

Broad-Band Dielectric Spectroscopy of Polymer Chains Containing Structurally Complex Side Groups

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ABSTRACT: The temperature dependence of the α and β relaxations of poly(2-phenyl-5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) is studied by broad-band dielectric spectroscopy. The strength of the α relaxation decreases with increasing temperature, pointing to an onset temperature ($\Delta\epsilon_\alpha = 0$) of ca. 97 °C. Seen from the high-temperature side, the α relaxation starts with zero intensity at the onset temperature and steeply increases with decreasing temperature until it levels off in the vicinity of T_g . Whereas in the glassy state the strength of the β relaxation is only slightly dependent on temperature, it undergoes a strong increase at temperatures above T_g . Arrhenius plots of both relaxations show that the β process remains operative at temperatures above the onset temperature of the α relaxation. The temperature dependence of the stretch exponent does not show a definite trend, most of the values obtained lying in the interval 0.3–0.5.

Introduction

In the liquid range, and even into the moderately supercooled regime, the relaxation response of glass formers to an external perturbation field is a single absorption in the frequency domain that upon approaching the glass transition splits into a pair of maxima, the slow α and the faster β relaxations.^{1–3} By expressing the functions that describe these relaxations in the time domain, the mean relaxation times associated with these processes are given by

$$\langle\tau_i\rangle = \int_0^\infty g_i(t) dt \quad (1)$$

where g_i ($i = \alpha, \beta$) is the relaxation response in the time domain in which the initial-time normalization $g_i(0) = 1$ is imposed. The temperature dependence of $\langle\tau_\alpha\rangle$ shows an anomalous increase in the vicinity of the glass transition temperature described by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation^{4–6}

$$\tau = \tau_0 \exp\left(\frac{DT_V}{T - T_V}\right) \quad (2)$$

where τ_0 is a preexponential factor and T_V is the Vogel temperature which is found to be of similar magnitude as the Kauzmann temperature³ (the temperature at which the entropy of the supercooled liquid extrapolated to low temperatures seems to be similar to that of the crystal). The so-called strength factor^{7,8} D is related to the depth and density of the minima in the potential energy landscape of glass formers. Its value is lower/larger than 10 for fragile/strong supercooled liquids. Whereas the α relaxation becomes frozen at T_g , the β relaxation remains operative in the glassy state. The temperature dependence of the β process obeys Arrhenius behavior.

The α relaxation in the time domain inevitably seems to display a Kohlrausch–Williams–Watts (KWW) stretched exponential decay given by^{1–3}

$$g_\alpha(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{\beta_K}\right] \quad (3)$$

in which $0 < \beta_K \leq 1$ and τ^* is comparable to τ_α of eq 1 when T is near T_g . The stretch exponent characterizes the relaxation strength of the α process in such a way that the wider is the relaxation, the lower β_K is. Thus, for a Debye type process, $\beta_K = 1$. From eqs 1 and 3 it follows that the average relaxation time associated with the α relaxation is given by

$$\langle\tau\rangle = \int_0^\infty g(t) dt = \left(\frac{\tau^*}{\beta_K}\right) \Gamma\left(\frac{1}{\beta_K}\right) \quad (4)$$

The Fourier transform of eq 3 allows the determination of the normalized loss in the frequency domain by means of the following expression

$$\frac{\epsilon''(\omega)}{\epsilon''_{\max}} = -\mathcal{F}\{i\omega F[g_\alpha(t)]\} \quad (5)$$

where ω is the angular frequency of the electric alternating field, the symbol F means the Fourier transform and ϵ''_{\max} is the value of the dielectric loss at the peak maximum of the absorption.

Usually, the β peak is more symmetric than the α peak. The normalized dielectric loss for this process is often described by the empirical Fuoss–Kirkwood equation⁹

$$\frac{\epsilon''(\omega)}{\epsilon''_{\max}} = \operatorname{sech}\left(m \ln \frac{\omega}{\omega_{\max}}\right); \quad 0 < m \leq 1 \quad (6)$$

where ω_{\max} represents the frequency at the peak maximum. The parameter m , like β_K in the α relaxation, accounts for the breadth of the β process in such a way that the larger is m , the narrower is the absorption.

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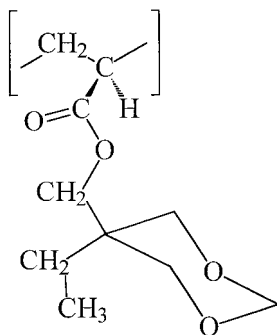


Figure 1. A rough sketch of the repeating unit of poly(5-(acryloxy)methyl-5-ethyl-1,3-dioxacyclohexane) (PAMED).

Polymers with cycloaliphatic and oxycycloaliphatic side groups in their structure display a prominent β absorption attributed to chair to inverse chair conformational transitions occurring in the rings.¹⁰ Although these motions may contribute to the β absorption, molecular dynamics simulations carried out on low molecular weight compound models of these polymers suggest that, aside from the conformational transitions taking place in the rings, other motions in the side groups may play an important role in the development of the β absorption.^{11,12} At any rate, the relative high strength of the fast process in these polymers makes them suitable to study the evolution with temperature of the strength of the α and β relaxations until they merge into the $\alpha\beta$ relaxation. For this purpose relaxation responses of poly(5-(acryloxy)methyl-5-ethyl-1,3-dioxacyclohexane) (PAMED) were studied using broadband frequency dielectric spectroscopy. The repeating unit of this polymer is shown in Figure 1. Earlier studies¹³ have shown that the mechanical and dielectric isochrones of PAMED exhibit a prominent β absorption centered in the neighborhood of -80°C at 1 Hz, followed by the glass-rubber relaxation located nearly 100°C above this temperature at the same frequency. In the frequency domain, the dielectric isotherms show two peaks, the low- and high-frequency peaks corresponding respectively to the α and β relaxations. Extrapolation methods suggest that the formation of a single peak would take place in the vicinity of 110°C . However, the lack of experimental data at high frequencies precluded the possibility of obtaining reliable information on the effect of temperature on the overlapping of the α and β relaxations. This paper focuses on this subject as well as the temperature dependence of the strengths of both relaxations. Finally, attention is paid to the variation of the stretch exponent of the α relaxation, β_K , with temperature.

Experimental Part

5-(Hydroxymethyl)-5-ethyl-1,3-dioxacyclohexane (HME) was obtained by reaction of 2-ethyl-2-(hydroxymethyl)propanediol with paraformaldehyde (1,1), using *p*-toluenesulfonic acid as catalyst. By adding dropwise acryloyl chloride to a solution of HME in chloroform, 5-((acryloxy)methyl)-5-ethyl-1,3-dioxacyclohexane (AMED) was obtained. This reaction was carried out in the presence of triethylamine to neutralize the hydrogen chloride evolved during the reaction. Poly(5-(acryloxy)methyl-5-ethyl-1,3-dioxacyclohexane) (PAMED) was synthesized by radical polymerization of 5-((acryloxy)methyl)-5-ethyl-1,3-dioxacyclohexane in toluene solution. The polymerization was carried out at 50°C , under nitrogen atmosphere, using azobis(isobutyronitrile) as catalyst. After attaining approximately 10% of conversion, the polymer was precipitated with metha-

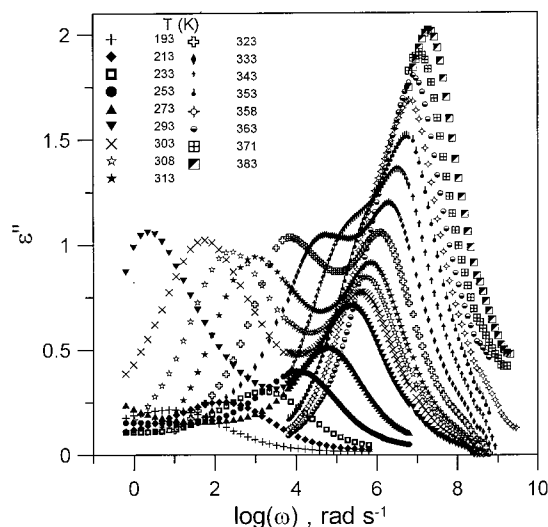


Figure 2. Loss component $\epsilon''(\omega)$ of the complex dielectric permittivity $\epsilon^*(\omega)$ of PAMED measured at several temperatures as a function of the angular frequency.

nol, dissolved in benzene, precipitated again with methanol, and dried at 60°C in a vacuum.

The complex dielectric permittivity, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and loss components of the permittivity, respectively, was measured with a SR 830 lock-in amplifier, the HP 4192, and the HP 4291 coaxial line reflectometer. The results were obtained at several temperatures in the frequency range 10^{-1} – 10^{10} Hz. The relative accuracy of the measurements is controlled by the sample thickness and has been estimated to be about $\pm 5\%$.

Experimental Results

Illustrative isotherms representing the dielectric loss in the frequency domain are shown in Figure 2. Below the glass transition temperature, about 20°C for the sample used in this study, the isotherms present a wide β relaxation whose maximum, as usual, shifts to higher frequency with increasing temperature. Also, the intensity of the β process increases with increasing temperature. In the supercooled liquid state and in the vicinity of T_g , isotherms display in the lower frequency range the slow α relaxation followed by the weaker β process in the high-frequency range. As the temperature augments, the distance separating the β from α peak decreases as a consequence of the high activation energy of the latter relaxation process. In the neighborhood of 371 K, both relaxations coalesce into a single peak, named $\alpha\beta$ relaxation, whose intensity seems to increase with increasing temperature.

To obtain information on the variation of the relative strengths of the α and β relaxation processes with temperature, it was proceeded to deconvolute the overlapping relaxations. Below T_g , i.e., for $T = 193, 213, 233, 253$, and 273 K, the experimental results were fitted to a β relaxation given by eq 6 disregarding the values of $\epsilon''(\omega)$ obtained in the low-frequency region that show an upturn. An illustrative example of these fittings is represented in Figure 3. Values obtained at intermediate temperatures, i.e., $293 \leq T \leq 363$ K, were fitted to a sum of a α plus a β relaxation according to the expression

$$\epsilon''(\omega) = \epsilon''_{\alpha}(\omega) + \epsilon''_{\beta}(\omega) = \epsilon''_{\max,\alpha} \mathcal{F}\{i\omega F[g_{\alpha}(t)]\} + \epsilon''_{\max,\beta} \text{sech}\left[m \ln\left(\frac{\omega_{\max}}{\omega}\right)\right] \quad (7)$$

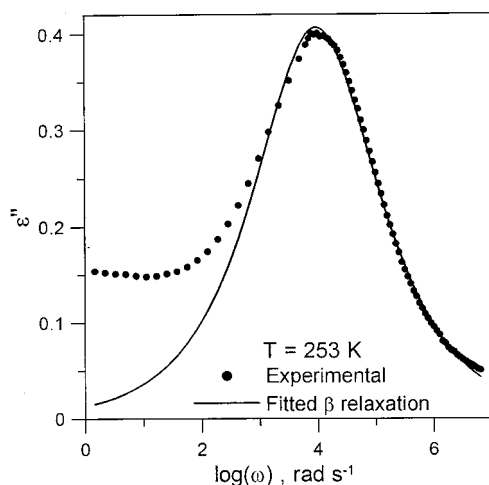


Figure 3. Fitting of the experimental values of $\epsilon''(\omega)$ measured at 253 K, i.e., below T_g , for PAMDED to a β relaxation according to eq 6 with the parameters of Table 1.

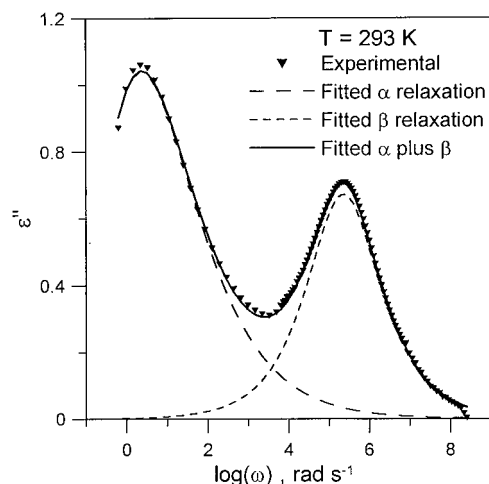


Figure 4. Deconvolution of the experimental values of $\epsilon''(\omega)$ measured at 293 K for PAMDED to fit the sum of an α plus a β relaxations according to eq 7 with the parameters given in Table 1. Individual contributions of α and β relaxations are indicated by broken lines while their sum is represented by a solid line.

where F represents the Fourier transform. Illustrative curves showing the goodness of the fittings are represented in Figures 4 and 5.

All the fittings were performed employing a numerical routine¹⁴ to minimize the sum of squared deviations between experimental and fitted values taking the height (ϵ''_{\max}) and position (ω_{\max}) of the maxima and the breadth (m and/or β_K) of the relaxations as independent parameters. All the values obtained in the fittings are summarized in Table 1. In particular, columns seven and four in Table 1 show respectively the results of m and β_K . It can be seen that m increases with temperature in the glassy region but remains practically constant in the supercooled and deep liquid state whereas most of the values of β_K lie in the range 0.3–0.5.

Arrhenius plots for the α and β relaxation processes are shown in Figure 6. The relaxation times associated with the α absorption are described by the VFTH equation assuming that $T_V = 243$ – 233 K and the strength factor D is equal to 4.76–6.14. On the other hand, the plot of the relaxation times associated with the β process is a straight line from whose slope the

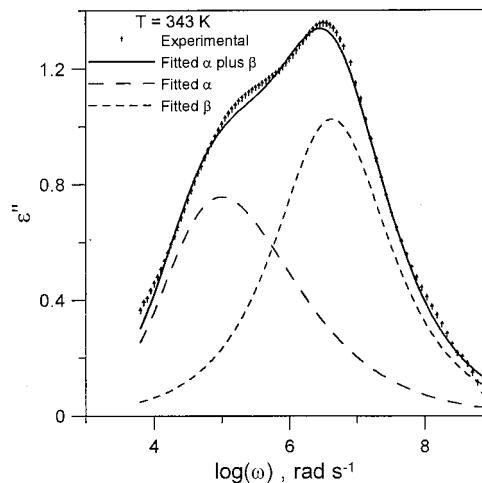


Figure 5. Same as Figure 4 for 343 K.

Table 1. Parameters Employed for the Fitting of Experimental $\epsilon''(\omega)$ Data to a β Relaxation According to Eq 6 or to the Sum of an α plus a β Relaxation According to Eq 7

T (K)	α relaxation			β relaxation		
	ϵ''_{\max}	ω_{\max} (rad/s)	β	ϵ''_{\max}	ω_{\max} (rad/s)	m
193				0.221	6.56	0.341
213				0.253	96.9	0.340
233				0.297	1.28×10^3	0.377
253				0.407	9.55×10^3	0.453
273				0.522	5.556×10^4	0.485
293	1.040	2.56	0.385	0.671	2.28×10^5	0.524
303	0.994	34.6	0.341	0.663	4.77×10^5	0.567
308	0.934	178	0.363	0.707	6.40×10^5	0.571
313	0.901	714	0.374	0.730	8.72×10^5	0.573
323	0.959	4.09×10^3	0.382	0.777	1.58×10^6	0.585
333	0.888	2.43×10^4	0.326	0.740	2.61×10^6	0.628
343	0.757	1.04×10^5	0.478	1.03	4.24×10^6	0.577
353	0.424	1.97×10^5	0.497	1.33	5.24×10^6	0.541
358	0.337	2.39×10^5	0.630	1.57	6.41×10^6	0.543
363	0.185	9.93×10^5	0.381	1.61	7.63×10^6	0.518
371				1.93	8.33×10^6	0.472
383				1.99	1.63×10^7	0.490

value of 11.5 kcal mol⁻¹ is obtained for the activation energy of this relaxation. This value is in good agreement with the value of 11.0 kcal mol⁻¹ obtained for this parameter from isochrones in the glassy state.¹³

The temperature dependence of the distance between the peaks of the α and β relaxations in the supercooled liquid state, expressed as $\Delta = \omega_{\max, \beta} / \omega_{\max, \alpha}$, is shown in Figure 7. As can be seen in this Figure, Δ is described by a Vogel type equation,

$$\ln \Delta = A' + \frac{m}{T - T_V} \quad (8)$$

This behavior presumably arises from the fact that the activation energy of the α relaxation is much higher than that of the β process.

The strength of the α and β relaxations was obtained from the corresponding deconvoluted isotherms by means of the expression

$$\epsilon_{ri} - \epsilon_{\infty i} = \frac{2}{\pi} \int_{-\infty}^{\infty} \epsilon''(\omega) d \ln \omega \quad (9)$$

where $i = \alpha, \beta$. Earlier results reported on the dielectric relaxation behavior of poly(*n*-alkyl methacrylate)s, specifically, poly(methyl, ethyl, propyl, and *n*-butyl methacry-

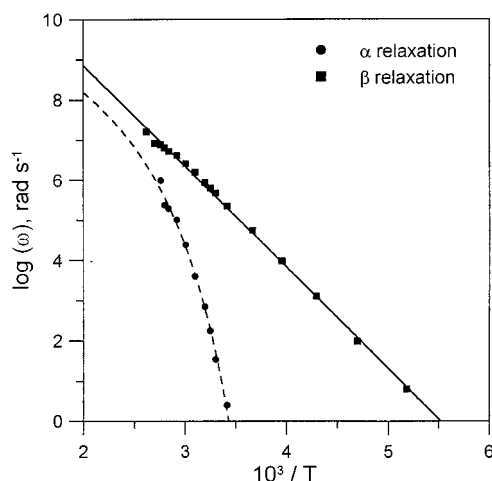


Figure 6. Arrhenius plots of the angular frequency at the maximum of the loss component ϵ'' . Experimental values for the β relaxation were fitted to the straight line: $\log(\omega_{\max}) = 13.87 - 2510/T$ shown as a solid line. The dashed line represents the VFTH equation: $\log(\omega_{\max}) = 10.49 - 614/(T - 233)$.

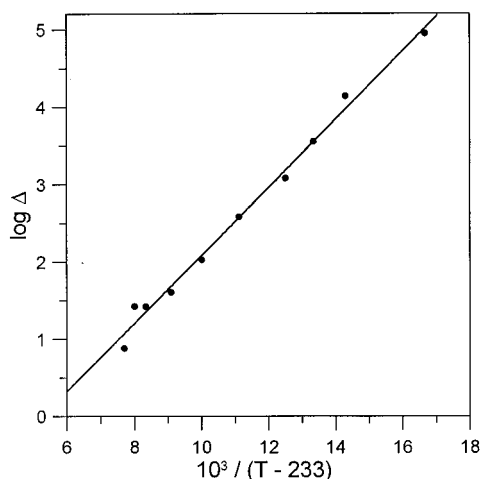


Figure 7. Distance between the peaks of the α and β relaxations in the supercooled liquid state expressed as $\Delta = \omega_{\max,\beta}/\omega_{\max,\alpha}$ plotted vs the reciprocal of $T - T_{\infty}$ according to eq 8.

late)s, show that the dielectric β relaxation of these polymers is symmetrical at low temperatures but becomes asymmetric at high temperatures.¹⁵ In our case, the β relaxation was rather symmetric in the whole temperature range in such a way that its relaxation strength at each temperature was determined by the expression

$$\Delta\epsilon_{\beta} = \epsilon_{r\beta} - \epsilon_{\infty\beta} = \frac{2\epsilon''_{\max}}{m} \quad (10)$$

resulting from substituting eq 6 into eq 9. Values of the strength of the β relaxation are plotted as a function of the reciprocal of temperature in Figure 8. In the glassy state the strength of the β process only exhibits a slight dependence on temperature. However, above T_g , $\Delta\epsilon_{\beta}$ experiences a steep increase with temperature.

From eqs 5 and 9 the strength of the α relaxation, $\Delta\epsilon_{\alpha} = \epsilon_{r\alpha} - \epsilon_{\infty\alpha}$, is obtained. Values of this quantity, plotted in Figure 8, show that the strength of this relaxation has a maximum value at temperatures just slightly above T_g , and then it undergoes a steep decrease

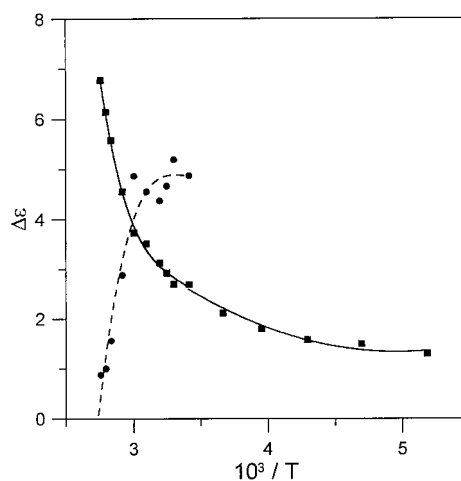


Figure 8. Strength of the α (circles) and β (squares) relaxation as a function of temperature obtained from eq 9.

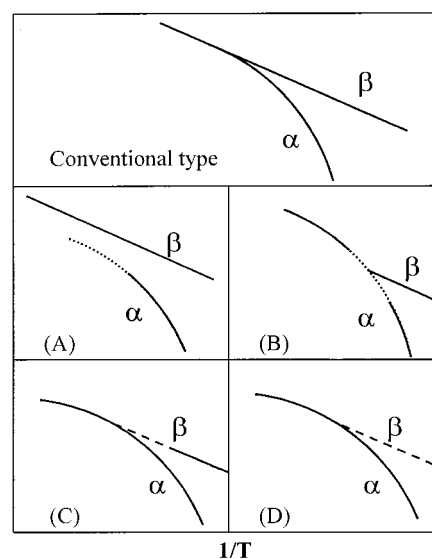


Figure 9. Five scenarios suggested for the splitting region in the Arrhenius diagram taken from ref 15: continuous line, trace with considerable intensity; dashed line, uncertainty in intensity and trace; points, intensity tending to zero. (See text for details.)

with increasing temperature. Extrapolation to $\Delta\epsilon_{\alpha} = 0$ (α onset) points to an onset temperature of 97 °C. Therefore, seen from the high-temperature side, the α relaxation starts with zero intensity at this temperature and steeply increases with decreasing temperature until it levels off in the vicinity of T_g . The strength of the isotherms expressed as $\Delta\epsilon = \Delta\epsilon_{\alpha} + \Delta\epsilon_{\beta}$ has a value of 7.9 ± 0.7 in the whole interval of temperatures in which the α and β relaxations coexist.

On the basis of the analysis of the splitting of the $\alpha\beta$ relaxation of condensed matter, including polymers, it has been speculated¹⁵ with the possibility of five scenarios schematically presented in Figure 9. In the first one, also called the conventional case, the β process continues deep in the liquid state whereas in the type A the separate α onset can be characterized by a minima cooperativity for α that cannot be continued to a local, noncooperative process. For the B type there is a locally coordinative β precursor for the cooperative α process at high temperatures. The topology of the diagram for the type C scenario is similar to that of the conventional one, but here the α relaxation is curved above and below

the splitting and β is not the tangent to α . In the type D scenario¹⁶ there are two different but touching α relaxations with a sharp crossover between them and a β trace aiming to this common tangential point with constant of increasing intensity again. Examples of conventional, A, B, C, and D scenarios are respectively solutions of chlorobenzene in *cis*-decalin, poly(*n*-butyl methacrylate), poly(ethyl methacrylate), poly(propylene glycol), and *o*-terphenyl. Although different approaches have been proposed to describe the origin of the observed dielectric response of polymer systems in the merging region,^{15,17} it seems that most of the experimental cases fall within any of the above-described scenarios. Comparison of the results of Figure 6 with the different scenarios suggests that the relaxation behavior of PAMED resemble the scenario A schematically depicted in Figure 9.

A few comments should be made concerning the temperature dependence of the stretch exponent in the supercooled and even in the deep liquid states. There is some dispute concerning the high-temperature behavior of β_K arising from inconsistent results reported in the literature.⁸ Experiments have been cited^{18–20} suggesting that β_K increases as the temperature goes up, approaching $\beta_K = 1$ at high temperatures. Variation of β_K with temperature was also found in some dielectric experiments.^{21–23}

Experimental evidence supporting the temperature independence of β_K mainly arises from light scattering experiments.^{24–30} For example, the α absorption in Brillouin spectra of the ionic glass formed by calcium potassium nitrate in the temperature range 120–190 °C is fitted by eq 2 with $\beta_K = 0.54$. Moreover, a comparative analysis of the broad-band dielectric behavior of propylene carbonate and glycerol, carried out recently,⁸ shows a tendency of β_K to level off at a constant value, smaller than unity, at high temperatures. Discrepancies observed in the experimental values of the stretch exponent obtained at high temperatures arise from various sources of error. The most important one is that when the loss peak shifts toward the high-frequency limit of the available frequency window, there are less and less experimental data in the high-frequency side of the peaks, and as a result the error involved in the determination of β_K is enhanced.

Recent studies³¹ on the relaxation behavior of poly(vinyl acetate), both in bulk and in solution, show an unexpected fact: the widths of the absorption simulated for isolated PVAc chains and for PVAc in bulk are quite similar. The values of β_K for the temperature range 400–600 K lie in the interval 0.54–0.51 in the former case and in the interval 0.51–0.60 in the second one. The simulations carried out in the solutions do not show a definite temperature dependence, and on the other hand, the values of β_K lie in the range of values obtained for PVAc. The scattering in the values of β_K obviously arises from the difficulty of fitting the simulated time-dipole correlation function to the KWW equation. However, the simulations suggest that a Debye behavior of the relaxation of liquids at high temperatures is quite unlikely. This conclusion is supported by the analysis of the temperature dependence of β_K for PVAc in the bulk and its toluene solutions. The extrapolation of these results to infinite temperature gives values of β_K of the order of 0.57 ± 0.05 .

Comparison of β_K for the responses of PVAc and PAMED in the time domain suggests a greater complexity in the response of the latter polymer, presumably arising from the conformational changes taking place in the bulky side group that involve complex chair-to-inverse chair conformational transitions presumably coupled with motions of the main chain.

Conclusions

The temperature dependence of the distance between the α and β peaks in the frequency domain, expressed in terms of the ratio of the frequencies at the peaks maximum ($\omega_{\max,\beta}/\omega_{\max,\alpha}$), obeys Vogel behavior. As the temperature increases, an onset temperature is reached at which the strength of the α relaxation vanishes whereas the β relaxation undergoes a sharp increase. Since side chains contain the electric dipoles, most of the polarization at temperatures not far above the glass transition temperature relaxes through the β relaxation and only a smaller part through the main chain dynamics reflected in the α relaxation.

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