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Dielectric Relaxations in Polymers Containing Dioxacyclohexane Rings by Thermostimulated Depolarization Currents

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Summary: The dielectric activity of poly{5-[(methacryloxy)methyl]-5-ethyl-1,3-dioxacyclohexane} (PMAMED) and poly[(5-methacryloxy)-1,3-dioxacyclohexane] (PMAD) in the glassy region and in the glass-rubber transition is investigated by using global and partial thermostimulated discharge current (TSDC) techniques. The global TSDC curve for each polymer displays an ostensible β absorption in the glassy region followed in increasing order of temperature for a prominent α glass rubber relaxation. Partial depolarisation curves show in detail the regions of the glassy state in which more dielectric activity occurs. The TSDC curves for PMAMED are compared with those of its acrylate homologous, poly{5-[(acryloxy)methyl]-5-ethyl-1,3-dioxacyclohexane} (PAMED), finding that the methyl group in the former polymer only hinders long range micro-Brownian motions in the chains, thus shifting the glass-rubber relaxation to higher temperatures, without affecting in a significant way molecular motions in the glassy region. Small changes in the neighbourhood of the 1,3-dioxacyclohexane ring, such as suppression of a methylene group or replacement of the equatorial hydrogen in position 2 of the ring for a phenyl group, depresses the dielectric activity and shifts the β absorptions to lower temperatures. The interconversion between TSDC and a.c. dielectric results in the glassy region is discussed.

Keywords: Relaxation, Dielectric properties, structure-property relations, dioxacyclohexane rings, Thermostimulated Depolarization Currents.

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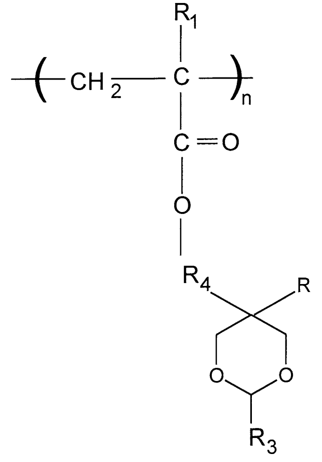
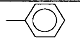
Introduction

Like the plots depicting the variation of the loss relaxation modulus of amorphous polymers with temperature, the isochrones representing the temperature dependence of the dielectric loss exhibit a cascade of subglass relaxations that reveal different modes of molecular mobility.[1] In particular, secondary relaxations in polymers with flexible side groups are attributed to motions taking place in the side chains. The mechanical and dielectric relaxation spectra of acrylic polymers with pendant flexible rings in their structure present ostensible subglass absorptions which traditionally have been attributed to chair-to-inverse chair conformational transitions in the rings.[2] The responses of this kind of polymers to perturbation fields are influenced not only by the chemical nature of the moieties linking the rings to the main chain but also by the substituents of the hydrogen atoms of the rings. In order to gain a better understanding on the influence of the fine structure of polymers on the relaxations taking place in these materials in the glassy state, it is advisable to carry out relaxation studies at the lowest available frequencies where overlapping of the different relaxational peaks decreases.

We present in this work the dielectric behaviour of acrylate polymers with 1,3-dioxane rings in their structure, whose structural characteristics slightly differ. The relaxation responses were studied at equivalent frequencies below 10^{-2} Hz, using the thermostimulated depolarization currents (TSDC) technique.[3] The TSDC discharge curves for poly{5-[(methacryloxy)methyl]-5-ethyl-1,3-dioxacyclohexane} (PMAMED) and poly(5-methacryloxy)-1,3-dioxacyclohexane (PMAD) were measured and compared with those reported earlier for poly{5-[(acryloxy)methyl]-5-ethyl-1,3-dioxacyclohexane} (PAMED) and poly{cis/trans-5-[(acryloxy)methyl]-2-phenyl-5-ethyl-1,3-dioxacyclohexane} (PAEDP).[4] Schematic representations of the repeating units of these polymers are given in Scheme I.

		R_1	**R_2**	**R_3**	**R_4**
	**PAMED**	$-H$	$-C_2H_5$	$-H$	$-CH_2-$
	PAEDP	$-H$	$-C_2H_5$		$-CH_2-$
	PMAMED	$-CH_3$	$-C_2H_5$	$-H$	$-CH_2-$
	PMAD	$-CH_3$	$-H$	$-H$	-

Scheme I. Sketch of the polymers used

Experimental Part

The monomers, 5-methacryloxymethyl-5-ethyl-1,3dioxacyclohexane and 5-methacryloxy-1,3-dioxacyclohexane, were synthesized by using the procedure described eleswhere.[4,7] Poly(5-methacryloxymethyl-5-ethyl-1,3dioxacyclohexane) (PMAMED) and poly(5-methacryloxymethyl-5-ethyl-1,3dioxacyclohexane) (PMAD) were obtained, respectively, by radical polymerization of 5-methacryloxymethyl-5-ethyl-1,3dioxacyclohexane and 5-methacryloxy-1,3-dioxacyclohexane, using AIBN as initiator. The polymerisation, carried out at 60° C in benzene solution, was stopped when a conversion of about 10% was reached. The polymers were precipitated with methanol, dissolved in benzene, precipitated again with methanol, and further freeze-dried from benzene solutions. The weight-average molecular weights of PMAMED and PMAD, determined by GPC, were 145,000 and 132,000, respectively.

The glass transition temperatures of the polymers were obtained with a Perkin Elmer DSC7 calorimeter at a heating rate of 10° C/min. The Tg's, taken as the temperatures at which the endotherms in the glassy region depart from the base line, were 125° C and 115° C for PMAMED and PMAD, respectively. The values of T_g for PAMED and PDAEP are, respectively, 36° C and 55° C.

Thermostimulated Depolarization Current measurements (TSDC) were performed with a TSC-RMA Termhold apparatus on polarized pills of the polymers. The global TSDC curves were obtained by poling the pills for 10 min. at temperatures close to the respective calorimetric glass transition temperatures of the polymers, under a potential of 500 V/mm. The poled samples were quenched at –150°C, the electric field removed, and the electrodes short-circuited and kept at the quenching temperature for 5 min to eliminate spurious charges. Then the samples were warmed at a constant heating rate of 7°C/min and the temperature dependence of the depolarization current density $(J = dP/dT)$ was measured. Partial depolarization curves were obtained by using windows of 5°C.

Theory

The linear theory of dielectrics predicts that under a static electric field **E**, the polarization at equilibrium of a sample of cross-sectional area A is given by

$$\mathbf{P} = \varepsilon_0 \Delta\varepsilon \mathbf{E} \qquad (1)$$

where $\varepsilon_0 (= 8.854 pF/m)$ is the vacuum permittivity and $\Delta\varepsilon$ is the strength of the relaxation at the poling temperature T_p. Let us assume that the poled sample is cooled at a temperature such that the relaxation times associated with dipolar mechanisms are much larger than the time scale of the experiment. If the sample is shortcircuited and subsequently heated at a constant rate $h(= dT/d$, the discharge current is related to the polarization by

$$\mathbf{P} = \frac{1}{A}\int_{t_0}^{\infty} \mathbf{I}dt = \frac{1}{Ah} {}_{T_0}^{T_f} \; d \qquad (2)$$

where t_0 is the starting time of the depolarization, $\mathbf{I}$ is the current density, and T_0 and T_f are respectively the initial and final temperatures of the interval at which the depolarization takes place. From eqs.(1) and (2) the relaxation strength is obtained as

$$\Delta\varepsilon(T_P) = \frac{1}{\varepsilon_0 E A h}\int_{T_0}^{T_f} I dT \tag{3}$$

If the electric field vanishes, the depolarization process is described by the following simple differential equation

$$\frac{dP(t)}{dt} = -\frac{P(t)}{\tau(T)} \tag{4}$$

where $\tau(T)$ is the relaxation time at temperature T. Integration of eq. (4) gives

$$P(T) = P_0 \exp\left[-\frac{1}{h}\int_{T_0}^{T}\frac{dT}{\tau(T)}\right] \tag{5}$$

where P_0 is the equilibrium polarization before starting the process and $h(=dT/dt)$ is the heating rate. By differentiating eq. (5), the current maximum is found to occur at

$$\frac{d}{dT}(\tau(T)) = -h^{-1} \tag{6}$$

For systems obeying Arrhenius behaviour, the temperature dependence of the relaxation time is given by

$$\tau = \tau_0 \exp E_a / RT \tag{7}$$

where E_a and R are respectively the activation energy and the gas constant. Eqs. (6) and (7), lead to the following expression for the frequency at the peak maximum

$$f_m = \frac{1}{\tau(T_{\max})} = \frac{hE}{2\pi R T_{\max}^2} \tag{8}$$

where T_m is the temperature at the peak maximum. From the experimental data available for most secondary relaxations in polymers, eq. 8 predicts that f_m lies in the vicinity of $10^{-3} Hz$.

Results

The global TSDC curves for PMAD and PMAMED are plotted as a function of temperature in Figure 1. In the same figure, and for comparison purposes, the TSDC curves for PAMED and PAEDP are also shown.

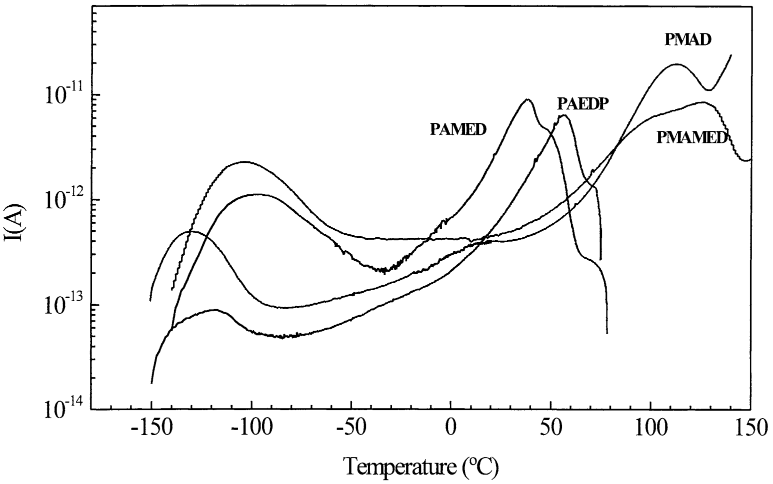


Figure 1. Global TSDC thermograms for PMAD, PMAMED, PAMED and PAEDP.

The curves exhibit well-developed *β* absorptions in the glassy region followed by prominent α relaxations associated with the glass transition. The intensities of the subglass absorptions follow the tends PMAMED > PAMED > PMAD >> PDAEP and the position of the β peaks of the two latter polymers in the spectra are shifted to lower temperatures with respect to that of the other two. The maximum of the α peaks are located at 35°C, 60° C, 110° C and 115-135° C for PAMED, PDAEP, PMAD and PMAMED, respectively. These values nearly coincide with the calorimetric glass transition temperatures of the polymers. In the high temperature side of the peak of PMAMED a shoulder arisen from space charges appears. The position and intensity of the α and β peaks are in qualitative agreement with those observed in conventional dielectric a.c. experiments.[7]

More detailed information about subglass dielectric processes can be obtained by partial depolarization (thermal windowing, TW) of poling samples. Typical curves for PMAMED are shown in Figure 2.

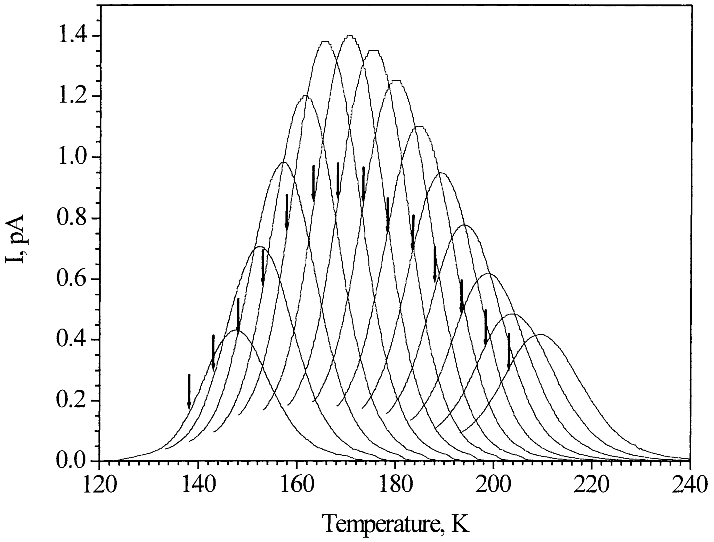


Figure 2. Partial depolarization curves for PMAMED in the glassy state. Arrows represent the polarization temperatures.

The temperature dependence of the relaxation time associated with each elementary peak was obtained by using the following equation

$$\tau(T) = \frac{\int_{T_0}^{T} I(T)dT}{hI(T)} \tag{9}$$

where T_0 is the lower temperature of the elementary peak. It is assumed that the relaxation times obtained from eq. (9) for each elementary peak, follow Arrhenius behaviour, at least in the central part of the peak. Accordingly, the central part of the Arrhenius plots was used to calculate the pre-exponential factor τ_0 and the activation energy E_a of each peak. The values of these magnitudes for PMAD and PMAMED, plotted as a function of the poling temperature in figure 3, show that the pre-exponential factor decreases as T_P increases, while the activation energy augments as the poling temperature goes up.

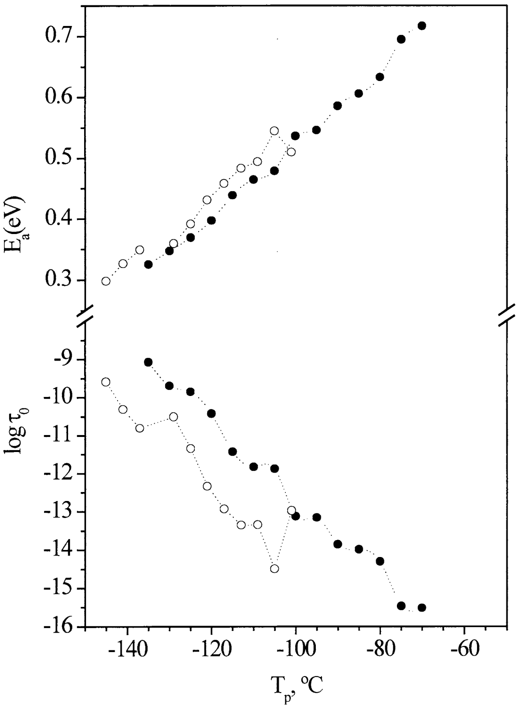


Figure 3. Activation energies and pre-exponential factor vs. polarization temperatures corresponding to PMAD (o) and PMAMED (•)

The relaxation strength of the elementary peaks obtained from eq. (3) increases as the poling temperature increases until a maximum is reached; then $\Delta\varepsilon$ falls as T_P increases; (Figure 4).

These tendencies are similar to those observed for PAMED and PAEDP.[4]

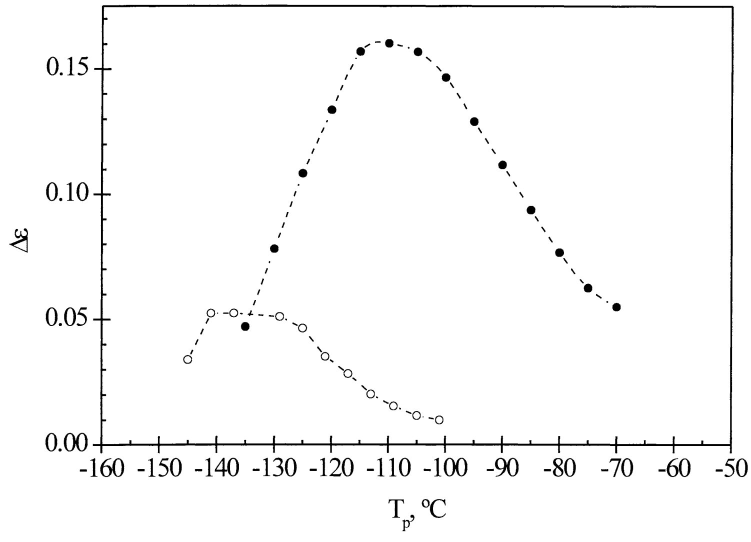


Figure 4. Relaxation strength of each partial depolarization curve vs. polarization temperatures for PMAD (o) and PMAMED (•)

TSD Currents and Dielectric a.c. measurements

Comparison between TSDC and conventional a.c. dielectric measurements can be helpful to elucidate the molecular origin of the subglass peaks. However, it should be taken into account that the two techniques are different. TSDC is basically a non-isothermal method, while conventional a.c. experiments are usually done either at constant frequency or constant temperature. The Fourier transform of a Curie-von Schweidler exponential[3, 9], like $I = I_0 t^{-n}$, allows to relate the dielectric loss with the depolarization current by means of the following expression

$$\varepsilon''(T,\omega)=\frac{1.475kT^2I(T)}{\varepsilon_0E_ahE} \tag{10}$$

with $\omega=\dfrac{\pi}{5t}$ and whose frequency at the maximum is given by eq. (8).

Partial depolarization data obtained from eqs. (3) and (9) suggest an alternative method to obtain the real and imaginary parts of the complex relative permittivity.[10,11] The pertinent equations are

$$\begin{aligned}\varepsilon' &= \varepsilon_\infty+\sum_{i=1}^{n}\frac{\Delta\varepsilon_i}{1+\omega^2\tau_i^2(T)}\\ \varepsilon'' &= \sum_{i=1}^{n}\frac{\omega\tau_i(T)}{1+\omega^2\tau_i^2(T)}\Delta\varepsilon_i\end{aligned} \tag{11}$$

where ε_∞ is the unrelaxed relative permittivity taken from a.c. data, and $\tau_i(T)$ is the relaxation time associated with the elementary peak at temperature T.

Illustrative curves calculated from eqs. (11) for PMAMED are depicted in Figure 5.

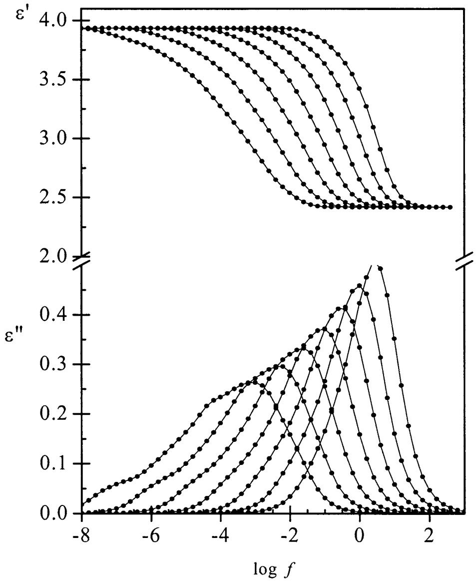


Figure 5. Dielectric permittivity and loss in the frequency domain for PMAMED at the temperatures indicated (-100°, -90°, -80°,-70°, -60°, -50°C).

The curves show a well-defined peak. Low temperature isotherms exhibit structure, which means that several single processes in this zone overlap. In Figure 6 the experimental a.c. loss data at 1Hz. are compared with those calculated from eqs. (10) and (11). Significant shifts to low and high temperatures with respect to the a.c. isochrone at the same frequency are observed, respectively, for the absorptions obtained from eqs. (10) and (11).

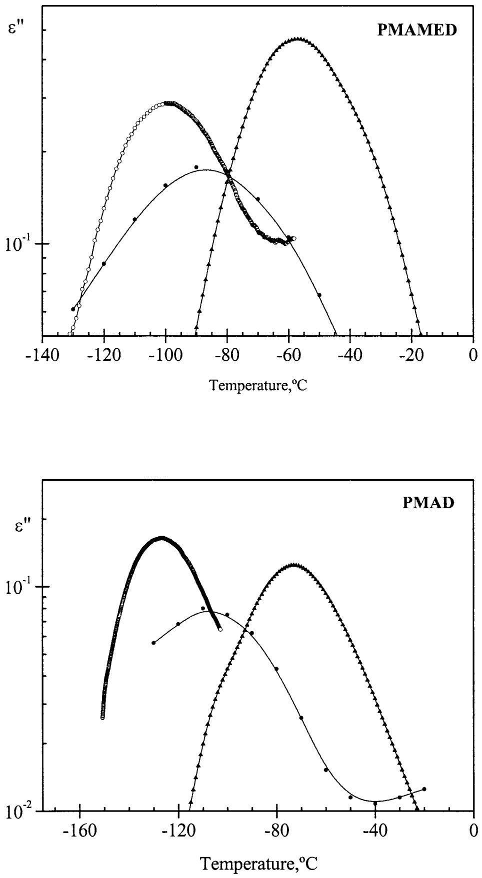


Figure 6. Imaginary parts of the complex permittivity obtained by DEA measurements (,), TSDC experiments employing eq. (10) with frequency at the maximum given by eq. (8), (–) and TW experiments employing eq. (11) (7) for the PMAD and PMAMED.

Discussion

The relaxation spectra of acrylate polymers containing cyclohexyl groups in their structure exhibit strong subglass activity centred in the vicinity of –80°C at 1 Hz.[7] Moreover, the activation energy of the relaxation is about 10-11 kcal·mol^{-1}, a value similar to that determined by NMR spectroscopy for chair-to-inverse-chair conformational transitions in cyclohexane. This fact led to postulate[2] that flipping motions in the cyclohexyl groups are responsible for the prominent subglass relaxations exhibited for these polymers. As the results of the present work indicate, polymers containing 1,3-dioxacyclohexane rings also exhibit ostensible subglass absorptions which, in principle, could be attributed to chair-to-inverse-chair conformational transitions in the oxycycloaliphatic rings. Earlier results show that the barriers associated with the conformational transitions in the dioxane rings of PAMED and PDAEP are similar.[12,13] This fact suggests that the well-developed subglass absorptions in these polymers not only arise from chair-to-inverse-chair conformational transitions, but also from motions of the side chains, possibly coupled with local motions of the main chain. Actually, the presence of the phenyl group in the 2,3-dioxacyclohexane ring of PDAEP hinders the motions about the CH_2-O bonds in this polymer. Therefore the low intensity of the β absorption of PDAEP could be attributed to the hindrance of motions about the bonds indicated. It is important to notice that the absence of a methylene group between the ester group and the dioxane ring depresses the subglass peak in PMAD, shifting it to lower temperatures. This behaviour also suggests that the diminishion of the flexibility of the side groups decreases the intensity of the β relaxation and therefore motions about the bonds of the side groups presumably are responsible for the dielectric activity observed in polymers with flexible rings in the side chains.

The α-methyl group hardly affects the intensity and location of the β absorption of homologous polyacrylates and poly(methacrylates) as a comparison of the global TSDC curves of PAMED and PMAMED show. The only effect of this group is to shift the glass-rubber relaxation to higher temperature. However, the bulkiness of the side groups increases the temperature at which the glass rubber relaxation appears, as a comparison of the glass transition temperatures of PMAD and PMAMED with that of poly(methyl methacrylate), 104° C, suggests.

Notice that the glass transition temperatures of PAMED and PDAEP are also higher than that of poly(methyl acrylate), 13 ° C. It seems therefore that the substituted dioxane rings hinder the micro-Brownian motions of the chains, shifting the location of the global α TSDC peaks to higher temperatures.

As can be seen in Figure 6, the agreement between the a.c. isochrones and those calculated from TSDC data is only qualitative. The absorptions in the calculated spectra have higher intensity and are narrower than those measured by a.c. Moreover, important frequency shifts in the position of the peaks are observed. The strong discrepancies between the location and intensity of the subglass a.c isochrones with those obtained from eq 11 mainly arise from the fact that the relaxation times associated with the partial thermal stimulated discharge curves do not follow Arrhenius behaviour in the whole range of temperatures underlying the elementary peaks. It occurs as whether different mechanisms were involved in partial thermal depolarisations. The procedure used in this work to calculate relaxation times from partial depolarisation curves seems to overestimate the values of these quantities and, as a result, the relaxation curves calculated by means of eqs(11) are shifted to higher temperatures.

Conclusions

This study shows that small differences in the chemical structure of the lateral chain produces significant incidences in the short time response for 1,3-dioxacyclohexane substituted polymers. The suppression of a methylene group linking the rings to the ester residue depresses the dielectric activity. The same occurs if the equatorial hydrogen in position 2 in he ring is replaced for a phenyl group. The ostensible subglass activity exhibited by these polymers arises from more complex motions than simple chair-to-inverse-chair conformational transitions.

The bulkiness of the ester residues hinders micro-Brownian motions of the chain thus shifting the glass-rubber relaxation to higher temperatures at a given frequency. It is worthy to point out, however, that the effect of the bulkiness groups in main chain motions is much less pronounced than that of the methyl group attacked to the main chain in polymethacrylates.

Global and partial TSDC curves give a good account of the intervals of temperature in which dielectric activity occurs. However, the interconversion of TSDC curves to dielectric a.c. results is only valid at the qualitative level, as a result of the structure that seems to display the elementary TSDC peaks obtained by partial depolarisation.

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