Equilibrium and Dynamic Dielectric Properties of Acrylate Polymers with (Phenyl)(4-chlorophenyl)methanone Groups in Their Structure

R. C. Nunes,[†] R. Díaz-Calleja,[‡] M. Pinto,[§] E. Saiz,[‖] and E. Riande*,[†]

Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006-Madrid, Spain, Departamento de Termodinámica, ETSII, UPV, Valencia, Spain, Instituto de Macromoléculas (IMA), UFRJ, Rio de Janeiro, Brazil, and Departamento de Química-Física, Universidad de Alcalá de Henares, 28871 Madrid, Spain

The curves describing the relaxation behavior of poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone at several frequencies present in the dielectric loss–temperature plane a β relaxation centered at $-76\ °\mathrm{C}$ at 10 Hz, whose activation energy shows a slight tendency to increase as the temperature goes up. The relaxation spectra exhibit an ostensible glass–rubber relaxation or α process centered at 106 °C at 10 Hz, in which free charge conductivity and blocking electrode phenomena become dominant at frequencies below 10 Hz. An electric model is used to separate the dipolar response from conductivity contributions in the glass–rubber relaxation, and the dipole time correlation function for this process is obtained at several temperatures. The intramolecular correlation coefficient g_{intra}, determined from dielectric measurements in solution, is somewhat larger than the coefficient g involving both intra- and intermolecular interactions, obtained from dielectric measurements in the bulk. A rotational state scheme is developed which gives a good account of the intramolecular dipolar correlation coefficient. Finally whereas the relaxation mechanisms involved in the glass–rubber relaxation seem to be governed by the volume, the conductive processes exhibit Arrhenius behavior.

Introduction

The physical properties of polymer chains with asymmetric carbon atoms in the backbone are strongly influenced by the chemical structure, length, and flexibility of the side groups. By restricting our attention to the polarity of polymers, one can see that the dipolar correlation coefficient for chains with dipoles rigidly attached to the skeletal bonds (poly(vinyl chloride), poly-(p-chlorostyrene), etc.) is governed by the statistics of the backbone.[1,2] However, for polymers with polar flexible side groups, such as poly(cyclohexyl acrylate), poly(methyl acrylate), etc., the dipolar correlation coefficient also depends on the relative orientations of the dipoles associated with the consecutive side groups.[2–5] In this later case an important difference between the conformational analysis of dipole moments and unperturbed dimensions arises in the sense that whereas only knowledge of the conformational statistics of the skeletal bonds is necessary for the dimensions, for dipole moments it is also important to develop statistics models in which the relative orientations of the side groups are properly considered.

The esterification of poly(acrylic acid) is a nearly unexhaustible source of polymeric materials whose properties are mainly conditioned by the chemical nature of the ester moiety. Thus polyacrylate chains with rigid side groups may develop mesomorphic order when the polar rods are separated from the main chain by means of flexible segments and, in some cases, even when they are directly linked to the COO group of the acrylate chains.[6] However, the study of the polarity of these chains presents some difficulties because in most cases the polymers are only soluble in polar solvents. Then it is necessary to devise methods by which the dipole moments of these chains can experimentally be determined. Therefore one of the aims of

this work is to measure the dipole moments of poly(4-acryloxy)-phenyl)(4-chlorophenyl)methanone (PAPCM), a polymer which is insoluble in nonpolar solvents (benzene, cyclohexane, dioxane, etc.). The polarity of PAPCM is then critically interpreted in terms of the rotational isomeric state model by using a scheme in which the orientations of the dipoles associated with the rigid side groups are properly accounted for.

Dielectric relaxation spectra of polymers with polar flexible side groups present subglass transition temperature relaxation processes which presumably arise from motions either taking place in the side groups alone or coupled with local motions of the main chain.[7–9] Whatever the mechanisms involved in the relaxations taking place in the glassy state, conformational transitions may occur through barrier energies whose heights may be affected by the surroundings and, consequently, both intramolecular and intermolecular interactions may play an important role in the dielectric response of PAPCM chains.[10] Therefore another goal of this work is to investigate how the presence of rigid polar moieties in the flexible side group may affect the dielectric response of these polymers in the glassy state and the glass–rubber transition. The phenomenological aspects of the description of the glass–rubber relaxation process of PAPCM chains are investigated paying special attention to the study of free charge conductivity and blocking electrode phenomena arising in the dielectric measurements.

Experimental Section

Synthesis of Poly(4-(acryloyloxy)phenyl)(4-chlorophenyl)-methanone. A suspension of 24.8 g (0.158 mol) of 4-chlorobenzoic acid (I) and 35.7 g (0.3 mol) of thionyl chloride in 300 mL of dry xylene was refluxed for ca. 6 h until complete solubilization was achieved. The solution was fractionated by distillation until the temperature at the top of the column reached 135 °C. The remaining solution was dropwise added to an aqueous cooled solution of 18.8 g (0.2 mol) of phenol, 8.0 g (0.2 mol) of sodium hydroxide, and 1 g of tetrabutylammonium

[†] Instituto de Ciencia y Tecnología de Polímeros (CSIC).
[‡] Departamento de Termodinámica, ETSII, UPV.
[§] Instituto de Macromoléculas (IMA), UFRJ.
[‖] Universidad de Alcalá de Henares.

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chloride, with strong stirring. The organic layer was evaporated, and the residue was recrystallized from isooctane. The yield of the compound thus obtained, 4-chlorophenyl benzoate (II), was 27.4 g (74%). A total of 26.7 g (0.2 mol) of aluminum chloride was quickly added to 22 g (0.094 mol) of II, and after 5 min of reaction the mixture was poured into an equal mixture of ice and 6 N HCl. The resulting mixture was slowly heated until complete neutralization of the inorganic compounds. The waxy residue was dissolved in hot toluene and then extracted with 200 mL of 2 N NaOH. The aqueous layer was treated with activated charcoal, filtered, and acidified with 6 N HCl. The precipitate (4-chlorophenyl)(4-hydroxyphenyl)methanone (III) was recrystallized from methanol and dried in a vacuum oven at 60 °C; yield 14.2 g (41.3%). (4-(Acryloyloxy)phenyl)-(4-chlorophenyl)methanone (IV) was obtained by reacting a solution of 7.2 g (0.08 mol) of acryloyl chloride in 100 mL of dichloromethane with a solution of 9 g (0.038 mol) of III, 1.6 g (0.0375 mol) of sodium hydroxide, and 0.5 g of tetrabutyl-ammonium chloride in 150 mL of distilled water at 0−5 °C with stirring. The organic layer was separated by chromatography using a basic aluminum oxide bead and dichloromethane as eluent. Finally it was recrystallized from toluene/hexane (1: 1); yield 7.6 g (68.8%). Anal. Found: C, 66.78%; H, 3.87%; Cl, 12.65%. Theoretical: C, 67.00%; H, 3.84%; Cl, 12.39%.

A 50% solution of (4-(acryloyloxy)phenyl)(4-chlorophenyl)-methanone in toluene and 1.5 mol % (in relation to monomer) AIBN was purged with N_2 and heated with stirring at 60 °C for 12 h. The resulting polymer was precipitated with methanol and dried under vacuum at 100 °C. The glass transition temperature of PAPCM was determined with a DSC7 calorimeter at a heating rate of 20 °C/min, and the value of this quantity taken at the onset of the thermogram peak was found to be 78 °C.

Dielectric Measurements. Values of the dielectric permittivity ϵ of solutions of PAPCM in a mixture of dioxane/dimethylformamide ($w_{dioxane} = 0.9444$) were obtained at 30 °C with a capacitance bridge (General Radio, type 1640 A) and a cylindrical three-terminal cell. The measurements were performed at 10 kHz, at which the real part ϵ' of the complex dielectric permittivity ϵ^* was observed to coincide with the static dielectric permittivity ϵ. Increments of the index of refraction of the solutions with respect to that of the solvent were also measured at 30 °C with a Brice Phoenix differential refractometer.

The real ϵ' and loss ϵ'' components of the complex dielectric permittivity of PAPCM in the bulk were performed with a three-terminal plane condenser and a capacitance apparatus TA DEA 2970. The experiments proceeded from −150 to 20 °C, over the frequency range 10^{-4} to 30 kHz, at a heating rate of 1 °C/min. In the temperature interval 20−150 °C measurements were made in the multiplexing mode (10^{-5} to 30 kHz) under isothermal conditions with steps of 5 °C.

Experimental Results

(A) Dielectric Results in the Bulk. Values at several frequencies of the dielectric loss for PAPCM are represented as a function of temperature in Figure 1. The curves exhibit a well developed relaxation process in the glassy state centered at ca. −76 °C at 10 Hz. This relaxation, named β, is followed at higher temperature by an ostensible glass−rubber relaxation (α process) in which the dipolar relaxation seems to overlap with conductive processes. Thus the peak associated with the glass−rubber relaxation is not observable at frequencies below 10 Hz; at this frequency the maximum of the α peak is located at 106 °C. Plots of the dielectric loss in the frequency domain are represented at several temperatures in Figure 2. At
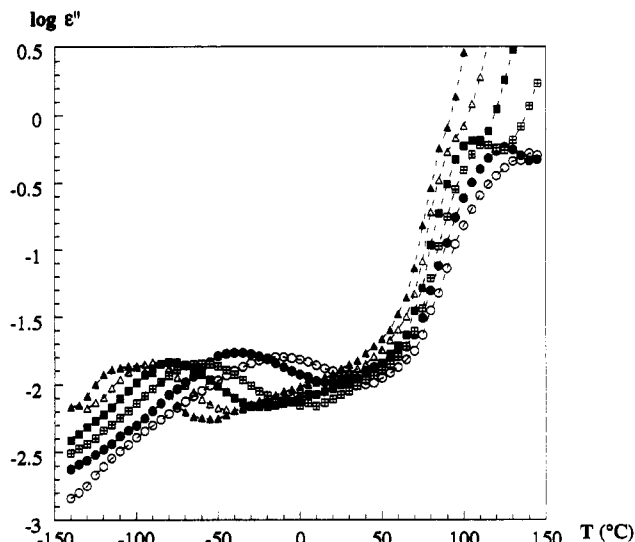

Figure 1. Double logarithmic plot showing the temperature dependence of the dielectric loss for poly(4-(acryloxy)phenyl)(4-chlorophenyl)-methanone (PAPCM) at several frequencyes (▲) 0.1, (△) 1, (■) 10, (+ in □) 10^2, (●) 10^3, and (○) 10^4 Hz.

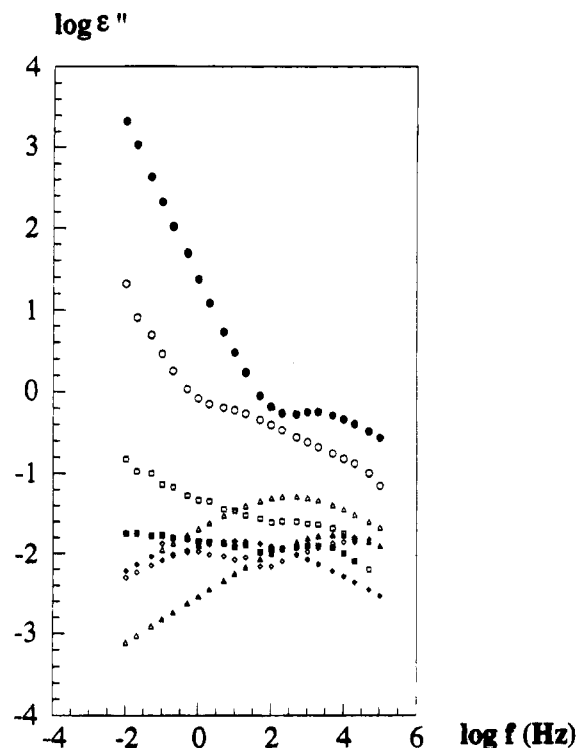**Figure 2.** Values of the dielectric loss in the frequency domain for poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM) at several temperatures: (◆) −80, (△) −50, (▲) −20, (◊) 10, (■) 40, (□) 70, (○) 100, and (●) 130 °C.

temperatures above T_g an anomalous increase in the dielectric loss with decreasing frequency in the low-frequency region occurs.

1. β Relaxation. As occurs with other amorphous polymers with highly polar side groups, the isochrones representing the β relaxation of PAPCM are well developed peaks reflecting the dielectric activity of the side groups. Usually subglass relaxations are nearly symmetric peaks, and therefore both isochrones and isotherms can be characterized by means of the Fuoss−Kirkwood equation[11]

$$\epsilon'' = \epsilon_{max} \, \text{sech}\left[m\frac{E_a}{RT}\left(\frac{1}{T} - \frac{1}{T_{max}}\right)\right]; \quad 0 < m \leq 1 \quad (1)$$

TABLE 1: Values of the Parameter m of the Fuoss—Kirkwood Equation and the Relaxation Strength $\Delta\epsilon$ for the Isochrones Corresponding to the β Relaxation Process of Poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM)

f, Hz	m	$\Delta\epsilon$
5000	0.249	0.134
2000	0.246	0.139
1000	0.236	0.145
500	0.240	0.137
200	0.238	0.126
100	0.239	0.119
50	0.278	0.100
20	0.255	0.120
10	0.256	0.115
5	0.234	0.129
2	0.235	0.124

where E_a is the activation energy, T_{max} is the temperature at the peak maximum, and m is an empirical parameter that increases as the broadening of the relaxation increases, in such a way that its value is 1 for a Debye type peak. Since the β relaxation obeys Arrhenius behavior with an activation energy of 11.4 ± 0.5 kcal mol^{-1}, the plot of $\cosh^{-1}(\epsilon''_{max}/\epsilon'')$ vs $1/T$ permits us to obtain m. The values of this parameter indicated in the second column of Table 1 do not show a noticeable dependence on the frequency of the isochrone.

Usually the determination of the activation energy is performed using only the maximum of the isochrones or isotherm curves, the remainder being neglected. However, methods have been developed that show temperature dependence for the activation energy through the relation[12]

$$E_a = \frac{\pi R T^2}{2\epsilon''} \frac{d\epsilon'}{dT} \qquad (2)$$

For illustrative purposes values of E_a at a typical frequency of 1 kHz are represented as a function of temperature in Figure 3, where it can be seen that although the value of this quantity in the central part of the relaxation is nearly constant (≈ 14 Kcal mol^{-1}), there is a global tendency toward a slight increase in the activation energy with temperature. Comparison of the temperature dependence of E_a at frequencies of 0.5 and 5 kHz in the same figure shows that except in the high-temperature region where the β relaxation may be contaminated by the α relaxation process, the activation energy is nearly independent of frequency.

In view of the small but still significant dependence of E_a on temperature, the values of m were also obtained from analysis of the β peaks in the frequency domain, that is, at constant temperature. In this case eq 13 becomes

$$\epsilon'' = \epsilon_{max} \text{sech}\left(m \ln\frac{f_{max}}{f}\right) \qquad (3)$$

where f_{max} is the frequency at the maximum of the peak. As an example, experimental values at -70 °C of the dielectric loss against frequency are shown in Figure 4. By plotting $\cosh^{-1} \epsilon''_{max}/\epsilon''$ against $\ln f$, the value of 0.257 is obtained for m. The values of ϵ'' calculated by means of eq 3 together with the experimental ones suggest that the β peaks are nearly symmetric. In the same way the values of m associated with other isotherms are shown in Table 2. It is worthy of note that the results for m evaluated from both the isochrones and the isotherms do not show a significant difference, presumably due to the symmetric shape of the β relaxation peaks.

The strength of the β relaxations $\Delta\epsilon_\beta$ ($=\epsilon_{r\beta} - \epsilon_{u\beta}$, where $\epsilon_{r\beta}$ and $\epsilon_{u\beta}$ denote respectively the relaxed and unrelaxed dielectric permittivities associated with the process) is commonly deter-
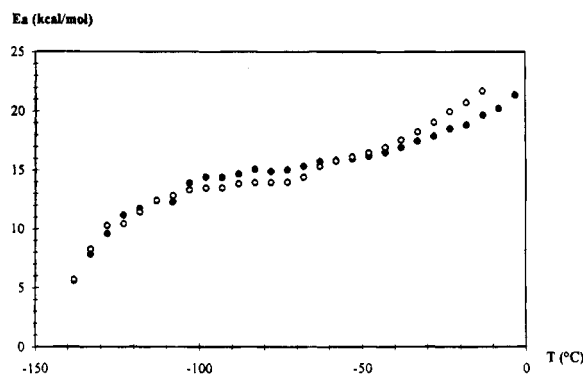

Figure 3. Variation of the activation energy associated with the β peak of the relaxation spectrum of poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM) at ($\bullet$) 0.5 and ($\bigcirc$) 5 kHz.
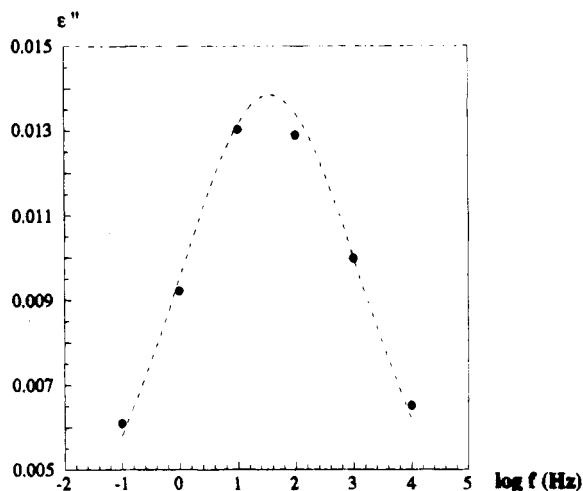

Figure 4. Experimental results in the frequency domain ($\bullet$), at -70 °C, for the β dielectric peak of poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM). (- - -) curve calculated by means of the Fuoss—Kirkwood equation assuming $m = 0.27$.

TABLE 2: Values of the Parameter m of the Fuoss—Kirkwood Equation, Relaxation Strength, $\Delta\epsilon$, and the Relaxed, $\epsilon_{r\beta}$, and Unrelaxed, $\epsilon_{u\beta}$, Dielectric Permittivities of the β Relaxation Process in the Frequency Domain

T, °C	m	$\Delta\epsilon^a$	$\epsilon_{r\beta}{}^b$	$\epsilon_{u\beta}{}^b$
-80	0.247	0.121	2.534	2.413
-70	0.257	0.108	2.537	2.429
-60	0.272	0.108	2.542	2.434
-50	0.274	0.118	2.553	2.434
-40	0.288	0.119	2.556	2.438
-30	0.287	0.120	2.559	2.439
-20	0.288	0.119	2.561	2.442

^{a} Calculated with eq 4. ^{b} Calculated with eqs 4 and 5.

mined from Cole—Cole plots. However, the lack in many cases of enough experimental results to construct the arcs with sufficient accuracy may produce significant errors in the determination of $\Delta\epsilon_\beta$. Then for nearly symmetric peaks it is better to determine the relaxation strength by means of the relation[13]

$$\Delta\epsilon_\beta = \frac{2\epsilon''_{max}}{m} \qquad (4)$$

Values of this quantity using values of m obtained from isochrones and isotherms are given respectively in Tables 1 and 2. Moreover for nearly symmetric peaks in the frequency domain, the maximum of the dielectric loss and the inflexion
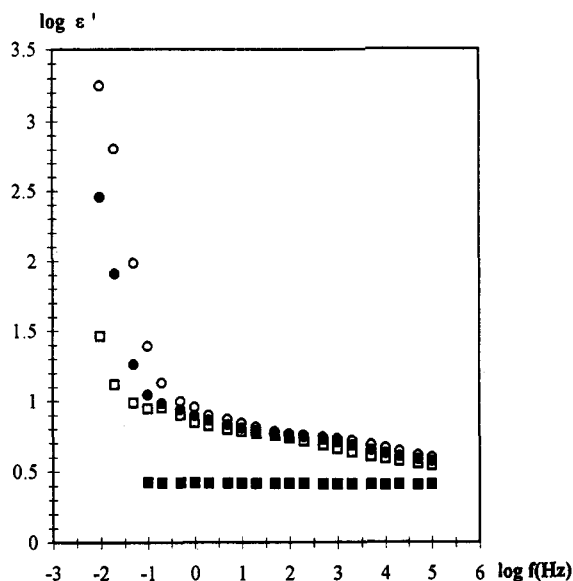
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Figure 5. Frequency dependence of the real component of the complex dielectric permittivity of poly(4-(acryloxy)phenyl)(4-chlorophenyl)-methanone (PAPCM) at several temperatures: (■) 20, (□) 120, (●) 130, and (○) 140 °C.

of the ϵ' curve ϵ'_{infl}, occur at the same frequency. Accordingly,

$$\epsilon'_{infl} = \frac{\epsilon_{r\beta} + \epsilon_{u\beta}}{2} \tag{5}$$

This expression in conjunction with eq 4 permits us to determine the values of $\epsilon_{r\beta}$ and $\epsilon_{u\beta}$ indicated in Table 2 for several isotherms.

2. Glass—Rubber Relaxation. Plots of ϵ'' vs frequency, f, for the α relaxation process show that the dielectric loss in the low-frequency region is a reciprocal function of f, that is, $\epsilon'' \sim f^{-1}$, and consequently, this contribution corresponds to a free charge conductive phenomenon (see Figure 2). According to the Kramers—Kronig equations, such behavior is only consistent with a constant value of ϵ' in this region. However, the experimental results represented for this polymer in Figure 5 also show a strong dependence of ϵ' on f in the low-frequency region, specifically, $\epsilon' \sim f^{-(1+\alpha)}$, where $0 < \alpha < 1$. These results suggest that a combination of free charge and blocking electrode phenomena may be held responsible for the apparently anomalous relaxation behavior exhibited by the PAPCM chains at low frequencies. These conductive effects preclude the possibility of obtaining the unrelaxed dielectric permittivity from complex dielectric plots, as indicated in Figure 6, where a representation of this kind at 130 °C is shown.

The complex dielectric permittivity associated with the dipolar α process is related to the normalized dipole time—correlation function $\Phi(t)$ by[14]

$$\frac{\epsilon(\omega) - \epsilon_{u\alpha}}{\epsilon_{r\alpha} - \epsilon_{u\alpha}} \frac{K(\omega)}{K(0)} = \int_0^\infty \left[-\frac{d\Phi(t)}{dt} \right] \exp(-i\omega t) \, dt \tag{6}$$

where ω ($= 2\pi f$) is the angular frequency, $\epsilon_{r\alpha}$ and $\epsilon_{u\alpha}$ are respectively the relaxed and unrelaxed dielectric permittivities in the glass—rubber relaxation, the factor $K(\omega)/K(0)$ accounts for the local field effects, and $\Phi(t)$ can be written as

$$\Phi(t) = \frac{\sum_k \langle \mu_k(0) \, \mu_k(t) \rangle + \sum_{k \neq k'} \langle \mu_k(0) \, \mu_{k'}(t) \rangle}{\langle \mu^2 \rangle + \sum_{k \neq k'} \langle \mu_k(0) \, \mu_{k'}(0) \rangle} \tag{7}$$
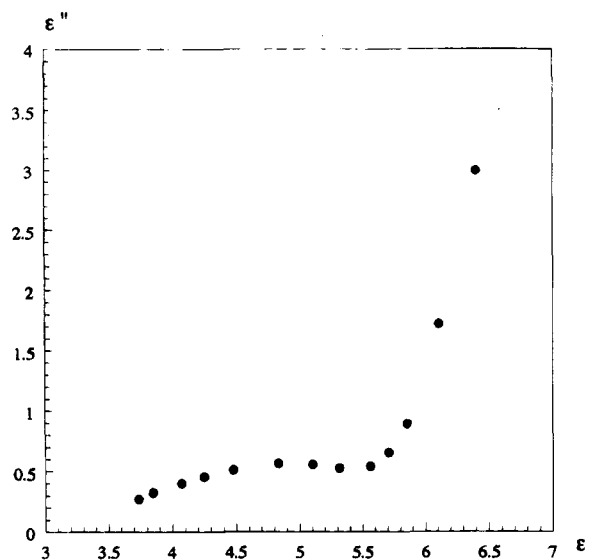

Figure 6. Complex dielectric plot at 130 °C for the glass—rubber relation of poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PA-PCM).

For most polymer systems the average of the cross correlation terms is negligible, so that this expression is reduced to

$$\Phi(t) = \frac{\sum_k \langle \mu_k(0) \, \mu_k(t) \rangle}{\langle \mu^2 \rangle} \tag{8}$$

The time correlation function $\Phi(t)$ can be evaluated from the sine or cosine inverse Fourier transform of the real or imaginary parts of $\epsilon^*(\omega)$ though, for computational purposes, it is more convenient to use the cosine form[15]

$$\Phi(t) = \frac{2}{\pi} \int_0^\infty \frac{\epsilon''(\omega)}{\Delta\epsilon} \frac{\cos \omega t}{\omega} \, d\omega \tag{9}$$

where $\Delta\epsilon = \epsilon_{r\alpha} - \epsilon_{u\alpha}$ is the relaxation strength. It is important to note that in this equation the field effect has been omitted so that the function $\Phi(t)$ thus obtained can be interpreted as a macroscopic (instead of microscopic) correlation function. The numerical evaluation of eq 9 can be performed[16] by depicting the dipolar α process by the HN relation[17] for which

$$\epsilon'(\omega) = \epsilon_{u\alpha} + \Delta\epsilon r^{-\nu} \cos \nu\psi$$

$$\epsilon''(\omega) = \Delta\epsilon r^{-\nu} \sin \nu\psi \tag{10}$$

where the parameters ν and ψ are given by

$$r = \left[1 + 2(\omega\tau_{HN})^\mu \cos \frac{\pi}{2}\mu + (\omega\tau_{HN}^{2\mu}) \right]^{1/2}$$

$$\psi = \arctan \frac{(\omega\tau_{HN})^\mu \sin \frac{\pi}{2}\mu}{1 + (\omega\tau_{HN})^\mu \cos \frac{\pi}{2}\mu} \tag{11}$$

τ_{HN} being the average relaxation time whereas μ and ν are respectively empirical parameters which account for the shape and skewness of the complex ϵ'' vs ϵ' plot.

In order to proceed with the evaluation of the exponents of the HN expression, it is necessary to split the dipolar contribution to the dielectric response from the contributions corresponding to free charge conductivity and blocking electrode phenomena. In an earlier work[18] an electric model was proposed to perform this task. The model is basically a parallel

TABLE 3: Values of the Parameters That Define the Kohlrauch–Williams–Watts (KWW) and Havriliak–Negami (HN) Equations for the Glass–Rubber Relaxation of Poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM)

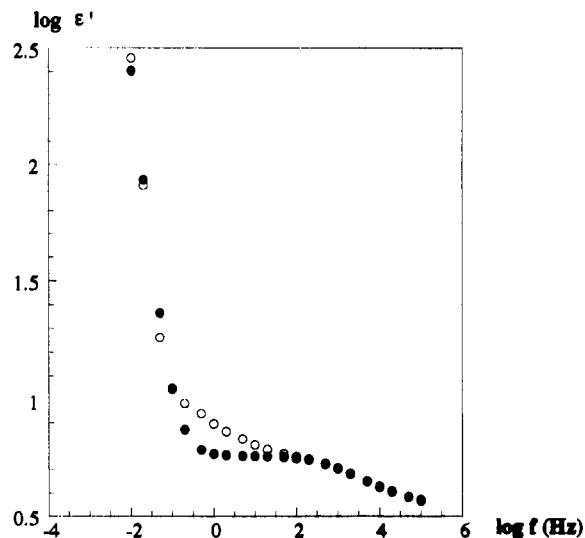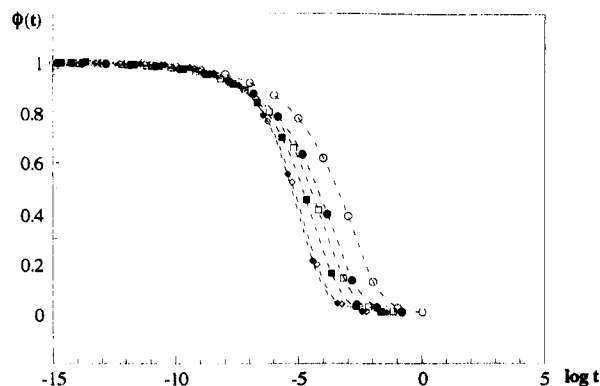| T, °C	$10^5\beta$	$10^5\tau_{KWW}$, s	$10^4\langle\tau\rangle$, s	μ	ν	$\mu\nu$	$\beta^{1.23}$	$10^5\tau_{HN}$, s
110	0.2960	115.93	385.5	0.7302	0.3170	0.2315	0.2237	284.5
120	0.3008	18.829	57.28	0.7198	0.3294	0.2371	0.2282	44.64
125	0.3129	9.7124	23.45	0.7106	0.3525	0.2505	0.2395	22.56
130	0.3446	4.2557	6.560	0.7083	0.3942	0.2792	0.2697	9.886
135	0.3870	1.8310	1.727	0.7010	0.4825	0.3382	0.3382	3.764
140	0.4046	1.3802	1.099	0.7000	0.5195	0.3637	0.3637	2.505
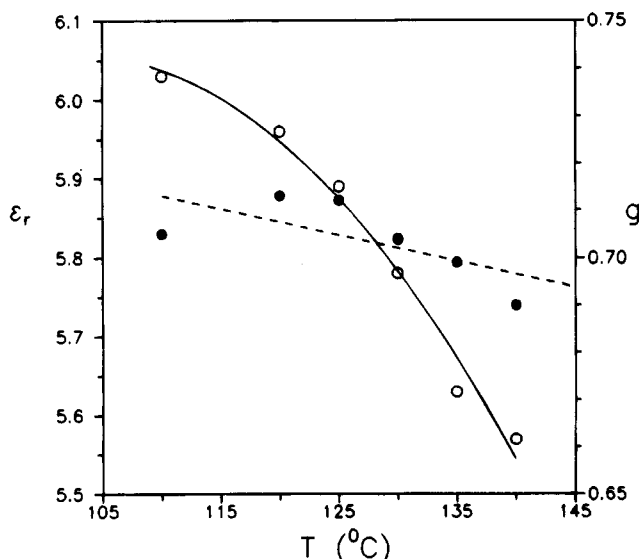
Figure 7. Temperature dependence of the relaxed dielectric permittivity (O) and the dipolar correlation coefficient (●) for poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM).

Figure 8. Plot showing the frequency dependence of the experimental (O) and calculated (●) values of the real component of the complex dielectric permittivity at 130 °C.

Figure 9. Evolution with time of the dipole correlation function.

configuration involving a condenser ($C_{r\alpha}$), a resistance (R), and an HN type impedance ($Z_{HN} = [1 + (i\omega\tau_\alpha)^\mu]^\alpha/(i\omega[C_{r\alpha} - C_{u\alpha}])$) coupled in series with an impedance ($Z_e^* = Z_e(-i\omega\tau_e)^{-\alpha}$) representing the electrode phenomena. By using a NLSR (nonlinear square regression) program developed by Mac-Donald,[19] the best set of parameters for the HN equation representing the dipolar contribution to ϵ'' was obtained. These values are given in Table 3, whereas those corresponding to the relaxed dielectric permittivity are represented as a function of temperature in Figure 7. Results at 130 °C for ϵ' in the frequency domain calculated by using the scheme described above together with the experimental ones are shown as an example in Figure 8. In all the isotherms the average residual values are below 4%. In the same way, good agreement between calculated and experimental values of the dielectric loss is obtained.

From the values of the components of ϵ^* obtained by means of the HN equation and using methods described elsewhere[16] to solve eq 9, the dipolar correlation function $\Phi(t)$ was obtained. Curves describing the evolution of this function with time at several temperatures are shown in Figure 9. Except in the high-frequency region, the α-relaxation is properly described by the Kohlrausch–Williams–Watts (KWW) dipolar correlation function[20]

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^\beta\right] \tag{12}$$

where τ_{KWW} is a characteristic relaxation time that corresponds to the time at which $\Phi(t)$ falls to its $1/e$ value and β is a parameter that describes the nonexponential character of the correlation function. An average relaxation time is also defined by

$$\langle\tau\rangle = \frac{\tau_{KWW}}{\beta}\Gamma\left(\frac{1}{\beta}\right) \tag{13}$$

where Γ is the gamma function. The correlation functions obtained at different temperatures were fitted to the KWW expression, and the values of β and τ_{KWW} are given in Table 3. It can be seen that the exponent β increases with temperature, indicating that the cooperativity rises when the temperature goes up. It is worthy of note that the values of τ_{KWW} are roughly half of those of the HN equation.

Comparison of the parameters appearing in the KWW equation with those in the HN expression has been performed, and it has been found that the KWW function parameters can be fitted to those of an HN function. However, the inverse is not true, as a consequence of the higher flexibility that the additional parameter confers to the latter function. In the zone where conversion between the HN and the KWW functions is possible, the parameters of both functions are related by the following equations[21]

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$$\ln\!\left(\frac{\tau_{KWW}}{\tau_{HN}}\right) = -2.6(1 - \beta)^{0.5}\exp(-3\beta) \tag{14}$$

$$\mu\nu = \beta^{1.23}$$

As can be seen in Table 3 the product $\mu\nu$ is roughly the value of $\beta^{1.23}$, in agreement with the second expression of the eq 12 prediction. However, the values of τ_{HN} calculated from the first expression of eq 12 in conjunction with the results for τ_{KWW} given in the second column of Table 3 are between 1.5 and 3.8 times lower than those of the last column of the same table. In this respect it is interesting to note the high sensitivity of the HN parameters to the fitting procedure.

(B) Dipolar Correlation Coefficients. The dielectric relaxation strength of polymers in the bulk can be interpreted in terms of Onsager type equations such as the Fröhlich expression[22]

$$\epsilon_r - \epsilon_u = \frac{4\pi\varrho N_A}{k_B M_0 T}\frac{3\epsilon_r}{2\epsilon_r + \epsilon_u}\!\left(\frac{\epsilon_u + 2}{3}\right)^{\!2} g\mu_0{}^2 \tag{15}$$

where $\mu_0{}^2 = \sum m_i{}^2$, m_i being the dipoles associated with the polar groups of the side chain, M_0 is the molecular weight of the repeating unit, k_B is the Boltzmann constant, N_A is Avogadro's number, and g is the dipolar correlation coefficient, involving both intra- and intermolecular dipolar interactions, given by[23]

$$g = 1 + \frac{\left\langle\sum\limits_{i\neq j} m_i m_j\right\rangle^{intram} + \left\langle\sum\limits_{k\neq l} m_k m_l\right\rangle^{interm}}{\mu_0{}^2} \tag{16}$$

Consequently, the larger g is, the larger is the dielectric strength of the polymer in the bulk. In the case that intermolecular correlations are nil, as occurs for isolated chains, then

$$g = g_{intram} = 1 + \frac{\left\langle\sum\limits_{i\neq j} m_i m_j\right\rangle^{itram}}{\mu_0{}^2} \tag{17}$$

The values of g were calculated by means of eq 15 and the values of ϵ_r shown in Figure 7. In the calculations it was assumed that $\epsilon_u = n^2$, and the value of this quantity was assumed to be 2.3 in the whole temperature interval. The results obtained, indicated in Figure 7, suggest significant correlations between dipolar entities.

1. Intramolecular Dipolar Correlation. In the experimental measurements of dipole moments of polymers, use is made of methods based on earlier theories developed for the determination of the polarity of molecules in the gaseous state.[2] This situation in the condensed matter is simulated by performing the measurements on dilute solutions of the solute in nonpolar solvents. In this case the solvent separates the solute molecules withuot distorting the electric field, so that the dielectric behavior of the diluted solutions is similar to that of the gaseous state. Owing to the fact that PAPCM is only soluble in high-polarity solvents, the approach used to determine the dipole moment of the chains involved the swelling of the polymer in a small amount of dimethylformamide and further addition of dioxane, achieving in this way solubility of the polymer in the medium. The weight fraction of dimethylformamide in the mixture of solvents was 0.055, and the dielectric permittivity amounted to only 3.689 at 30 °C.

Experimental values at 30 °C of the increment of the dielectric permittivity of the solutions with respect to that of the solvent
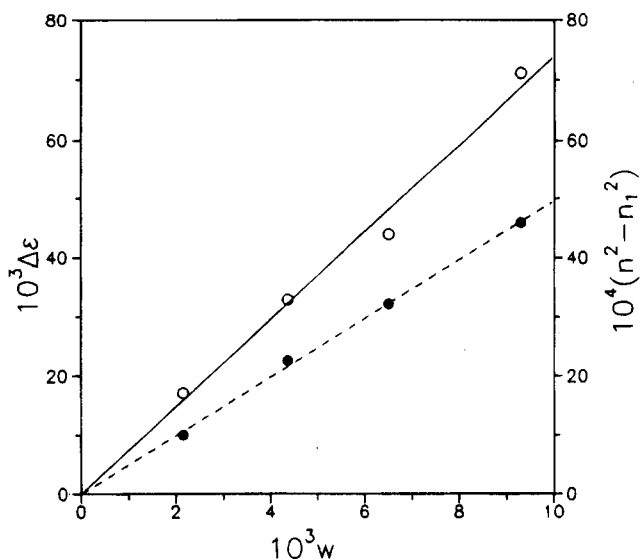

Figure 10. Concentration dependence of the increments in dielectric permittivity (O) and squared index of refraction (●) at 30 °C for poly-(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM).
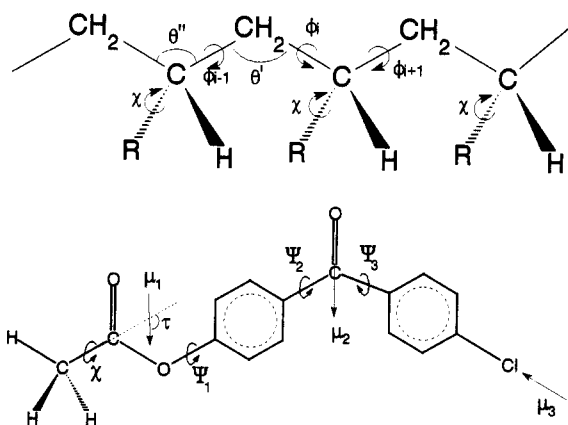

Figure 11. (a, top) Schematic representation of a sequence of meso diads for poly(4-acryloxy)phenyl)(4-chlorophenyl)methanone (PA-PCM). (b, bottom) (4-(Acetyloxy)phenyl)(4-chlorophenyl)methanone, model compound of the side group, in the all trans conformation.

$(\Delta\epsilon = \epsilon - \epsilon_1)$ are plotted as a function of the weight fraction of solute, w, in Figure 10. In the same figure plots of the increments of the squares of the indexes of refraction of the solution with respect to that of the solvent $(\Delta n = n - n_1)$ are plotted against w. The mean-square dipole moment per repeating unit, $\langle\mu^2\rangle/x$, was calculated from the experimental results by means of the equation of Guggenheim[24] and Smith[25]

$$\frac{\mu^2}{x} = \frac{27k_B T M_0}{4\pi\varrho N_A(\epsilon_1 + 2)^2}\!\left[\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right] \tag{18}$$

where k_B and N_A are respectively the Boltzmann constant and Avogadro's number, T is the absolute temperature, M_0 is the molecular weight of the repeating unit, and ϵ_1 and n_1 are respectively the dielectric permittivity and index of refraction of the solvent. The values of the derivatives $d\epsilon/dw$ and $2n_1$ dn/dw obtained by least square analysis from the results plotted in Figure 10 are 7.39 and 0.49, respectively, and consequently, $\langle\mu^2\rangle/x$ for PAPCM amounts to 10.3 ± 0.4 D². The intramolecular correlation coefficient, g_{intra}, evaluated from the expression

$$g_{intra} = \frac{\langle\mu^2\rangle}{x\mu_0{}^2} \tag{19}$$

amounts to 0.92.

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2. Theoretical Calculations. Figure 11 shows a schematic representation of a segment of the isotactic chain together with the structure of (4-acetoxyphenyl)(4-chlorophenyl)methanone (ACM), which was used as a model compound for the side group of PAPCM. In both cases the planar all trans conformations shown in the figure were taken as the origin for the rotational angles.

The rotational state model used in this work has been used before for the analysis of oligomers of poly(methyl acrylate) (PMA),[3] phenyl and chlorophenyl esters of poly(acrylic acid),[4] and several model compounds.[5] In brief, two conformational states, trans (t) and gauche (g), are allowed for the skeleton bonds (rotational angles ϕ in Figure 11). Two rotational angles are also permitted for the rotational angle χ about the $C^\alpha - C^*$ bond of the side group, namely $\chi = 0$, which places the carbonyl group cis to the $C-H$ bond on the side of the polymer backbone (this orientation is represented in Figure 11b), and $\chi = 180°$, which places these two bonds in the trans conformation. The conformations thus generated can be represented by a four-state scheme with the isomers in the order $t_c(\phi = 0, \chi = 0)$, $t_t(\phi = 0, \chi = 180)$, $g_c(\phi = 0, \chi = 0)$ and $g_t(\phi = 120, \chi = 180)$, whose statistical weight matrices are[3-5]

$$U' = \begin{vmatrix} 1 & 0 & \varrho & 0 \\ 0 & \varrho & 0 & \varrho \\ 1 & 0 & 0 & 0 \\ 0 & \varrho & 0 & 0 \end{vmatrix} \qquad (20)$$

for the interdiad $CH_2-C^\alpha-CH_2$ pair of bonds, and

$$U''_m = A \times \begin{vmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{vmatrix} \qquad U''_r = \begin{vmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} \qquad (21)$$

respectively, for meso and racemic configurations of the diad $C^\alpha-CH_2-C^\alpha$ pair of bonds.

The statistical weight of the $\chi = 180$ orientations relative to the $\chi = 0$ orientations is denoted by ϱ. The factors γ, γ_1, and γ_2 arise from the differences in Coulombic interactions for the allowed orientations of two consecutive ester groups in the diad. The constant $A = \omega'' \delta_m / \delta_r$ represents a combination of second-order (ω'') and Coulombic (δ_m and δ_r) factors whose exact values are not required for the calculations performed in the present work, since it is the same for all the allowed states represented in the U''_m matrix.

The values of the conformational parameters were taken from previous works.[1-3] Thus, the valence angles were taken as $\theta' = 114°$ for $C^*-CH_2-C^*$ and $\theta'' = 112°$ for $CH_2-C^*-CH_2$. Rotational isomers were placed $(\phi_{i-1}, \phi_i) = (16°, 16°)$, $(3°, 114°)$, $(114°, 3°)$, and $(3°, 3°)$, respectively, for the meso-tt, meso-tg, and racemic-tt conformations. The statistical weights $\varrho = 1.1$, $\beta = 5.0$, $\gamma_1 = 0.1$, $\gamma_2 = 1.8$, and $\gamma = 0.2$ were taken from the analysis of para-substituted phenyl esters of poly-(acrylic acid).[4,5]

The molecule ACM, represented in Figure 11b, was used as a model compound for the side group of the polymer. The conformational analysis of this molecule[26] shows that the allowed orientations for its three rotatable bonds (besides the rotation χ that it is irrelevant for the molecule) are $\Psi_1 = \pm 90°$ and Ψ_2, $\Psi_3 = 0 \pm 30°$ and $180 \pm 30°$, with displacements of the same sign in both angles (i.e., $\Psi_2 = 30$, $\Psi_3 = 30$ is permitted while $\Psi_2 = 30$, $\Psi_3 = -30°$ is forbidden). The dipole moment of this molecule was calculated in a previous work[26] by assigning partial charges to each atom and then performing a molecular dynamics simulation. However, it is possible to

TABLE 4: Dipole Moment for the Allowed Conformations of the (4-(Acetyloxy)phenyl)(4-chlorophenyl)methanone (ACM) Used as a Model Compound for the Side Group of Poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM)[a]

Ψ_2	Ψ_3	$\chi = 0$ (cis)			$\chi = 180°$ (trans)		
		μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
90	30	1.009	−3.314	0.859	1.134	0.138	3.381
90	150	2.695	−2.176	0.859	−0.552	−1.000	3.381
90	−150	2.215	−1.466	1.661	−0.057	−1.733	2.609
90	−30	0.529	−2.603	1.661	1.629	−0.596	2.609
−90	30	2.215	−1.466	1.661	−0.057	−1.733	2.609
−90	150	0.529	−2.603	1.661	1.629	−0.596	2.609
−90	−150	1.009	−3.314	0.859	1.134	0.138	3.381
−90	−30	2.695	−2.176	0.859	−0.552	−1.000	3.381

[a] Components of the dipoles are written in the reference frame attached to the skeleta bond $C^\alpha-CH_2$.

obtain a reasonable approximation, which is much easier to incorporate into the scheme of calculation for the polymer, by adding three contributions represented by μ_1, μ_2, and μ_3 in Figure 11b. The sum of these contributions depends on the rotations Ψ_1 and Ψ_2 but not on Ψ_3, and consequently eight conformations of the molecules should be taken into consideration for the calculation of its dipole moment. Table 4 summarizes the total dipole moment $\mu = \mu_1 + \mu_2 + \mu_3$ for each of the allowed conformations of the ACM molecule written in the reference frame attached to the skeletal bond $C^\alpha-CH_2$ of the backbone,[7] which reproduces the experimental dipole moment of the model compound of the repeating unit of the polymer.

The calculation of the mean-square dipole moment $\langle \mu^2 \rangle$ for the polymeric chain was performed according to the standard procedures of the matrix multiplication scheme.[1,2,27] Thus chains containing $x = 200$ repeating units with predetermined values of the meso fraction w_m ranging from 0 to 1 and Bernouillian placement of meso and racemic units were generated. The values of $\langle \mu^2 \rangle$ computed for these chains were converted into the intramolecular correlation coefficient $g_{intra} = \langle \mu^2 \rangle / x\mu_0^2$ by means of eq 19) assuming $\mu_0^2 = 11.2$ D^2. The rotations Ψ_1, Ψ_2 of the side groups were incorporated into the scheme of calculation by means of a random routine that decided which of the eight allowed orientations (i.e. which one of the rows of Table 4) should be used for each repeating unit of the chain.[4,28]

All the values of g_{intra} shown below are averages of over 200 independent chains generated as explained. We have used such a large number of chains to ensure that all the orientations of the side group were evenly sampled and the predetermined values of w_m coincided with those actually generated. On the other hand, the number of repeating units contained in each chain, $x = 200$, is large enough to ensure that g_{intra} has reached its asymptotic limit.

The solid line in Figure 12 shows the vlaues of g_{intra} computed as a function of w_m with all the parameters indicated above. As the figure shows, the value of the intramolecular correlation coefficient is rather low for the pure syndiotactic chain, i.e. $g_{intra} = 0.25$ when $\omega_m = 0$. The reason for this small value of g_{intra} is that only tt conformations are allowed for the racemic diad. In this conformation, the z components of the dipole moment of the two consecutive side groups point in the opposite direction and therefore subtract their values. This cancellation is strongest when both units have the lateral group with $\chi = 180°$, since in this case the z component is the largest one (see Table 4). A few units in the meso configuration are enough for breaking down the racemic all trans sequences and consequently relieving
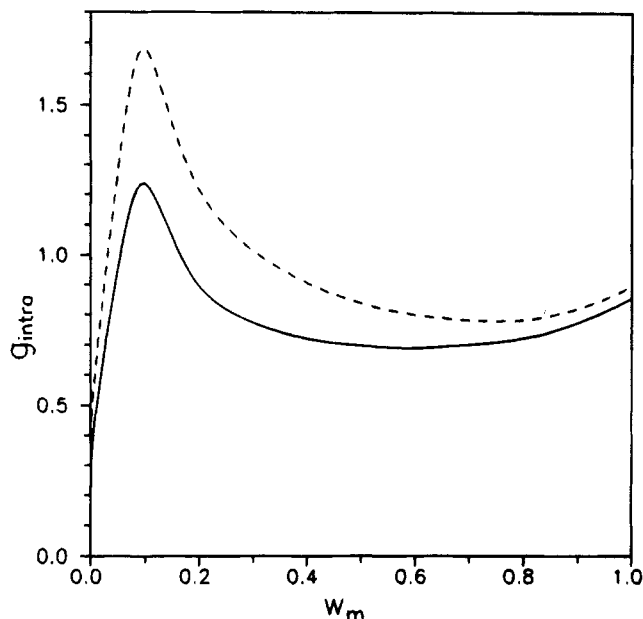
Figure 12. Plot showing the dependence of the intramolecular correlation coefficient on the isotactic content for poly(4-(acryloxy)-phenyl)(4-chlorophenyl)methanone (PAPCM). See text for details.

the cancellation of contributions, so that the values of g_{intra} increase sharply when the fraction of meso diads increases to 0.1.

If this steep variation of g_{intra} with w_m in the region of highly syndiotactic chains is excepted, the polarity of the polymer is almost insensitive to tacticity. Thus $g_{intra} = 0.8 \pm 0.1$ is obtained for chains with $w_m > 0.2$. The values of g_{intra} can be raised by means of small adjustments of the conformational parameters, as is indicated by the dashed line of Figure 12, which was computed with $\varrho = 1.0$, $\gamma_1 = 0.2$, $\gamma_2 = 1.7$ and all other parameters as before. The value $g_{intra} = 1.2-0.9$ obtained with this set of parameters for the range of tacticities 0.2−0.4 is in good agreement with the experimental results.

Discussion

In spite of the relatively large polarity of the side groups, the dielectric strength of the β relaxation of PAPCM is relatively small and similar to that exhibited by other much less polar acrylate polymers such as poly(phenyl acrylate) (PPA)[4] and poly(cyclohexyl acrylate) (PCHA).[29] The study of the evolution with time of the polarity of (4-(acetyloxy)phenyl)(4-chloro-phenyl)methanone (ACM), a model compound for PAPCM, shows that most of the conformations adopted by ACM have values of dipole moment in the range 3.0 ± 0.5 D. The closeness of the polarity of the conformations may be held responsible for the relatively weak β relaxation exhibited by PAPCM chains.

The activation energy associated with the mechanisms intervening in the β relaxation process does not show a significant temperature dependence, suggesting that the energy barriers involved in the conformational transitions vary little over the interval of temperature in which the relaxation occurs. By shifting horizontally the normalized curves representing the β relaxation in the frequency domain, the master curve shown in Figure 13 is obtained. The relaxation is described in terms of the KWW relation or stretch function with exponent 0.24. It is worth noting the closeness of this exponent to that corresponding to the glass−rubber relaxation, whose value at 110 °C is only 0.29.

Relaxation processes have been recently interpreted in terms of the coupling scheme that assumes that, without consideration
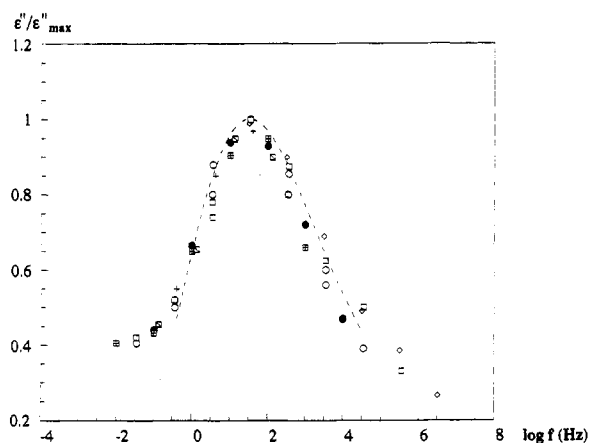

Figure 13. Normalized master curve at −70 °C for the β relaxation of poly(4-(acryloxy)phenyl)(4-chlorophenyl)methanone (PAPCM).

of the interactions between the relaxing species, the relaxation process can be described[29] by a single linear exponential with time τ_0. However, coupling between the relaxing species produces a slowdown of the relaxation. According to the model, the relaxation rate in the absence of coupling, τ_0^{-1}, is slowed down and modified to have a time dependence of $\tau_0^{-1}(\omega_c t)^{-n}$. The model leads to the following expression for the dipolar correlation function

$$\Phi(t) = \exp[-(t/\tau^*)]^{1-n} \qquad (22)$$

which is similar to the KWW equation. In this expression, τ^*, named the effective relaxation time, is related to τ_0 by[30]

$$\tau^* = [(1 - n)\omega_c^n\tau_0]^{1/(1-n)} \qquad (23)$$

where ω_c^{-1} is a time characteristic of the connections of the system and n is a constant characterizing the coupling among the relaxing species. By comparing eqs 12 and 23, one obtains $\beta = 1 - n$ and $\tau_{KWW} = \tau^*$. Consequently, the relatively low value of β (high n) for the glass−rubber relaxation is related to a strong coupling interaction between the relaxing species. Therefore the closeness of the exponents for the α and β relaxations suggest that the hindered motions that give rise to the β relaxation process may also play an important role in the development of the α relaxation.

In most amorphous systems relaxation times in the glass−rubber relaxation process in the case of polymers or glass−liquid relaxation in the case of monomers are governed by the free volume. Consequently, the relaxations are related to temperature by the empirical Vogel expression[31]

$$\tau = A \exp\left(\frac{m'}{T - T_\infty}\right) \qquad (24)$$

where T_∞ is an empirical temperature at which the free volume would be zero were it not for the formation of the glassy state. The KWW and HN relaxation times of Table 3, τ_{KWW} and τ_{HN}, respectively, are described by the Vogel expression, obtaining the best fit of the experimental results to this equation for $T_\infty = 45$ °C. The values of m' of eq 24 thus obtained from the plot of $\ln \tau_{KWW}$ or $\ln \tau_{HN}$ vs $1/(T - T_\infty)$ amount to 1134 and 1063 K, respectively. The relaxation times can also be interpreted in terms of the Doolittle equation,[32] $\tau = A \exp(B/\phi)$, where ϕ is the relative free volume and B is a parameter close to unity that according to the Cohen−Turnbull theory[33] can be written as
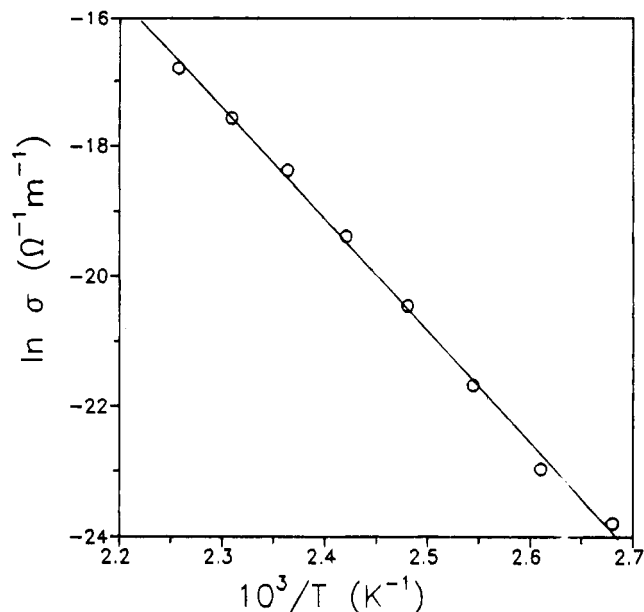
$$B = \gamma v^*/v_m \qquad (25)$$

Figure 14. Arrhenius plot for the conductivity of poly(4-(acryloxy)-phenyl)(4-chlorophenyl)methanone (PAPCM) above the glass transition temperature.

where γ is a constant whose value is $0.5-1$ and ν^* and ν_m are respectively the critical volume for a relaxation process to take place and the volume of the relaxing segments. In fact the assumption that the specific volume is a linear function of temperature leads from the Doolittle equation to the Vogel equation, finding that $m = \nu_0 B/\alpha_f$, where ν_0 is the occupied volume and α_f is the expansion coefficient in the liquid state. Comparison of the Vogel equation with the Doolittle equation yields the expression

$$\frac{\Phi}{B} = \frac{T - T_\infty}{m'} \tag{26}$$

which relates the relative free volume that appears in the Doolittle equation with the value of m' in the Vogel relationship. By using the values of m' given above, one finds that the relative free volume at T_g (ϕ_g/B) amounts to 0.033 (KWW) and 0.035 (HN), which is somewhat larger that the value of 0.025 ± 0.005 reported for most amorphous polymers. If the isovolume theory at T_g holds, eq 28 suggests that $B > 1$; that is, the critical volume of the relaxing species is smaller than the volume of the segments intervening in the relaxation. It is worth pointing out that the analyses of the free volume using the relaxation times of the KWW and HN equations give nearly similar results for the relative free volume. Moreover, assuming that $\nu_0 \approx 1$, one finds that $\alpha_f/B \approx 9.1 \times 10^{-4}\ K^{-1}$, a value that is on the order of magnitude of the expansion coefficient reported for polymers in the liquid state.

On approaching the temperature of the glassy state T_g, the orientation of the gradually unfreezing dipoles as well as contributions of other less well defined entities causes a step increase in the components of the complex dielectric permittivity. As indicated above, free charge conductivity and blocking electrode phenomena are the most important contributions to the raise observed in these components at low frequencies. In the region where $\epsilon'' \simeq \omega^{-1}$, the loss is related to the conductivity σ by the equation

$$\epsilon''_c = \frac{\sigma}{\epsilon_0 \omega} \tag{27}$$

where ϵ_0 is the permittivity of free space. From the values of ϵ''_c in the double logarithmic plot ϵ''_c of vs ω, the results for

the conductivity at several temperatures were obtained. The dependence of σ on temperature obeys Arrhenius behavior, as indicated in Figure 14. From the slope of this plot the value of 34.1 ± 0.5 kcal mol^{-1} is obtained for the activation energy associated with the process. This behavior is somewhat different from that reported for solutions of LiCl in polypropylene glycol,[33] where the conductivity neither follows Arrhenius behavior nor obeys the Vogel relation.

Finally, the statistics used in this work gives a good account of the intramolecular correlation coefficient. In fact g_{intra} is close to unity, suggesting that the dipole entities behave as if they were nearly uncorrelated. In spite of this, the analysis indicates that the orientation of the carbonyl bonds of two consecutive diads in the trans conformation is favored with respect to that of the alternative cis conformation. On the other hand, the small but still important differences between g and g_{intra} indicate that intermolecular dipolar correlations should not be ruled out.

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