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Dynamic-Mechanical Behavior of Phenyl and Chlorophenyl Esters of Poly(acrylic acid)

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ABSTRACT: The dynamic-mechanical behavior of poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*m*-chlorophenyl acrylate) (PMCPA), and poly(*o*-chlorophenyl acrylate) (POCPA) in the glassy and glass–rubbery regions is reported. Analysis of the results by using the biparabolic model indicates that the width of the distribution of relaxation times follows the trend PPA < PMCPA ≤ PPCPA < POCPA. The decay function associated with the glass–rubbery process is affected by an exponent that is smaller than that corresponding to the decay function of the dielectric α process. Both PPA and PPCPA exhibit a weak subglass β process, whereas this relaxation is strong for PMCPA and POCPA. The values of the activation energy associated with the β absorption increase from 12.3 and 13.0 kcal mol^{-1} for PPCPA and PPA, respectively, to 15.0 and 18.4 kcal mol^{-1} for POCPA and PMCPA, respectively, presumably as a consequence of the fact that the sweeping energy involved in the rotation about O–Ph bonds is smaller for polymers with symmetric side groups. Molecular motions, which can produce localized mechanical activity, are discussed.

Introduction

The glass–rubber relaxation in polymers occurs at temperatures at which the molecular chain have accessibility to the available conformational space through cooperative segmental motions, which are long range in nature. Although the relaxation times are governed by the volume, the distribution of relaxation times depends on the experimental probe.[1-6] Thus the dielectric relaxation times have been found to be shorter than either the light scattering relaxation times or the mechanical relaxation times.[7] Below the glass transition temperature, molecular processes take place that are characterized by Arrhenius temperature behavior of the relaxation times and by a broad distribution of relaxation times.[8] The molecular motions proposed to account for the subglass dispersions are uncoordinated torsional oscillations of skeletal bonds without crossing the barrier separating the rotational states of minimum energy, crankshaft and kink motions, and rotations of side groups either alone or coupled with local motions of the main chain.[9] Computer simulations[10] carried out on symmetric isolated chains, immersed in a viscous medium, suggest that the only way of reducing the motions of the tails and the frictional resistance that the tails present to the transition is by means of counterrotational cooperative motions involving two second-neighbor bonds. The resultant is not rotation of the attached tails, and therefore the motions are not molecular weight dependent.

The fact that the molecular motions involved in the subglass relaxation are localized in nature offers the possibility that they can be effectively modeled by molecular mechanics.[8] Therefore, it is important that there be appropriate experimental data for systems that are amenable to molecular modeling. In a recent work[11] the dielectric subglass dispersions corresponding to phenyl and chlorophenyl esters of poly(acrylic acid) were studied. In general, it was found that the strength of the β process for chains with symmetric side groups (phenyl and *p*-chlorophenyl derivatives) is small in comparison with that of the chains with asymmetric side groups (*o*-chlorophenyl and *m*-chlorophenyl derivatives). Moreover, the activation energy associated with the process is higher in chains with asymmetric side groups, suggesting that molecular motions about the O–Ph bond presumably play an important role in the relaxation process of *o*- and *p*-chlorophenyl esters of poly(acrylic acid).

Table I
Values of the Number-Average Molecular Weight M_n, Glass Transition Temperature T_g, T_∞ in Equation 8, and the Fractional Free Volume Φ_g/B at T_g for Phenyl and Chlorophenyl Esters of Poly(acrylic acid)

polymer	$10^{-3}M_n$	T_g, °C	T_∞, °C	Φ_g/B
PPA	240	50	−7	0.033
PPCPA	600	57	0	0.023
PMCPA	350	39	−16	0.033
POCPA	150	45	−12	0.024

The dielectric studies reported for poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*o*-chlorophenyl acrylate) (POCPA), and poly(*m*-chlorophenyl acrylate) (PMCPA) are now extended to the dynamic-mechanical behavior of the same polymers. These systems offer the opportunity of investigating how the location of the halogen atom in the phenyl group affects the mechanical response in comparison with the dielectric response.

Experimental Part

Synthesis and Characterization of the Samples. Homopolymerization reactions of phenyl acrylate and *o*-, *m*-, and *p*-chlorophenyl acrylates were carried out at 50 °C in benzene solutions,[12] keeping the conversion below 12%. The polymers were precipitated with methanol, washed with methanol, and dried in vacuo. The values of the number-average molecular weight of the samples used in the dynamic-mechanical experiments, measured in benzene solutions with a Knauer high-speed membrane osmometer, are given in the second column of Table I. The stereochemical composition of the polymers, determined with a Varian XL-300 NMR spectrometer at 75 MHz, was similar in all the polymers, amounting to 0.62, 0.33, and 0.04 for the molar fraction of syndio- (rr), hetero- (mr + rm), and isotactic (mm) triads, respectively.[11] The glass transition of the samples was determined with a Perkin-Elmer DSC-4 calorimeter, and the results obtained are shown in the third column of Table I.

Dynamic-Mechanical Measurements. Molded samples 1 mm thick and 10 mm wide were used in the viscoelastic experiments. Dynamic experiments were performed by flexion deformation in a DMTA apparatus Mark II. Values of the

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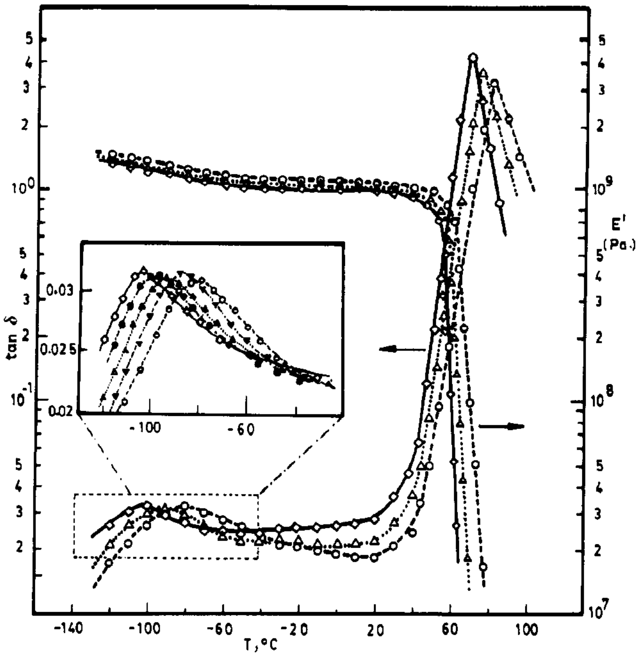

Figure 1. Storage relaxation modulus E' and loss tan δ dependence on temperature for poly(phenyl acrylate) (PPA) at five frequencies: (◇) 0.3, (●) 1, (△) 3, (▽) 10, (○) 30 Hz. For the sake of clarity the relaxation spectra in the α absorption are only shown at three frequencies.

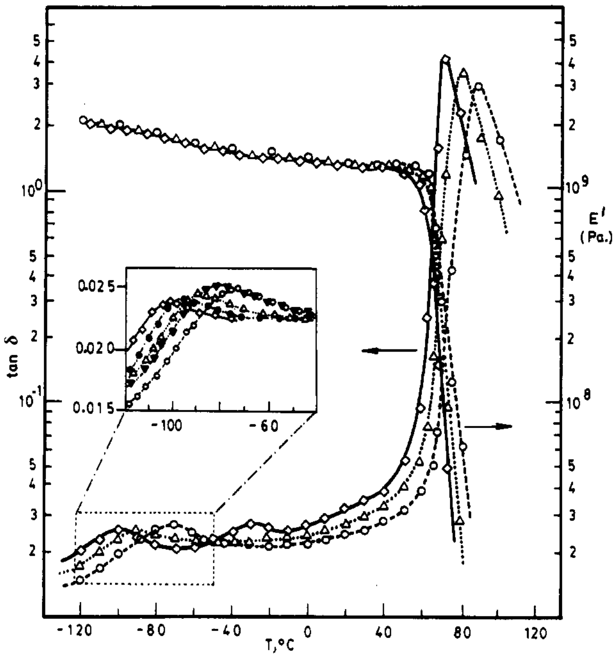

Figure 2. Values of both the storage relaxation modulus E' and the loss tan δ against temperature for poly(p-chlorophenyl acrylate) (PPCPA). (See Figure 1 for the values of the frequencies attached to the symbols.)

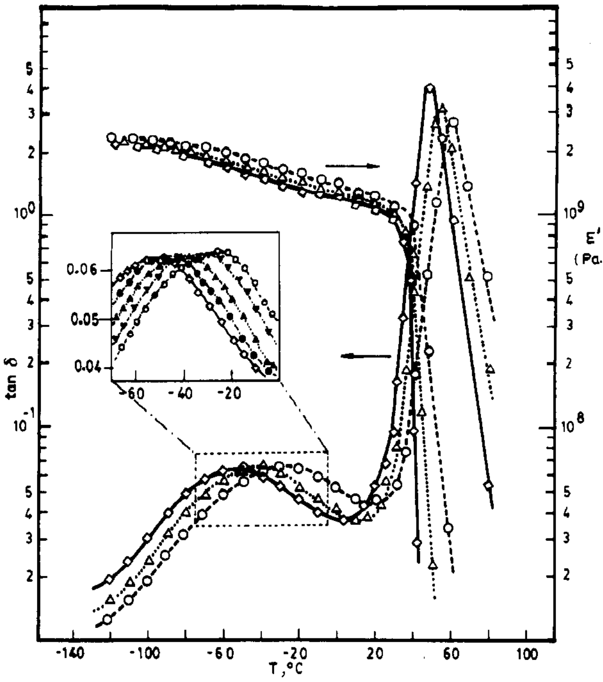

Figure 3. Variation of the storage relaxation modulus E' and the loss tan δ with temperature for poly(m-chlorophenyl acrylate) (PMCPA). (See Figure 1 for the values of the frequencies attached to the symbols.)

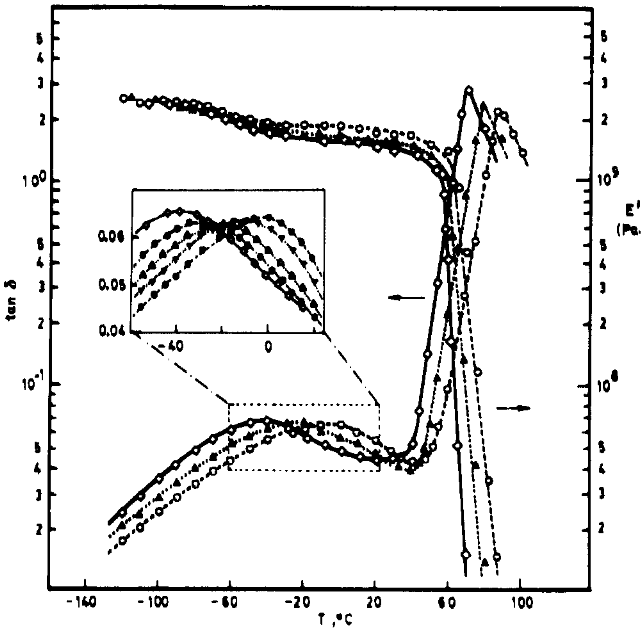

Figure 4. Dependence of the storage relaxation modulus E' and the loss tan δ on temperature for poly(o-chlorophenyl acrylate) (POCPA). (See Figure 1 for the values of the frequencies attached to the symbols.)

components of the complex relaxation modulus were obtained at 0.3, 1, 3, 10, and 30 Hz from -120 °C to about +40 °C above the glass transition temperature of each polymer.

Results and Discussion

Values of both the real part E' of the complex modulus E^* and the loss tan δ for the phenyl and chlorophenyl esters of poly(acrylic acid) are shown, as a function of temperature, in Figures 1-4. An inspection of the relaxation spectra shows, as usual, a prominent relaxation, labeled α and clearly associated with the glass-rubber relaxation, followed by in all cases for a single subglass absorption labeled β, whose strength and location are strongly dependent on the symmetry of the side groups. Thus, the β absorption at 0.3 Hz for PPA and PPCPA, represented in Figures 1 and 2, is centered in both cases at -100 °C, whereas the maximum of the absorption at the same frequency is shifted to -56 and -44 °C for PMCPA and POCPA, respectively. The strength of the β dispersion, expressed in terms of the values of loss tan δ associated with the maximum of the peaks, follows the trend PPCPA < PPA < PMCPA < POCPA. The subglass dispersion follows Arrhenius behavior, with activation energies E_a of 13.0 and 12.3 kcal mol^{-1} for PPA and PPCPA, respectively, whereas the values of this parameter amount to 15.0 and 18.4 kcal mol^{-1}, respectively, for POCPA and PMCPA.

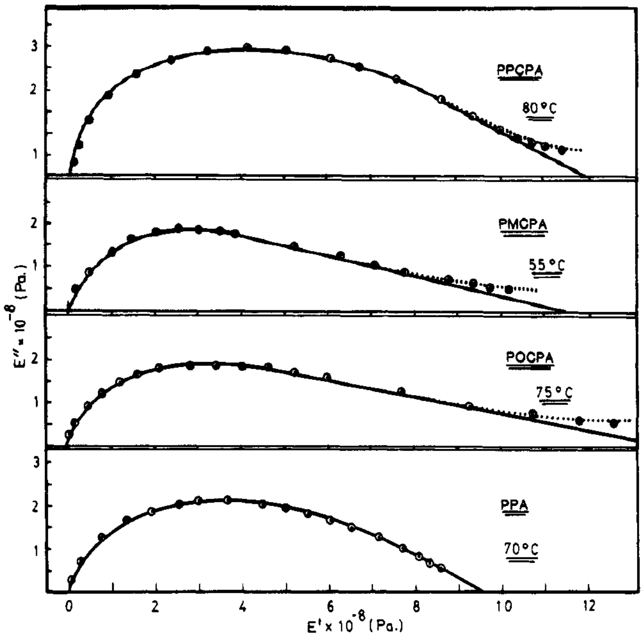

Figure 5. Cole–Cole plots for PPA, POCPA, PMCPA, and PPCPA at the temperatures indicated.

Table II
Values in Pascals of the Storage Relaxation Modulus at Infinite Frequency E_∞ and the Parameters Corresponding to the Biparabolic Model (Equation 1) That Describe the α Relaxation of Phenyl and Chlorophenyl Esters of Poly(acrylic acid) at the Temperatures Indicated Below

polymer	T, °C	$10^{-9}E_\infty$	κ	h	δ	$10^3\tau$, s
PPA	70	0.95	0.40	0.90	1.61	3.75
PPCPA	80	1.20	0.225	0.885	0.77	0.318
PMCPA	55	1.15	0.17	0.77	1.225	0.179
POCPA	75	1.40	0.156	0.834	1.70	0.56

The activation energy of the β process is therefore dependent on the nature of the side group, this quantity being lower for the polymers with symmetric side groups.

Master curves of both log E' and log E'' versus log ω were obtained by horizontal shifting of the corresponding experimental isotherms determined at temperatures in the vicinity of the glass transition temperature. The results corresponding to the α relaxation were then interpreted in terms of the Cole–Cole formalism, obtaining skewed arcs in the high-frequency region, which are represented in Figure 5. The curves were fitted to the biparabolic model[13,14]

$$E^* = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-\kappa} + (i\omega\tau)^{-h}} \tag{1}$$

where E_0 and E_∞ represent the relaxed and unrelaxed modulus, respectively, and k and h are given by

$$\kappa = 2\frac{\bar{\alpha}}{\pi};\quad h = 2\frac{\bar{\beta}}{\pi} \tag{2}$$

$\bar{\alpha}$ and $\bar{\beta}$ being the angles formed by the skewed arcs with the horizontal axis at zero and infinite frequencies, respectively, and τ is the characteristic relaxation time. Values of E_∞ and the parameters $\bar{\alpha}$, $\bar{\beta}$, and τ for the polymers studied here are given in Table II. The low values obtained for κ in POCPA and PMCPA are due to the presence of a secondary relaxation, whose maximum is located near the maximum of the corresponding mechanical α peak of these polymers. The magnitude of the real residues for both E' and E'', expressed in terms of the difference between the experimental and predicted values, was for all the polymers, with the exception of POCPA, lower than 0.05 Pa, that is, somewhat lower than the error band associated with replication studies. For POCPA the residual residues were somewhat higher presumably as a consequence of the closeness of the β relaxation.

The viscoelastic analogue of the expression proposed by Havriliak and Negami[15] to represent the dielectric dispersion of many polymers is

$$D^* = D_\infty + \frac{D_0 - D_\infty}{(1 + (i\omega\tau)^{1-\bar{\alpha}})^{\bar{\beta}}} \tag{3}$$

where D^* is the complex compliance and D_0 and D_∞ are, respectively, the compliances at zero and infinite frequencies. Since the complex relaxation modulus is given by the reciprocal of the complex compliance, eq 3 can also be written as

$$E^* = \frac{E_\infty}{1 + (E_\infty/E_0)(1 + (i\omega\tau)^{1-\bar{\alpha}})^{-\bar{\beta}}} \tag{4}$$

The residual errors obtained by analyzing the experimental results with eq 4 are significantly larger than those obtained from eq 3, presumably as a consequence of the fact that the term E_∞/E_0 that appears in the denominator of the former equation is highly imprecise. Actually, $E_0 \ll E_\infty$ (see Figures 1–4), and its value lies near the limit of measurement of the DMTA apparatus.

The analysis of the secondary relaxations was carried out by using the model of Fuoss and Kirkwood[16] in which the loss relaxation modulus is given by

$$E'' = E''_{\max} \operatorname{sch} mx \tag{5}$$

with

$$x = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\max}}\right) \tag{6}$$

and m is a parameter that it is related to the width of the relaxation. For example, $m = 1$ for a process described by a single relaxation time, whereas its value is 0.4–0.5 if the process is governed by an intramolecular barrier. For a complex process, $m = 0.1$–0.25, the value of m decreasing as the complexity of the system increases. Values of m were obtained at 0.3 Hz by plotting $\operatorname{ch}^{-1}E_{\max}''/E''$ against $1/T$, taking for the activation energy E_a the values given above. The values obtained for m were 0.17, 0.15, and 0.115 for PPA, PPCPA, and PMCPA, respectively. These results reflect the fact that the complexity of the system increases with the asymmetry of the side group.

The glass–rubbery relaxation is governed by the volume so that the relaxation time associated with a viscoelastic mechanism is related to the relative free volume Φ by the Doolittle equation[17]

$$\tau_i = A \exp(B/\Phi) \tag{7}$$

where B is thought to be close to unity. The assumption in this equation that the volume is a linear function of temperature leads to the Vogel relationship[18]

$$\ln \tau_i = A' + \frac{m}{T - T_\infty} \tag{8}$$

where T_∞ is the temperature at which Φ would be zero were it not for the formation of the glassy state. When the natural logarithm of the relaxation time associated with the maximum of the α peaks is plotted against the reciprocal of $T - T_\infty$, straight lines with correlation coefficients $\rho > 0.9996$ are obtained if the values of T_∞ indicated in the fourth column of Table I are used. From the slopes of the straight lines, the ratio Φ_g/B is determined

Table III
Values of the Exponent n for the Decay Function of the Dielectric and Mechanical α Relaxation (n_{dr} and n_{mr}, Respectively) in the Coupling Model, and Values of the Vogel Parameters B_{dr} and B_{mr}

polymer	n_{mr}	n_{dr}[a]	B_{mr}, K	B_{dr},[a] K
PPA	0.64	0.58	1727	2220
PPCPA	0.58	0.51	2457	1750
PMCPA	0.58	0.48	1687	1500
POCPA	0.62		2425	2420

[a] Taken from ref 11.

by means of the equation

$$\frac{\Phi_g}{B} = \frac{T_g - T_\infty}{m} \tag{9}$$

where Φ_g is the relative free volume at T_g. The values of Φ_g/B for the phenyl and chlorophenyl esters of poly(acrylic acid) are given in Table I. As usual, these values are close to the average value of 0.025 ± 0.005 reported for the relative free volume at T_g for most polymers.

According to the phenomenological theory of linear viscoelasticity, the complex relaxation modulus $E^*(\omega)$ corresponding to the relaxation α process can be written as[19]

$$\frac{E_\infty - E^*(\omega)}{E_\infty - E_0} = \int_0^\infty \left[-\frac{d\psi(t)}{dt} \right] e^{-i\omega t} dt \tag{10}$$

where $\psi(t)$ is the normalized decay function, which in most relaxation phenomena is given by the Kohlrausch–Williams–Watts (KWW) equation[20,21]

$$\psi(t) = \exp(-t/\tau_0)^{\bar{\gamma}} \tag{11}$$

Recently, Ngai and co-workers[22] have interpreted the KWW equation by means of the coupling model. The model assumes that the primary relaxation mechanism arises from interactions between the relaxing species and the heat bath that can be described by a single linear exponential with a constant relaxation time τ_0. As a consequence of the coupling between the relaxing species, which produces time-dependent effects on the relaxation already in progress, due to the interactions between the relaxing species and the heat bath, the model gives for the decay function the expression[22]

$$\psi(t) = \exp(-t/\tau^*)^{1-n} \tag{12}$$

where n is a constant characterizing the coupling among the relaxing species and τ^*, called the effective relaxation time, is given by

$$\tau^* = [(1-n)w_c\tau_0]^{1/(1-n)} \tag{13}$$

where w_c is the reciprocal of a time characteristic of the complexity of the system and τ_0 has the Vogel form

$$\tau_0 \propto \exp[B_0/(T - T_\infty)] \tag{14}$$

The normalized E''/E''_{max} curves corresponding to the α absorption of the relaxation spectra of the phenyl and chlorophenyl acrylate polymers were fitted by the decay function given be eq 12. Since the relaxation times obtained by using different probes are not the same, the parameter n is not invariable, but it is dependent on the probe. The values obtained for n from mechanical and dielectric results, represented by n_{mr} and n_{dr}, respectively, are given in Table III. It can be seen that $n_{dr} < n_{mr}$ for the relaxation spectra of PPA, POCPA, PMCPA, and PCPA, in agreement with results reported for other systems.[7]

By substituting eq 14 into eq 13, one obtains for the effective relaxation times of the dielectric and mechanical processes[7] the expressions

$$\tau_{dr}^* \propto \exp\{[B_0/(1-n_{dr})]/(T - T_\infty)\} \tag{15}$$

$$\tau_{mr}^* \propto \exp\{[B_0/(1-n_{mr})]/(T - T_\infty)\} \tag{16}$$

A prediction of the coupling model is that in the relations

$$B_{dr} = B_0/(1 - n_{dr}) \tag{17}$$

$$B_{mr} = B_0/(1 - n_{mr}) \tag{18}$$

B_0 is invariant and hence

$$(1 - n_{dr})B_{dr} = (1 - n_{mr})B_m = B_0 \tag{19}$$

where B_{dr} and B_{mr} are represented by m in eq 8, and their values are given in Table III. Values of B_0 obtained from eqs 17 and 18 for the phenyl and chlorophenyl esters of poly(acrylic acid) show some discrepancy for each polymer. However, the average values of 856 ± 75 and 820 ± 188 determined for the polymers from dielectric and mechanical results show a reasonable agreement.

The β relaxation for the polymers with asymmetric side groups is wide, and it seems to be the result of several overlapping processes presumably produced by motions of different parts of the side groups coupled with motions of the main chain. Molecular motions in the side groups arise from rotations about both O–Ph and C^α–C^* bonds, where C^* represents the carbonyl carbon. Potential calculations show that the rotational state angles about the former bonds are $\chi = \pm 60°$ and $\pm 120°$ for phenyl and p-chlorophenyl groups in PPA and PPCPA, respectively.[23] The presence of a Cl atom in the ortho position, as occurs in POCPA, causes strong interactions with the carbonyl group, and the rotational angles are reduced to[23] ±75°. For PMCPA the interactions between the Cl atom and the carbonyl group are smaller than those for POCPA; potential minima about 0–Ph bonds occur at the same angles as in PPA and PPCPA. The O–C^* bonds in the side groups of the esters of poly(acrylic acid) are restricted to trans states, whereas the rotational angles about C^α–C^* bonds are[24] 0 and 180°.

As can be seen in Figures 1–4, the intensity of the β relaxation of the polymers with symmetric side groups is significantly lower than that of the polymers with asymmetric side groups. Similar behavior appears in the dielectric relaxation of these polymers. The analysis of the ^{1}H NMR relaxation spectra of the phenyl and p-chlorophenyl esters of poly(acrylic acid) suggests that their stereochemical configuration is predominantly racemic, and in this configuration the trans conformation is strongly favored over the alternative gauche conformation. The critical interpretation of the dielectric conformation-dependent properties of PPA and PPCPA indicates that $t\pi,t\pi$ conformations about the skeletal bonds of racemic diads are favored over the alternative[25] t0,t0 and $t0,t\pi$. Occasional transitions $t\pi,t\pi \rightleftharpoons t\pi,t0$ in PPA, which involve moderate dielectric activity, might account for the low dielectric strength of the β absorption of PPA.[11] However, transitions involving rotations about C^α–C^*, though dielectrically active, would not produce significant mechanical activity. This would be produced by motions of the side groups coupled, for example, with transitions $...ttt... \rightleftharpoons ...g^\pm t g^\mp...$ or $...g^\pm tt... \rightleftharpoons ...ttg^\pm...$ about isolated sequences CH_2–C^α–CH_2–C^α in the racemic configuration. These transitions reduce the motions of the tails and therefore should not be dependent on molecular weight.[10] Transitions of this kind are accompanied by rotations about O–Ph bonds where the mechanical sweeping energy is presumably larger in POCPA and PMCPA than in PPA and PPCPA. As a result the strength of the β mechanical absorption should be higher in polymers with asymmetric side groups than in those with symmetric ones. Rotations about O–Ph bonds in PMCPA and POCPA also produce considerable dielectric activity caused by the changes of orientation of the dipole associated with the C^{ph}–Cl bond with respect to that of the ester group within each side group.[11] As a consequence, these polymers exhibit a β dielectric relaxation, whose strength is significantly larger than that of both PPA and PPCPA. However, the fact that the activation energy for the mechanical β relaxation of POCPA is somewhat lower than that of PMCPA suggests that molecular motions about O–Ph bonds in the latter case probably involve oscillating motions in the vicinity of the rotational minima without transitions between two rotational states taking place.

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