Dielectric Relaxation Studies on Phenyl and Chlorophenyl Esters of Poly(acrylic acid)

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ABSTRACT: Dielectric measurements have been made on phenyl and chlorophenyl esters of poly(acrylic acid). Phenomenological analysis of the data indicates that the strength of the β subglass process for both poly(phenyl acrylate) (PPA) and poly(*p*-chlorophenyl acrylate) (PPCPA) is weak in comparison with the strength of this process for poly(*o*-chlorophenyl acrylate) (POCPA) and poly(*m*-chlorophenyl acrylate) (PMCPA). The latter two polymers exhibit a relatively strong β process compared with the α glass–rubber relaxation. Information on the intramolecular and intermolecular correlation factors was obtained from the values of the mean-square dipole moments determined from dielectric measurements in solution and in the bulk. The α relaxation is governed by the free volume, and the coupling model gives a good account of this process. Attempts are made to explain the molecular origin of the subglass relaxations.

Introduction

Below the glass–rubber transition, molecular motions in polymers give rise to subglass relaxations characterized by Arrhenius type temperature dependence of the relaxation times and a broad distribution of relaxation times.[1,2] These processes take place in polymers either with or without flexible side groups, and it is believed that the subglass absorptions are produced by local molecular motions of the main chain and/or motions of the side groups. The relaxation response is dependent on the experimental probe (dipole polarization, dynamic stress–strain, density fluctuations, etc.) since time correlation functions of different dynamic variables are involved. Therefore different responses (dielectric relaxation, dynamic mechanical relaxation, dynamic light scattering, volume recovery, etc.) give complementary information that can further be used to develop molecular models that successfully account for the experimental observations.[3]

For critical interpretation of the dynamics of molecular chains we need, in addition to the use of different probes, experimental data on polymer chains in which the response is sensitive to conformational changes of determined bonds in the molecular chains. Suitable candidates for this purpose, in the case of the dielectric response, are the phenyl and chlorophenyl esters of poly(acrylic acid). The dielectric activity of poly(phenyl acrylate) (PPA), for example, will be dependent on the rotations about the C^{α}–C^{*} bonds of the side group (where α and * identify a substituted carbon of the chain skeleton and the carbonyl carbon, respectively), which, as is known, are restricted to 0 and 180° with respect to the methine C^{α}–H bond.[4,5] The substitution of hydrogen atoms of the phenyl ring for halogen atoms gives rise to additional dielectric activity that will be strongly dependent on the location of the substitution. In this regard, it is expected that the dielectric relaxation spectra are similar for poly(*p*-chlorophenyl acrylate) (PPCPA) and PPA. However, for those polymers in which the halophenoxy group is asymmetric, dielectric activity can also arise in each side group as a result of combined rotations about C^{α}–C^{*} bond and Ph–O bonds. Major contribution to mechanical activity does not come from motions of the side but from motions of segments of the main chain.

At temperature above the subglass absorptions, amorphous polymers exhibit a prominent glass–rubber relaxation, labeled α, which is characterized by WLF temperature behavior of the relaxation times.[6] The results at hand seem to suggest that, independent of the nature of the probe, the appropriate correlation function of the segmental motions in amorphous polymers, near and above the glass transition temperature, is well described by the Kohlrausch–Williams–Watts function,[7-9] whereas the temperature dependence of the relaxation times obeys the Vogel equation.[1,6]

The present work reports dielectric data on phenyl and chlorophenyl esters of acrylic acid, and attempts are made to explain the molecular origin of the subglass relaxations. The coupling model is used to interpret the α relaxation on PPA, PPCPA, poly(*o*-chlorophenyl acrylate) (POCPA), and poly(*m*-chlorophenyl acrylate) (PMCPA).

Experimental Section

Synthesis and Characterization of the Polymers. Phenyl acrylate and *o*-, *m*-, and *p*-chlorophenyl acrylates were synthesized from a solution of the phenolic reagent and freshly distilled acryloyl chloride, following the procedures described in detail elsewhere.[10] Homopolymerization reactions were carried out at 50 °C in benzene solutions, and the conversions were kept below 12%. The polymers were precipitated with methanol, filtered, washed with methanol, and dried under vacuum. The number-average molecular weight M_n of the chains was determined in benzene solutions at 34 °C with a Knauer high-speed membrane osmometer. The values of $10^{-3}M_n$ amounted to 240, 150, 350, and 600 for PPA, POCPA, PMCPA, and PPCPA, respectively. The stereostructure of the polymers was determined with a Varian XL-300 spectrometer at 75 MHz, using TMS as internal reference. The molar fraction of syndio (rr), hetero (mr + rm), and isotactic (mm) structures was similar in all the polymers, amounting to ca. 0.62, 0.33, and 0.04, respectively.

The glass transition temperature of the polymers was determined with a Perkin-Elmer DSC-4 calorimeter, and the results obtained are shown in the second column of Table I.

Dielectric Measurements. Dielectric results were obtained on films of 0.8-mm thickness, coated with gold, with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell. Values of the complex dielectric permittivity were obtained at several frequencies lying in the range 0.1–100 kHz.

Dielectric Results

General Results. Values of the loss dielectric constant for PPA chains are shown as a function of both frequency

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Table I
Values of the Vogel Parameters for Poly(phenyl acrylate) (PPA), Poly(*p*-chlorophenyl acrylate) (PPCPA), Poly(*m*-chlorophenyl acrylate) (PMCPA), and Poly(*o*-chlorophenyl acrylate) (POCPA)

polymer	T_g, °C	T_∞, °C	m, K	Φ_g/B
PPA	50	-7	2220	0.026
PPCPA	57	0	1750	0.033
PMCPA	39	-16	1500	0.037
POCPA	45	-12	2420	0.024

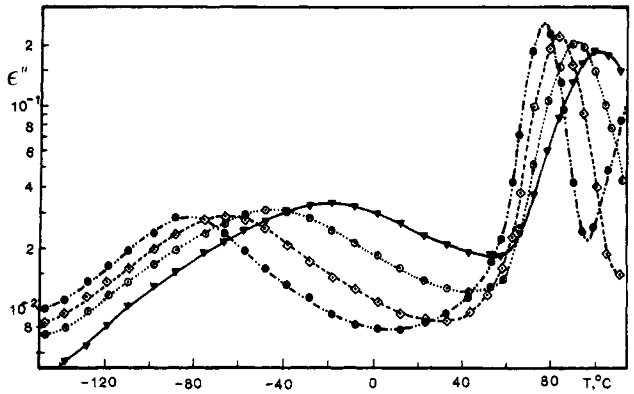

Figure 1. Dielectric loss plotted isocronally versus temperature for PPA at several frequencies: (●) 0.1, (◇) 1, (○) 10, and (▼) 100 kHz.

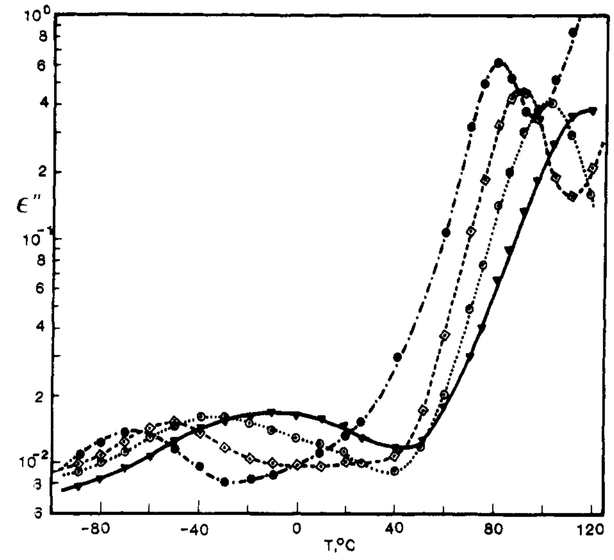

Figure 2. Temperature dependence of the loss dielectric permittivity for PPCPA. (See Figure 1 for the values of the frequencies attached to the symbols indicated.)

and temperature in Figure 1. The dielectric spectrum exhibits at 0.1 kHz a prominent relaxation peak, centered at 76 °C, which is clearly associated with the glass–rubber relaxation, and therefore it will be labeled α. In descending temperature a well-developed subglass absorption appears, labeled β, whose maximum at 0.1 kHz is located at -85 °C. By substituting the hydrogen atom in the para position of the phenyl group of the repeat unit of PPA chains with a Cl atom, PPCPA chains are obtained. The relaxation spectrum of this polymer, shown in Figure 2, indicates that both the α and β relaxations are shifted to higher temperatures with regard to the corresponding relaxations of PPA chains, the shifting being lower for the former relaxation than for the latter. Moreover, the intensities of the α and β relaxations of PPCPA chains are respectively higher and lower than those corresponding to PPA chains.

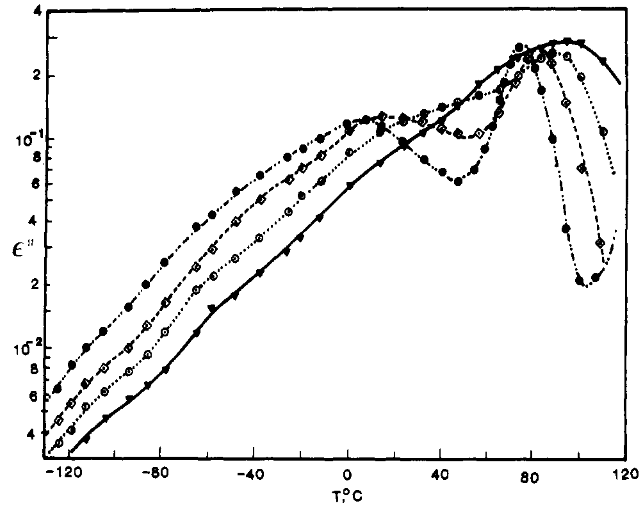

Figure 3. Dielectric loss versus temperature plot for POCPA at several frequencies. (See Figure 1 for the values of the frequencies attached to the symbols indicated.)

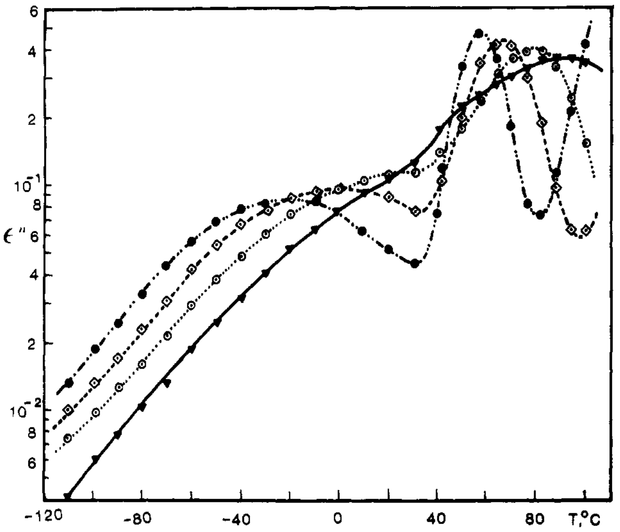

Figure 4. Dielectric loss dependence on temperature for PMCPA. (See Figure 1 for the values of the frequencies attached to the symbols indicated.)

The effect of the asymmetry of the chlorophenoxy residue on the dielectric behavior of chlorophenyl esters of poly(acrylic acid) was studied on POCPA and PMCPA, whose relaxation spectra are presented in Figures 3 and 4, respectively. Comparison of the relaxation spectra of the phenyl and chlorophenyl esters of poly(acrylic acid) seems to suggest that the presence of the Cl atom on the phenyl ring tends to overlap the glass–rubber and subglass absorption domains; for POCPA and PMCPA both relaxations coalesce into an $\alpha + \beta$ absorption at frequencies above 50 kHz.

The dielectric results were also analyzed by using the Cole–Cole formalism.[1] Plots representing the values of the loss component ϵ'' of the complex dielectric permittivity ϵ^* versus the real component ϵ' are indicated in Figure 5 for PPA and PPCPA chains at 83.5 and 92.2 °C, respectively. As usual, the Cole–Cole plots corresponding to the α relaxation are circular in the low-frequency region, but at high frequencies the curves approach the abcissa along straight lines.[1,2] An anomalous increase in the values of the loss dielectric permittivity occurs for PPCPA as a consequence of conductivity effects that become important for this polymer at low frequencies. The Cole–Cole curves for POCPA and PMCPA, shown in Figure 5 at 83.6 and

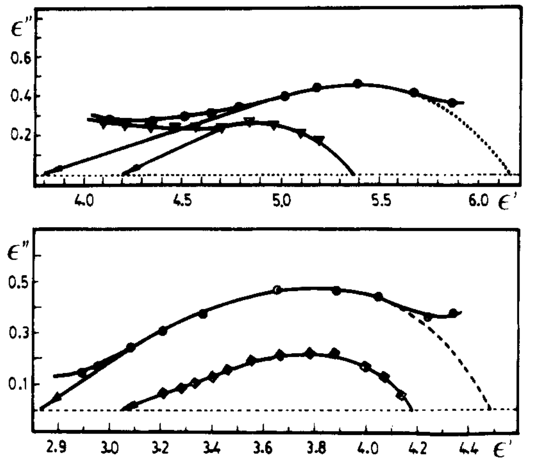

Figure 5. Complex-plane plot of dielectric loss versus dielectric constant of the glass-rubber relaxation in PPA (◇) at 83.5 °C, PPCPA (○) at 92.2 °C, POCPA (▽) at 83.6 °C, and PMCPA (●) at 64.8 °C.

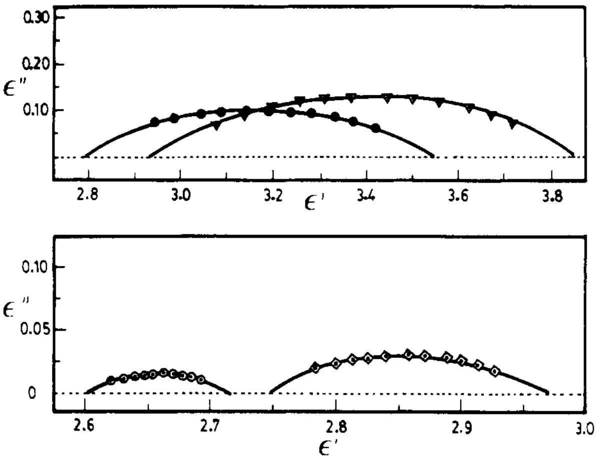

Figure 6. Cole–Cole plots for the β subglass relaxation in PPA (◇) at −66.5 °C, PPCPA (○) at −50 °C, POCPA (▽) at 23.2 °C, and PMCPA (●) at −1.4 °C.

64.8 °C, respectively, are not well resolved in the high-frequency region owing to the coalescence of the α and β absorptions into a single α + β relaxation. In order to quantify the relaxation strength of the α process, the dielectric results were fitted by means of the Havriliak–Negami equation[11]

$$\epsilon^* = \epsilon_{u\alpha} + \frac{\epsilon_{r\alpha} - \epsilon_{u\alpha}}{(1 + (i\omega\tau_0)^{\bar{\alpha}})^{\bar{\beta}}} \tag{1}$$

where $\epsilon_{r\alpha}$ and $\epsilon_{u\alpha}$ are the related and unrelaxed dielectric constants in the process, τ_0 is the central relaxation time, ω is the angular frequency, $\bar{\alpha}$ is the width parameter, and $\bar{\beta}$ represents the skewing in the α process. The β processes of POCPA and PMCPA are extremely broad arcs in the frequency domain at most temperatures, and their relaxation characteristics were obtained by fitting the experimental results to the Cole–Cole equation[12]

$$\epsilon^* = \epsilon_{u\beta} + \frac{\epsilon_{r\beta} - \epsilon_{u\beta}}{1 + (i\omega\tau_0)^{\bar{\alpha}}} \tag{2}$$

It can be seen in Figure 6 that the relaxation strength $\Delta\epsilon_\beta = \epsilon_{r\beta} - \epsilon_{u\beta}$ of the β process is relatively small for PPA and PPCPA chains; for example, the dielectric strength $\Delta\epsilon$ is only 0.1 (at −50.0 °C) and 0.21 (at −66.5 °C) for PPCPA and PPA, respectively. However, this difference amounts to 0.73 (at −1.4 °C) and 0.94 (at 23.2 °C) for PMCPA and POCPA, respectively. Consequently, an important fraction of the apparent dipole moment of the relaxing groups in POCPA and PMCPA chains will relax in the β process, and the remainder will relax in the α process. For PPA and PPCPA, however, the relaxation will take place, almost in its totality, in the α process. Values of the unrelaxed and relaxed values of ε of the β absorption at temperatures above T_g, given in Table II, were obtained by the methods outlined by Buerger and Boyd.[13] As was indicated above, the α process for both PPA and PPCPA chains is well resolved isocronically from the α process in the whole range of frequencies studied, but for POCPA and PMCPA severe interferences between the α and β processes occur, so that there is not a single temperature at which accurate enough α complex-plane plots can be constructed for these polymers. Therefore the relaxed dielectric constant of the β absorption ($\epsilon_{r\beta}$) was considered to be the unrelaxed dielectric constant ($\epsilon_{u\alpha}$) of the α relaxation. The relaxation parameters, $\bar{\alpha}$, $\bar{\beta}$, and τ_0 are given in Table II together with the values of $\epsilon_{r\alpha}$ and $\epsilon_{u\beta}$ for the combined α + β relaxations of the phenyl and chlorophenyl esters of acrylic acid.

Intermolecular and Intramolecular Correlations between Relaxing Dipoles. The relaxation strengths for the combined α + β processes can be represented as dipolar correlation factors, g, from the Onsager equation[1,14]

$$\epsilon_{r\alpha} - \epsilon_{u\beta} = \frac{3\epsilon_{r\alpha}}{2\epsilon_{r\alpha} + \epsilon_{u\beta}} \left(\frac{\epsilon_{u\beta} + 2}{3}\right)^2 \frac{4\pi\rho N_{\rm A}}{3_{\rm A}} \frac{g\langle\mu_0{}^2\rangle}{\kappa M_0 T} \tag{3}$$

where κ is the Boltzmann constant, ρ is the density, M_0 is the molecular weight of the repeating unit, $N_{\rm A}$ is Avogadro's number, and $\langle\mu_0{}^2\rangle$ is the mean-square dipole moment of the relaxing group associated with each repeating unit. The values of $\langle\mu_0{}^2\rangle$ used, given in the fourth column of Table III, were those reported earlier[15] for model compounds of the repeating unit of the polymers used in this study. For completely relaxed systems and in the absence of inter- and intramolecular interactions, $g = 1$; that is, the mean-square dipole moment of the chains per repeating unit should coincide with the value of this quantity for the relaxing group. Intramolecular dipole correlations were accounted for from the dipole moment ratio $\langle\mu^2\rangle/x\langle\mu_0{}^2\rangle$, where $\langle\mu^2\rangle$ is the mean-square dipole moment of a chain of x repeating units, obtained earlier[16] for these chains from dielectric measurements in solutions of nonpolar solvents. Values of $\langle\mu^2\rangle/x$ at the temperatures indicated in the second column of Table II were obtained by extrapolating the values of the dipole moment ratio determined for these polymers in the temperature range 30–60 °C. The uncertainty of these values was estimated to be ±5%. From the effective mean-square dipole moment per repeating unit $(\mu_{\rm eff})_{\rm isol} = \langle\mu^2\rangle/x$ and the values of $\langle\mu_0{}^2\rangle$ one easily obtains the values of $g_{\rm intra}$. The results for $(\mu_{\rm eff})_{\rm isol}$, $\langle\mu_0{}^2\rangle$, and $g_{\rm intra}$ are indicated in the second, fourth, and fifth columns of Table III, respectively. It can be seen that the intramolecular correlation factors are relatively large for PPA, PPCPA, and PMCPA, but they seem to be negligible for POCPA chains. The values of $g = g_{\rm intra} + g_{\rm inter}$, where $g_{\rm inter}$ accounts for the intermolecular correlation factor, were obtained from the results of the third and fourth columns of Table II, in conjunction with eq 3. The error involved in the determination of g was estimated to be ±7%. An inspection of the fourth and fifth columns of Table III leads to the conclusion that for the phenyl and chlorophenyl esters of poly(acrylic acid), with the exception of POCPA, the intermolecular and intramolecular correlation factors are similar in value.

Table II

Dielectric Relaxation Parameters for the α Process of Poly(phenyl acrylate) (PPA), Poly(*p*-chlorophenyl acrylate) (PPCPA), Poly(*m*-chlorophenyl acrylate) (PMCPA), and Poly(*o*-chlorophenyl acrylate) (POCPA)

polymer	T, °C	$\epsilon_{u\beta}$	$\epsilon_{r\alpha}$	$\epsilon_{r\beta}$	$1-\bar{\alpha}$	$\bar{\beta}$	$10^4\tau_0$, s
PAP	83.5	2.85	4.18	3.05	0.245	0.294	8.38
PPCPA	92.2	2.63	4.47	2.73	0.140	0.418	4.08
PMCPA	64.8	2.95	6.16	3.77	0.240	0.246	15.9
POCPA	83.6	3.20	5.36	4.20	0.355	0.496	5.49

Table III

$(\mu_{\text{eff}})_{\text{isol}}$, $(\mu_{\text{eff}})_{\text{bulk}}$, $\langle\mu_0^2\rangle$, g_{intra}, and g for Poly(phenyl acrylate) (PPA), Poly(*p*-chlorophenyl acrylate) (PPCPA), Poly(*m*-chlorophenyl acrylate) (PMCPA), and Poly(*o*-chlorophenyl acrylate) (POCPA) at the Temperatures Indicated in Table II

polymer	$(\mu_{\text{eff}})_{\text{isol}}$,[a] D^2	$(\mu_{\text{eff}})_{\text{bulk}}$,[b] D^2	$\langle\mu_0^2\rangle$,[c] D^2	g_{intra}[d]	g[e]
PPA	2.10	1.13	3.00	0.70	0.38
PPCPA	3.76	1.83	7.83	0.48	0.23
PMCPA	3.78	2.41	6.15	0.61	0.39
POCPA	3.68	1.68	3.43	1.0	0.49

[a] Mean-square dipole moment per repeating unit for isolated chains. [b] Mean-square dipole moment per repeating unit for chains in the bulk. [c] Mean-square dipole moment of the side group. [d] Intramolecular interaction parameter. [e] Interaction parameter $g = g_{\text{intra}} + g_{\text{inter}}$.

The Glass-Rubber Relaxation. According to the phenomenological theory of linear dielectric relaxation, the complex permittivity corresponding to the α process can be written as[9]

$$\frac{\epsilon^*_\alpha - \epsilon_{u\alpha}}{\epsilon_{r\alpha} - \epsilon_{u\alpha}} = \int_0^\infty \left[-\frac{d\psi(t)}{dt}\right] e^{-i\omega t}\, dt \qquad (4)$$

where $\psi(t)$ is the normalized decay function, which in most relaxation phenomena is given by the Kohlrausch-Williams-Watts (KWW) equation[7,8]

$$\psi(t) = \exp(-t/\tau)^{\bar{\gamma}} \qquad (5)$$

The physical meaning of the exponent $\bar{\gamma}$ was recently interpreted by Ngai and co-workers[17] by means of the coupling model. The model assumes that without consideration of the interactions between the relaxing species, the relaxation process can be described by a single linear exponential with a constant relaxation time τ. There is a slowing down of the relaxation which comes from the coupling between the relaxing species. The coupling model suggests that the relaxation rate τ_0^{-1} is slowed down and modified to have the time dependence of $\tau_0^{-1}(\omega_c t)^{-n}$. The model leads to an expression for the decay function[18]

$$\psi(t) = \exp(-t/\tau^*)^{1-n} \qquad (6)$$

which is similar to the KWW equation. Here τ^*, named the effective relaxation time, is given by

$$\tau^* = [(1-n)\omega_c^{\ n}\tau_0]^{1/(1-n)} \qquad (7)$$

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. It can be considered that τ_0 is goverened by the free volume, so that this parameter can be expressed by the Doolittle equation[19]

$$\tau_0 = A_0 \exp(B_0/\Phi_0) \qquad (8)$$

where Φ_0 is the ratio of the free volume to the occupied volume and B_0 is related to the minimum hole size required for local segmental motions, whose value is believed to be close to unity. Equation 8 may lead to the Vogel equation[20]

$$\ln \tau_0 = A_0' + \frac{m_0}{T - T_\infty} \qquad (9)$$

if the specific volume is assumed to be a linear function of T over the whole temperature range. Here T_∞ is the temperature at which the free volume would be zero were it not for the formation of the glassy state. By comparing the Doolittle and Vogel equations, one can obtain the free-volume ratio at T_g

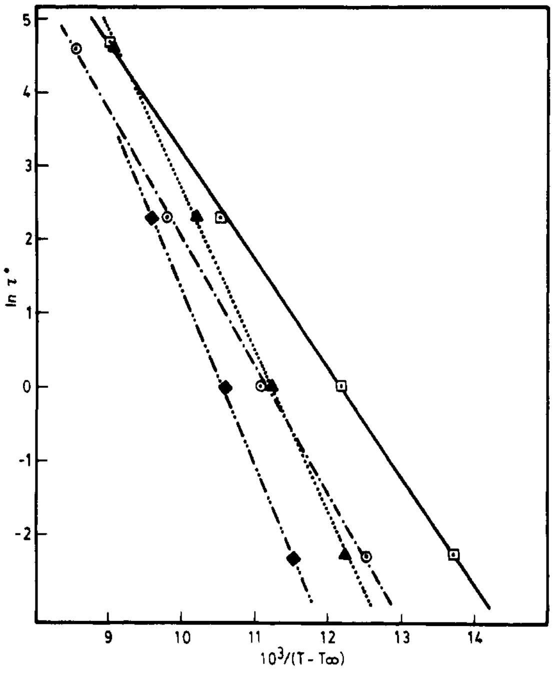

Figure 7. Temperature dependence of the α relaxation of PPA (▲), PPCPA (○), POCPA (◆), and PMCPA (□). The values of T_∞ are given in Table I.

$$(\Phi_0)_g/B_0 = (T_g - T_\infty)/m_0 \qquad (10)$$

It follows from eq 7 that the relations corresponding to eqs 8-10 for τ^* are

$$\tau^* = A \exp(B/\Phi) \qquad (11)$$

$$\ln \tau^* = A' + \frac{m}{T - T_\infty} \qquad (12)$$

and

$$\Phi_g/B = (T_g - T_\infty)/m \qquad (13)$$

where

$$m = m_0/(1-n) \qquad (14)$$

Plots of $\ln \tau^*$ versus $1/(T - T_\infty)$ are shown in Figure 7, where it can be seen that straight lines are obtained for the values of T_∞ indicated in the third column of Table I. The values of Φ_g/B for PPA and POCPA, shown in the fifth column of this table, lie within the interval 0.025 ± 0.005 reported for most systems;[6] however, these values are somewhat larger for PPCPA and PMCPA, suggesting that the minimum hole size required for a relaxation process to take place is apparently somewhat smaller in the latter polymers.

The dielectric losses expressed in terms of $\epsilon''/\epsilon''_{\max}$ were also represented as a function of the frequency at different

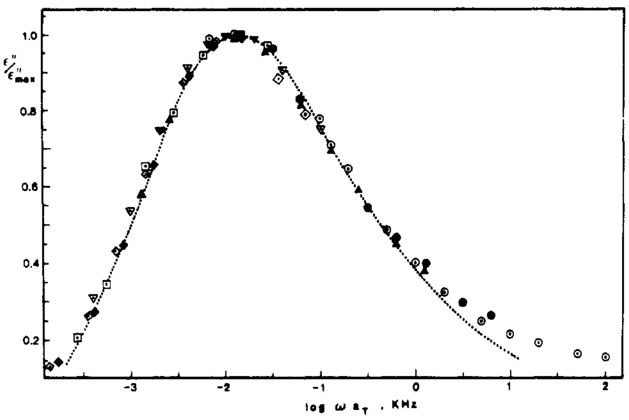

Figure 8. Master curve for the glass-rubber relaxation of PPA chains at 71.8 °C. The discontinuous curve was obtained from eqs 4 and 5 by assuming that $\bar{\gamma}$ in the KWW equation is 0.42.

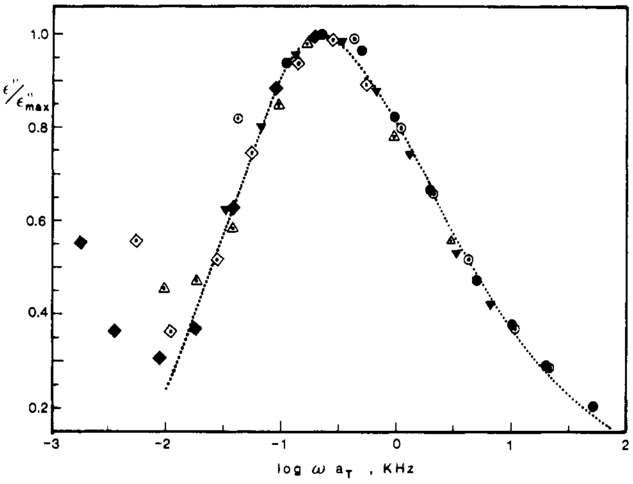

Figure 9. Master curve for the glass-rubber relaxation of PPCPA chains at 86.1 °C. The discontinuous curve was obtained from eqs 4 and 5 by using $\bar{\gamma}$ = 0.49 in the KWW equation.

temperatures. Master curves were then obtained by horizontal empirical shifts of the isotherms along the frequency axis. The master curves corresponding to PPA and PPCPA are shown in Figures 8 and 9, respectively. Overlapping of the α and β relaxations precludes the possibility of obtaining the master curve for POCPA in the whole frequency region, and the same occurs for PMCPA in the high-frequency zone. Values of $\epsilon''/\epsilon''_{max}$ were obtained from eq 4 by the procedures outlined by Williams et al.,[9] and the values of n that best fit the experimental results are 0.58 and 0.51 for PPA and PPCPA (see Figures 8 and 9), whereas $n \approx 0.48$ for PMCPA if only the low-frequency side of the master curve is fitted. It should be pointed out that the values of m_0 calculated by the product of $(1 - n)m$ for the polymers lie inside the narrow interval 780–930 K, the average value being 855 K, which is very close to the results obtained for this quantity from different probes in poly(vinyl acetate).[3] Similarly, the values $(\Phi_0)_g/B_0$ calculated by $(\Phi)_g/B(1 - n)$ are about the same for the three polymers.

Molecular Motions in the Subglass Process. As usual, the central relaxation times associated with the β process fit to an Arrhenius relation, and the values of the activation energies associated with this process amount to 10.4, 35.0, 15.7, and 12.5 kcal mol^{-1}, respectively, for PPA, POCPA, PMCPA, and PPCPA. The overlapping of the α and β processes at high frequencies in the relaxation spectra of POCPA and PMCPA suggests that at temperatures not far above the glass transition temperature of this polymer the decay functions for the α and β processes will become comparable. Both processes will coalesce, giving rise to the $\alpha + \beta$ process in the frequency domain through which the whole dipolar entities will relax.[21] This behavior resembles that of certain polymers containing flexible side groups, such as atactic poly(ethyl acrylate), which present a well-developed $\alpha + \beta$ absorption at temperatures above their respective glass transition temperatures.[1,21]

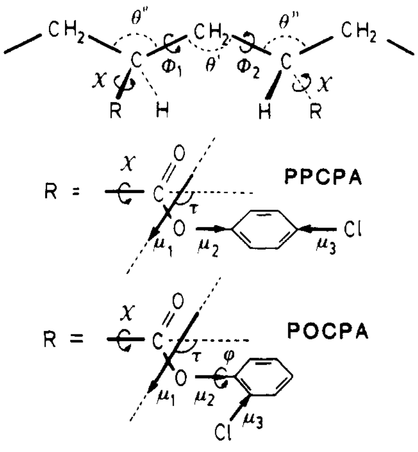

Figure 10. Schematic representation of a racemic diad for PPCPA chains.

The structural characteristics of PPA and PPCPA suggest that the molecular motions that produce dielectric activity are presumably associated with conformational changes about C$^\alpha$–C* bonds of the side chains coupled with local conformational transitions of the main chain. The dipole moment of each side group for PPA can be represented by the sum of two contributions μ_1 and μ_2 (see Figure 10) assigned as to reproduce the dipole moment $(\mu_0{}^2)^{1/2}$ of phenyl propionate.[16] The value of μ_2 amounts of 0.3 D, whereas a third contribution μ_3 = 1.6 D corresponding to Ph–Cl bonds has to be considered in chlorophenyl esters of poly(acrylic acid). The contribution of the ester group μ_1 was assumed to have a value of 1.757 D and an orientation defined by the angle τ = 123° with respect to the CH$_2$–C* bond. The sensitivity of the polarity of the diads of PPA and PPCPA to the conformational changes of the side groups was studied by assuming that the ∠CC*O, ∠C*OC, and ∠CCC bond angles have values of 114, 113, and 110°, respectively. As is known C*–O bonds are restricted to trans states, whereas the rotational angles about C$^\alpha$–C bonds are χ = 0, π, the former and latter angles representing the conformations in which the carbonyl group is trans and cis, respectively, to the methine bond.[4,5]

The critical analysis of the NMR spectra of model compounds of phenyl and chlorophenyl esters of poly(acrylic acid) suggests that the fraction of gauche states in racemic diads is only[22] 0.14; that is, the diads are predominantly trans. The values of μ^2 for racemic diads in the trans conformation are shown in the third and fourth columns of Table IV for PPA and PPCPA, respectively. It can be seen that the polarity reaches a maximum value for $\chi,\chi = \pi,\pi$, as a consequence of the fact that these rotational states place the overall dipole moments of the two side groups in nearly parallel direction. The polarity reaches a minimum value for χ,χ = 0,0, the value of μ^2 being only ≈0.1 D^2 for PPCPA; intermediate values are obtained for $\chi,\chi = 0,\pi$ in both polymers. For tg conformations the polarity reaches maximum and minimum values for χ,χ = 0,0 and $0,\pi$, respectively.

Table IV
Square Dipole Moments μ^2 (D^2 for Racemic Diads of Poly(phenyl acrylate) (PPA) (in the tt and tg Conformations) and Poly(*p*-chlorophenyl acrylate) (PPCPA) (in the tt Conformation)

rot. angles about C$^\alpha$–C* bonds				
χ	χ	$(\mu^2_{\mathrm{PPA}})_{\mathrm{tt}}$	$(\mu^2_{\mathrm{PPCPA}})_{\mathrm{tt}}$	$(\mu^2_{\mathrm{PPA}})_{\mathrm{tg}}$
0	0	2.5	0.1	10.3
π	π	9.9	25.8	6.7
0	π	3.6	10.3	1.2

Table V
Square Dipole Moments μ^2 (D^2) for Meso Diads of Poly(phenyl acrylate) (PPA) and Poly(*p*-chlorophenyl acrylate) (PPCPA) in the tt and tg Conformations

rot. angles about C$^\alpha$–C* bonds					
χ	χ	$(\mu^2_{\mathrm{PPA}})_{\mathrm{tt}}$	$(\mu^2_{\mathrm{PPCPA}})_{\mathrm{tt}}$	$(\mu^2_{\mathrm{PPA}})_{\mathrm{tg}}$	$(\mu^2_{\mathrm{PPCPA}})_{\mathrm{tg}}$
0	0	10.4	29.3	3.2	7.0
π	π	10.3	29.3	5.0	13.2
0	π	1.7	20.3	8.3	21.2

Table VI
Influence of the Rotational Angles about O–PhCl Bonds for Racemic Diads of Poly(*o*-chlorophenyl acrylate) (POCPA)

rot. angles about C$^\alpha$–C* bonds		rot. angles about O–PhCl bonds		
χ	χ	φ	φ	μ^2, D^2
0	0	75	75	3.4
		75	−75	10.9
π	π	75	75	2.3
		75	−75	9.7
0	π	75	75	9.2
		75	−75	1.7

In meso diads rotational angles $\chi,\chi = 0,0$ and π,π about C$^\alpha$–C* bonds place the dipole moments of the ester residue in nearly parallel direction, and hence the polarity reaches the maximum value for these conformations (see Table V).

The critical interpretation of the dielectric conformation dependent properties of phenyl and p-chlorophenyl esters of 2,4-dimethylglutaric acid[5,21] suggests that tπ,tπ conformations about CH$_2$–C$^\alpha$–CH$_2$ bonds of racemic diads are favored over the alternative t0,t0 and tπ,t0 conformations. Occasional t0,t0 $\rightleftharpoons$ tπ,t0 transitions in PPA, which involve moderate dielectric activity, might contribute to the small dielectric strength of the β absorption of PPA chains. However, these transitions involve considerable dielectric changes in the polarity of racemic diads of PPCPA, and therefore they cannot explain the very small strength exhibited by the subglass relaxation of these chains. On the other hand, since racemic diads are predominantly trans, contributions from conformational transitions through CH$_2$–C$^\alpha$ bonds of the backbone should in comparison be small. Consequently, the results of Tables IV and V seem to suggest that the low strength of the β relaxation of PPCPA chains can only be explained by assuming that the absorption involves rotations about C$^\alpha$–C* bonds of the side groups in such a way that the distribution of rotational angles χ in racemic sequences before and after the relaxation remains practically constant.

The strength of the β relaxation of POCPA is only somewhat lower than that of the α absorption, suggesting that a great part of the polarity of the chains relaxes through this process and the rest in the α relaxation. It should be pointed out that in most polymers with flexible dipolar side groups the strength of the α absorption ($\Delta\epsilon_\alpha$) is larger than that of the β absorption ($\Delta\epsilon_\beta$).[21] However, certain polymers containing dipolar side groups have $\Delta\epsilon_\beta > \Delta\epsilon_\alpha$ at certain temperature–pressure conditions: e.g., atactic poly(methyl methacrylate) and poly(ethyl methacrylate).[1,21] The value of the $\Delta\epsilon_\beta/\Delta\epsilon_\alpha$ ratio for POCPA (0.88) is almost 3 times the value of this quantity (0.33) for PMCPA. The values of this ratio for PPA and PPCPA only amount of 0.15 and 0.05, respectively, so that the polarity of these two polymers relaxes almost in its totality through the α process.

The dielectric activity in PMCPA and POCPA also arises from motions about O–PhCl bonds. Semiempirical potential calculations indicate that the rotational angles ϕ about O–Ph bonds are located[16] at ±75°, taking as reference the conformation indicated in Figure 10. For PMCPA the rotational angles are located at $\phi = \pm 60$ and ±120°. The results of Table VI suggest that motions of O–Ph bonds can produce considerable activity, even in the cases in which the χ angles remain constant. Therefore the β dielectric relaxation of POCPA is presumably the consequence of coupled motions about C$^\alpha$–C* and O–Ph bonds of the side groups. Similar motions could also explain the well-developed β relaxation exhibited by PMCPA chains. The connection between the subglass relaxation of both POCPA and PMCPA chains and the molecular motions about O–Ph bonds is supported by the values of the apparent activation energy E_β associated with the relaxation. Thus the value of this quantity for POCPA (35.0 kcal mol^{-1}) is larger than the value of 12.4 kcal mol^{-1} obtained for this quantity in PPA, as a consequence of the fact that rotation about O–Ph bonds in the former polymer gives rise to severe interactions between the halogen atom and the carbonyl group; as a consequence the maximum of the β absorption in POCPA is displaced to higher temperature. Interactions between the Cl atoms and the C=O group decrease when this atom is located in the meta position of the phenyl ring, and therefore the value of E_β for PMCPA is smaller.

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