

Comparative study of the relaxation behaviour of acrylic polymers with flexible cyclic groups in their structure

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Abstract

The synthesis and radical polymerization of 1,3-dioxan-5-yl-acrylate and 1,3-dioxan-5-yl-methacrylate are described. The mechanical and dielectric relaxation spectra of poly(1,3-dioxan-5-yl-acrylate) and poly(1,3-dioxan-5-yl-methacrylate) exhibit prominent subglass absorptions, the locations of which are not affected by the rigidity of the main chain. The subglass relaxations of poly(1,3-dioxan-5-yl-acrylate) and poly(1,3-dioxan-5-yl-methacrylate) are shifted nearly 20°C toward lower temperatures with respect to those of poly(cyclohexyl acrylate) and poly(cyclohexyl methacrylate). The locations of the mechanical glass–rubber relaxations are not affected by the different nature of the rings located in the side groups. A study of the conductive contributions to the dielectric glass–rubber relaxation of poly(1,3-dioxan-5-yl-acrylate) and poly(1,3-dioxan-5-yl-methacrylate) is carried out using a theory that assumes that the dispersion displayed by the loss $\tan \delta$ at high temperatures, in the frequency domain, arises from the Maxwell–Wagner–Sillars effect combined with Nernst–Planck electrodynamic effects caused by interfacial polarizations in the polymer–electrodes interface. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The study of the response of glass formers to the perturbations of force fields is a subject of great interest in condensed matter physics. The interactions between the constituent particles of glass formers (atoms, ions or molecules) are comprised in a potential energy function $\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ that depends on the spatial location and the chemical nature of the particles. These interactions condition the restructuring kinetics, resulting from interbasin transitions, of the perturbed system. The particle dynamics of the system is described for most applications of interest by the classical Newton equations of motion incorporating forces specified by ϕ .

Relaxation responses of liquids in the time domain, $g_\chi(t)$ to a variety of weak external perturbations, χ , provide information on the actual restructuring kinetics resulting from interbasin transitions appearing in the multidimensional topographic map of ϕ . For a unit step-off perturbation function $\chi(t)$, the area under the normalized response function

$g_\chi(t)$ gives the mean-relaxation time τ_χ associated with the relaxation [1]. In a cooling experiment, a temperature can be reached at which $g_\chi(t)$ splits into two relaxations, one fast, called β -relaxation, and another slow, named α -relaxation [1–3]. The mean relaxation times associated with the β - and α -relaxations obey to the Arrhenius and Vogel–Fulcher–Tamman–Hesse (VFTH) equations [4], respectively. As the temperature of the perturbed liquid decreases, a temperature is reached at which the mean-relaxation time associated with the α relaxation is larger than the time scale of the experiment, whatever large this time may be. A transition from the liquid state to the glassy state occurs and the α -relaxation is frozen out whereas the β -relaxation remains operative in the glassy state.

Since $g_\chi(t)$ is related to the energy potential function ϕ , which depends implicitly on time for a dynamical system in thermal equilibrium, the temperature at which the α -relaxation of a polymer becomes frozen, at very low frequencies, is affected by the chemical structure of the material [5]. In this regard, bulky side-chain substituents, that hinder the motions of the chains, increase the temperature at which the α -relaxation freezes. On the other hand, the relaxation spectra of chains with flexible side groups may exhibit

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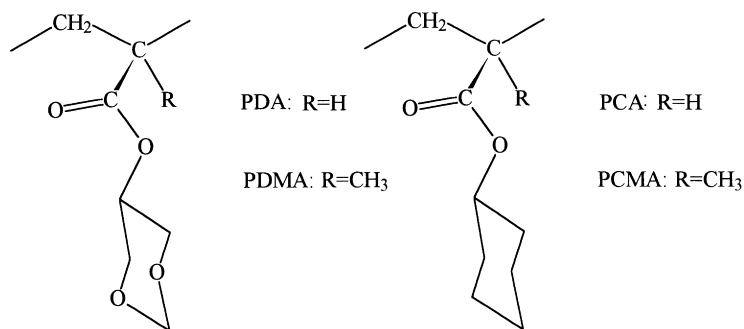


Fig. 1. Repeating units of PDA, PDMA, PCA and PCMA.

ostensible β -relaxations. For example, the spectra of acrylic and methacrylic polymers with cyclohexane rings in the side groups display well-developed β -relaxations, located in the vicinity of -80°C at 1 Hz, attributed to chair-to-inverse chair conformational transitions of the rings [6]. This relaxation, however, disappears when the cyclohexane ring is located in the main chain [7,8], or when the cyclohexane ring has two identical substituents in the same carbon that makes undistinguishable the chair-to-chair conformational transition.

In order to gain a better understanding on the relation between secondary relaxations and chemical structure it is advisable to investigate the relaxation behaviour of polymers with only slight differences in their chemical structure. With this aim, the responses of poly(1,3-dioxan-5-yl-acrylate) (PDA) and poly(1,3-dioxan-5-yl-methacrylate) (PDMA) to electric and mechanical force fields were studied in this work, and the results obtained compared with those reported for poly(cyclohexyl acrylate) (PCA) and poly(cyclohexyl methacrylate) (PCMA). A schematic representation of the repeating unit of these polymers is given in Fig. 1.

2. Experimental part

2.1. Synthesis of 5-hydroxy-1,3-dioxane

5-Hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxane-cyclopentane were obtained by reaction of glycerol with *p*-formaldehyde (molar ratio 10/15), in aqueous solution, using *p*-toluene sulfonic acid as catalyst. The reaction process was carried out at the boiling temperature of the reaction medium, eliminating water by evaporation. The mixture of acetals was purified by distillation at reduced pressure and the yield of the reaction was 74%. Benzoyl chloride was added dropwise to the mixture of acetals in pyridine solution. The reaction was performed at 20°C , for 48 h, under stirring; the products formed were dissolved in ether and separated from the pyridinium chloride salt by filtration. The solution in ether of the mixture of benzoates was washed successively with water, 1 N sulfuric acid and, finally, with a dilute solution of sodium bicarbonate. Then

the solution was dried with calcium chloride anhydride and the solvent was separated by evaporation. 1,3-Dioxan-5-yl benzoate was isolated from the acetals by fractionated crystallization in ethyl ether (m.p. $72-74$. Lit. 70°C). Hydrolysis of the ester at 75°C , carried out in an aqueous solution of potassium hydroxide, yielded 5-hydroxy-1,3-dioxane. This product was extracted from the reaction medium with ethyl ether and further dried with calcium chloride. The ether was then eliminated by evaporation and the 5-hydroxy-1,3-dioxane was finally purified by distillation at reduced pressure ($51-53^\circ\text{C}$, 0.5 mmHg). This compound was characterized by gas chromatography (GC-MS) and by ^1H , ^{13}C NMR spectroscopies.

2.2. Synthesis of 1,3-dioxan-5-yl-acrylate and 1,3-dioxan-5-yl-methacrylate

1,3-Dioxan-5-yl-acrylate (DA) and 1,3-dioxan-5-yl-methacrylate (DMA) were obtained, respectively, by adding acryloyl chloride and methacryloyl chloride dropwise to benzene solutions of 5-hydroxy-1,3-dioxane, using triethylamine as absorbent of the hydrogen chloride formed. The reactions were carried out at 0°C , under stirring and nitrogen atmosphere, for 5 h. Triethylamine chlorhydrate formed in the reaction was separated by filtration. The reaction medium was washed several times with distilled water to eliminate the triethylamine in excess, and then it was dried with anhydrous calcium chloride. The solvent was eliminated at room temperature by evaporation at low pressure, and the monomers were purified by distillation at reduced pressure ($60-65^\circ\text{C}$, 0.5 mmHg) (yield, 60%) and ($74-75^\circ\text{C}$, 0.5 mmHg) (yield, 50%) for DA and DMA, respectively.

DMA, a solid below room temperature, was further purified by recrystallization from ether obtaining a crystalline compound with melting point $29-30^\circ\text{C}$.

Both monomers were characterized by ^1H and ^{13}C NMR spectroscopies. The resonance spectra were registered with a Varian XL-300 operating at 75.4 MHz for ^1H and 300 MHz for ^{13}C , using deuterated chloroform as solvent and tetramethylsilane as internal reference. The ^1H characteristic chemical shifts, δ (in ppm, corresponding to the monomer DA were: (4.1, m/4H), (4.9, m/3H), (6.0, dd/1H), (6.3, dd/1H), (6.4, dd/1H); for DMA: (1.9, m/3H), (3.9, m/4H), (4.8,

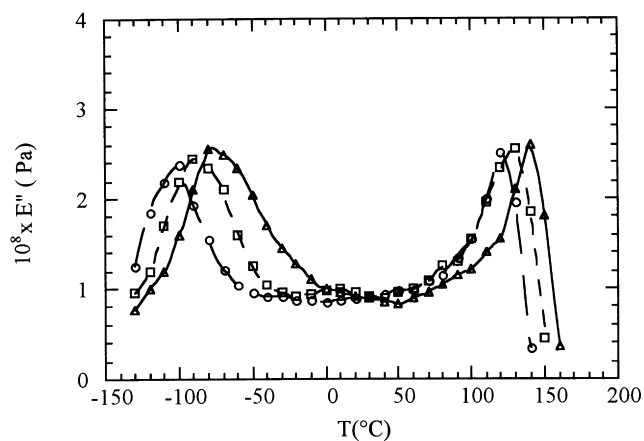


Fig. 2. Temperature dependence of the loss relaxation modulus for PDMA at several frequencies: 0.3 Hz (○); 3 Hz (□); and 30 Hz (△).

m/3H), (5.6, m/1H), (6.2, m/1H). The ^{13}C NMR spectra of both monomers showed six and seven resonance signals for the carbons belonging to DA and DMA, respectively.

2.3. Polymerization

Poly(1,3-dioxan-5-yl-acrylate)(PDA) and poly(1,3-dioxan-5-yl-methacrylate) (PDMA) were obtained, respectively, by radical polymerization of 1,3-dioxan-5-yl-acrylate and 1,3-dioxan-5-yl-methacrylate in benzene solution, using azobisisobutyronitrile (AIBN) as initiator. The polymerizations were carried out at 60°C and the reactions were stopped once 10% of conversion was achieved. The polymers were precipitated with methanol, dissolved in benzene, precipitated again with methanol. PDA was dried overnight in vacuum at 70°C while PDMA was freeze-dried from benzene solution. The ^1H and ^{13}C NMR spectra of the polymers showed their purity. The values of the fractions of syndiotactic dyads calculated from the spectra were ca. 0.65 and 0.75 for PDA and PDMA, respectively.

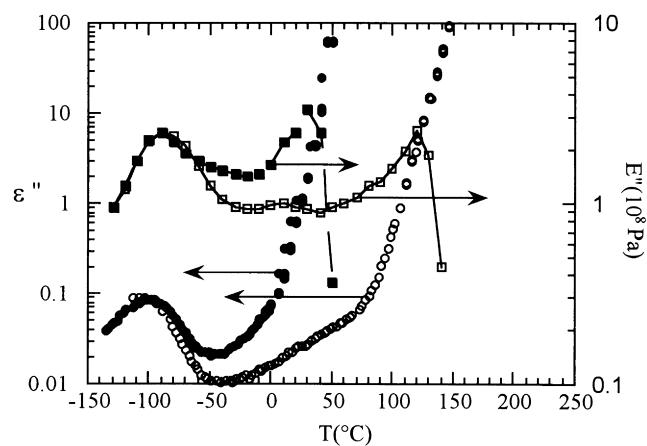


Fig. 3. Temperature dependence of the loss relaxation modulus (squares) and the dielectric loss (circles), at 1 Hz, for PDA (filled symbols) and PDMA (open symbols).

The glass transition temperatures of PDA and PDMA were measured with a Perkin–Elmer DSC 4 calorimeter at a heating rate of 10°C/min. The values of T_g , taken at the onset of the separation of the thermograms of the baseline, were 115 and 25°C for PDMA and PDA, respectively.

2.4. Mechanical and dielectric measurements

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

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

2.5. Mechanical and dielectric results

Illustrative plots depicting the temperature dependence of the loss relaxation modulus of PDMA at three frequencies are shown in Fig. 2. The isochrones exhibit a prominent subglass β -absorption, centred at ca. -100°C at 0.3 Hz, followed in increasing order of temperature by the glass–rubber process or α -relaxation. The β mechanical relaxations of PDA and PDMA, at a given frequency, are located at nearly the same temperature while the α -relaxation of the former polymer is located ca. 100°C below that of the latter. This behaviour is reflected in Fig. 3 where the values of the loss modulus at 1 Hz for PDA and PDMA are plotted against temperature. The variation of the storage relaxation modulus with temperature, measured at 0.3 Hz and represented in Fig. 4, is quite different for the two polymers. For example, E' for PDA decreases moderately with increasing temperature in the glassy region, and then sharply drops in the vicinity of T_g , whereas the isochrone corresponding to PDMA experiences a strong decrease in the interval -130 to -20°C followed by a pseudo-plateau region lying in the temperature range -20 to -50°C ; finally the isochrone sharply decreases in the vicinity of the glass–rubber transition.

The isochrones showing the temperature dependence of the dielectric loss of PDMA are plotted at several frequencies in Fig. 5. Although the curves also present a prominent α -absorption, the strong conductive contributions to the α -absorption preclude the possibility of measuring the dipolar α -relaxation process for these polymers at frequencies below 10^5 Hz. The isochrones corresponding to the dielectric and mechanical losses of PDA and PDMA are shown, for comparative purposes, in Fig. 3. An inspection of the curves reveals that the dielectric β -absorptions appear

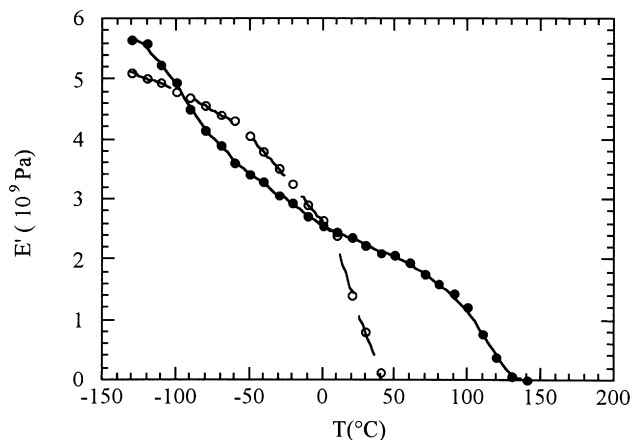


Fig. 4. Variation of the storage relaxation modulus with temperature for PDA (○) and PDMA (●), at 1 Hz.

at slightly lower temperatures than the mechanical β -relaxations.

The dielectric β -absorption of PDMA in the frequency domain is shown at several temperatures in Fig. 6 where it can be seen that the absorptions become narrower as the temperature increases. The departure of the β -relaxation from Debye behaviour is customarily studied by analyzing the dielectric results in terms of the Fuoss–Kirkwood equation given by [9]:

$$\varepsilon''(f, T) = \varepsilon''(f_{\max}, T) \operatorname{sech} \left[m \ln \frac{f}{f_{\max}} \right] \quad (1)$$

where m is an empirical parameter lying in the interval $0 < m \leq 1$ and f_{\max} the frequency associated with the maximum of the isotherm at temperature T . The parameter m is related to the relaxation times distribution in such a way that the higher m is, the narrower is the distribution, in such a way that for a Debye type relaxation, $m = 1$. The loss curves in the frequency domain fit very well to Eq. (1) at low temperatures. The fit is not so good in the high frequency side of the

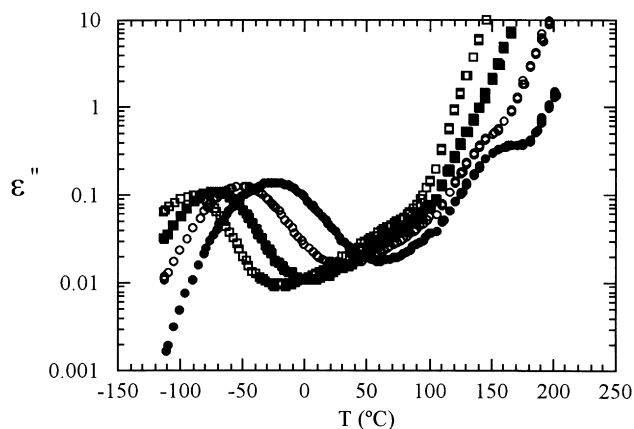


Fig. 5. Isochrones representing the variation of the dielectric loss with temperature for PDMA at several frequencies: (□) 0.1 kHz; (■) 1 kHz; (○) 10 kHz, and (●) 100 kHz.

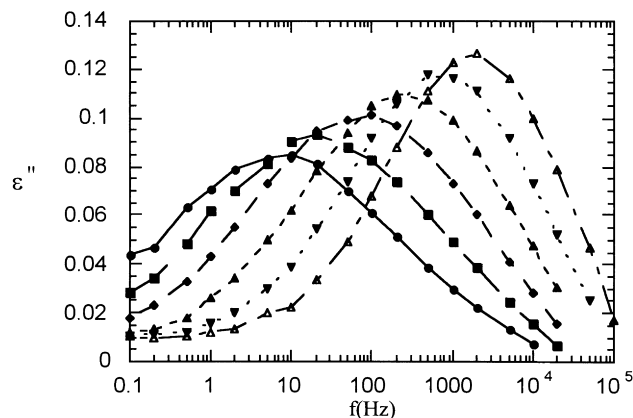


Fig. 6. Curves showing the dielectric β -relaxation for PDMA in the frequency domain at several temperatures: -100°C (●); -90°C (■); -80°C (◆); -70°C (▲); -60°C (▼); and -50°C (Δ).

curves at high temperatures. The results shown for m at different temperatures in Tables 1 and 2 indicate that this parameter is somewhat higher for PDMA than for PDA. Moreover, m increases with increasing temperature, the temperature dependence of m being slightly higher for PDMA than for PDA.

The mechanical β -relaxation appearing in the isochrones at a given frequency is described by the Fuoss–Kirkwood equation expressed in terms of the temperature as

$$E''(T, f) = E''(T_{\max}, f) \operatorname{sech} \left[\frac{mE_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\max}} \right) \right] \quad (2)$$

where T_{\max} is the temperature associated with the maximum of the isochrone at frequency f and E_a the activation energy of the relaxation process. The values obtained for m fitting the mechanical results to Eq. (2), shown in Table 3, are lower than the dielectric ones. The values of m are similar for PDA and PDMA and somewhat lower than those found for this parameter from dielectric results.

The strength of the β -relaxation expressed as $\Delta\varepsilon_{\beta} = \varepsilon_{r\beta} - \varepsilon_{u\beta}$, where $\varepsilon_{r\beta}$ and $\varepsilon_{u\beta}$ are, respectively, the relaxed and unrelaxed dielectric permittivities, can be obtained either from the expression

$$\Delta\varepsilon = 2 \frac{\varepsilon''_{\max}}{m} \quad (3)$$

Table 1

Variation of the parameter m of the Fuoss–Kirkwood equation and the relaxation strength of the dielectric β -relaxation with temperature for PDA

T ($^{\circ}\text{C}$)	f_{\max} (Hz)	ε''_{\max}	m	$\Delta\varepsilon$
-100	4	0.087	0.28	0.62
-95	10	0.090	0.30	0.61
-90	20	0.099	0.31	0.61
-85	40	0.097	0.31	0.62
-80	80	0.102	0.32	0.64
-75	150	0.104	0.33	0.64
-70	250	0.108	0.33	0.65

Table 2
Variation of the parameter m of the Fuoss–Kirkwood equation and the relaxation strength of the dielectric β -relaxation with temperature for PDMA

T (°C)	f_{\max} (kHz)	ε''_{\max}	m	$\Delta\varepsilon$
–100	0.007	0.084	0.31	0.54
–90	0.02	0.093	0.34	0.55
–80	0.08	0.102	0.37	0.56
–70	0.25	0.104	0.40	0.54
–60	0.65	0.117	0.44	0.53
–50	1.8	0.128	0.48	0.53
–40	4.3	0.133	0.51	0.53
–30	10	0.1380	0.535	0.516

or from the Cole–Cole equation [10]

$$\varepsilon^*(\omega) = \varepsilon_{u\beta} + \frac{\varepsilon_{r\beta} - \varepsilon_{u\beta}}{1 + (i\omega\tau_0)^{\bar{\gamma}}} \quad (4)$$

where ω ($= 2\pi f$) is the angular frequency. The values of the relaxation strength obtained from Eq. (3) and represented in the last columns of Tables 1 and 2 are in rather good agreement with those determined from Eq. (4). As usual, the relaxation strength of the β process increases as the temperature increases for PDMA. However, the strength of the relaxation seems to be nearly independent of the temperature for PDA.

2.6. Temperature dependence of the β - and α -relaxations

The relaxation times associated with the β -relaxations usually display Arrhenius behaviour so that the activation energy of these processes are obtained from the slopes of $-\ln \omega$ against $1/T$. The values of the activation energies corresponding to the mechanical and dielectric β -relaxations obtained from the pertinent Arrhenius plots are, respectively, 10.8 and 9.6 kcal mol^{–1} for PDA, and 10.7 and 9.3 kcal mol^{–1}, respectively, for PDMA.

The temperature dependence of the mean relaxation time associated with the glass–rubber relaxation obeys the Vogel–Fulcher–Tammann–Hesse equation [11–13]:

$$\tau = A \exp\left(\frac{m}{T - T_{\infty}}\right) \quad (5)$$

The plots in τ against $1/(T - T_{\infty})$ for the mechanical relaxations fit reasonably well into straight lines by assuming, as usual, that T_{∞} lies 50 K below the corresponding glass tran-

Table 3
Values of m and strength ΔE ($= E_{r\beta} - E_{u\beta}$) for the mechanical β -relaxation strength of PDA and PDMA

T (°C)	PDA		PDMA	
	m	$10^{-9} \times \Delta E$ (Pa)	m	$10^{-9} \times \Delta E$ (Pa)
–100	0.23	2.18	0.23	2.07
–90	0.22	2.15	0.23	2.16
–75	0.20	2.61	0.21	2.40

sition temperatures. The slopes of the straight lines are 1050 and 1140 K^{–1} for PDA and PDMA, respectively. By comparing the VFTH and the free volume Doolittle equations [14], the fractional free volumes of PDA and PDMA at their respective T_g s are exceptionally high, of the order of 0.048 and 0.044, nearly two times larger than the value of 0.025 ± 0.005 reported for most polymers [15]. Unfortunately, strong conductive effects associated with the α -relaxation preclude the possibility of determining the fractional free volume for these polymers from dielectric experiments.

2.7. Conductivity and electrokinetic phenomena in the glass–rubber relaxation

Double logarithmic plots of the dielectric loss permittivity against frequency, at temperatures above T_g , give curves for which $\varepsilon'' \sim f^{-1}$ when $f \rightarrow 0$ (see Fig. 7). This behaviour suggests that the frequency dependence of the dielectric loss in this region can be described by the Maxwell–Wagner–Sillars (MWS) equation [16–18]:

$$\varepsilon''(\omega) = \frac{\sigma}{2\pi\varepsilon_0 f} \quad (6)$$

where σ and ε_0 are, respectively, the specific conductivity and the dielectric permittivity in vacuum. Values of the specific conductivity obtained by means of Eq. (6) are listed in the fourth column of Table 4.

Conductivity by free charges requires that the real dielectric permittivity remains constant in the region of the spectra in which Eq. (6) holds. However, as can be seen in Fig. 8, $\varepsilon' \sim f^{-a}$ for $f \rightarrow 0$ suggesting that, besides free charges, other conductivity phenomena may be involved in the electric responses at low frequencies. Moreover, the isotherms corresponding to the experimental values of $\tan \delta$ in the frequency domain present a maximum at low frequencies which is shifted to higher frequencies as the temperature of the isotherms increases. The values of both $\tan \delta$ and frequency at the peak maximum are collected for different isotherms in Tables 4 and 5. The presence of a maximum in the $\tan \delta$ peaks was explained earlier as due to an excess impedance, in addition to the MWS impedance, arising from interfacial polarization near the electrodes [19]. A theory has been developed, based on the Trukhan model [20], that assumes that the dispersion arises from both MWS effects, taking place in the bulk, and Nernst–Planck electrodynamic effects arising from interfacial polarization in the films [19,21]. According to the theory, $\tan \delta_{\max}$ is related to the Debye length κ by the following expression [21]:

$$\tan \delta_{\max} = \left(\frac{\kappa L}{8}\right)^{1/2} \quad (7)$$

where L is the thickness of the sample. Moreover, the theory predicts that the dimensionless angular frequency at the peak maximum is related to the diffusion coefficients of anions and cations, D_1 and D_2 , by the following relationship

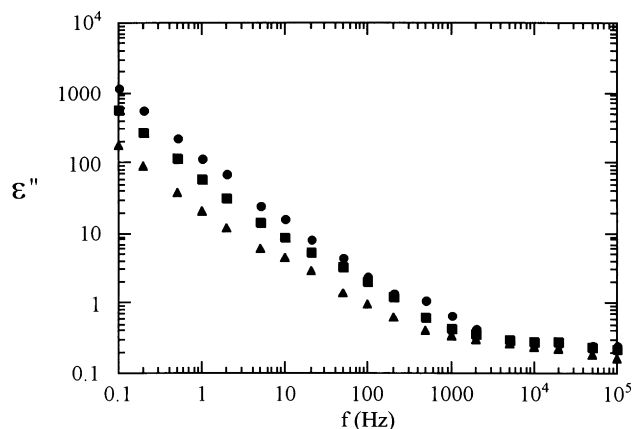


Fig. 7. The dielectric loss in the frequency domain for PDMA at high temperatures: 160°C (■); 170°C (▲); and 180°C (●).

[21]:

$$D_1 D_2 = \frac{4\pi^2 f_{\max}^2 L^4}{2(\kappa L)^3} \quad (8)$$

This equation allows the estimation of the product of the apparent diffusion coefficients of the cationic and anionic species from the data obtained in the dielectric experiments at low frequencies. By assuming $D_1 \cong D_2 \cong D$, Eq. (8) becomes

$$D = \frac{2\pi f_{\max} L^2}{[2(\kappa L)^3]^{1/2}} \quad (9)$$

The estimation of D by means of Eq. (9) involves the determination of κL from the experimental data by means of Eq. (7). The values of κL and D for PDA and PDMA, obtained by the procedure outlined above, are listed in Tables 4 and 5, respectively. The results obtained for D are of the same order of magnitude as those reported for other polymers.

Table 4

Summary of conductive and electrokinetic parameters for the α -relaxation of PDMA at different temperatures

T (°C)	f (Hz)	$\tan \delta_{\max}$	$10^8 \times \sigma$ (S m ⁻¹)	$10^{-3} \times \kappa L$	$10^{13} \times D$ (m ² s ⁻¹)	$10^2 \times c_s$ (mol m ⁻³)
160	0.7	38	2.0	11.552	2.25	1.7
170	1.3	40	5.8	12.800	3.59	3.2
180	2	60	12.5	28.800	4.08	6.2

Table 5

Summary of conductive and electrokinetic parameters for the relaxation of PDA at different temperatures

T (°C)	f (Hz)	$\tan \delta_{\max}$	10^8 (S m ⁻¹)	κL	$D \times 10^{13}$ (m ² s ⁻¹)	$c_s \times 10^2$ (mol m ⁻³)
50	0.1	35	0.39	9800	0.41	1.4
60	0.3	47	1.4	17700	0.51	4.1
70	0.5	55	3.5	24200	0.53	10.1
80	1	63	6.2	32000	0.70	13.9
90	2	72	6.7	48700	0.74	14.6

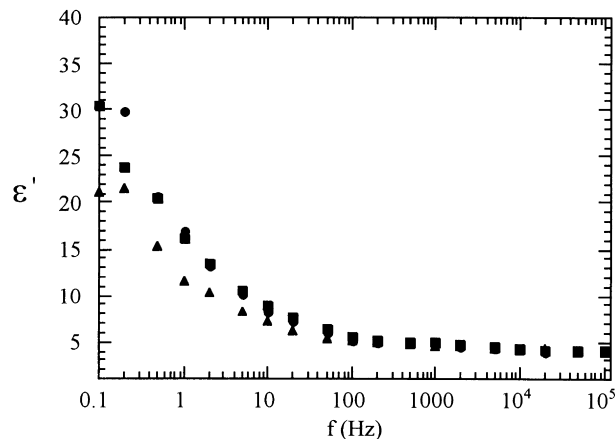


Fig. 8. Isotherms showing the real permittivity in the frequency domain for PDMA at high temperatures: 160°C (■); 170°C (▲); and 180°C (●).

3. Discussion

For comparative purposes, the mechanical and dielectric β -relaxations of PDA, PDMA, PCA, PCMA and poly(cyclohexylmethyl methacrylate) (PCMMA) are shown in Figs. 9 and 10, respectively. The relevant data concerning these absorptions, given in Table 5, suggest that the activation energy associated with the dielectric β -relaxation of each polymer is roughly 1.2–2.5 kcal mol⁻¹ below that of the mechanical relaxation. At first sight, the higher activation energy for the mechanical relaxation could be explained by assuming that the development of this relaxation involves motions of the side groups coupled with local motions of the main chain, while the dielectric relaxation arises from motions taking place only on the side groups. The fact, however, that the activation energies of the mechanical relaxation of acrylates and methacrylates are similar, in spite of the fact that local motions in the main chain of the latter polymer are severely hindered with respect to similar motions in acrylates, seems to suggest that coupling

Table 6

Relevant parameters for the subglass absorptions of poly(cyclohexyl acrylate) (PCA), poly(cyclohexyl methacrylate) (PCMA), poly(methylcyclohexyl methacrylate) (PMCMA), PDA, PDMA, poly(5-acryloxy-5-methyl-1,3-dioxacyclohexane) (PAMMD) and poly(neopentyl glycol methacrylate) (PNGMA)

Polymer	Mechanical		Dielectric			$\Delta\varepsilon$
	E_a (kcal/mol)	T_{\max} , (°C) (1 Hz)	E_a (kcal/mol)	T_{\max} , (°C) (1 Hz)	T_{\max} , (°C) (1 kHz)	
PCA	14.2	-78	11.9	-82	-25	0.20
PCMA	14.0	-74	12.0	-80	-20	0.15
PMCMA	12.5	-82	11.8	-	-30	0.11
PDA	10.8	-94	9.6	-105	-53	0.61
PDMA	10.7	-95	9.3	-106	-51	0.55
PAMMD	11.1	-74	9.6	-80	-20	1.23
PNGMA	12.6	-85	10.2	-90	-30	2.41

motions of the side groups and the main chain do not play a determinant role in the development of the mechanical subglass relaxation. On the other hand, the ostensible subglass relaxation displayed in the spectra of acrylic polymers with cyclohexyl groups in their structure disappears in the polymers resulting of substituting the cyclohexyl rings by phenyl groups.

The peak maxima of the mechanical β -relaxation of the polymers shown in Table 6 are located at temperatures 4–11°C above those corresponding to the dielectric relaxation. An important difference between the dielectric and mechanical relaxation spectra is that the intensity of the mechanical subglass relaxations only shows a weak dependence on the chemical structure, in contrast with what occurs with dielectric relaxations the intensities of which can vary in more than one order of magnitude, specifically, from 0.01 for PCMA [22] to 0.21 for poly(5-acryloxy-5-methyl-1,3-dioxacyclohexane) (PAMMD) [23].

By schematically replacing the methylene groups located at the 3- and 5-positions of the cyclohexyl groups of PCA and PCMA for two oxygen atoms, PDA and PDMA are obtained. The activation energy of the β dielectric relaxation

is similar for PDA and PDMA and the same occurs with the mechanical activation energy. However, the activation energy associated with the mechanical β -relaxation of PDA and PDMA is more than 3 kcal mol⁻¹ lower than that of PCA and PCMA, this difference being only 1.5 kcal mol⁻¹ for the dielectric β process.

The shift of nearly 20°C toward the low temperatures region of the locations of the mechanical and dielectric β -relaxations of both PDA and PDMA with respect to those of PCA and PCMA could, in principle, be attributed to the lower activation energies of the acrylic polymers with 1,3-dioxane groups in their structure. However, the location of the dielectric β -relaxation of PAMMD is located at nearly the same temperature as that of PCA in spite of the fact that the activation energy of the former polymer is similar to that of PDA. This behaviour suggests that the frequency factor in the Arrhenius equation, which represents the frequency of formation of relaxing conformations susceptible of crossing the barrier energies, is lower in PAMMD than in PDA.

The fact that the activation energy associated with the β -relaxation of PCA is similar to that determined for

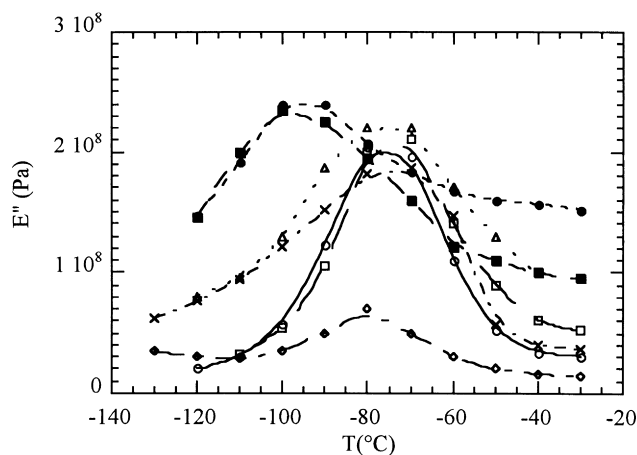


Fig. 9. Isochrones showing the temperature dependence of the mechanical β -relaxation at 1 Hz for the following polymers: poly(5-acryloxy-5-methyl-1,3-dioxacyclohexane) (Δ); poly(neopentyl glycol methacrylate) (\times); PDA (\bullet); PDMA (\blacksquare), poly(cyclohexyl acrylate) (\circ); poly(cyclohexyl methacrylate) (\square); and poly(methylcyclohexyl methacrylate) (\diamond).

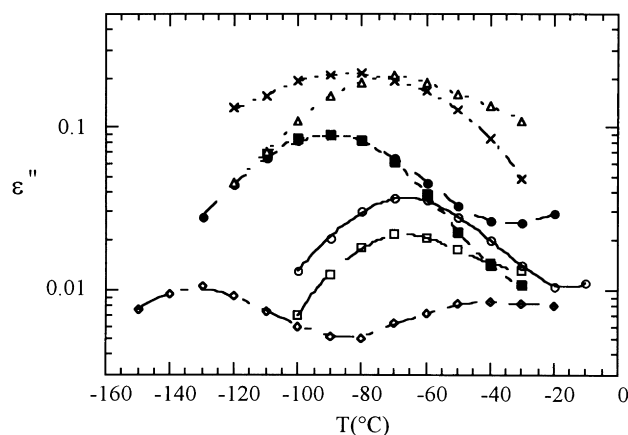


Fig. 10. Isochrones showing the temperature dependence of the dielectric β -relaxation at 10 Hz for the following polymers: poly(5-acryloxy-5-methyl-1,3-dioxacyclohexane) (Δ); poly(neopentyl glycol methacrylate) (\times); PDA (\bullet); PDMA, poly(cyclohexyl acrylate) (\circ); poly(cyclohexyl methacrylate) (\square); and poly(methylcyclohexyl methacrylate) (\diamond). The isochrone for the latter polymer corresponds to 1 kHz.

chair-to-inverse chair conformational transitions in cyclohexane by NMR spectroscopy, led Heijboer [6] to conclude that the relaxation could be caused by flipping motions of the cyclohexane ring. Accordingly, flipping motions of this kind occurring in the 1,3-dioxane rings of PDA and PDMA could also explain the mechanical and dielectric activity displayed by these polymers in the glassy state. However, PAMMD presents the β -relaxation nearly 20°C above that of PDA in spite of the fact the conformational energy involved in the flipping motions of the rings is similar in both cases. Simulation studies carried out in 2-chlorocyclohexane isobutyrate [24,25] and 5-acetoxy-5-ethyl-1,3-dioxacyclohexane [26] suggest that flipping motions in acrylic polymers with saturated cyclic and heterocyclic side groups may not play a central role in the important mechanical and dielectric activity developed by these polymers in the glassy state. It is important to note that prominent β -absorptions not only appear in the relaxation of polymers containing cycloaliphatic or dioxacycloaliphatic rings in their structures. The relaxation spectra of acrylate polymers with bulky side groups, such as poly(neopentyl glycol methacrylate) (PNGMA) [27], with structural unit $[-\text{CH}_2-\text{C}(\text{CH}_3)_2-\{\text{COOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}\}]$ also present ostensible β -relaxations. As can be seen in Table 6, the activation energies of the mechanical and dielectric subglass absorptions of PNGMA are intermediate to those of acrylate polymers with cyclohexane and 1,3-dioxane rings in their structure, and the absorptions are centred at nearly the same temperatures as those of the acrylic polymers with flexible cyclic groups.

In order to get a glimpse of the cause of the high conductivity presented by this polymer at low frequencies, the concentration of conducting species that would be required to produce the conductivity observed was calculated. For that purpose, use was made of the Nernst–Planck electrodiffusion equations following the methods described elsewhere [21]. According to these methods, the conductivity of a polymer arisen from 1:1 electrolytes embedded in a matrix is given by

$$\sigma = \frac{\varepsilon_s}{L^2} (\kappa L)^2 D \quad (10)$$

where ε_s is the static absolute dielectric permittivity. The apparent salt concentration, c_s , is related to the Debye's length by

$$\kappa^2 = \frac{2F^2}{RT\varepsilon_s} c_s \quad (11)$$

where F is the Faraday's constant. By combining Eqs. (10) and (11) we obtain

$$c_s = 4.459 \times 10^{-10} \frac{\sigma T}{D} \quad (12)$$

This equation gives c_s in mol m^{-3} when D is expressed in $\text{m}^2 \text{s}^{-1}$, σ in S m^{-1} and T in Kelvin. The values of c_s obtained at different temperatures by means of Eq. (12) for PDA and given in the last column of Table 5 lie in the

range 1.4×10^{-2} – $6.2 \times 10^{-2} \text{ mol m}^{-3}$ in the temperature interval 150–180°C. Similar results are obtained for c_s in PDMA. It is worth noting that the values obtained for the concentration of salt embedded in the polymer is of the order of that one would expect taking into account the purification steps carried out on the polymer.

4. Conclusions

The substitution of the two methylene groups in the 3- and 5-positions of the cyclohexane rings in poly(cyclohexyl acrylate) and poly(cyclohexyl methacrylate) for two oxygen atoms shifts nearly 20°C to lower temperatures the locations of the mechanical and dielectric absorptions of the resulting polymers, at a given frequency. However, the location of the glass–rubber relaxations is not altered by the substitutions.

Comparison of the dielectric and relaxation spectra of acrylic and methacrylic polymers with cyclohexane and dioxane rings in their structures shows that the hindering effect of the methyl groups in the local motions of the main chain hardly affects the intensity and location of the subglass relaxations. However, this effect is important in the location of the α -relaxation.

Finally, electrodiffusion Nernst–Planck methods allow the semiquantitative determination of salts embedded in the polymeric matrices that cause the high conductivity observed in the dielectric relaxation spectra of these polymers.

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