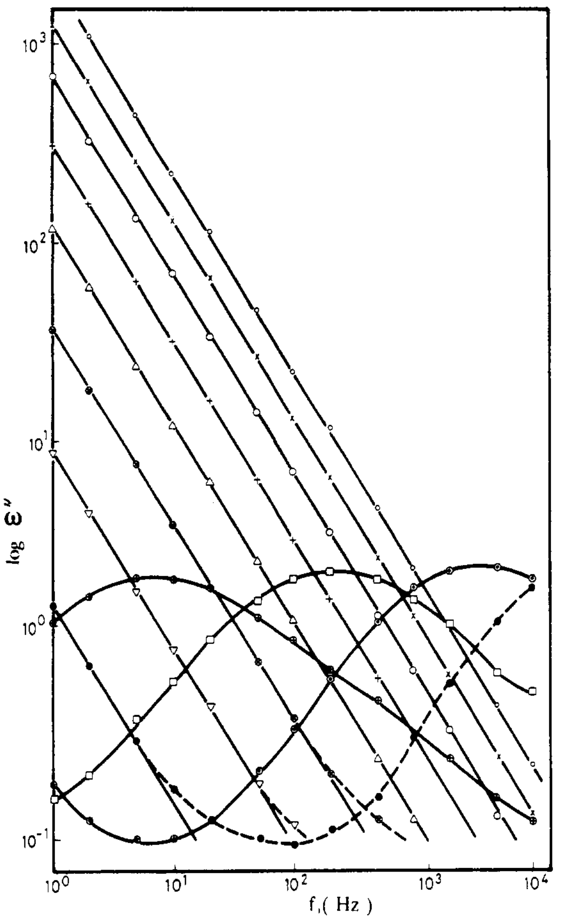

Figure 13. Plot showing the contributions of the dipolar relaxation and the free charges conductive process to the dielectric loss of 2-chlorocyclohexyl acrylate at several temperatures: (⊕) −90, (□) −85, (◎) −80, (●) −75, (▽) −70, (⊗) −65, (△) −60, (+) −55 (○) −50, (×) −45 and (○) −40 °C.

with an RC parallel circuit which represents the conductive component. In this RC circuit the capacity C would represent the dipolar component completely relaxed and, as a consequence, $\epsilon_{\infty c} = C/C_o = \epsilon_{r\alpha}$, where $\epsilon_{\alpha r}$ and C_o are, respectively, the relaxed permittivity in the α-glass rubber relaxation process and the capacity of the empty capacitor. The interfacial phenomena, however, may include the diffusion of charges in the vicinity of the electrodes together with specific charges adsorption processes. Some adsorption models imply an inductive type behavior and an arc in the complex impedance plane which partially or totally falls below the real axis. In analyzing this phenomenon, Franceschetti and Macdonald[16] have concluded that it is preferable to consider that adsorption leads to negative resistance and negative capacitance contributions, rather than to a large positive inductance. We should note that a negative capacitance, $-1/i\omega C$, is equivalent to a positive inductance, $i\omega L$, where $L = 1/\omega^2 C$. The negative value for the resistance can be explained in terms of a progressive accumulation of adsorbed charges on the surface of the electrode.[17-21] From a physical point of view, this would correspond to an active ⇄ passive states transition in the corresponding electric circuit, a relatively frequent phenomenon that appears in the corrosion of metals. The carriers responsible for the interfacial phenomena detected in our experiments may be ionic impurities as a result of the preparative methods used in the synthesis of the monomer and, therefore, the problematic involved in the interface PCCHA-electrode may be similar to that observed in electrode/solid electrolyte interfaces.

The apparent additivity of interfacial ϵ^*_i and free charge ϵ^*_c permittivity in the low-frequency region can be accounted for by assuming a negative interfacial impedance, $Z_i^* = -z_i(i\omega)^{-\alpha}$, in series with a parallel RC circuit for the free charge conduction. If the latter is represented by a complex admitance, $Y = G + i\omega C$, the measured values of both the capacitance, $\bar{C}$, and the conductance, $\bar{G}$, are related to C and G by the following approximate expressions

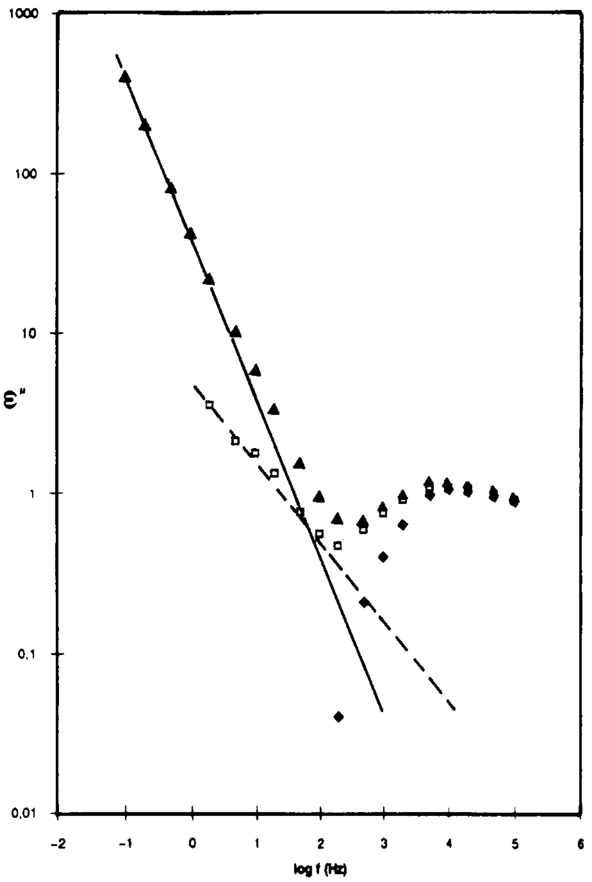

Figure 14. Separation of the free charges (slope −1) interfacial (−0.5) and dipolar contributions to the glass-rubber process of poly(2-chlorocyclohexyl acrylate) (PCCHA) at 100 °C.

$$\bar{C} \cong C - G^2 z_1 \sin\left(\frac{\pi\bar{\alpha}}{2}\right)\omega^{-(1+\bar{\alpha})}$$
$$\bar{G} \cong G + G^2 z_1 \cos\left(\frac{\pi\bar{\alpha}}{2}\right)\omega^{-\bar{\alpha}} \qquad (15)$$

which are valid for $(\omega C)^2 \ll G^2$ and $(Z_1 G)^2 \ll 1$, conditions which are held in the present case at low frequencies where the dipolar entities are nearly fully relaxed. The value and sign of α also depend on the type of electric network representing the V-shaped groove between the sample and the electrodes (ref 15, page 81). If it is assumed that $\alpha < 0$, eqs 15 lead to

$$\bar{\epsilon}' = \epsilon_\infty - \frac{z_1 G^2}{C_o}\sin\left(\frac{\pi h}{2}\right)\omega^{-h} = \epsilon_{\infty c} + \mathcal{R}\epsilon_{\infty i}[1 + (i\omega\tau_i)^{-h}] \qquad (16)$$

$$\bar{\epsilon}'' = \frac{\sigma}{\epsilon_o\omega} + \frac{z_1 G^2}{C_o}\cos\left(\frac{\pi h}{2}\right)\omega^{-h} = \frac{\sigma}{\omega\epsilon_o} + |\mathcal{F}\epsilon_{\infty i}[1 + (i\omega\tau_i)^{-h}]| \qquad (17)$$

where $\sigma/\epsilon_o = G/C_o$, $\epsilon_{\infty c} = C/C_o$, $\epsilon_{\infty i} = (G^2/C_o)z_1\tau_i^h$, $\epsilon_\infty = \epsilon_{\infty c} + \epsilon_{\infty i}$, C_o and τ_i being, respectively, the capacity of the empty condenser and the relaxation time associated with the interfacial phenomena. According to eqs 16 and 17, the complex conductive permittivity is obtained by adding the free charge and interfacial complex permittivities, the latter parameter being given by

$$\epsilon_i^* = \epsilon_{\infty i}[1 + (i\omega\tau_i)^{-h}] \tag{18}$$

which in terms of the electric modulus can be written as

$$M_i^* = M_{\infty i}\left(\frac{1}{1 + (i\omega\tau_i)^{-h}}\right) = M_{\infty i}\left(1 - \frac{1}{1 + (i\omega\tau_i)^{h}}\right) \tag{19}$$

Therefore by subtracting the free charges and interfacial contributions from the dielectric loss, the glass-rubber dipolar peaks are obtained. In Figure 14 are shown, as an example, the dipolar, interfacial, and conductive contributions to the dielectric loss of 100 °C.

By assuming that additivity holds in the low–frequency region, the components of the conductive modulus can be written as

$$\bar{M}' = \frac{\alpha\omega^{-h} + d}{(a^2 + b^2)\omega^{-2h} + 2ad\omega^{-h} + 2bc\omega^{-(1+h)} + c^2\omega^{-2} + d^2} \tag{20}$$

$$\bar{M}'' = \frac{b\omega^{-h} + c\omega^{-1}}{(a^2 + b^2)\omega^{-2h} + 2ad\omega^{-h} + 2bc\omega^{-(1+h)} + c^2\omega^{-2} + d^2} \tag{21}$$

where the parameters a, b, c, and d are given by

$$\begin{gathered} a = \epsilon_{\infty i}\tau_i^{-h} cos\,\frac{\pi}{2}h \\ b = \epsilon_{\infty i}\tau_i^{-h} sin\,\frac{\pi}{2}h \\ c = \frac{\sigma}{\epsilon_0} \\ d = \epsilon_{\infty c} + \epsilon_{\infty i} \end{gathered} \tag{22}$$

The complex dielectric plot M'' *vs* M' shows asymptotic behavior

$$\bar{M}', \bar{M}'' \rightarrow 0, \text{ for } \omega \rightarrow 0$$

$$\bar{M}' \rightarrow (\epsilon_{\infty c} + \epsilon_{\infty i})^{-1}; \qquad \bar{M}'' \rightarrow 0, \text{ for } \omega \rightarrow \infty \tag{23}$$

in agreement with the experimental results. The value of $d = \epsilon_{\infty c} + \epsilon_{\infty i} = \bar{M}_\infty^{-1}$ can straightforwardly be obtained from the $\bar{M}''$ *vs* $\bar{M}'$ plot. However, separation of the free charge and interfacial contributions to d requires some assumptions. Thus, since $\epsilon'_c = \epsilon_{\infty c}$ and $\epsilon'_i \approx \omega^{-h}$, it is expected that $\epsilon'_i \gg \epsilon_{\infty c}$ and $\epsilon'_i \ll \epsilon_{\infty c}$, at low and high frequencies, respectively, which leads to $\epsilon_{\infty i} \approx 0$ and $d \approx \epsilon_{\infty c}$. On the other hand, and as a consequence of the fact that the double logarithmic plots of ϵ''_c and ϵ''_i *vs* ω exhibit slopes of −1 and −0.5, respectively, it is expected that $\epsilon''_c \gg \epsilon''_i$ and $\epsilon''_c \ll \epsilon''_i$, at low and high frequencies, respectively.

Values of the experimental dielectric results, expressed in terms of the complex electric modulus, are given in Figure 15, where it can be seen that two arcs appear, one in the low frequency region produced by both free charges and interfacial conductive effects, followed by another one of lower curvature in the high frequency region caused by dipolar processes. Both arcs are assumed to intersect at $(\bar{M}_\infty)^{-1} = (\epsilon_{\infty c} + \epsilon_{\infty i}) = \epsilon_{\alpha r}$, where $\epsilon_{\alpha r}$ is the relaxed dipolar permittivity. Since in the low-frequency region the loss electric modulus $\bar{M}''$ can be written as

$$\bar{M}'' = \frac{\bar{\epsilon}''}{(\epsilon_{\infty c} + \epsilon'_i)^2 + \bar{\epsilon}''^2} \tag{24}$$

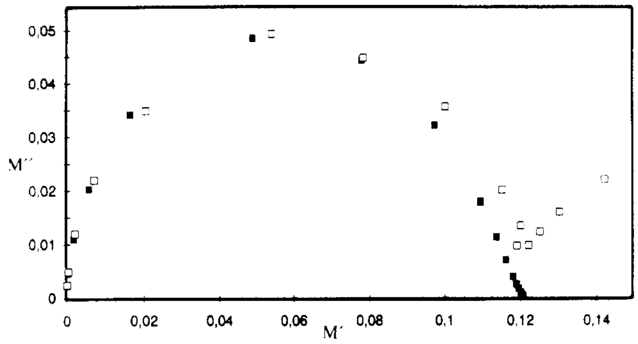

Figure 15. Complex electric modulus plot for poly(2-chlorocyclohexyl acrylate) (PCCHA) at 100 °C. The symbols (□) and (■) represent, respectively, experimental results and calculated values by means of the model described in the text.

Table 3. Dielectric Results in Benzene and Dipole Moments for 2-Chlorocyclohexyl Isobutyrate (CCHI) and Poly(2-chlorocyclohexyl acrylate) (PCCHA)

T, °C	$2n_1 dn/dw$	$d\epsilon/dw$	$\langle\mu^2\rangle$, D^2	$\langle\mu^2\rangle/x$, D^2
		CCHI		
20	−0.05	4.58	8.46	
30	−0.05	4.31	8.44	
40	−0.06	4.13	8.55	
50	−0.06	3.95	8.64	
		PCCHA		
20	0.04	4.30		7.18
30	0.05	4.15		7.30
40	0.06	3.91		7.24
50	0.07	3.73		7.34

the term $\epsilon_{\infty c} + \epsilon'_i$ can directly be obtained from $\bar{M}''$ and $\bar{\epsilon}''$. By plotting log $(\epsilon' - \epsilon_{\infty c})$ *vs* log ω for different values of $\epsilon_{\infty c}$, in the low-frequency region, the value of this quantity is considered to be that one for which the slope of the plot is −0.5. For example, the slope of this plot at 100 °C goes up from −0.28 ($p = -0.985$) for $\epsilon_{\infty c} = 6$ to −0.49 ($\rho = 0.960$) for $\epsilon_{\infty c} = 8.26$, where ρ is the correlation coefficient of the straight line obtained by least-squares analysis. This result confirms the previous assumption $\epsilon_{\infty i} \approx 0$ and, at the same time, indicates that the uncertainties involved in the evaluation of $\epsilon_{\infty i}$ preclude the possibility of obtaining the values of the parameters a and b in eqs 20 and 21. An important conclusion of this analysis is that the extremes of the $\bar{M}''$ *vs* $\bar{M}'$ arc seem to be governed by the free charge conductivity. However, the depature of the Debye arc observed in Figure 15 is caused by the interfacial contribution to the total conductive process.

C. Dipole Moments. Values of the mean-square dipole moments $\langle\mu^2\rangle$ for the model compound and the polymer were determined from dielectric measurements in solution by means of the equation of Guggenheim and Smith[22,23]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi\rho N_A(\epsilon_1 + 2)^2}\left(\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right) \tag{25}$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, N_A is Avogardro's number, ρ is the density of the solvent, and ϵ and n are, respectively, the static dielectric permittivity and index of refraction of the solutions (the same terms with subindex 1 refer to the solvent). Values of $d\epsilon/dw$ and dn/dw in benzene were obtained, respectively, from the slopes of the plots $\epsilon - \epsilon_1$ and $n - n_1$ *vs* the weight fraction of solute w in the limit w → 0. Values of the slopes at different temperatures are indicated in Table 3. In the last column of the table the values of $\langle\mu^2\rangle$ for CCHI are indicated; however, the results for the polymer are expressed in terms of $\langle\mu^2\rangle/x$, the mean-square dipole

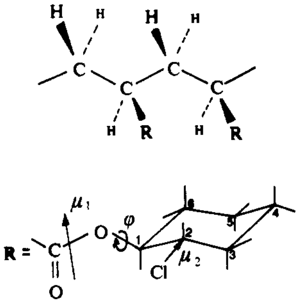

Figure 16. Scheme showing a meso diad in trans conformation and the side group of poly(2-chlorocyclohexyl acrylate) (PCCHA). Arrows represent the orientation of the dipoles.

moment per repeating unit. The uncertainty involved in the determination of $\langle \mu^2 \rangle$ was estimated to be ±3%.

Theoretical Analysis of the Polarity of Isolated Chains

A scheme of a meso diad of PCCHA is shown in Figure 16. The dipole moment associated with the side group may be considered to be the result of two contributions: μ_1, the dipole moment of methyl acetate whose value is 1.76 D and its orientation forms an angle of 123° with the C–CO bond,[24] and μ_2, the dipole moment of the C–Cl bond whose value was assumed to be[25,26] 1.9 D. The dipole moment μ of the side group depends on the relative orientation of μ_1 and μ_2 as defined by the rotational angle about the C_{cy}–O bond φ; this is the only rotational angle that governs μ since the O–CO bond in the ester group is restricted to trans states. Moreover, μ also will depend on the type of linkage, equatorial or axial, of the chlorine and oxygen atoms to the cyclohexane ring. This problem was investigated by ^{1}H NMR spectroscopy as will be discussed below.

The hydrogen bound to the C_2 atom of the cyclohexyl ring in CCHI gives eight signals in the interval 3.786 to 3.865 δ, whereas the hydrogen bound to the C_1 carbon atom gives six signals in the range 4.729 to 4.806 δ. The location of these signals in the spectrum indicates that these hydrogens are in axial position in the cyclohexyl ring with a chair conformation; i.e., the halogen and oxygen 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 analysis of the spectrum reveals coupling constants of $J(H_{2a},H_{1a})$ = 9.0 Hz, $J(H_{2a},H_{3a})$ = 10.4 Hz, and $J(H_{2a},H_{3e})$ = 4.2 Hz for the hydrogen at 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, which can only be justified considering a chair conformation with equatorial arrangement of the heteroatoms.

By comparing the values of μ with the conformational energies about the C_{cy}–O bond, calculated by molecular mechanics, one can see that the minimum of energy is located in the vicinity of $\varphi = 0$ ($\mu^2 = 8.42$ D^2) and $\varphi = 180°$ ($\mu^2 = 3.16$ D^2). However, the conformational energy in the latter case is more than 2 Kcal mol^{-1} higher in energy than in the former and, consequently, the rotational angle about the C_{cy}–O bond was assumed to be zero. Moreover, the calculations were performed assuming that the Cl atom can be located, with the same probability, linked to either of the 2 and 6 carbons of the cyclohexyl moiety.

A 2 × 2 rotational states scheme was used to perform the theoretical calculations of $\langle \mu^2 \rangle$ which assumes that the skeletal bonds are restricted to t y g states; however, since the carbonyl group only can adopt two conformations, each of these states is split into two in order to account for the conformations in which the carbonyl group is cis ($\chi = 0$) and trans ($\chi = \pi$) to the methine bond. The statistical weight matrices in the order (t,χ=0), (t,χ=π), (g,χ=0), and (g,χ=π) are[27,38]

Table 4. Components in D of the Resulting Dipole Moment of the Side Group, in the Reference Frame of the C$^\alpha$–CH$_2$ Bond of the Backbone, for Different Rotational Angles (χ) about the C$^\alpha$–CO Bond in Figure 16

loc. Cl atom in Fig 15	x^0	μ_x	μ_y	μ_z
2	180	0.094	−2.595	−0.883
2	0	0.295	2.101	1.737
6	180	2.410	−0.839	−0.954
6	0	−2.022	0.399	1.809

$$\boldsymbol{U'} = \begin{pmatrix} 1 & 0 & \rho & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{pmatrix} \tag{26}$$

for the CH$_2$–C$^\alpha$–CH$_2$ bond pair and

$$\boldsymbol{U''}_{\mathrm{r}} = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad \boldsymbol{U''}_m = \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix} \tag{27}$$

for racemic and meso configurations of the C$^\alpha$–CH$_2$–C$^\alpha$ bond pair. The skeletal bond angles were considered to be 112.5°, whereas the rotational angles about the backbone of meso diads are $\langle \phi_1,\phi_2 \rangle_{tt}$ = 16,16°, $\langle \phi_1,\phi_2 \rangle_{tg}$ = 3,-114° and $\langle \phi_2,\phi_1 \rangle_{gt}$ = 114,3°. For racemic diads, $\langle \phi_1,\phi_2 \rangle_{tt}$ = 3,3°. The components of the dipole moments of the side groups in the reference frame of the C$^\alpha$–CH$_2$ bond are given in Table 4.

The mean-square dipole moment per repeating unit was calculated by matrix methods described in detail elsewhere.[29] According to these methods, $\langle \mu^2 \rangle / x$ is given by

$$\frac{\langle \mu^2 \rangle}{x} = \frac{1}{Zx} \boldsymbol{P}_1 \prod_{k=2}^{x-1} (\boldsymbol{S'P}_k) \boldsymbol{P}_x \tag{28}$$

where Z is the rotational partition function, and $\mathbf{P}_k$ can be written as[30,31]

$$\boldsymbol{P}_k = \begin{pmatrix} \boldsymbol{G'}_k(t,\chi=0) & & & \\ & \boldsymbol{G'}_k(t,\chi=\pi) & & \\ & & \boldsymbol{G'}_k(g,\chi=0) & \\ & & & \boldsymbol{G'}_k(g,\chi=\pi) \end{pmatrix} \times (\boldsymbol{U''}_k \otimes \boldsymbol{E}_5) \times \begin{pmatrix} \boldsymbol{G''}_k(t,\chi=0) & & & \\ & \boldsymbol{G''}_k(t,\chi=\pi) & & \\ & & \boldsymbol{G''}_k(g,\chi=0) & \\ & & & \boldsymbol{G''}_k(g,\chi=\pi) \end{pmatrix} \tag{29}$$

where the elements of the diagonal of $\mathbf{P}_k$, $\mathbf{G}_k$, are 5 × 5 generator matrices given by the familiar expression[29]

$$\boldsymbol{G}_k = \begin{pmatrix} 1 & 2\mu^T \boldsymbol{T} & \mu^2 \\ 0 & \boldsymbol{T} & \mu \\ 0 & 0 & 1 \end{pmatrix}_k \tag{30}$$

In this equation $\boldsymbol{T}$ is the transformation matrix that by premultiplication converts the transformation matrix in reference frame $k+1$ to its representation in the reference frame k and μ^T is the vector transpose of μ. The term $\mathbf{S}'$

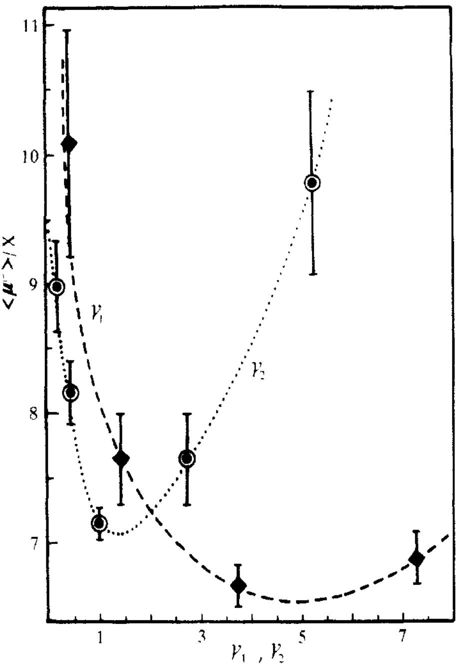

Figure 17. Plot showing the variation of the mean-square dipole moment per repeating unit of poly(2-chlorocyclohexyl acrylate) (PCCHA) with the statistical weights that define the orientations of the dipoles in a racemic diad.

in eq 28 corresponds to $\mathbf{U}'\otimes\mathbf{E}_5$, where the symbol $\otimes$ denotes the direct product and $\mathbf{E}_5$ represents the identity matrix of order 5. Finally, the terms $\mathbf{P}_1$ and $\mathbf{P}_x$ are, respectively, row and column vectotrs to convert eq 28 in a scalar; specifically, $\mathbf{P}_1$ = row($\mathbf{G}_{11}$, 0, 0, 0) and $\mathbf{P}_x$ = column-($\mathbf{G}_{xf}(\chi=0)$, $\mathbf{G}_{xf}(\chi=\pi)$, $\mathbf{G}_{xf}(\chi=0)$, $\mathbf{G}_{xf}(\chi=\pi)$), $\mathbf{G}_{11}$ and $\mathbf{G}_{xf}$ being, respectively, the first row and last column of the generator matrix $\mathbf{G}$.

Values of $\langle\mu^2\rangle/x$ were obtained by using the set of statistical weights $\rho = 1.1$, $\beta = 1.8$, $\gamma = 1.4$, $\gamma_1 = 1.4$, and $\gamma_2 = 2.7$ that describe the polarity of PCHA[6] and poly(phenyl acrylate) (PPA).[28] The calculations were carried out by generating 100 chains of 100 repeating units each by Monte Carlo methods, in which the probability of isotactic replacement was 0.45. The locations of the chlorine atom in each repeating unit was decided by a random routine so that the probability of the location in each of the two positions was 0.5. The dipole moments are very sensitive to γ_2, as can be seen in Figure 17 where the dependence of $\langle\mu^2\rangle/x$ on this parameter is depicted. The polarity of the chains strongly increases when the fraction of racemic diads having carbonyl groups with the same conformation increases. On the contrary, the dependence of $\langle\mu^2\rangle/x$ on γ_1 shows that the polarity of the chains decreases as the fraction of racemic diads having carbonyl groups with alternating cis and trans conformations with respect to the methine bond increases. As for the dependence of $\langle\mu^2\rangle/x$ on the parameters of the statistical weight matrices associated with meso diads, the calculations indicate that whereas the polarity of the chains is nearly insensitive to the value of β, it is moderately dependent on γ. Thus in increasing γ from 0.14 to 3.77, $\langle\mu^2\rangle/x$ goes down from 9.41 to 7.64 D^2, whereas the value of this quantity only changes from 7.40 to 8.06 when β goes up from 1 to 4.8. In view of these results the best set of statistical weights that give a good account of the dipole moments of the chains is $\beta = 1.79$, $\rho = 1.1$, $\gamma = 1.79$, $\gamma_1 = 1.4$, and $\gamma_2 = 1$. The results obtained with these values for $\langle\mu^2\rangle/x$ and the temperature coefficient $d \ln \langle\mu^2\rangle/\mathrm{d}T$ are 7.15 ± 0.09 D^2 and (5.5 ± 0.6) × 10^{-4} K^{-1}, in pretty good agreement with the experimental results 7.2 D^2 and 5.8 × 10^{-4} K^{-1} ($\rho = 0.775$), respectively.

Discussion

By comparing the mean-square dipole moment of PCCHA with that of poly(cyclohexyl acrylate) (PCHA) one finds that the presence of a halogen atom in PCCHA nearly triples the value of this quantity corresponding to PCHA. Actually, the value of $\langle\mu^2\rangle/x$ at 30 °C increases from 2.68 D^2 for PCHA[6] to 7.30 D^2 for PCCHA. One of the reasons for this difference lies not only in the lower polarity of the side group in the former polymer, but also in that the dipole moment associated with the side group in PCHA is located in the plane defined by the C$^\alpha$–CO–O bonds, and, therefore, it is very sensitive to γ_2, the statistical weight that accounts for the relative orientation of two consecutive dipoles in racemic diads. As γ_2 increases in PCHA, the probability of conformations in which the dipoles are in nearly antiparallel direction also increases and hence $\langle\mu^2\rangle/x$ shows a decreasing dependence on γ_2. In PCCHA, on the contrary, the resulting dipole moment of the ester and C–Cl contributions are not located in the C$^\alpha$–CO–O plane as occurs in PCHA. Here the halogen atom contributes to increase the polarity of the PCCHA chains as the fraction of conformations in which the carbonyl group is either in cis or trans conformation with respect to the methine bond increases. Disruption of this conformational *order* diminishes $\langle\mu^2\rangle/x$, as can be seen in Figure 17 where a decreasing dependence of this quantity on γ_1 can be detected. Although tg conformations are undoubtedly preferred over the alternative tt conformation in the meso diads of both PCHA and PCCHA chains, the dipole moments of these polymers, contrary to the molecular dimensions, do not seem to be dependent on the fraction of tg conformations as the insensitivity of $\langle\mu^2\rangle/x$ to β suggests. The dipole moments are only sensitive to the parameter γ that governs the fraction of tt states in meso diads in which the carbonyl groups are in cis conformation with respect to the alternative trans. The higher is this fraction; the lower is the polarity of the chains.

Both intramolecular and intermolecular dipolar correlations are responsible for the polarity exhibited by polymers in the bulk. The correlation coefficient that accounts for both the intramolecular and intermolecular interactions may be written as[2]

$$g = 1 + \sum_{i\neq j} \cos\left(\langle\gamma_{ij}\rangle\right)^{\text{intram}} + \sum_{k\neq l} \cos\left(\langle\gamma_{kl}\rangle\right)^{\text{interm}} \qquad (31)$$

The intramolecular dipolar correlation coefficient can directly be obtained from the experimental results by means of the expression

$$g_{\text{intra}} = \frac{\langle\mu^2\rangle}{x(\mu_1^2 + \mu_2^2)} \qquad (32)$$

where μ_1 and μ_2 represent the dipoles associated with the ester and the C–Cl bonds whose values, as indicated before, amount to 1.76 and 1.9 D, respectively. The value of g_{intra} at 30 °C for PCCHA amounts to 1.1, a surprisingly high value if it is compared with that observed in PCHA which is only 0.75 at the same temperature.[6] This value, however, is somewhat lower than that obtained (1.2) for CCHI. Accordingly, correlations between dipoles enhance the polarity of both isolated CCHI molecules and isolated PCCHA chains.

The high value of g_{intra} is deeply related to the angular correlation between the dipoles associated with the ester and the C–Cl bond. Interactions between the chlorine atom and the carbonyl group restricts the rotational angle about O–C$_{\text{Cy}}$ bond to zero raising the mean-square dipole moment of the side group to the value of 8.4 D^2. This

Table 5. Values of the Conductivity for 2-Chlorocyclohexyl Isobutyrate (CCHI) and Poly(2-chlorocyclohexyl acrylate) (PCCHA)

CCHI		PCCHA	
T, °C	$10^9\sigma$ (S/m)	T, °C	$10^9\sigma$ (S/m)
−75	0.08	90	0.48
−70	0.49	100	2.29
−65	2.03	110	13.8
−60	6.67	115	20.9
−55	17.5		
−50	37.8		
−55	69.5		

value is already larger than the sum of the squares of the dipole moments of the two dipoles of the side groups. In fact, if only the resulting dipole moment of the side group is considered, then the intramolecular correlation coefficient decreases to 0.87 and, therefore, PCCHA chains exhibit slight intramolecular dipolar correlations.

The intermolecular correlation coefficient g for the polymer may be evaluated from dielectric measurements carried out in the bulk using Onsager type equations[32] such as the Fröhlich relation[33]

$$g = \frac{9(\epsilon_r - \epsilon_u)(2\epsilon_r + \epsilon_u)}{x(\mu_1^2 + \mu_2^2)\epsilon_r(\epsilon_u + 2)^2}\frac{MkT}{4\pi\rho N_A} \qquad (33)$$

where ϵ_r and ϵ_u are the relaxed and unrelaxed dielectric permittivities, the value of the latter quantity being assumed to be n^2 (≈ 2.16); the other parameters have the usual meaning. The value of ϵ_r at 100 °C, 8.26, was obtained from the Cole–Cole plot of Figure 4. By using this result one finds $g = 1.2$, in pretty good agreement with the value obtained for g_{intra}. As a consequence, intermolecular dipolar correlations seem to be negligible in the dielectric behavior of PCCHA.

The evaluation of g for CCHI at room temperature was carried out using a procedure that may involve some lack of precision. Actually, the results shown in Figure 2 seem to suggest that ϵ' is a decreasing linear function of temperature, independent of the frequency, for temperatures above T_g. By using this method one finds that $\epsilon_r \approx 7.0$ at 20 °C; this quantity in conjunction with the fact that $n^2 = 2.10$ gives $g = 0.91$ for CCHI. Contrary to what occurs for the polymer g is somewhat lower than g_{intra} presumably as a consequence of the uncertainties involved in the determination of the relaxed dielectric permittivity.

PCCHA exhibits a β absorption whose intensity is nearly three times larger than that corresponding to PCHA. An ostensible β relaxation has also been reported for poly(chlorocyclohexyl methacrylate)s, specifically the 2- and 4-chlorocyclohexyl derivatives. This absorption has been partially attributed to dielectric activity caused by conformational transitions from one chain conformation to the other, so that the chlorine atom would move from axial to equatorial position as the cyclohexyl group flips.[2,34] However, a close inspection of the spectrum of PCCHA shows that the halogen atom remains in equatorial position and, therefore, conformational chair to chair transitions in the cyclohexyl group of chlorocyclohexyl esters of polyacrylic and polymethacrylic esters are unlikely. This relaxation may rather be the result of molecular motions about the O–C$_{\text{Cy}}$ bonds; conformational transitions between the two states of lower energy ($\phi = 0 \rightleftarrows \phi = 180°$) change the square dipole moment of the side group from 8.42 to 3.16 D^2. Although the energy associated with the state $\phi = 180°$ has an energy ca. 2 kcal mol^{-1} above that of the alternative state, it is sufficiently populated to hold these transitions mainly responsible for the secondary relaxation. The β relaxation observed in cyclohexyl isobutyrate is not detected in the relaxation spectrum of CCHI, presumably because it is shifted to the right side of the spectrum and it overlaps with the glass–rubber relaxation.

Finally, the conductivities exhibited by the relaxation spectra of both CCHI and PCCHI at temperatures above their respective values of T_g, shown in Table 5, obey Arrhenius behavior with activation energies of 20.0 and 42.6 kcal mol^{-1}, respectively. The fact that the conductivity increases with temperature suggests that the carriers may be of ionic type.

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