Relaxation behaviour and dipolar correlations for polyacrylate-based polymers with aromatic side groups

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Dielectric experiments are carried out on poly(4-phenoxyphenyl acrylate) (PPOA) and 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG), a low-molecular-weight analogue of PPOA. The intramolecular dipolar correlation coefficient g_{intra} for the polymer changes from 0.821 at 30°C to 0.835 at 60°C. This coefficient is similar to that of PPODG (0.817 at 30°C), suggesting that the asymptotic value of g_{intra} is reached for rather low molecular weights. The dipolar correlation coefficient g that accounts for both the intramolecular and intermolecular dipolar interactions is smaller than g_{intra} for both the polymer and the low-molecular-weight compound. The dielectric spectrum of PPOA in the bulk presents a prominent glass–rubber relaxation followed by a subglass absorption that seems to be the combination of a process in the high-temperature zone (named β) that overlaps with the glass–rubber relaxation and a well developed absorption (named γ) in the low-temperature region. This latter process can be explained in terms of motions of the dipole associated with the C^{ar}–O–C^{ar} bonds whereas motions about the C^{α}–$C^{*}O^{*}$ bonds may also intervene in the β process. The low-molecular-weight compound only exhibits a prominent glass–liquid absorption followed by a diffuse and weak subglass relaxation; this behaviour cannot be explained in terms of only intramolecular interactions, and therefore intermolecular interactions must play an important role in this process. The mechanical and the dielectric glass–rubber relaxations are interpreted in terms of the coupling scheme. This study suggests that the complexities of both processes are similar, in contrast with what occurs in many other systems.

(Keywords: polyacrylates; aromatic side groups; dipolar correlation; dielectric relaxation; mechanical relaxation)

INTRODUCTION

Thermotropic side-chain liquid-crystalline polymers can be obtained by placing flexible spacers between the main chain and the mesogenic groups that partially decouple the mobility of the main chain from that of the mesogenic moiety[1–11]. However, liquid-crystalline order may also be achieved by direct attachment of the mesogenic groups to the backbone in highly flexible polymers in which the main chain can be significantly distorted. In this context, polyacrylate-based polymers are good candidates to develop two-dimensional order[5].

Direct attachment of bulky mesogenic groups to the backbone of polyacrylates might affect in a significant way the relaxation behaviour of these polymers even though liquid-crystalline order is not developed. As a first step to more ambitious goals connected with the determination of the molecular parameters that govern development of mesogenic phases in polymers with mesogenic side groups attached to the main chain, it is convenient to carry out a systematic work on the relationship between molecular relaxations and structure on polyacrylates containing side groups whose structure resembles that of those with the capability to develop mesogenic order. This work addresses this subject, taking as a model poly(4-phenoxyphenyl acrylate) (PPOA) whose structure is shown in *Figure 1*. An inspection of the molecular structure of these chains suggests that significant dielectric activity can be produced by motions of the side groups totally decoupled from the motions of the main chain. It is also expected that the bulkiness of the side group will restrict the coupling of motions of these groups with motions of localized segments in the backbone necessary to develop mechanical activity in the glassy state.

Another important subject is the quantification of the intramolecular and intermolecular contributions to the dielectric strength of polyacrylates. Earlier studies carried out on phenyl, cyclohexyl, 2-biphenyl and chlorophenyl esters of poly(acrylic acid) (PA) suggest that, the larger the effective dipole moment of the chains, the larger are the intermolecular interactions[12,13]. Thus, whereas significant intermolecular interactions were found for the chlorophenyl esters of PA, these interactions are relatively small for poly(phenyl acrylate) (PPA)[12,13],

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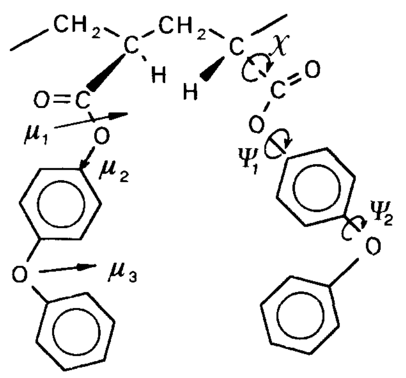

Figure 1 Scheme of a *racemic* diad of poly(4-phenoxyphenyl acrylate) (PPOA) in *trans* conformation

poly(cyclohexyl acrylate)[14] (PCA) and poly(2-biphenyl acrylate)[15] (PBPA). An important result only observed in the latter polymer is that coupling between the relaxing species in the glass–rubber relaxation seems to be more important in the dielectric process than in the mechanical one, presumably as a consequence of the bulkiness of the side group, which increases the barrier energies across which conformational changes of the side groups take place.

The aim of this work is the theoretical and experimental determination of the intramolecular dipolar correlation coefficient for PPOA and its comparison with the total dipolar correlation coefficient evaluated from the relaxed and unrelaxed values of the real component of the complex dielectric permittivity. The effects of the volume and the conformational versatility of the side group of this polymer on the subglass absorptions are investigated, and attention is also paid to the effects of the bulkiness of the side group on the temperature dependence of the glass–rubber relaxation. Dielectric experiments have been conducted in parallel on 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG), a low-molecular-weight analogue of the polymer, with the aim of obtaining a better understanding of the relaxation behaviour of molecular chains.

EXPERIMENTAL

The 4-phenoxyphenyl ester of 2,4-dimethylglutaric acid was synthesized by direct condensation of 0.07 mol of the acid with 0.1 mol of the corresponding phenol derivative in 100 ml of dry toluene by using an equivalent amount (0.1 g) of *p*-toluenesulfonic acid and boric acid as catalyst. The reaction mixture was refluxed for 24 h in a Pyrex glass reactor equipped with a Dean–Stark distillation separator under a nitrogen atmosphere. The solution of the crude ester was concentrated at reduced pressure and purified by column chromatography (Kiesegel 60, Merck) using a mixture of chloroform/heptane (80:20 v/v) as eluent. The yield was 70% and the purity of the diester, determined by g.l.c. and i.r., exceeded 99.5%.

4-Phenoxyphenyl acrylate was obtained by dropwise addition of freshly distilled acryloyl chloride to a solution of 4-phenoxyphenol in an aqueous medium containing 20% of dioxane and 5% of NaOH. The product was extracted with ether, washed with distilled water, dried successively with calcium sulfate and calcium hydride and finally distilled under vacuum. The monomer was polymerized in benzene solution at 50°C by using azobisisobutyronitrile (AIBN) as initiator; the conversion was kept below 12%. The polymer thus obtained, poly(4-phenoxyphenyl acrylate), was precipitated with methanol, washed several times with this compound and dried under vacuum. The number-average molecular weight of the unfractionated polymer, measured by osmometry, amounted to 210 000. The glass transition temperatures of both PPODG and PPOA were measured with a DSC-4 calorimeter at a heating rate of 5°C min^{-1} and the results obtained were −34 and 55°C, respectively. Additional transitions were not detected in the interval of temperatures −100 to 200°C.

^{13}C n.m.r. spectra of the polymer and the dimer (4-phenoxypheyl-2,4-dimethylglutarate) (PPODG) were recorded in chloroform with a Varian XL-300 at 75 MHz. The analysis of the C=O and C–H signals in the spectra indicates that the values of the molar fraction of meso-, syndio- and heterotactic triads in the polymer chains amount to 0.16, 0.37 and 0.47, respectively. This analysis also suggests that the molar fraction of both the *meso* and *racemic* diads in 4-phenoxy-2,4-dimethylglutarate is 0.5.

Values of the real component, ε', of the complex dielectric constant, ε^*, of solutions of the samples in benzene were determined at 10 kHz with a capacitance bridge (General Radio, type 1620 A) operating with a three-terminal cell. At this frequency $\varepsilon' \approx \varepsilon$, where ε is the static dielectric constant. Increments of the indices of refraction of the solution with respect to the solvent were measured at $\lambda = 632.8$ nm with a differential refractometer (Chromatix Inc.).

Dielectric measurements were performed on the samples in the bulk with a plane condenser and a dielectric analyser (DuPont DEA 2970) in the frequency range and temperature interval 0.001 to 30 kHz and −140 to 90°C, respectively. The real E' and loss E'' components of the complex relaxation modulus were measured with a PL-DTMA Mark II apparatus in single cantilever bending in the frequency range 0.3–30 Hz and temperature interval −140 to 120°C. The heating rate was 1°C min^{-1}.

DIELECTRIC AND MECHANICAL RESULTS IN BULK

The dielectric relaxation spectrum of the dimer PPODG presents a strong peak centred at −29°C at 1 Hz clearly associated with the glass–liquid relaxation followed by a weak subglass absorption that at first sight does not present a well defined maximum. However, careful inspection of the subglass zone in *Figure 2* permits detection of a maximum located at −127°C at 10^3 Hz, which shifts to −104°C at 10^4 Hz, suggesting that a relatively low activation energy is associated with the process. The curves showing the dependence of the dielectric loss on temperature for PPOA, presented in *Figure 3*, exhibit an ostensible absorption located at 65°C at 2 Hz, corresponding to the α glass–rubber absorption, and a wide subglass relaxation that seems to be composed of two peaks: one, named β, detected at low frequencies in the high-temperature zone that overlaps with the glass–rubber absorption, and another well differentiated peak, named γ, whose width and intensity seem to decrease as the frequency decreases. This latter peak centred at −106°C at 2 Hz obeys Arrhenius behaviour with an activation energy of only 9.6 kcal mol^{-1}.

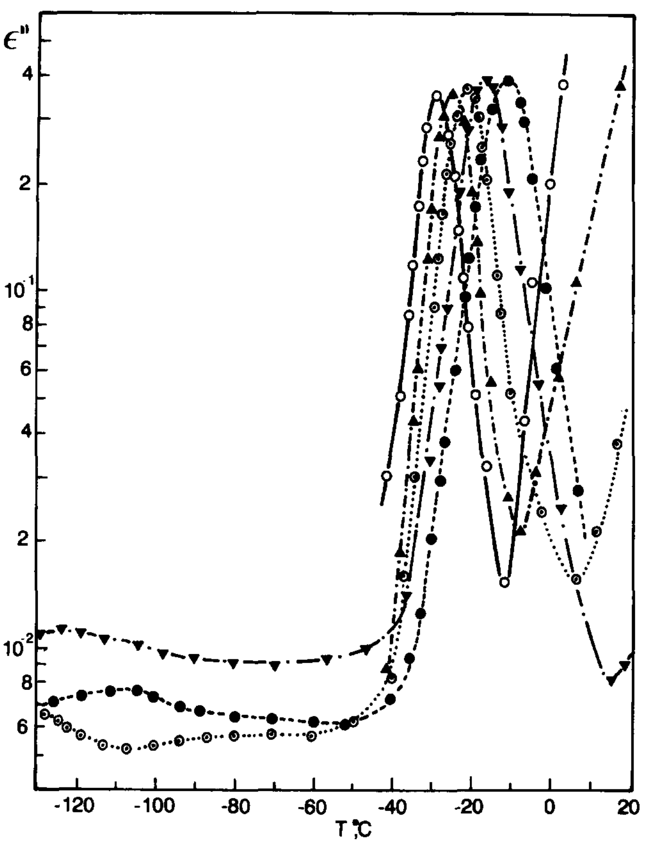

Figure 2 Variation of the dielectric loss with temperature for 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG) at several frequencies: (○) 0.001, (▲) 0.01, (⊙) 0.1), (▼) 1, (●) 10 kHz

The dielectric complex-plane plots depicting the glass–rubber and glass–liquid transitions for PPOA and PPODG are shown in *Figure 4*. Both plots are slightly skewed arcs that approach the abscissa axis in the high-frequency region through a straight line and, as usual, they obey the Havriliak–Negami formalism[16]:

$$\varepsilon^*_\alpha(\omega) - \varepsilon_{\alpha u} = \varepsilon_{\alpha u} + \frac{\varepsilon_{\alpha r} - \varepsilon_{\alpha u}}{[1+(i\omega\tau_0)^{1-\bar{\alpha}}]^{\beta}} \qquad (1)$$

where $\varepsilon_{\alpha r}$ and $\varepsilon_{\alpha u}$ are, respectively, the relaxed and the unrelaxed dielectric constants in the α region. The parameters that define the Cole–Cole arcs are given in *Table 1*. The Cole–Cole curves for the glass–liquid transition of PPODG presents some unexpected features. On the one hand, the unrelaxed permittivity for the α transition has a relatively high value (3.15) and, on the other hand, a Cole–Cole arc for the subglass transition is not observed.

The Cole–Cole plot for the dielectric subglass relaxation of the polymer is an arc with an unusually low curvature in the highest-frequency region that renders difficult the determination of $\varepsilon_{\gamma u}$; however, its intercept with the abscissa axis in the low-frequency region is easily determined, giving $\varepsilon_{\gamma r} \approx 2.70$ at -90°C, which nearly coincides with $\varepsilon_{\alpha u}$ at 70°C (2.72). Therefore, the relaxed dielectric permittivity of the γ process may not be significantly dependent on temperature. Evaluation of $\varepsilon_{\gamma u}$ was carried out using the empirical Fuoss–Kirkwood expression[17]:

$$\varepsilon'' = \varepsilon''_{\max}\,\mathrm{sech}(mx) \qquad (2)$$

with

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

where $T_{\max}$ is the temperature at which the γ peak reaches a maximum and E_a is the activation energy of the process. This approach leads to $\Delta\varepsilon_\gamma = (2/m)\varepsilon''_{\max}$. The value of m obtained from the plot of $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ vs. $1/T$ at 0.2 kHz amounts to 0.19. Since $\varepsilon''_{\max} \approx 0.014$ at -90°C, one obtains $\Delta\varepsilon_\gamma \approx 0.15$, from which $\varepsilon_{\gamma u} \approx 2.55$.

The storage E' and loss E'' relaxation moduli for PPOA are plotted as a function of temperature at several frequencies in *Figure 5*. The loss modulus exhibits a glass–rubber relaxation centred at 57°C at 0.3 Hz

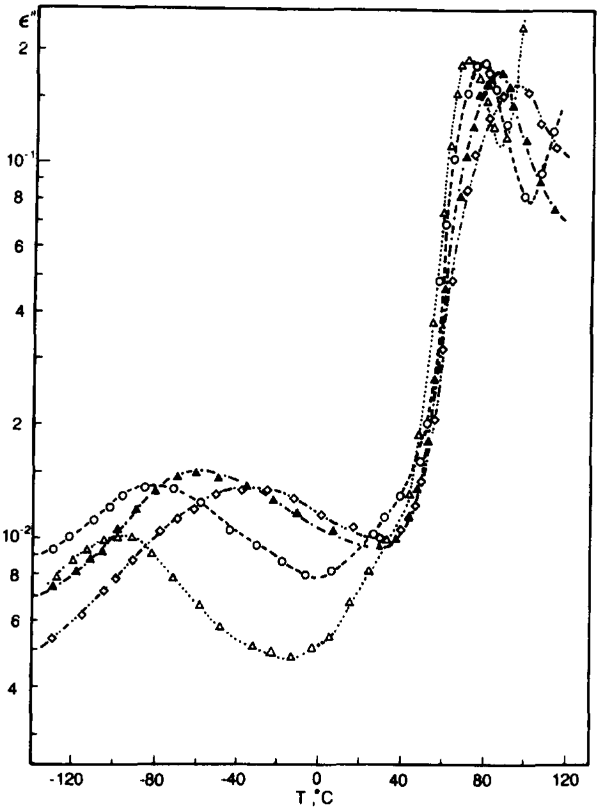

Figure 3 Dependence of the dielectric loss on temperature for poly(4-phenoxyphenyl acrylate) (PPOA) at several frequencies: (△) 0.02, (○) 0.2, (▲) 2, (◇) 10 kHz

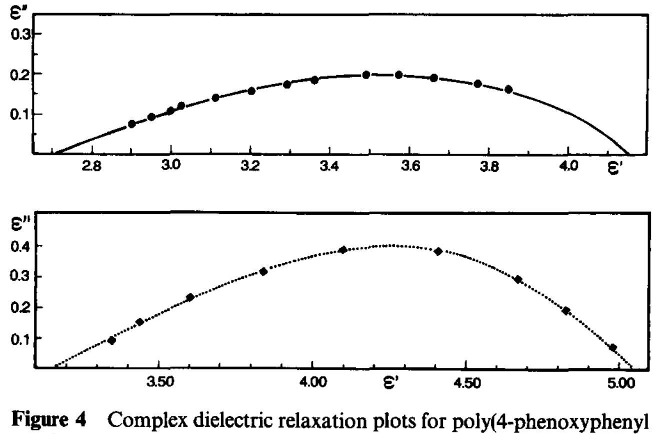

Figure 4 Complex dielectric relaxation plots for poly(4-phenoxyphenyl acrylate) (PPOA) (●) and 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG) (◆) at 70°C and -20°C, respectively

Table 1 Cole–Cole parameters for the α relaxations of poly(phenoxyphenyl acrylate) (PPOA) and 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG)

Sample	T (°C)	$\varepsilon_{\alpha r}$	$\varepsilon_{\alpha u}$	$\bar{\alpha}$	$\bar{\beta}$	$10^3 \times \tau_0$ (s)
PPOA	70	4.15	2.70	0.563	0.508	53.0
PPODG	−20	5.05	3.15 (2.46)^a	0.40	0.50	3.2

^{a} Value obtained from $\varepsilon_\infty = n^2$

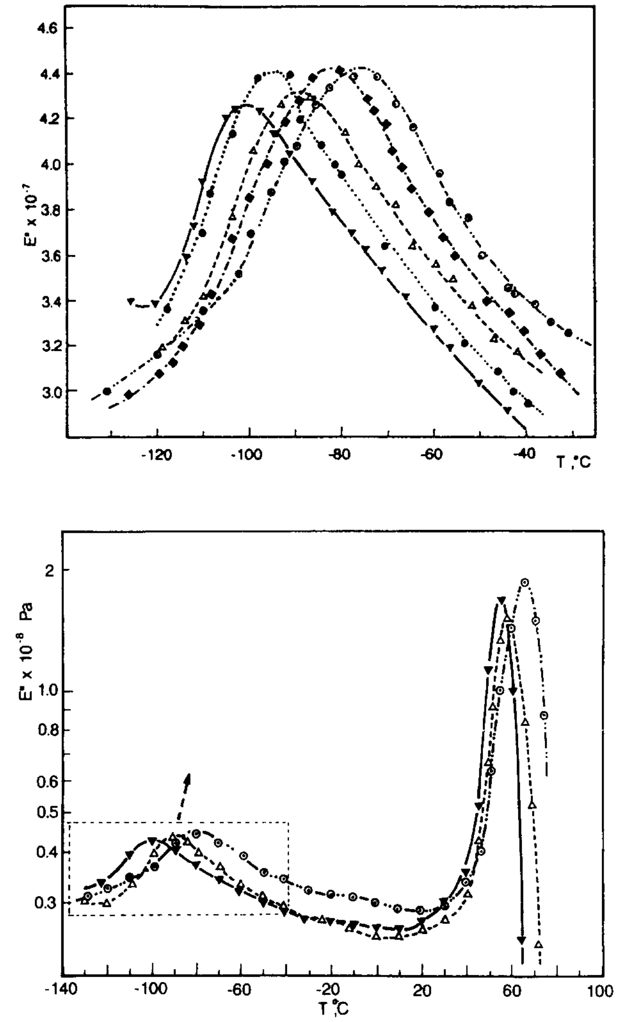

Figure 5 Dependence of the loss relaxation modulus on temperature for poly(4-phenoxyphenyl acrylate) (PPOA) at several frequencies: (▼) 0.3, (●) 1, (△) 3, (◆) 10, (⊙) 30 Hz

followed by a moderate subglass absorption that presents a maximum at −100°C. Details of the mechanical relaxation spectrum in the low-temperature region of the glassy zone are also inserted in *Figure 5*. This relaxation is a thermally activated process with an activation energy of 12.4 kcal mol^{-1}, a value nearly 3 kcal mol^{-1} above that corresponding to the dielectric relaxation.

PHENOMENOLOGICAL DESCRIPTION OF THE GLASS–RUBBER RELAXATION

A complex compliance function Γ^*, such as the dielectric permittivity and the tensile compliance D^*, is related to the decay function $\psi(t)_\Gamma$ of a relaxation process by the familiar expression[18]:

$$\frac{\Gamma^*(\omega)-\Gamma_u}{\Gamma_r-\Gamma_u}=\int_0^\infty\left(-\frac{d\psi(t)_\Gamma}{dt}\right)\exp(-i\omega t) \qquad (4)$$

where, as before, the indices r and u refer, respectively, to the relaxed and unrelaxed compliance function, ω is the angular frequency and $\psi(t)$ obeys the Kohlrausch–Williams–Watts equation[19,20]:

$$\psi(t)_\Gamma=\exp(-t/\tau_0)^{\bar{\gamma}} \qquad 0<\bar{\gamma}\leqslant 1 \qquad (5)$$

Since $E^*=1/D^*$, the relationship between the complex tensile modulus and the decay function is straightforwardly obtained from equation (4).

A detailed description of the dependence of the real and loss components of the complex dielectric permittivity on temperature in the α process is shown for PPOA in *Figure 6*. Composite curves for the dielectric and mechanical α relaxations, depicting the dependence of the losses on frequency at a reference temperature, were obtained by horizontal shifting of the normalized loss isotherms measured in the vicinity of the glass transition temperature. The dielectric curves for PPOA and PPODG, shown in *Figure 7*, fit the KWW equation for values of $\bar{\gamma}$ of 0.30 ± 0.02 and 0.42 ± 0.02, respectively. The composite curves for the mechanical α process of the

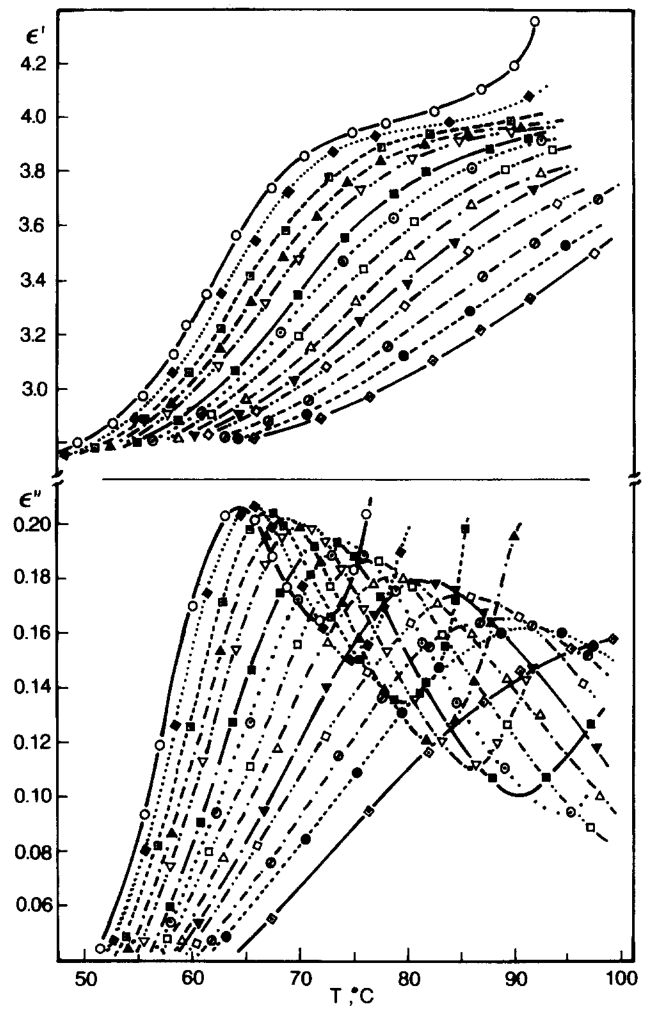

Figure 6 Detailed description of the dependence of the components of the complex dielectric permittivity on temperature for poly(4-phenoxyphenyl acrylate) (PPOA) in the glass–rubber transition at various frequencies: (○) 0.001, (◆) 0.002, (□) 0.005, (▲) 0.01, (▽) 0.02, (■) 0.05, (⊙) 0.1, (□) 0.2, (△) 0.5, (▼) 1, (◇) 2, (⊘) 5, (●) 10, (◇) 50 kHz

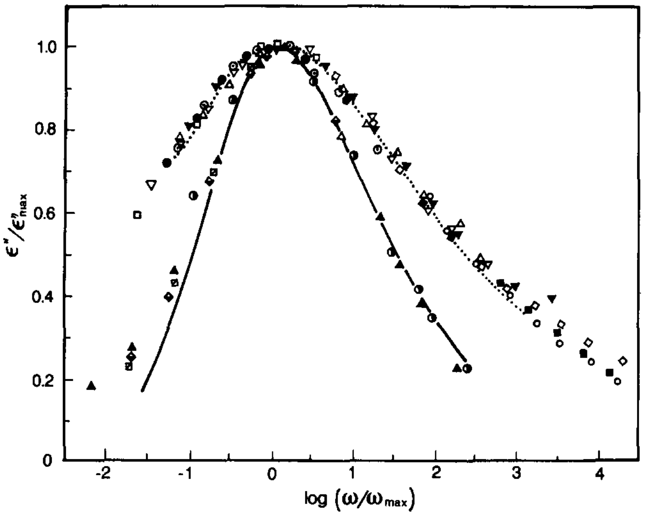

Figure 7 Composite curves for the dielectric glass–rubber relaxation of 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG) (——) and poly(4-phenoxyphenyl acrylate (PPOA) (···). The curves were calculated from equation (4) by using the values of 0.30 and 0.42, respectively, for the exponents of the KWW equation

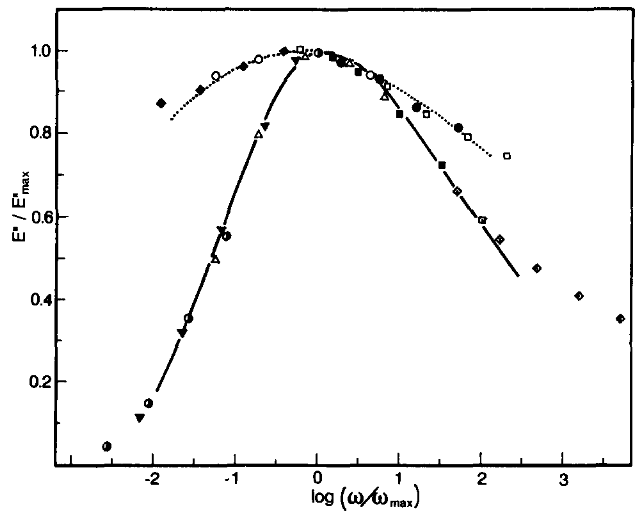

Figure 8 Composite curves for both the mechanical glass–rubber process (——) and the mechanical subglass absorption (···) of poly(4-phenoxyphenyl acrylate) (PPOA). The curves were calculated from equation (4) by using the values of 0.30 and 0.20, respectively, for the exponents of the KWW equation

polymer are represented in *Figure 8*, where it can be seen that the KWW exponent that fits the experimental results is also 0.30±0.02. It should be pointed out that, even though the relaxation peak for PPOA is much broader than a typical α process for conventional amorphous polymers, d.s.c. transitions that would suggest a liquid-crystalline order are not detected.

There is a wealth of experimental results that suggest that the α relaxation is governed by the free volume so that the relaxation time is related to the free volume by the empirical Doolittle expression[21]:

$$\tau^* = A\exp(B/\Phi) \tag{6}$$

where Φ is the relative free volume and *B* is a parameter close to unity that seems to be closely related to the critical volume necessary for a relaxation process to take place. By assuming that the volume is linearly dependent on temperature, equation (4) converts into the empirical expression formerly proposed by Vogel[22]:

$$\ln\tau^* = A' + m/(T - T_\infty) \tag{7}$$

where *m* may be considered as the ratio of *B* to the expansion coefficient and T_∞ is an empirical parameter that is customarily considered as the temperature at which the free volume would be zero were it not for the formation of the glassy state. The values of this parameter are usually assumed to be those for which the plots of $\ln\tau^*$ against $1/(T - T_\infty)$ fit better to a straight line.

By assuming that the average relaxation time associated with the process is the reciprocal of the frequency at the temperature associated with the peak maximum, the plots represented in *Figure 9* are obtained. The values of T_∞ were considered to be those for which a better fit for the experimental results to equation (7) is obtained. The values of the Vogel parameters for both the mechanical and dielectric glass–rubber relaxations of the polymer and for the dielectric glass–liquid relaxation of PPODG are given in *Table 2*. The ratio of the relative free volume to the parameter *B* at T_g, Φ_g/B, can be obtained from the

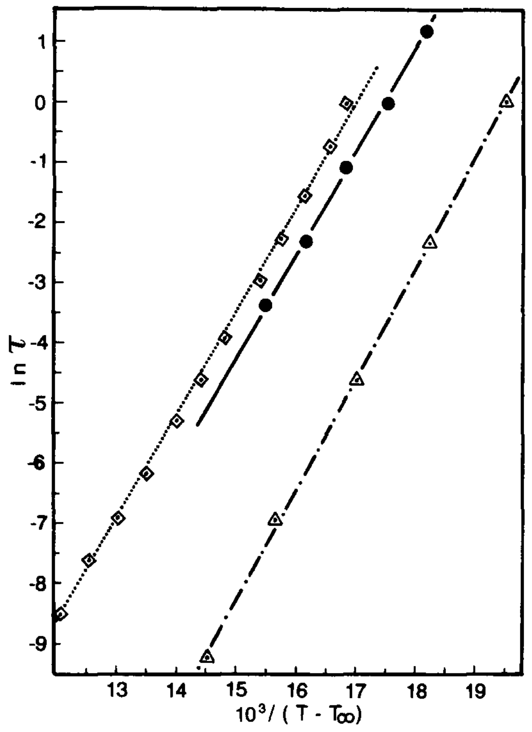

Figure 9 Temperature dependence of the relaxation mechanisms involved in the dielectric α relaxation of both poly(4-phenoxyphenyl acrylate) (PPOA) (◇) and 4-phenoxyphenyl-2,4-dimethylglutarate (PPODG) (△) and in the mechanical α process of PPOA (●)

Table 2 Values of the Doolittle and Vogel parameters (*m* and T_∞ (equation (5)), Φ_g/B (equation (6))) for the dielectric and mechanical glass–rubber relaxations of poly(phenoxyphenyl acrylate) (PPOA) and phenoxyphenyl-2,4-dimethylglutarate (PPODG)

Sample	Relaxation	*m* (K)	T_∞ (K)	Φ_g/B
PPOA	Dielectric	1710	283	0.026
PPODG	Dielectric	1850	193	0.025
PPOA	Mechanical	1700	273	0.032

Table 3 Dielectric results and intramolecular dipolar correlation coefficient g_{intra} at different temperatures for poly(4-phenoxyphenyl acrylate) (PPOA)

T (°C)	$2n_1\,\mathrm{d}n/\mathrm{d}w$	$\mathrm{d}\varepsilon/\mathrm{d}w$	g_{intra}
30	0.002	1.593	0.821
40	0.002	1.520	0.828
50	0.001	1.438	0.826
60	0.001	1.380	0.835

expression:

$$\Phi_g/B=(T_g-T_\infty)/m \tag{8}$$

which, in turn, can easily be deduced from equations (6) and (7). The values of this ratio for the mechanical and dielectric results, given in the fifth column of *Table 2*, are in very good agreement with the average value of 0.025 ± 0.005 reported for this quantity in most polymer systems.

DIPOLAR CORRELATION COEFFICIENTS

The dipolar correlation coefficient between relaxing dipoles, g, can be written as[23]:

$$g=1+\sum_{i<j}\langle\cos\gamma_{ij}\rangle^{\mathrm{intra}}+\sum_{i<j}\langle\cos\gamma_{ij}\rangle^{\mathrm{inter}} \tag{9}$$

where the superscripts intra and inter refer, respectively, to the intramolecular and intermolecular cross-correlations. The intramolecular correlation coefficient g_{intra} is given by:

$$g_{\mathrm{intra}}=\frac{\langle\mu^2\rangle/x}{\langle\mu^2\rangle_0} \tag{10}$$

where $\langle\mu^2\rangle/x$ and $\langle\mu^2\rangle_0$ are, respectively, the mean-square dipole moments of the both the repeat unit of the chains and the flexible polar side group. The values of g_{intra} can be determined by using the method of Guggenheim[24] and Smith[25] that relates $\langle\mu^2\rangle$ to the dependence of both the dielectric permittivity ε and the index of refraction n on the weight fraction w of the solute in solutions of non-polar solvents, in the limit $w\to 0$. According to this approach:

$$g_{\mathrm{intra}}=\frac{27\kappa TM_0}{4\pi\rho N_A x\langle\mu^2\rangle_0(\varepsilon_1+2)^2}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}w}-2n_1\frac{\mathrm{d}n}{\mathrm{d}w}\right) \tag{11}$$

where κ and N_A are respectively the Boltzmann constant and Avogadro's number, M is the molecular weight of the solute, x is the degree of polymerization, T is the absolute temperature and ρ is the density of the solvent; the parameters ε_1 and n_1 represent, respectively, the dielectric permittivity and the index of refraction of the solvent. Values at different temperatures of $2n_1\,\mathrm{d}n/\mathrm{d}w$ and $\mathrm{d}\varepsilon/\mathrm{d}w$ in benzene for PPOA are given in the second and third columns of *Table 3*, respectively. By using for $(\langle\mu^2\rangle_0)$ the value of 4.40 D^2 reported for 4-phenoxyphenyl isobutyrate[26] one finds that g_{intra} increases from 0.821 to 30°C to 0.835 at 60°C (see *Table 3*), that is, the cross-correlation terms are slightly dependent on temperature. These values are similar to those reported earlier for PPODG[26] and, consequently, the asymptotic value of g_{intra} is reached for rather low molecular weights in PPOA chains.

The coefficient g that accounts for the intramolecular and intermolecular dipolar interactions was determined from dielectric measurements carried out in bulk by using Onsager-type[27] equations such as the Fröhlich relationship[28]:

$$g=\frac{9\kappa TM}{4\pi x\langle\mu\rangle_0^2\rho N_A}\,\frac{(\varepsilon_r-\varepsilon_u)(2\varepsilon_r+\varepsilon_u)}{\varepsilon_r(\varepsilon_u+2)^2} \tag{12}$$

Evaluation of g for the polymer by using the values of ε_r and ε_u shown in *Table 1* gives for this quantity the value of 0.54 at 70°C; the value of g for PPODG is estimated to be 0.64 at −22°C if the index of refraction is used to determine ε_u.

Three contributions to the polarity of the side groups can be devised[26]: a dipole μ_1 of 1.7 D associated with the ester group that forms an angle[29] of 123° with the C^α–C*; a second contribution of 0.3 D, represented by μ_2 in *Figure 1*, pointing from the oxygen atom of the ester group to the phenyl group; and finally a dipole μ_3 of 1.15 D bisecting the C^{ar}–O–C^{ar} bond angle[26]. The contribution of the side group to the polarity of the chains depends on χ, Ψ_1 and Ψ_2, the rotational angles about C^α–C*, O–C^{ar} and C^{ar}–O bonds, shown in *Figure 1*. By symmetry, the average dipole moment of the side group does not depend on the rotational state of the Ψ_2 angle, so that only the rotational angles χ and Ψ_1 will be considered in the calculations. Earlier studies carried out on model compounds suggest that the values of χ are 0 and 180°, taking as zero the angle for which the carbonyl group is *cis* to the methine bond. On the other hand, $\Psi_1 = \pm 60°$ and $\pm 120°$, taking as reference the angle for which the phenyl group is coplanar with the ester group. The components of the dipoles for each conformation of the side group in a reference frame associated with the C^α–CH_2 bonds of the main chain are given in *Table 4*.

Although the skeletal bonds of the main chain are restricted to t and g states, the consideration of all the rotational states of the side groups would lead to the formulation of a 16 × 16 rotational-states scheme. The use of huge matrices was avoided by using a four-rotational-states scheme that accounts for the splitting of each conformational state of the backbone into two corresponding to the conformations in which the carbonyl bond is *cis* ($\chi=0$) and *trans* ($\chi=\pi$) to the methine bond, in combination with a Monte Carlo simulation of the state about the O–C^{ar} bond of each repeat unit. The statistical weight matrices required

Table 4 Components of the dipole (in debye, D) in the reference frame of the C^α–CH_2 bond of the repeat unit as a function of the rotational angle about C^α–C* (χ) and O–C^{ar} (Ψ_1) bonds

χ (deg)	Ψ_1 (deg)	μ_x	μ_y	μ_z
0	60	0.714	−2.363	−0.020
180	60	0.272	1.111	2.187
0	−60	2.039	−1.390	−0.061
180	−60	−1.053	0.139	2.228
0	120	0.273	−1.738	0.542
180	120	0.713	0.468	1.625
0	−120	1.597	−0.765	0.501
180	−120	−0.611	−0.486	1.666

are[26,30]:

$$U' = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{pmatrix} \tag{13}$$

for the CH_2–C^{α}–CH_2 bonds and:

$$U''_{r} = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$U''_{m} = \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix} \tag{14}$$

for the C^{α}–CH_2–C^{α} bonds in the *racemic* and *meso* diads. Twenty chains of 100 repeat units each were generated by Monte Carlo techniques in which the isotactic replacement was 0.39; for each of these chains, 50 chains were also generated in which the probability of finding Ψ_1 in each one of the four permitted rotational states is 0.25 ± 0.02. Computation of g_{intra} was carried out by statistical mechanics methods described in detail elsewhere[31,32], using the set of statistical weights already utilized in the evaluation of the mean-square dipole moments of PPODG[26], specifically, $\rho = 1.1$, $\beta = 3.68$, $\gamma = 0.2$, $\gamma_1 = 1.4$ and $\gamma_2 = 1.90$. In the calculations the valence angles were taken as $\theta = 111.5°$ and the average values for the rotational angles about the skeletal bonds of the main chain were assumed to be: $\langle \Phi_1, \Phi_2 \rangle_{tt} = 16°, 16°$, $\langle \Phi_1, \Phi_2 \rangle_{tg} = 3°, 14°$ for the *meso* diad and $\langle \Phi_1, \Phi_2 \rangle_{tt} = 3°, 3°$ for the *racemic* diad.

The theoretical values of g_{intra} are extremely sensitive to the statistical weight γ_2 that governs the orientation of the dipoles associated with the ester groups in two consecutive side chains of a *racemic* diad. Thus g_{intra} decreases from 1.58 ± 0.1 to 0.54 ± 0.02 when γ_2 increases from 0.19 to 4.45. Good agreement between theoretical and experimental results is found for $\gamma_2 = 1.90$. The polarity of the chains is somewhat less sensitive to the γ_1 parameter because the value of g_{intra} only drops from 0.94 to 0.69 when this parameter decreases from 2.71 to 0.37. The correlation coefficient is much less sensitive to β, the statistical weight parameter that accounts for the probability of finding *tg* conformations in *meso* diads. For example, the value of g_{intra} changes from 0.85 to 0.81 when β increases from 1.39 to 3.68, suggesting that the increase of *tg* conformations in *meso* diads slightly decreases the polarity of the chains. It is expected that the molecular dimensions will be much more sensitive to this conformation.

The temperature coefficient calculated with the main set of statistical weights amounts to $(1.7 \pm 0.13) \times 10^{-3}$, in fair agreement with the experimental result. Better agreement between the theoretical and experimental results can be achieved by slightly refining the values of the γ_2 and γ_1 statistical parameters. Finally, it should be pointed out that the set of statistical weights indicated before also reproduces the experimental intramolecular dipolar correlation coefficient for the dimer[26].

DISCUSSION

The relaxation behaviour is typical of that exhibited by conventional amorphous polymers and therefore two-dimensional order is not developed in PPOA. Recent advances in the description of the α processes in thermo-rheologically simple systems lead to two coupled predictions[33,34]: the KWW relaxation function $\Phi(t) = \exp[-(t/\tau^*)^{1-n}]$ and the relation $\tau^* = [(1-n)\omega_c^n \tau_0]^{1/(1-n)}$ between the effective relaxation time in the KWW expression and the primitive relaxation time τ_0, where ω_c is the reciprocal of the characteristic time after which interactions between the primary relaxing species occur and τ_0 has the Vogel form, that is, $\tau_0 \approx \exp[B_0/(T - T_{\infty})]$. If B_0 is invariant then[34]:

$$(1 - n_{\mathrm{dr}})B_{\mathrm{dr}} = (1 - n_{\mathrm{mr}})B_{\mathrm{mr}} = B_0 \tag{15}$$

where B_{dr} and B_{mr} are represented by m in equation (7) (the indices dr and mr refer to the dielectric and mechanical relaxations, respectively) and n_{dr} and n_{mr} are constants relating the coupling between the relaxing species, respectively. The values of B_0 for PPOA obtained from the mechanical and dielectric results amount to 513 and 510 K, respectively, thus supporting the invariance of this parameter for a given system; however, this invariance does not seem to hold for the low-molecular-weight compound PPODG, for which B_0 has a value of 770 K. The parameter B_0 may be interpreted in terms of the free-volume theory of Cohen and Turnbull[35] that predicts for B_0 the following expression:

$$B_0 = \gamma^* v^* / v_{\mathrm{m}} \tag{16}$$

where γ^* is a constant whose value lies in the interval 0.5 to 1, v_{m} is the mean volume of the segment intervening in the relaxation and v^* is the critical free volume required for a relaxation process to take place. Therefore, the comparatively high value of B_0 for PPODG suggests that the ratio v^*/v_{m} may be higher for the low-molecular-weight compound than for the polymer.

For most polymer systems the KWW exponent is smaller for the mechanical glass–rubber relaxation than for the dielectric glass–rubber process, in opposition with what occurs in PPOA where $\bar{\gamma} \approx 0.30$ for both relaxations. This result suggests that complicated coupled motions of the side groups and the main chain intervene in the dielectric glass–rubber relaxation. The dielectric and mechanical γ relaxations of PPOA are also described by the KWW equation with exponents of $\bar{\gamma} = 0.16$ and 0.20 for the former and latter processes, respectively, corresponding to the fact that the subglass relaxations spread over a wide range of frequencies. Moreover the activation energy times the γ exponent seems also to be invariant in the present case. However, whereas the polymer exhibits a moderate γ relaxation, only a diffuse and wide distribution can be detected in PPODG.

A model was recently developed by Smith and Boyd[36] that permits evaluation of the dipolar correlation coefficient of polymer chains with flexible side groups in the glassy region. The model assumes that the flexible groups in the glassy state relax relative to a fixed main chain and are not able to relax individually over all space. This causes the relaxation strength to decrease with decreasing temperature as individual dipoles become confined in their lowest energy state. It should be pointed out that this model is formally equivalent to the model of partial relaxation of dipoles for the β process described by Williams[37], but now the conformations are specified. According to this model, the correlation coefficient g_γ for the γ process can be written as:

$$g_\gamma \approx (N/N_p\langle\mu_0^2\rangle)\left(\sum_k \mu_k^2 - \sum_k \langle\boldsymbol{\mu}_k\rangle^2\right) \qquad (17)$$

where it has been considered that the dipole–dipole correlation contributions $\langle\mu_j\cdot\mu_k\rangle - \langle\mu_j\rangle\cdot\langle\mu_k\rangle$ to g_γ are relatively small at low temperatures[14,36]. In this equation N and N_p are the number of molecular chains and relaxing dipoles, respectively. Whereas the C^α–C^* bond has access to two conformational states ($\chi = 0, \pi$), four states of the same energy located at $\Psi_1 = \pm 60°$, $\pm 120°$ are accessible to the dipole associated with the C^{ar}–O–C^{ar} group. Moreover, since these states are equivalent in energy, all of them have the same probability. Evaluation of g_γ by assuming that the C^α–C^* bonds in the γ region are in the state of lowest energy gives for this quantity the value of 0.05, in fair agreement with the experimental result that amounts to 0.02 at −90°C, this latter quantity being obtained from equation (7) using the relaxed and unrelaxed values of the dielectric permittivity corresponding to the γ relaxation, discussed in previous sections. Accordingly, the γ absorption is apparently produced through conformational changes about the O–C^{ar} bonds, whereas motions about the C^α–C^* bonds probably intervene in the β absorption that overlaps with the glass–rubber relaxation. It should be pointed out in this regard that the latter absorption is located in the temperature–frequency domain not far away from the glass–rubber relaxation corresponding to PPODG, and therefore one is tempted to attribute the β relaxation to generalized conformational changes about the bonds of the side groups.

The dielectric relaxation spectrum of PPODG only exhibits an extremely weak subglass absorption in spite of the conformational versatility of this compound. Similar behaviour was detected in other diesters such as the phenyl and chlorophenyl esters of 2,4-dimethylglutaric acid and cyclohexyl-2,4-dimethylglutarate[38]. This behaviour is even more surprising if it is considered that apparently rigid low-molecular-weight compounds such as bromobenzene present a fair subglass absorption. This apparently contradictory behaviour could be explained by considering that a number of low-density regions, statistically distributed, may exist in the glass in which the dipoles are located in many possible orientations. Dielectric activity would arise from non-cooperative but highly hindered motions of some of these molecules in these local zones, which are encaged by large regions where requirements of cooperative motions make relatively inmobile the arrangement of the majority of dipoles[39]. According to this model, transitions of opposite polarity could occur in small islands that would produce negligible dielectric activity.

A four-rotational-states scheme in conjunction with Monte Carlo techniques that simulate both the stereochemical composition and the rotational states of the dipole moment associated with the C^{ar}–O–C^{ar} bonds reproduce in a satisfactory way the intramolecular correlation coefficient of the chains determined from dielectric measurements in solution. This scheme also gives a good account of the mean-square dipole moment of the diester. However, the correlation factor g for the polymer that involves both inter- and intramolecular correlation contributions departs by nearly 34% from the value found for this quantity from dielectric measurements carried out in solution. These results suggest that intermolecular interactions play an important role in the development of the dielectric relaxation behaviour of the polymer. These interactions seem to be somewhat lower in PPODG, for which g is only 17% lower than the value of the intramolecular interaction coefficient.

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