Macromol. Symp. **2006**, 237, 39–52 DOI: 10.1002/masy.200650505

Chain Dynamics of Polymers with Highly Flexible Side Groups

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Summary: The relaxation behaviour of poly(5-acryloxy-5-methyl-2,3-dioxacyclohexne), poly(2,3-dichlorobenzyl methacrylate) and poly(3-chlorobenzyl methacrylate) was thoroughly studied by broadband dielectric spectroscopy with the aim of investigating how the chemical structure affects the response of polymers to electric perturbation fields over a wide temperature window. Retardation spectra calculated from dielectric isotherms utilizing linear programming regularization parameter techniques were used to deconvolute strongly overlapped absorptions. Special attention is paid to both the splitting region and the fitting of the Williams ansatz to the experimental results. Attempts are made to explain the molecular origin of the relaxations observed in the retardation spectra of the polymers.

Keywords: chain dynamics; dielectric spectroscopy; frequency domain; retardation spectrum; Williams ansatz

Introduction

In the moderate supercooled regime, the spectrum of the loss response of supercooled liquids to perturbation fields displays a single absorption in the frequency domain. In cooling the system, a temperature is reached at which the single absorption splits into a slow process or α relaxation associated with cooperative molecular motions, and a fast absorption or β process arising from local motions in a variety of environments.[1–3] The distance between the α and β relaxations expressed in terms of log ($f_{\beta;max}/f_{\alpha;max}$), where f_{max} is the frequency at the peak maximum, increases with decreasing temperature owing to the high activation energy of the α relaxation in comparison with that of the β absorption. The mean relaxation time associated with the α absorption undergoes an anomalous increase in the vicinity of the glass transition temperature described by the Vogel-Fulcher-Tammann-Hesse (VFTH) equation[4] whilst the β relaxation obeys Arrhenius behaviour. Near T_g ergodicity is lost, the mechanisms responsible for the α relaxation become frozen, but the β relaxation remains operative in the glassy state.[5] Since the VFTH equation also describes the temperature dependence of the viscosity, the α relaxation may be considered a precursor of the flow and the glassy state.

The study of the dynamic behaviour of the glassy state and its precursor, the supercooled liquid, is paramount to get a better understanding of the glass transition, one of the most important unresolved issues in Condensed Matter physics.[6–18] Thorough studies on the splitting behaviour of poly(n-alkyl methacrylates) have been carried out in the last decade by Donth and coworkers,[19] Colmenero and coworkers,[20] etc. To take this matter further we undertook the study of the relaxation behaviour of polymers with polar highly flexible side groups. In this work we report recent studies[21] on the relaxation behaviour of polymers with polar highly side groups such as poly(5-acryloxy-5-methyl-1,3-dioxacyclohexane) (PAMD), poly(2,3-dichlorobenzyl

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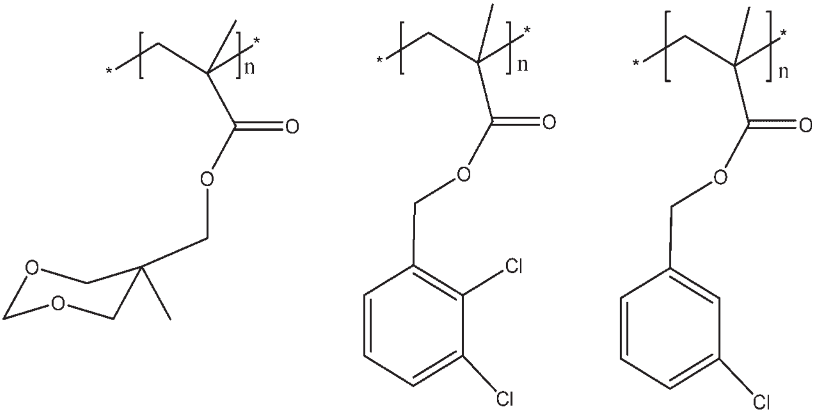
methacrylate) (P23CBM) and poly(3-chlorobenzyl methacrylate) (P3CBM) carried out at several temperatures over a wide frequency window. The structural units of the polymers are given in Scheme I and their respective glass transition temperatures are 313, 313 and 296 K , respectively.

Experimental Results

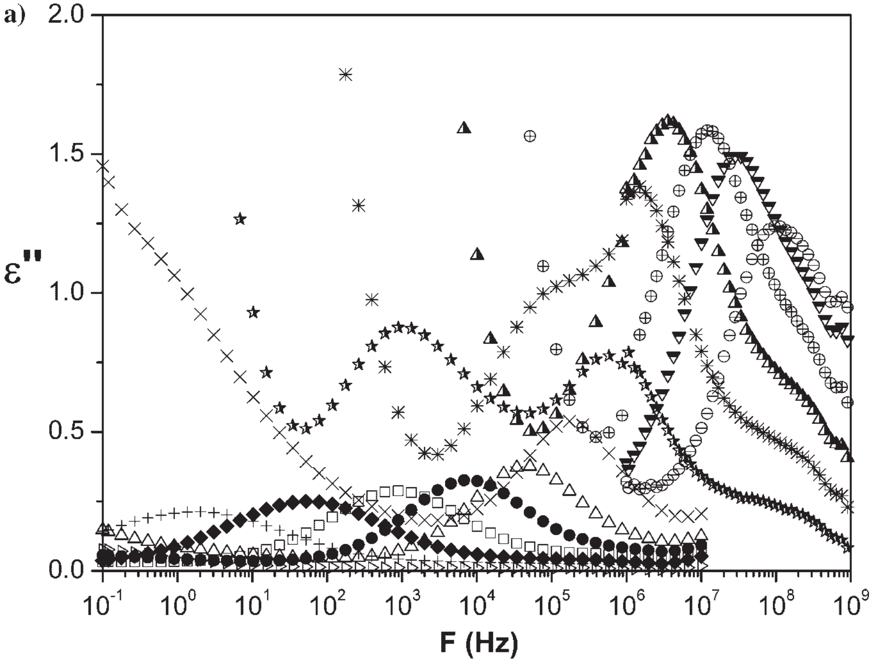
Dielectric loss isotherms in the frequency domain for PAMMD, are shown in Figure 1a. Above T_g, the isotherms corresponding to PAMMD exhibit an α relaxation followed in increasing order of frequency by the β absorption the intensity of which increases with temperature. The degree of overlapping between the α and β relaxations increases with increasing temperature forming a single absorption or αβ relaxation at 403 K. An additional absorption named γ relaxation appears as a shoulder in the high frequency side of the β absorption. The dielectric loss isotherms for P23CBM (Figure 1b) and P3CBM (Figure 1c) differ from those of PAMMD in that they apparently present only two absorptions, α and β. Notice that the α and β relaxations for P23CBM appear strongly overlapped. At high temperatures these two relaxations form a single αβ absorption for P23CBM whereas the two processes remain separated for P3CBM, even at high temperatures,. Notice that above T_g, in the low frequency region, the dipolar contribution to the α process is in all the cases negligible in comparison with that of the ionic conductivity.

Retardation Spectra

At high temperatures the dielectric loss isotherms are characterised for the strong overlapping between the α and β relaxations whereas at temperatures slightly higher than T_g the contribution of the dipolar relaxation to the dielectric loss at low frequency may be negligible in comparison with that of the ionic conductivity. Deconvolutions of the α and β absorptions can be carried out fitting Havriliak Negami type equations[22] to the loss isotherms. However, since a Debye type relaxation in the time domain is a delta Dirac function whilst it covers more than two decades in the frequency domain, deconvolution of the overlapping peaks is better performed on the retardation spectra obtained from the loss isotherms. The dielectric loss can be written in terms of the retardation spectrum



Scheme I.
From left to right repeating units of poly(5-acryloxy-5-methyl-2,3-dioxacyclohexane), poly(2,3-dichlorobenzyl methacrylate) and poly(3-chlorobenzyl methacrylate).



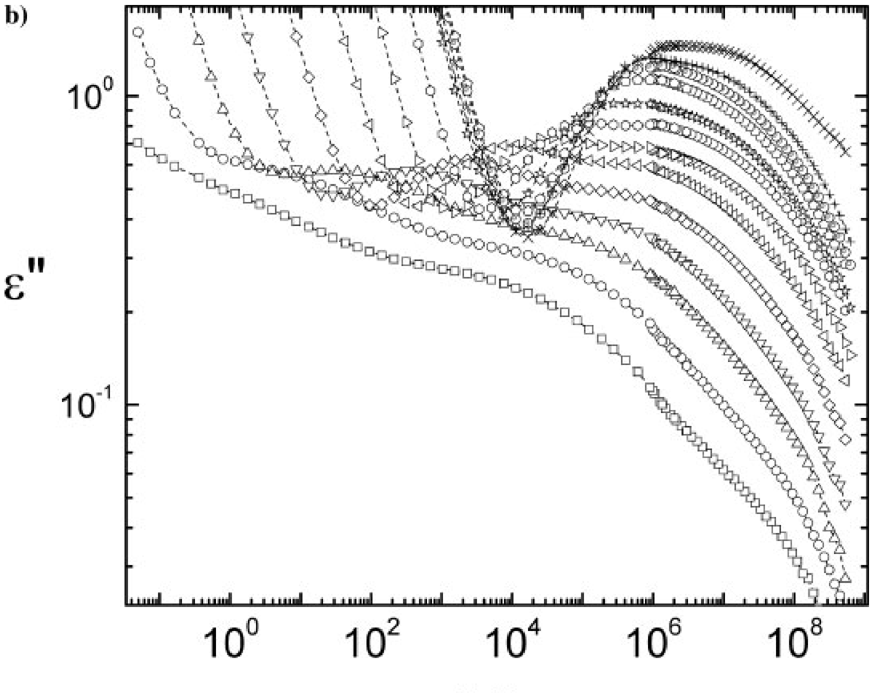


Figure 1.

Isotherms showing the dielectric loss in the frequency domain for: (a) poly(5-acryloxy-5-methyl-2,3-dioxacyclohexane), from 198 K, at 25 K steps (b) poly(2,3-dichlorobenzyl methacrylate), from 303 K, at 10 K steps and (c) poly(3-chlorobenzyl methacrylate).from 293 K at 10 K steps.

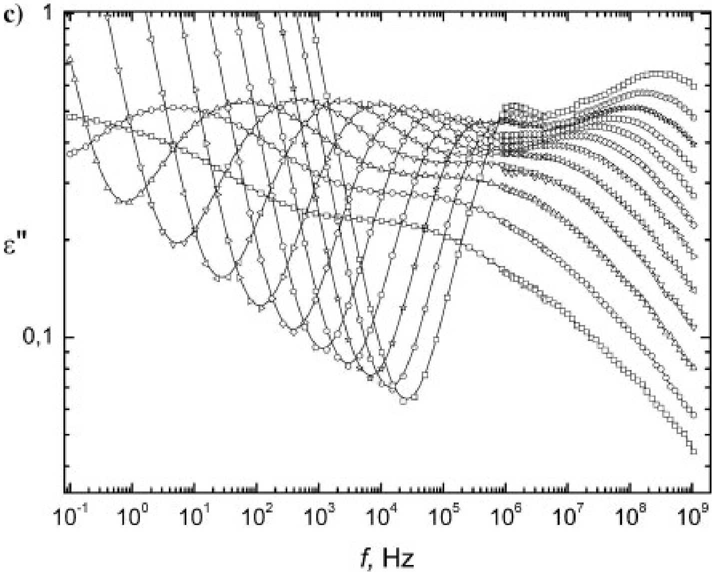


Figure 1. Continued.

L by means of the following expression[23]

$$\varepsilon''(\omega) = \left(\frac{\sigma}{\varepsilon_0\omega}\right)^S + \int_{-\infty}^{\infty} L(\ln\tau)\,\frac{\omega\tau}{1+\omega^2\tau^2}\,d\ln\tau = \left(\frac{\sigma}{\varepsilon_0\omega}\right)^S + \int_{-\infty}^{\infty} L(\ln\tau)\,K(\omega\tau)\,\ln\tau \tag{1}$$

where σ is the conductivity, ε_0 is the dielectric permittivity in vacuum and ω is the angular frequency. The inversion of eq. (1) can be performed by obtaining different L's for various physically admissible values of s and selecting the one that optimizes it. In short, assuming ρ_i the uncertainties in the experimental measurements of $\varepsilon''(\omega_i)$ at ω_i ($i = 1, 2, \ldots, n$), Eq. (1) can approximately be written as

$$\frac{\varepsilon''(\omega_i)}{\rho_i} \cong \left(\left(\frac{\sigma}{\varepsilon_0\omega_i}\right)^s + \sum_{k=1}^{m} R_{ik}\,L(\ln\tau_k)\right)\Big/\rho_i \tag{2}$$

where

$$R_{ik} = \frac{\omega_i\tau_\mathrm{k}}{1+\omega_i\tau_k^2}\,\ln\left(\frac{\tau_{k+1}}{\tau_{k-1}}\right)^{1/2} \tag{3}$$

or in matricial form as

$$\varepsilon = \mathbf{RL} \tag{4}$$

The solution of the ill-conditioned eq. (4) is similar to that of the also ill-posed quadratic programming problem *min*-$|\varepsilon'' - \mathbf{RL}|^2$, equivalent to[24]

$$\min|\varepsilon'' - \mathbf{RL}|^2 + \lambda(\mathbf{L}^\mathrm{T}\mathbf{HL}) \tag{5}$$

where λ (>0) is known as the regularization parameter and **H** is a definite positive quadratic form. The election of the matrix **H** must be based on the a priori knowledge of the solution. If the solution is thought to be piecewise linear, a good choice is $\mathbf{H} = \mathbf{B}^\mathrm{T}\mathbf{B}$ where **B** is the $(\mathrm{m}-2)\times\mathrm{m}$ matrix given by[24]

$$\mathbf{B} = \begin{bmatrix} -1 & 2 & -1 & 0 & 0\ldots & 0 \\ 0 & -1 & 2 & -1 & 0\ldots & 0 \\ \ldots. & & & & & \\ 0 & \ldots.. & -1 & 2 & -1 & 0 \\ 0 & \ldots.. & 0 & -1 & 2 & -1 \end{bmatrix} \tag{6}$$

and B^T reads for the transpose matrix of B. The best values of the regularization parameter λ were determined by means of the Morozov's discrepancy method[25].

The retardation spectra of PAMMD below T_g, above T_g and in the splitting region are shown in Figures 2a, 2b and 2c, respectively. Below T_g, the spectra exhibit two peaks named, in increasing order of time, γ and β. At temperatures not far

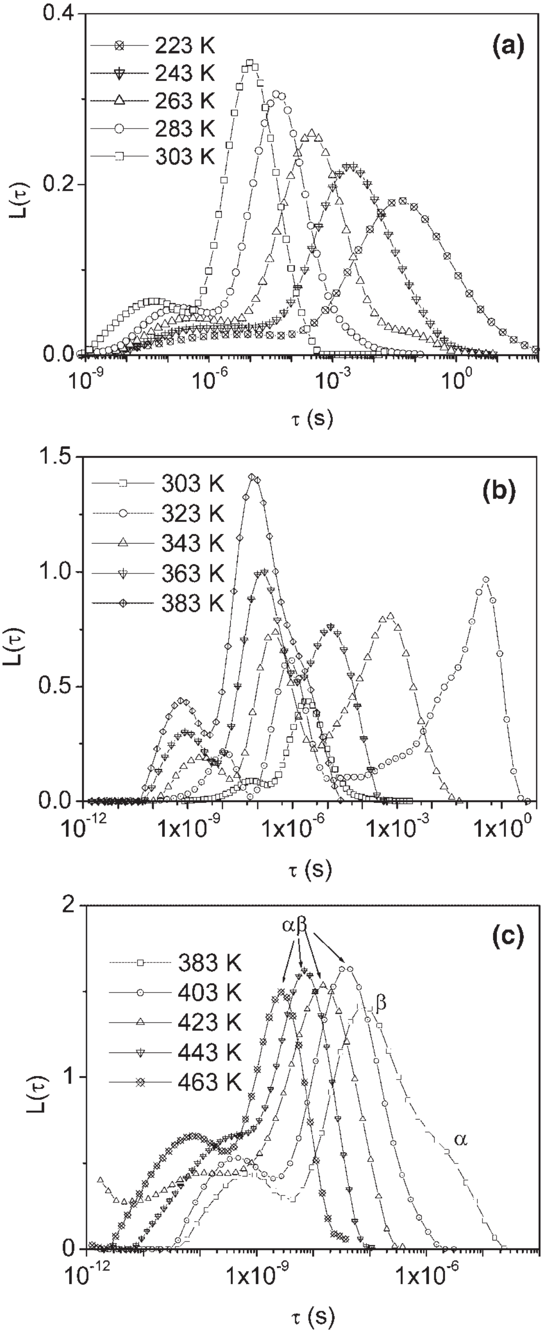


Figure 2.

Retardation spectra for poly(5-acryloxy-5-methyl-2,3-dioxacyclohexane) in (a) the glassy state, (b) at moderate temperatures in the rubbery state and (c) in the splitting region.

above T_g the spectra display three peaks corresponding to the γ, β and α absorptions whose overlapping increases with temperature. The α and β relaxations apparently form at 403 K a single absorption, named αβ relaxation. Notice that the γ and β relaxations are symmetric whilst the α peak is asymmetric dropping, as expected, more slowly on the left side than on the right side of the peak.

The α and β absorptions for P23CBM are strongly overlapped, even at temperatures slightly higher than the glass transition temperature, as the spectra of Figure 3a show. As temperature increases, the two relaxations form an apparent single peak or $\alpha\beta$ relaxation which, at difference of the $\alpha\beta$ absorption of PAMMD, can be deconvoluted into two peaks (α and β). The retardation spectra of P3CBM, shown in Figure 3b, presents two at first sight well separated peaks, even at temperatures well above T_g. However, a single Havriliak-Negami equation cannot fit the higher relaxation times peak; only a combination of H-N and Fuoss-Kirkwood[26] equations can do it. This means that the high retardation times absorption is the result

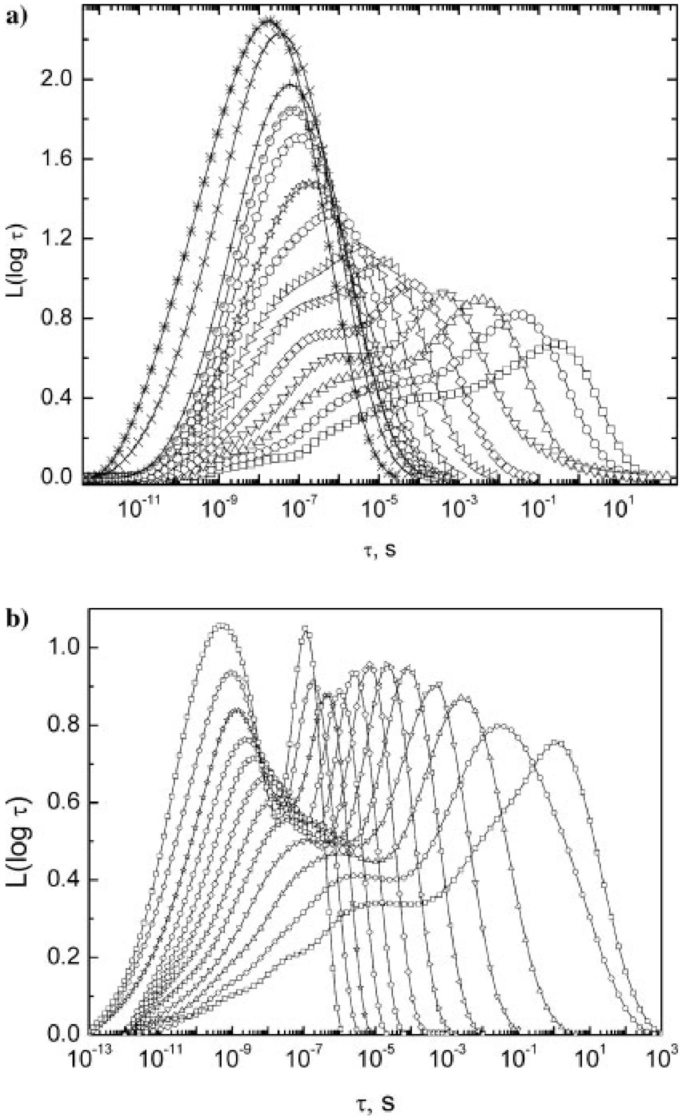


Figure 3.
Retardation spectra for: (a) poly(2,3-dichlorobenzyl methacrylate) from 303 K at 10 K steps and (b) poly(3-chlorobenzyl methacrylate) from 293 K at 10 K steps.

of a strong overlapping between the α and β relaxations. Therefore the well defined lowest relaxation time absorption that firstly was believed to be a β relaxation is really a γ process.

The strength of the relaxations can be calculated from

$$\varepsilon_{r,k} - \varepsilon_{u,k} = \int_{-\infty}^{\infty} L_k(\ln \tau)\, d \ln \tau \qquad (7)$$

where the subscripts r and u refer, respectively, to the relaxed and unrelaxed dielectric permittivities corresponding to the *k* relaxation (α,β,γ). The evolution of the strength of the relaxations of PAMMD with temperature is shown in Figure 4a. The strength of the β relaxation that remains nearly constant in the glassy state, increases with temperature above T_g. Notice that above the onset temperature of the α

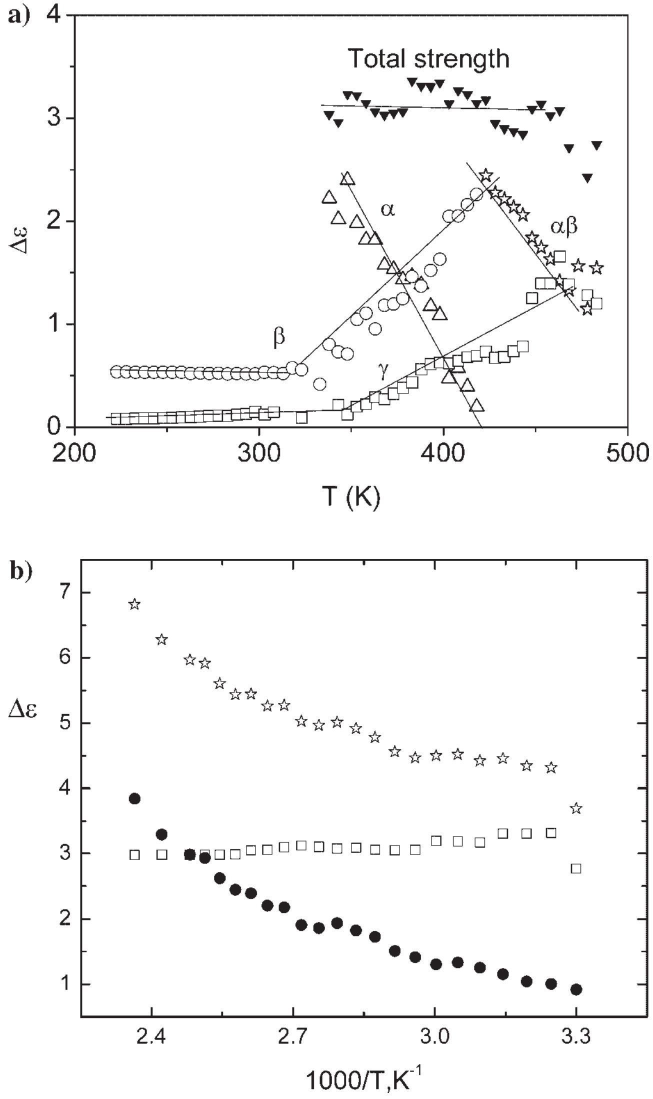


Figure 4.
Temperature dependence of the relaxations of (a) poly(5-acryloxy-5-methyl-2,3-dioxacyclohexane) and (b) poly(2,3-dichlorobenzyl methacrylate).

relaxation, the β process decreases with increasing temperature. The strength of the α relaxation decreases with increasing temperature eventually vanishing at 403 K. It seems that the α relaxation feeds the β and in turn the αβ process feeds the γ absorption. This behaviour differs from that exhibited by P23BCM and P3BCM. Unlike PAMMD, an onset temperature is absent in the α relaxations of P23CBM and P3CBM as the results of Figure 4b for P23BCM show. It can be seen that the strength of the α relaxation of P23CBM only slightly decreases with increasing temperature, though the β absorption undergoes a relatively strong increase.

Williams Ansatz

Williams$^{[1,2,27]}$ assumes that the β relaxation arises from restricted motions in a range of local environments, which permit a partial relaxation that leads to an initial drop in ϕ(t). When the α relaxation mechanisms are able to cause fluctuations of local environments that lead to the total randomization of the dipoles, ϕ(t) becomes zero. If the γ relaxation is well separated from the β absorption as occurs for P3BCM, neglecting cross correlation contributions Williams's assumption can be written as

$$\phi(t) = \phi_\alpha(t)[f_\alpha + f_\beta\phi_\beta(t)] + f_\gamma\phi_\gamma(t) \qquad (8)$$

where $\phi_\alpha(t)$ and $\phi_\beta(t)$ and $\phi_\gamma(t)$ are the normalized correlation functions for the α, β and γ relaxations. The parameter f_α is the fraction of polarization relaxing through the α process alone, f_β is the fraction of polarization relaxing through the β absorption via de α relaxation whilst $f_\gamma = 1 - f_\alpha - f_\beta$ represents the fraction of polarization relaxing via the γ process. Eq(16) is known as Williams-Watts (WW) ansatz. If the α, β and γ processes are well separated, the relaxation of the α process is not important until the total relaxation of the secondary absorptions is not complete; i.e. $\phi_\alpha(t) \approx 1$ when $\phi_\beta(t) \approx 0$ and $\phi_\gamma(t) \approx 0$. In this situation, eq. (8) becomes

$$\phi(t) = f_\alpha\phi_\alpha(t) + f_\beta\phi_\beta(t) + f_\gamma\phi_\gamma(t) \qquad (9)$$

This expression is known as the extended Williams ansatz. The normalized time-dipole autocorrelation function or decay function for the k process is given by

$$\phi_k(t) = \frac{\int_{-\infty}^{\infty} L_k(\ln\,\tau)e^{-t/\tau}d\,\ln\,\tau}{\int_{-\infty}^{\infty} L_k(\ln\,\tau)d\,\ln\,\tau} \qquad (10)$$

As an example, the decay function calculated from the retardation spectrum of P3CBM is shown in Figure 5. In the frequency domain, Eq. (8) can be written

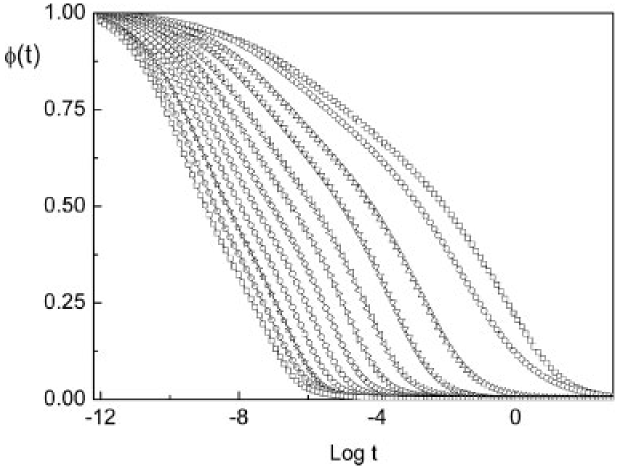


Figure 5.
Decay relaxation function for poly(2,3-dichlorobenzyl methacrylate).

as[1,2,27]

$$\begin{aligned}\phi*(\omega) &= \frac{\varepsilon*(\omega)-\varepsilon_u}{\varepsilon_r-\varepsilon_u} = L_{i\omega}\left(-\frac{d\phi(t)}{dt}\right)\\ &= f_\alpha\phi*_\alpha(\omega) + f_\beta\phi*_\alpha(\omega)\phi*_\beta(\omega)\\ &\quad + f_\gamma\phi*_\gamma(\omega)\end{aligned} \tag{11}$$

where $L_{i\omega}$ is the Laplace operator and $\phi_k*(\omega) = L_{i\omega}(-d\phi_k/dt)$, the subscript k meaning α or β. Illustrative plots showing the dielectric loss calculated from eq. (11) for P3CBM at 333 K together with the experimental results are presented in **Figure 6**. In general the dielectric loss obtained from the William ansatz fits rather well to the experimental results.

In the frequency domain, the extended ansatz is given by

$$\begin{aligned}\phi*(\omega) &= L_{i\omega}\left(-\frac{d\phi(t)}{dt}\right)\\ &= f_\alpha\phi*_\alpha(\omega) + f_\beta\phi*_\beta(\omega)\\ &\quad + f_\gamma\phi*_\gamma(\omega)\end{aligned} \tag{12}$$

For illustrative purposes, the temperature dependence of the values of f_α, f_β an f_γ obtained for P3CBM using eqs.(11) and (12) are shown in **Figure 7**. As usual, f_α decreases with increasing temperature whereas f_γ clearly increases. However, f_β does not follow a definite trend. The values of f_α an f_γ obtained by the two methods agree very satisfactorily, but the agreement is not so satisfactory in the case of the β process presumably as a consequence of the errors involved in the determination of the comparatively small contribution of this process to the total relaxation. Similar behaviour is displayed by the other polymers below the splitting temperature.

Influence of Temperature on the Retardation Times of the Relaxation Processes

Arrhenius plots for the relaxation processes of PAMMD, P23CBM and P3CBM, represented in **Figure 8**, show a strong dependence on the chemical structure of the polymers investigated. Thus the activation energies associated with β and γ relaxations of the first polymer seem to remain constant in the whole temperature window. The values of these quantities are 11.3 kcal/mol and 8.5 kcal/mol for the β and γ processes, relatively. The β relaxation of P23CBM presents a crossover temperature, T_{CO},

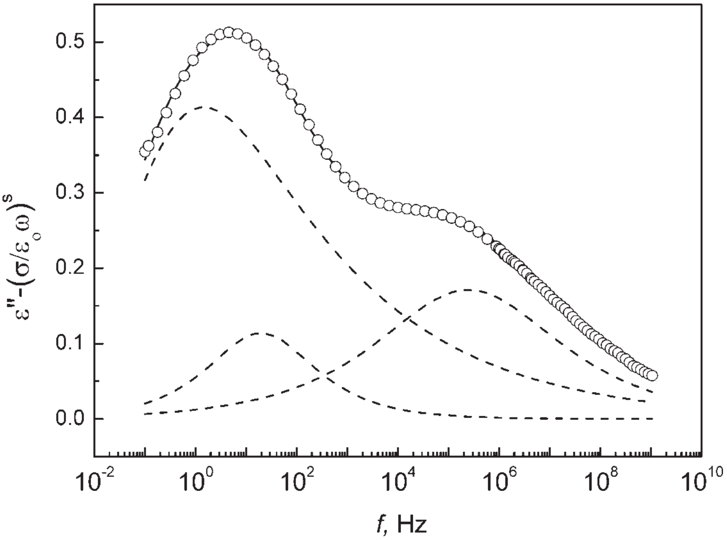


Figure 6.

Illustrative plot showing the fitting (continuous line) of the Williams ansatz to the experimental dielectric loss results of P3CBM (circles) at 333 K. Discontinuous lines correspond to the contributions in order of increasing frequency of the α, β and γ absorptions.

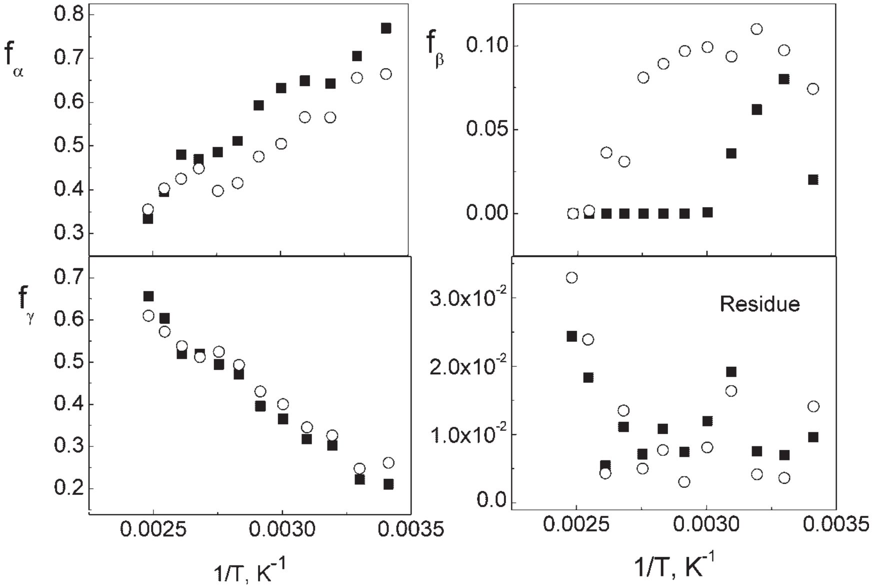


Figure 7.
Temperature dependence of the parameters f_α,f_β and f_γ for poly (3-chlorobenzylmethacrylate) and the residue of the fit. Open and filled symbols correspond, respectively, to the Williams and extended ansatz.

below which the activation energy is higher than above T_{CO}, the activation energies being 29.1 kcal/mol and 13.6 kcal/mol, respectively. It is worth noting that above T_{CO} the α and β relaxations of P23CBM have the same temperature dependence. Finally the activation enrgies associated with the β and γ relaxations of P3BCM amount to 26.7 and 6.4 kcal/mol, respectively.

As usual, the mean relaxation time associated with the α absorption is described by the Vogel-Fulcher-Tammann-Hesse (VFTH) equation[4]

$$\tau = \tau_0 \exp\left[\frac{m}{T - T_V}\right] \tag{13}$$

where τ_0 is a prefactor of the order of picoseconds and T_V is the Vogel temperature which lies in the vicinity of the

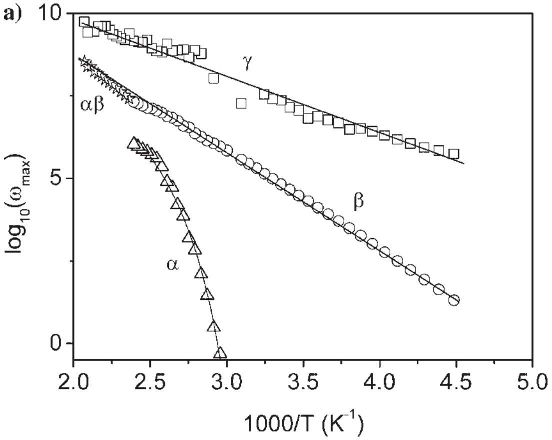
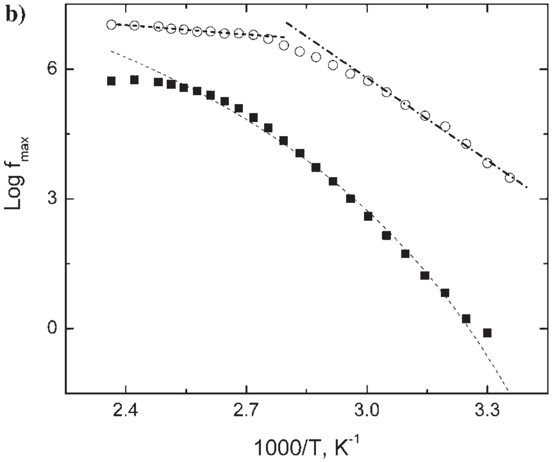


Figure 8.
Arrhenius plots for PAMMD (Fig. 8a), P23CBM (Fig. 8b) and P3CBM (Fig. 8c).



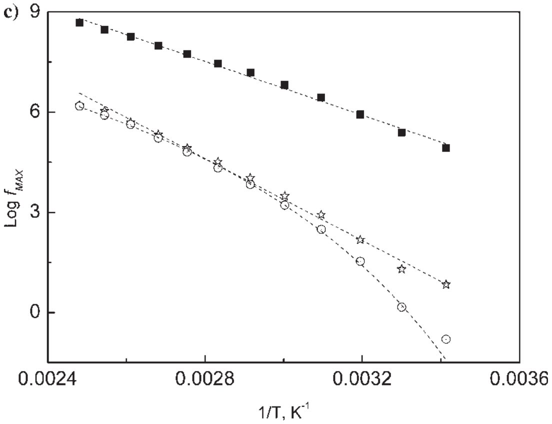


Figure 8. **Continued.**

Kauzmann temperature, that is, the temperature at which the crystal and the glass of the supercooled liquid have the same entropy.[3] By comparing eq. (13) with the Doolittle equation[28] $f_{\max} = f_0 \exp(-B/\Phi)$, where Φ is the relative free volume and B is a parameter close to 1, the relative free volume at T_g is given by

$$\frac{\Phi_g}{B} = \frac{T_g - T_V}{m} \tag{21}$$

The values of Φ_g/B for PAMMD, P23BCM and P3BCM, calculated by this procedure are 0.027, 0.046 and 0.048, respectively. It is worth noting that the values of Φ_g/B for P23BCM and P3BCM are well above the average result of 0.025 ± 0.005 obtained for most polymers.[29] Since B is related to ν^*/ν_m,[30] where ν^* and ν_m are, respectively, the critical volume necessary for a relaxation to take place and the volume of the segments intervening in the relaxation, the high volume of Φ_g/B suggests that $\nu^* < \nu_m$ if the isofree volume theory holds.

Discussion

By similarity with what occurs for poly(n-alkyl methacrylate)s[19,20] a great part of the β relaxation in benzyl methacrylates can be

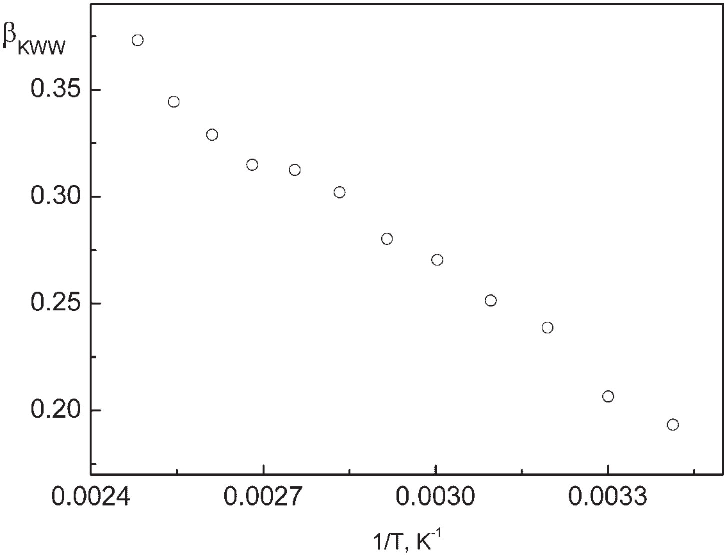


Figure 9.
KWW stretch exponent for P3CBM as a function of the temperature.

postulated to arise from motions about the $C(CH_3)$–C(O) bonds connecting the alcohol residue to the main chain. In support of this assumption we should point out that the activation energy associated with the β absorptions of P3CBM and P23BCM is of the same order of magnitude as that reported for poly(n-alkyl meathacrylate)s where dielectric activity mainly arise from motions about the $C(CH_3)$–C(O) bonds. The strong overlapping between the β and α processes in these polymers presumably is due to the similarity of the molecular motions for both processes. The β relaxations may arise from generalized molecular motions of the bonds of the side chains whereas motions of the side groups coupled with generalized motions of the main chain may cause the α relaxation. The γ relaxation in P3CBM probably arises from motions about CH_2–C^{ar} bonds that change the orientations of the dipole associated with C^{ar}–Cl bonds. The comparison of the activation energy of the γ absorption of P3BCM and that of the (β of P23BCM above T_{CO} suggests a common molecular origin for both processes.

The great increase taking place in the β relaxation of PAMMD with increasing temperature suggests that generalized motions about the skeletal bonds of the side groups (excluding theCH(O)–CO bond which is restricted to trans state) are responsible for the β process. The low barrier energy about CH(O)–CO bonds in polyacrylates, in comparison with that about CCH_3(O)–CO bond in poly(n-alkyl methacrylates), explains the comparatively low activation energy, 11.3 kcal mol^{-1}, of the β process of PAMMD. Chair-to-inverse chair conformation transitions may give rise to the γ absorption. Actually, the barrier energy involved in the conformational transition of the dioxacyclohexane ring has been calculated using Molecular Dynamics simulation methods. The value of this barrier amounts to 9.0 kcal mol^{-1}, close to the experimental activation energy of the γ process, 8.5 kcal/mol.[31] Moreover, the symmetry of the αβ relaxation in conjunction with the fact that the Arrhenius behaviour is common for the αβ and β relaxations suggests that both processes have the same nature.

The α relaxation is inevitably described by a KWW stretched exponential decay[1,2]

$$\phi(t) = \exp[-(t/\tau*)^{\overline{\beta}}] \qquad (14)$$

where the stretch exponent lies in the range $0 < \overline{\beta} \leq 1$. The temperature dependence of the stretch exponent increases from nearly 0.22 in the vicinity of T_g up to ca. 0.4 in the splitting region as the results for P3BCM show. The small values of the exponent at low temperatures indicates a rather wide distribution of relaxation times for the α relaxation, which presumably arises from a pronounced dynamic heterogeneity, a feature displayed by other systems. One would expect that due to the fast thermal fluctuations, each relaxing entity would see the same environment at high temperatures leading to a Debye relaxation.[16] However, this and other dielectric results do not show a stretch exponent independent of temperature in the splitting region.

A new scenario appears in the splitting region of P3CBM, which has been earlier postulated but not found in polymers.[9] It refers to the fact that the temperature dependence of the α and β processes not only have the same activation energy in the splitting region but also the prefactor of the exponential term in the Arrhenius equation is rather similar for both processes. This behaviour suggests a profound interdependence between the α and β processes in P3BCM.

The absence of an onset temperature for the α relaxations of P23BCM and P3BCM can be explained by assuming the configurational space above T_g as formed by craters and basins, the latter located not only in the space between craters but also inside the craters. The α and β relaxations would take place across the depth craters and the basins, respectively.[3] As temperature decreases, the craters become rare until a temperature is reached at which the α relaxation cannot occur, remaining below T_g only the basins through which the β process relaxes. At high temperatures the difference between the depths of the craters and the basins decrease eventually disappearing for PAMMD. However, this difference though small still persists for P23BCM and P3BCM thus avoiding the disappearance of the α relaxation in the range of temperatures investigated for these polymers.

Conclusions

The analysis of the dielectric broad-band experiments performed in terms of the retardation spectra allows a rather *unbiased* deconvolution of the overlapped α and β relaxations. This and other studies show that the splitting region is a rather complex governed by the fine chemical structure of the condensed matter. Theoretical approaches explaining the splitting scenarios as a function of chemical structure are needed.

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