ELSEVIER

Polymer 42 (2001) 4339–4346

polymer

www.elsevier.nl/locate/polymer

Response of acrylate polymers containing substituted 1,3-dioxacyclohexane groups in the ester residue to mechanical and electric perturbation fields

V. Compañ[a], R. Díaz-Calleja[b], J. Guzmán[c], E. Riande[c,*]

[a]*Dipartamento Ciencias Experimentals, Universitat Jaume I, 12080, Castellón, Spain*
[b]*Dipartamento Termodinámica Aplicada, ETSII, UPV, 46071 Valencia, Spain*
[c]*Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006 Madrid, Spain*

Received 27 July 2000; received in revised form 27 September 2000; accepted 20 October 2000

Abstract

The responses of poly(2-phenyl-5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) (PDAEP) to alternating mechanical and electric fields are studied. Molecular dynamics simulations, together with the comparative analysis of the dielectric spectra of PDAEP and poly(5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) lead to conclude that flipping motions of the 1,3-dioxacyclohexane ring may not be exclusively responsible, as it is often assumed, for the prominent β relaxations present in the spectra of polymers containing dioxane and cyclohexane pendant groups in their structure. The dipole-correlation coefficient of PDAEP obtained from the dielectric spectra is ca. 0.62, a value similar to that reported for the dipole auto-correlation coefficient of most acrylate chains. This fact suggests that intramolecular dipolar-correlations play a dominant role in the dielectric relaxation of PDAEP. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylate polymers; 1,3-Dioxacyclohexane groups; Mechanical and electrical fields

1. Introduction

The response of flexible molecular chains in entangled systems involves, at very short times, rearrangements on the scale of a chain unit. The rearrangement rate is probably not different from that of low molecular weight compounds or monomers at the same temperature, relative to the glass transition temperature [1]. As a result of these local motions a process, called β relaxation, appears at high frequencies in the frequency domain. Relaxations propagate to larger distances with time. Generalised micro-Brownian motions or segmental motions that give rise to the α relaxation occur. Although the α relaxation appears at lower frequencies than the β, a temperature ($T \gg T_g$) can be reached at which both relaxations overlap forming the αβ relaxation. For high molecular weight chains, the mean-relaxation time associated with the α process is nearly independent of the chain length and chain architecture. Therefore motions in this process involves some sort of cooperation. Relaxation propagates to larger and larger distances with time, and the longest times are strongly dependent on molecular weight and molecular architecture [1]. As a consequence, a relaxation called normal mode process appears at very low frequencies in the frequency domain.

Going from high temperatures to the glassy state, the mean-relaxation time associated with the α process changes over many orders of magnitude. A temperature can be reached at which the relaxation time is larger than the time scale of the experiment. The temperature at which this occurs is called glass transition temperature [2], T_g. This parameter is a dynamic property and it is often defined as the temperature at which the relaxation time becomes 200 s, a reasonable time for a dynamic experiment [2,3]. Molecular motions associated with the α relaxation are frozen below T_g, but the β relaxation remains operative in the glassy state [4,5].

Since the relaxation times associated with processes involving local motions are very small at temperatures above T_g, their detection requires sophisticated experimental devices. However, these fast relaxation processes are slow enough in the glassy state so their study is feasible using conventional experimental instruments. Subglass relaxations in polymers have traditionally been attributed to motions taking place in the side groups [6–10]. In this context, acrylic polymers containing cycloaliphatic and

---

* Corresponding author. Tel.: +34-91-562-2900; fax: +34-91-564-4853.
E-mail address: riande@ictp.csic.es (E. Riande).

PII: S0032-3861(00)00788-6

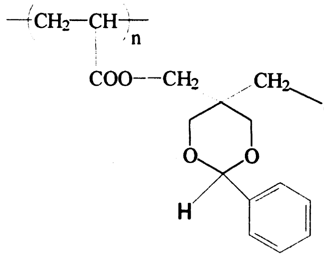

Fig. 1. Schematic representation of the repeating unit of PDAEP.

oxycycloaliphatic rings in the ester moiety have higher activity (mechanical, dielectric, optical and so forth) than their counterparts with aromatic groups [11]. In order to gain a better understanding on the mechanisms underlying subglass relaxations, it is advisable to investigate the relaxation behaviour of polymer chains having side groups with different structures.

In an earlier work the dielectric and mechanical relaxations of poly(5-acryloxy-5-ethyl-1,3-dioxacyclohexane) (PAMED) have been investigated finding that this polymer exhibits ostensible mechanical and dielectric subglass absorptions [11]. It would be important to study how the increase of the bulkiness of the side group of PAMED, for example, the substitution of a hydrogen located in the 2 position of the dioxane ring for a phenyl group would affect the relaxation behaviour of the resulting polymer. In this context, the responses of poly(2-phenyl-5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) (PDAEP) to dynamic force fields (electric and mechanical) is studied in both the glassy state and the glass–rubber transition, and the results obtained are compared with those reported for PAMED. A schematic representation of the repeating unit of PDAEP is shown in Fig. 1.

2. Experimental part

Synthesis of cis/trans 2-phenyl-5-ethyl-5-hydroxymethyl-1,3-dioxacyclohexane: A mixture of *cis/trans* 2-phenyl-5-ethyl-5-hydroxymethyl-1,3-dioxacyclohexane (HEDP) was obtained by reaction of 2-ethyl-2-hydroxymethyl-1,3-propanediol with benzaldehyde. The reaction was carried out in refluxing toluene, under nitrogen atmosphere, using *p*-toluene sulphonic acid (0.5%) as catalyst. Water produced in the reaction was azeotropically removed. The mixture of *cis/trans* alcohol isomers was dried with sodium sulphate and further distilled and collected under vacuum.

Characterisation of 2-phenyl-5-ethyl-5-hydroxymethyl-1,3-dioxacyclohexane: This product was characterised by ^{1}H and ^{13}C NMR spectroscopy with a Varian apparatus operating at 200 MHz for ^{1}H, and 50.4 MHz for ^{13}C,

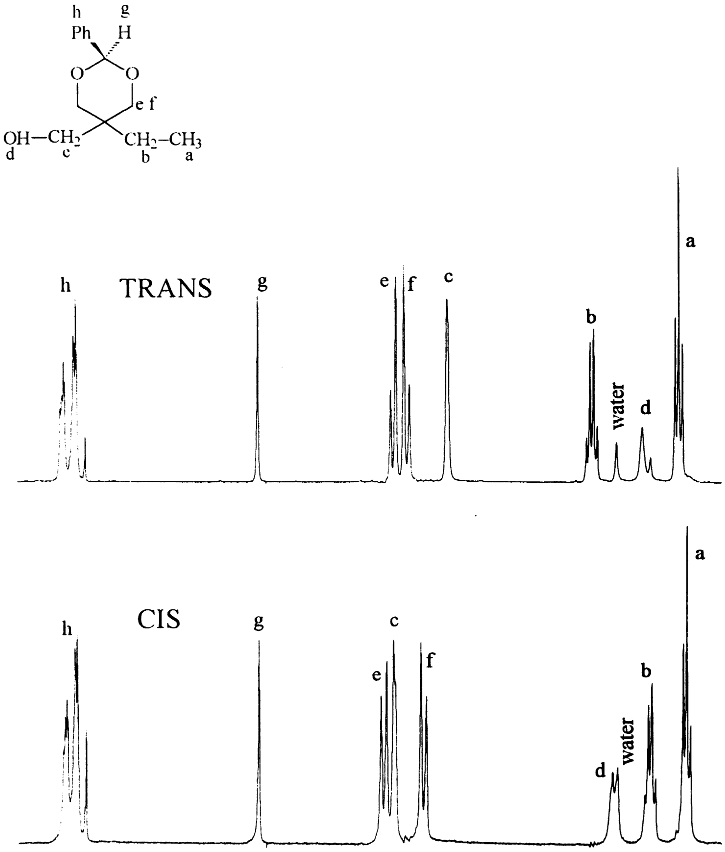

Fig. 2. ^{1}H NMR spectra of the *cis* and *trans* configurations of 2-phenyl-5-ethyl-5-hydroxymethyl-1,3-dioxacyclohexane.

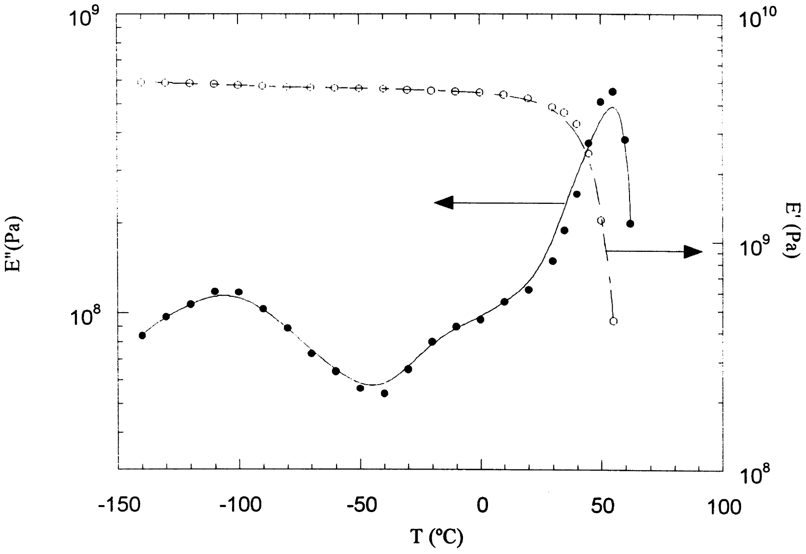

Fig. 3. Storage and loss relaxation moduli of PDAEP.

using deuterated chloroform as solvent and tetramethylsilane as reference. The ^{13}C NMR spectrum showed the high purity of the product.

Two tiny fractions of *cis* and *trans* isomers of HEDP were separated from *cis/trans*-HEDP by flash chromatography in a column of silica 60 (230–400 mesh ASTM), using a mixture 1/1 of ethyl acetate/chloroform as eluent. The ^{1}H NMR spectra of the *cis* and *trans* isomers of HEDP, represented in Fig. 2, show an AB system corresponding to the axial and equatorial protons of the ring. The values of the geminal coupling constants were 11.7 Hz for the e and f protons centred, respectively, at 4 and 3.80 pm in the *trans* configuration and 4.10 and 3.62 pm in the *cis* configuration. These assignments were made on the basis of NMR data reported for similar compounds in the literature [12,13]. The ^{1}H NMR spectra of the two pure isomers allowed the determination of the values of the mole fractions of the *cis* and *trans* isomers in *cis/trans* HEDP which were 0.70/0.30, with an uncertainty of 0.02.

Synthesis and polymerisation of cis/trans 2-phenyl-5-ethyl-5-acryloxymethyl-1,3-dioxane: Acryloyl chloride was added dropwise to a solution of HEDP in chloroform (1/1), under nitrogen atmosphere, using triethylamine to neutralise the hydrogen chloride evolved. The reaction was carried out at 0°C for 5 h. The triethylamine salt was removed by filtration and the reaction medium was washed several times with water, dried successively with sodium sulphate and calcium hydride. The monomer, *cis/trans* 2-phenyl-5-ethyl-5-acryloxymethyl-1,3-dioxacyclohexane (HEDPA), was finally distilled from the reaction medium under vacuum.

PDAEP was obtained by radical polymerisation of HEDPA. The polymerisation was carried out at 65°C in dioxane solution, under vacuum, using AIBN as initiator. The reaction was stopped once 10% of conversion was reached. The polymer was isolated from the reaction medium by precipitation in *n*-hexane. The polymer was freeze-dried from dioxane solutions. The value of the glass transition temperature of PDAEP, determined with a Perkin–Elmer DSC8 calorimeter at a heating rate of 10°C/min, is 55°C.

3. Mechanical and dielectric relaxation measurements

The complex relaxation modulus E^* of PDAEP was measured in flexion with a dynamic mechanical thermal analyser (Rheometrics-DMTA Mark II) in double cantilever flexural mode. The measurements were carried out at a heating rate of 1°C/min from -140°C up to a temperature 30°C above the glass transition temperature of the polymer. In the interval of temperatures $T_g - 30 < T < T_g + 30$, the measurements were also performed in isothermal conditions using steps of 5°C to ensure thermal equilibrium. The frequencies used in the mechanical experiments were 0.3, 1, 3, 10 and 30 Hz.

The complex dielectric permitivity ε^* was measured with a dielectric thermal analyser (TA-DEA 2970), in the frequency range 10^{-4}–10^{2} kHz, using the same thermal history as in the mechanical measurements.

4. Results

Illustrative curves depicting the temperature dependence of the storage E' and loss E'' relaxation moduli of PDAEP, at 1 Hz, are shown in Fig. 3. The loss relaxation modulus exhibits a secondary or β absorption, centred at -110°C, followed by an ostensible glass–rubber or α relaxation, whose peak is located at 54°C. A reminiscent β^* relaxation, probably due to the motion of the ester group as a whole, is observed in the neighbourhood of 0°C.

The curves representing the variation of the dielectric loss with temperature for PDAEP, shown in Fig. 4, also display

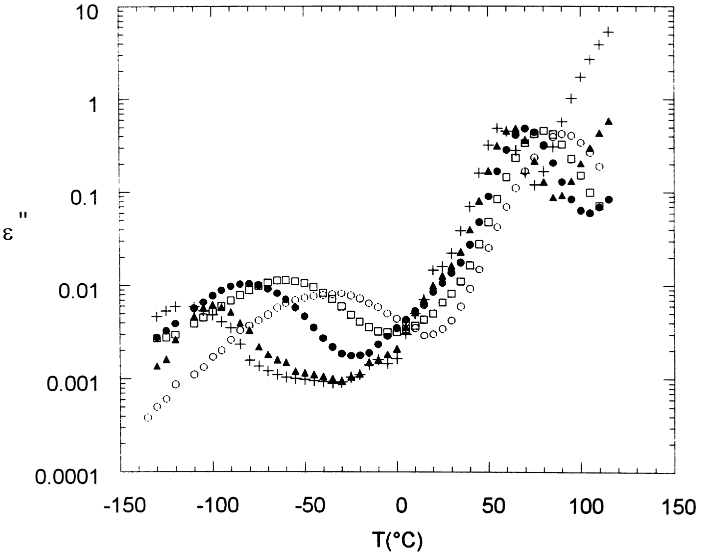

Fig. 4. Isochrones showing the temperature dependence of the dielectric loss on temperature at several frequencies: (○) 10^4 Hz; (□) 10^3 Hz; (●) 10^2 Hz; (▲) 10 Hz; and (+) 1 Hz.

two absorptions associated with the β and α processes centred, respectively, at −115 and 56°C, at 1 Hz. A β^* relaxation is observed as a noise at the level of $\varepsilon'' \approx 10^{-3}$ at 1 Hz. The two main relaxations are shown in the frequency domain in Figs. 5 and 6, respectively. Usually subglass absorptions are described by the Fuoss–Kirkwood equation[14]

$$\varepsilon''(f) = \varepsilon''_{\max} \sec h\left(m \ln \frac{f}{f_{\max}}\right); \qquad 0 < m \leq 1, \tag{1}$$

where $f_{\max}$ is the frequency at the peak maximum, and m an empirical parameter the value of which decreases as the complexity of the process increases. For a single relaxation time process $m = 1$. Values of m at different temperatures, obtained from Eq. (1), are given in Table 1. Apparently the complexity of the β relaxation seems to decrease as the temperature increases.

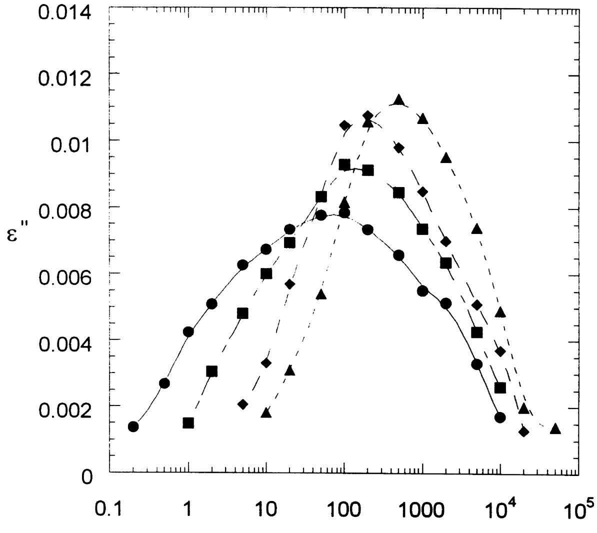

Fig. 5. The dielectric β relaxation of PDAEP in the frequency domain at several temperatures: (●) −100°C; (■) −90°C; (◆) −80°C; and (▲) −70°C.

The rather limited set of frequencies available in the mechanical dynamic apparatus precluded the possibility of obtaining the values of m from Eq. (1) for the mechanical β relaxation. This task, however, could be accomplished by considering that the frequency associated with subglass absorptions follows Arrhenius behaviour. In this case the Fuoss–Kirkwood equation can be written in terms of the temperature as

$$E''(T) = E''_{\max} \sec h\left[\frac{mE_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\max}}\right)\right]; \qquad 0 < m \leq 1, \tag{2}$$

where E_a is the activation energy of the subglass process, R is the gas constant and $E''_{\max}$ is the relaxation loss modulus associated with the temperature at the peak maximum, $T_{\max}$. In the calculation of m, the value of 7.8 kcal mol^{-1} was used for the activation energy of the β process (see below). The values of m obtained at different frequencies lie in the vicinity of 0.19.

The relaxation strength of the dielectric β relaxation $\Delta\varepsilon_\beta$ can be obtained from Eq. (1) by means of the expression

$$\varepsilon_{r\beta} - \varepsilon_{\infty\beta} = \frac{2}{\pi}\int_{-\infty}^{\infty} \varepsilon''(\omega)\, d\ln\omega = 2\frac{\varepsilon''_{\max}}{m}, \tag{3}$$

where $\varepsilon_{r\beta}$ and $\varepsilon_{\infty\beta}$ are, respectively, the relaxed and unrelaxed dielectric permitivities of the β process, and $\omega = (2\pi f)$ is the angular frequency. The results for the relaxation strength are shown in the sixth column of Table 1.

The isotherms representing the α relaxation in the frequency domain, shown in Fig. 6, display Wagner–Sillars

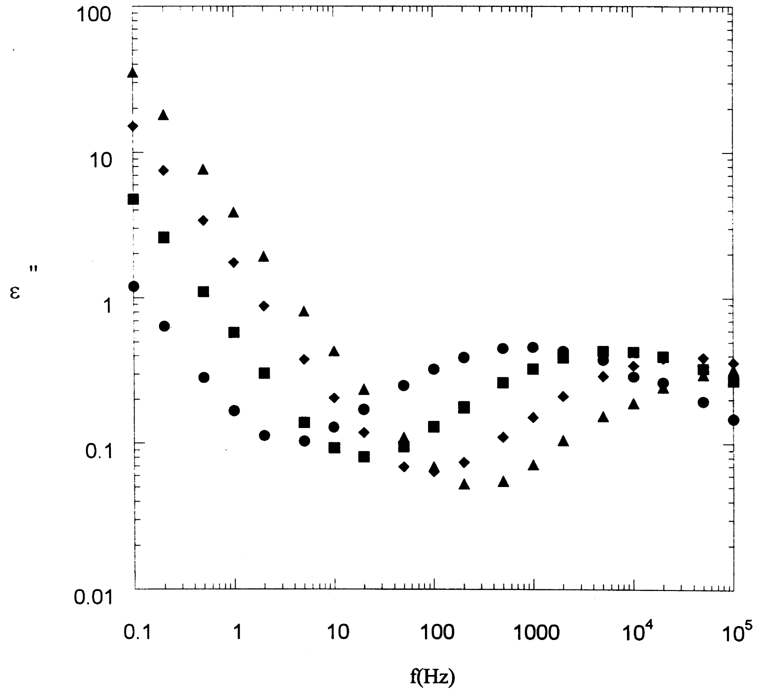

Fig. 6. The dielectric α relaxation of PDAEP in the frequency domain at several temperatures: (●) 80°C; (■) 90°C; (◆) 100°C; and (▲) 110°C.

behaviour [15–17] at high temperatures, that is,

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 f}, \tag{4}$$

where σ is the conductivity, f the frequency in Hz and ε_0 the dielectric permitivity in vacuum. The dipolar α relaxation was obtained by subtracting from ε'' the free charges conductivity contribution to the loss. The experimental values of the relaxed, $\varepsilon_{r\alpha}$, and unrelaxed, $\epsilon_{\infty\alpha}$, dielectric permitivities were obtained from Cole–Cole plots. As usual, the complex dielectric plots are skewed arcs that approach the abscissa axis in the high-frequency region along a straight line. The curves are described by the Havriliak–Negami equation [18]

$$\varepsilon^*_\alpha(\omega) = \varepsilon_{\alpha\infty} + \frac{\varepsilon_{r\alpha} - \varepsilon_{\alpha\infty}}{\left(1 + (j\omega\tau_0)^{\bar{\alpha}}\right)^{\bar{\beta}}}, \tag{5}$$

where τ_0 is the mean-relaxation time. The parameters of this equation were obtained by means of the LEVM6 program [19] and the corresponding values are compiled in Table 2. For illustrative purposes, the complex dielectric plots for the α relaxation of PDAEP at 70, 80 and 90°C are shown in Fig. 7.

Both the mechanical and dielectric β relaxations follow Arrhenius behaviour, the activation energies associated with these processes being 7.8 ± 0.4 and 8.9 ± 0.5 kcal mol^{-1}, respectively. As usual, the temperature dependence of the α relaxation obeys the Vogel–Fulcher–Tammann–Hesse (VFTH) equation [20–22], $f = f_0 \exp(-m/T - T_\infty)$, where m is a constant and T_∞ a temperature ca. 50°C below T_g. The plot $\ln f$ against $1/(T - T_\infty)$ gives a straight line ($\rho = 0.998$) of slope $m = 1403 \pm 200$ K. Comparison of the VFTH and the Doolittle equations [23] yields $\phi_g/B = 0.036$, where ϕ_g is the fractional free volume at T_g and B is a parameter close to unity. The value of ϕ_g/B obtained from the analysis of the temperature dependence of the mechanical glass–rubber relaxation of the polymer is 0.041.

5. Discussion

Taking the acryloxymethyl residue as reference, in the *trans* configuration this residue and the phenyl group are

Table 1
Variation of the Fuoss–Kirwood parameter m and the relaxation strength ($\epsilon_{r\beta} - \epsilon_{\infty\beta}$) for the β relaxation

Polymer	T (°C)	$f_{\max}$ (Hz)	$\varepsilon''_{\max}$	m	$\varepsilon_{r\beta}-\varepsilon_{\infty\beta}$
PDAEP	−100	100	0.0079	0.35	0.045
	−90	200	0.0095	0.44	0.043
	−80	300	0.0108	0.50	0.043
	−70	500	0.0112	0.52	0.043

Table 2
Havriliak–Negami parameters for PDAEP at several temperatures

Polymer	T (°C)	$\varepsilon_{\alpha\infty}$	ε_α	$10^3 \times \tau_0$ (s)	$\bar{\alpha}$	$\bar{\beta}$
PDAEP	70	2.48	4.60	2.3	0.73	0.33
	80	2.44	4.54	1.7	0.70	0.31
	90	2.42	4.44	1.0	0.68	0.30
	100	2.41	4.42	0.5	0.65	0.37

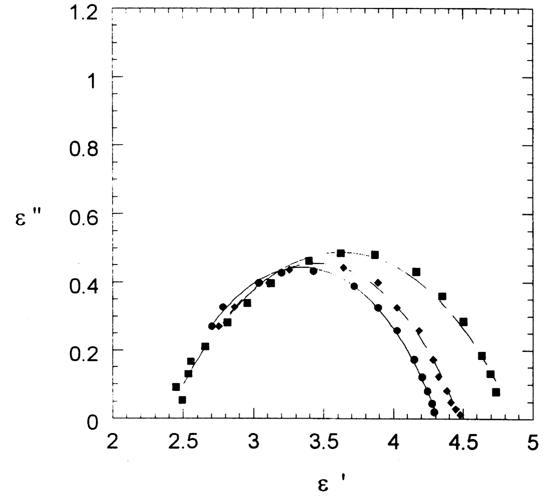

Fig. 7. Complex dielectric plots for the dielectric α relaxation of PDAEP at several temperatures: (●) 90°C; (◆) 80°C; and (■) 70°C.

in the same position (equatorial–equatorial or axial–axial) in the 1,3-dioxane ring. In the *cis* configuration, the acryloxymethyl residue and the phenyl group are located in different positions, either equatorial–axial or axial–equatorial. Molecular dynamics (MD) simulations carried out in 2-phenyl-5-acetoxymethyl-5-ethyl-1,3-dioxacyclohexane (HEDPA) show that for both the *cis* and *trans* configurations, the trajectory starting with the ester residue in the axial position presents dipole moments that are significantly larger than those exhibited by the equatorial trajectory [24]. Thus the averaged values at 30°C of the dipole moments along the axial–axial conformation of the *trans* configuration and axial–equatorial of the *cis* are, respectively, $\langle\mu^2\rangle_{\text{ax-ax}} = 14.29$ debye^2 and $\langle\mu^2\rangle_{\text{ax-eq}} = 9.87$ debye^2. For the trajectories starting with the ester residue in the equatorial position, the values of the mean-square dipole moments for the *trans* and *cis* configurations are, respectively, $\langle\mu^2\rangle_{\text{eq-eq}} = 3.73$ debye^2 and $\langle\mu^2\rangle_{\text{eq-ax}} = 3.82$ debye^2.

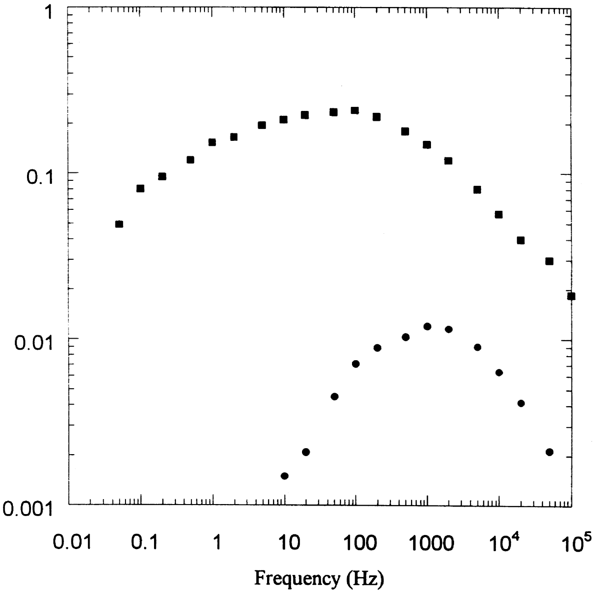

Fig. 8. The β relaxation in the frequency domain at −60°C for PDAEP (●) and poly(5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) (■).

The life times of both axial–axial and equatorial–equatorial conformations in the *trans* configuration are 0.14 and 18 ns at 27°C, respectively. For the *cis* configuration, the life time of the conformation in which the ester residue is in axial and the phenyl in equatorial is 23 ns, but it is only 0.20 s for the alternative conformation (ester residue in equatorial and phenyl group in axial). According to the simulations the mean-square dipole moment of the mixture of *cis/trans* HEDPA will be $\langle\mu^2\rangle \cong 0.30 \times 3.73$ debye^2 + 0.70×9.87 debye$^2 = 8.0$ debye^2, in very good agreement with the experimental result, 7.9 debye^2. Although chair to inverse chair conformational transitions involving eq–eq ↔ ax–ax for the *trans* configuration and ax–eq ↔ eq–ax for the *cis* configuration should produce high dielectric activity, the relaxation strength of the β relaxation of PDAEP is rather low in comparison with that of PAMED, as can be seen in Fig. 8 where the dielectric loss in the frequency domain, at −80°C, is shown for this latter polymer. MD simulations carried out on the model of the repeating unit of PAMED, 5-acetoxymethyl-5-ethyl-1,3-dioxacyclohexane (AMED) suggests that the acetoxymethyl residue spends nearly the same time in axial and equatorial positions, specifically, 1.14×10^{-2} and 1.08×10^{-2} ns, respectively, at 27°C [25]. The mean-square dipole moment of the two chair conformations of AMED is strongly dependent on the equatorial/axial locations of the acetoxymethyl moiety in the 1,3-dioxacyclohexane ring. From the simulations, $\langle\mu^2\rangle_{\text{ax}} = 15.2$ debye^2 and $\langle\mu^2\rangle_{\text{eq}} = 2.1$ debye^2 at 30°C, so $\langle\mu^2\rangle = 8.7$ debye^2, is in good agreement with the experimental result, 9.2 debye^2. Therefore ax ↔ eq conformation should produce considerable dielectric activity. By extrapolating the time dependence of the life times of the equatorial (or axial conformations) given for AMED in Ref. [24], the chair to chair inverse transition at −80°C would be detected at nearly 10^3 Hz. This result corresponds to the chair → chair inverse conformational transition in vacuum. Obviously, in the glassy state the transition would be shifted to lower frequencies, coming nearer to the frequency of 1 Hz at which the β relaxation in PAMED occurs at −80°C.

The analysis of the trajectories of the side groups of PAMED seem to suggest that in the development of the dielectric activity detected in the glassy state of this polymer chair-to-chair inverse conformational transitions may intervene. This is not so clear in *cis/trans*PDAEP because the acetoxymethyl moiety is located in its nearly totality in axial position. Moreover, chair-to-inverse chair conformational transitions in the latter polymer would cause high dielectric activity. Therefore the β absorption of relatively low intensity appearing in the spectra of PDAEP may arise mainly from motions about the O–CH$_2$–C$_y$ bonds which in turn presumably are hindered by the bulky side groups.

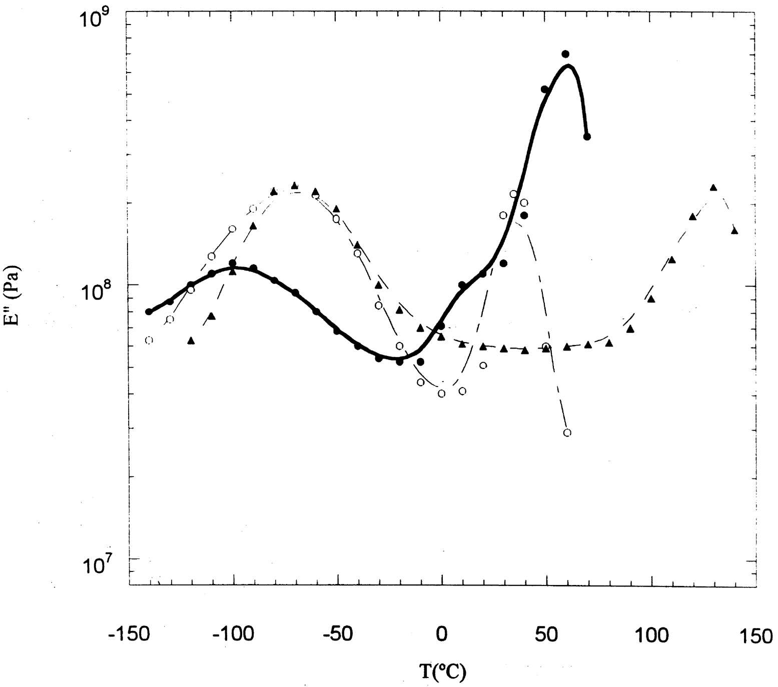

Fig. 9. Comparative ischrones at 1 Hz for PDAEP (●),poly(5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) (○) and poly(5-methacryloxymethyl-5-ethyl-1,3-dioxacyclohexane).

The strength of the β relaxation in most polymers increases with temperature. This, however, is not the case for PDAEP. According to the results of Table 1, the dielectric strength of the subglass absorption of PDAEP is nearly independent of temperature. Moreover, the single subglass absorption in PDAEP seems to suggest that the molecular motions intervening in the responses in the *cis* and *trans* configurations have similar barrier energies.

In most polymers with dioxacyclohexane groups in the side chains, the β absorption appears to be independent on the rigidity of the main chain. Actually, as can be seen in Fig. 9, both PAMED and poly(5-methacryloxymethyl-5-ethyl-1,3-dioxane) (PMAMED) present β relaxations of similar strength which are located in the same region of the spectra [11]. The same occurs with poly(1,3-dioxacyclohexane acrylate) and poly(1,3-dioxacyclohexane methacrylate) [26]. Therefore the intensities of the mechanical and dielectric β absorptions of poly(2-phenyl-5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) should be similar to those of PDAEP.

The glass transition temperature of PDAEP is nearly 30°C above that of PAMED presumably as a consequence of the bulkiness of the 2-phenyl-1,3-dioxacyclohexane moiety that hinders the micro-Brownian motions in the former polymer. As usual the dielectric strength of the α relaxation decreases as the temperature increases (see Fig. 7). The total dielectric activity of PDAEP can roughly be expressed in terms of the relaxation strengths of the α and β relaxation processes by

$$\varepsilon_{r\alpha} - \varepsilon_{\infty\beta} \cong \varepsilon_{r\alpha} - \varepsilon_{\infty\alpha} + \varepsilon_{\infty\alpha} - \varepsilon_{\infty\beta}, \tag{6}$$

where $\varepsilon_{\infty\alpha} \cong \varepsilon_{r\beta}$ are, respectively, the unrelaxed and relaxed dielectric permitivities corresponding to the α and β relaxations, respectively. The total dielectric strength $\Delta\varepsilon = (\varepsilon_{r\beta} - \varepsilon_{\infty\beta})$ can be obtained from Onsager type equations such as the Fröhlich equation [27,28]

$$\varepsilon_{r\alpha} - \varepsilon_{\infty\beta} = \frac{3\varepsilon_{r\alpha}}{2\varepsilon_{r\alpha} + \varepsilon_{\infty\beta}} \left(\frac{\varepsilon_{\infty\beta} + 2}{3} \right) \frac{4\pi\rho N_A \langle \mu^2 \rangle}{3M_0 k_B T}, \tag{7}$$

where N_A and k_B are, respectively, Avogadro's number and Boltzmann constant, M_0 and $\langle \mu^2 \rangle$, respectively, the molecular weight and the mean-square dipole moment of the repeating unit, T the absolute temperature and ρ the density of the polymer. The experimental value of $\varepsilon_{r\alpha}$ at 70°C is 4.60. Since, $\varepsilon_{\infty\beta}$ seems to be nearly independent of temperature, the value of this quantity was taken to be 2.38. These results in combination with Eq. (7) give $\langle \mu^2 \rangle = 5.1$ debye^2 at 70°C. Hence the dipole auto-correlation coefficient $g = (\langle \mu^2 \rangle / \langle \mu^2 \rangle_0)$ is 0.62 at 70°C, a value similar to that reported for most polyacrylates in solution [29]. The closeness of the values obtained for g from dielectric measurements in the bulk to those reported for isolated chains of this kind suggest that intramolecular dipolar-correlations play a dominant role in the dielectric relaxation of PDAEP. This means that the intermolecular dipolar cross-correlation contributions, although present, do not significantly affect the time dependence of the macroscopic dipole-moment time-correlation function as suggested by Williams earlier [30,31].

6. Conclusions

The substitution of a hydrogen atom bonded to the carbon atom located in position 2 of the 1,3-dioxane ring of poly(5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane) severely reduces the mechanical and dielectric activity of the resulting polymer, PDAEP. The mechanical and dielectric absorptions of the latter polymer are shifted to lower temperatures (higher frequencies). MD simulations suggest that chair-to-inverse chair are not responsible for the subglass dielectric activity of PDAEP but rather motions about the skeletal bonds of the side groups. However, the bulky side groups hinder these motions and hence the low intensity dielectric β absorption displayed by this polymer. The bulky side group also hinders the segmental motions and as a consequence the glass–rubber relaxation of PDAEP appears at higher temperature (lower frequencies) than that of poly(5-acryloxymethyl-5-ethyl-1,3-dioxacyclohexane).

References

[1] Graessley WW. In: Mark JE, editor. Physical properties of polymers. Washington, DC: American Chemical Society, 1984 (chap. 3).

[2] Lunkenheimer P, Schneider U, Brand R, Loidl A. Contemp Phys 2000;41:15.

[3] Angell CA. Science 1995;267:1924.

[4] Ngai K, Riande E, Wright G., editors. Proceedings of the 2nd Conference on Relaxations in Complex Systems. J Non Cryst Solids 1994; 172–4.

[5] Richert R, Blumen A, editors. Disorder effects on relaxational processes. Berlin: Springer, 1994.

[6] Heijboer J. In: Meier DJ, editor. Molecular basis of transitions and relaxations. New York: Gordon and Breach, 1978.

[7] Gomez-Ribelles JL, Díaz-Calleja R. J Polym Sci, Polym Phys Ed 1985;23:1297.

[8] Garwe F, Schönhals A, Beiner M, Schröter K, Donth E. Macromolecules 1996;29:247.

[9] Buerger DE, Boyd RH. Macromolecules 1989;22:2649.

[10] Smith GD, Boyd RH. Macromolecules 1991;24:2731.

[11] Pérez-Feito R, Díaz-Calleja R, Guzmán J, Riande E. J Polym Sci, Part B Polym Phys 1999;37:2486.

[12] Eliel EL, Banks HD. J Am Chem Soc 1972;94:171.

[13] Coxin AC, Stoddart JF. J Chem Soc Perkin Trans 1 1977:767.

[14] Fuoss RM, Kirkwood JG. J Am Chem Soc 1941;63:385.

[15] Wagner KW. Arch Elektrotechnol 1914;2:371.

[16] Wagner KW. Arch Elektrotechnol 1914;3:67.

[17] Sillars RW. Proc Inst Electr Engng Lond 1937;80:378.

[18] Havriliak Jr. S, Havriliak SJ. Dielectric and mechanical relaxation in materials. Munich: Hanser Publishers, 1997, 14 p.

[19] MacDonald JR, Complex non linear least squares immitance fitting program. LVM6, 1993.

[20] Vogel H. Z Phys 1921;22:645.

[21] Fulcher GSA. J Am Ceram Soc 1925;8:339.

[22] Tammann G, Hesse WZ. Anorg Allgem Chem 1926;156:245.

[23] Doolittle AK, Doolittle DB. J Appl Phys 1957;28:901.

[24] Saiz E, Guzmán J, Iglesias MT, Riande E. J Phys Chem 1996;100:18 345.

[25] Saiz E, Riande E, Guzmán J, Iglesias MT. J Phys Chem 1996;100:3818.

[26] García N, Compañ V, Díaz-Calleja R, Guzmán J, Riande E. Polymer 2000;41:6603.

[27] Fröhlich H. Trans Faraday Soc 1948;44:238.

[28] Fröhlich H. Theory of dielectrics. London: Oxford University Press, 1958.

[29] Salort J, Salom C, Riande E. Dipole moments of polymer solutions. In: Brandrupp, Immergut, editors. Polymer handbook. New York: Wiley-Interscience, 1999.

[30] Williams G. Adv Polym Sci 1979;33:60.

[31] Williams G. Dielectric relaxation spectroscopy of amorphous polymers: the modern approaches. In: Riande E, editor. Keynote lectures in selected topics of polymer science. CSIC, 1995. p. 7.