Dielectric relaxation behaviour of poly(mono-n-alkyl itaconates)

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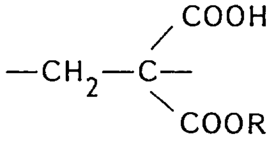
Dielectric relaxation measurements on a family of poly(mono-n-alkyl itaconates) have been performed. Two relaxation peaks have been observed within the temperature range studied. The first one at lower temperature (153 K at 1 kHz), which we call the γ peak and have attributed to motion in the lateral chains involving methylene sequences, depends on the length of the side-chain. The second relaxation labelled β (233 K at 1 kHz) is related mainly to motion of the lateral group. A peculiar behaviour has been observed in the case of poly(mono-tetradecyl itaconate). The results have been discussed in terms of the different possible motions of the side-chains.

(Keywords: dielectric relaxation; poly(mono-n-alkyl itaconates); films)

INTRODUCTION

Polymers derived from itaconic acid are of interest owing to the possibility of preparing mono- and diesters with different kinds of side-chains. Poly(mono-alkyl itaconates) may be considered as typical comb-like polymers[1]. Even though they have been widely studied in regard to their preparation and solution properties[1–4], studies dealing with their mechanical dynamical behaviour are scarce[5,6]. This is particularly so in the case of poly(mono-alkyl itaconates), owing to the fragility of the polymers in the bulk state, and in all cases non-absolute results have been reported.

The aim of this work is a systematic study of the dielectric relaxation for a family of poly(mono-alkyl itaconates) (PMAI), in order to obtain information about the effect of the side-chain structure of the polymer on the dielectric relaxation and to compare the results with those of poly(acrylic acid) derivatives previously reported[7,8]. The structure of the PMAI is:



$$-CH_2-\overset{\diagup COOH}{\underset{\diagdown COOR}{C}}-$$

$$R = -CH_2-(CH_2)_n-CH_3$$

where $n = 6$, 8, 10 and 12 (as can be seen in *Table 1*).

EXPERIMENTAL

Monomer and polymer preparation

Monomers were prepared by esterification of itaconic acid with the corresponding alcohol in the presence of octyl chloride, to ensure slightly acidic conditions, according to the method previously reported[2,9].

The reaction product was crystallized from ether, and the procedure was repeated at least twice to ensure total elimination of unreacted alcohol. The purity was confirmed by ^1H n.m.r. and i.r. spectroscopy.

The polymer was prepared in bulk using azobisisobutyronitrile (AIBN) (0.3 mol%) as initiator, under N_2 atmosphere. Polymerization time was 4 h and conversion of monomer to polymer was 75%.

The polymer samples were dissolved in about the same weight of chloroform/ethanol mixture (1:1 by vol) and then precipitated in methanol, repeating the same procedure for the total elimination of unreacted monomer. The polymer was vacuum dried and weighed.

The polymer was fractioned by standard precipitation procedures. Fractions with polydispersity indices of 1.25 and similar molecular weights ($M_w \simeq 1 \times 10^5$), determined by light scattering, were chosen for the present study.

Measurements

Dielectric relaxation measurements were performed on films prepared by evaporation from a polymer solution in tetrahydrofuran. The solution was deposited over metallic discs, which act as electrodes, and dried in vacuum at 313 K for several weeks. The thickness of the formed films is about 0.3–0.4 mm.

Table 1 Molecular characteristics and names of samples

Code	*n*	Name
PMOI	6	Poly(mono-octyl itaconate)
PMDI	8	Poly(mono-decyl itaconate)
PMDoI	10	Poly(mono-dodecyl itaconate)
PMTDI	12	Poly(mono-tetradecyl itaconate)

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High-frequency dielectric measurements were carried out by means of a Genrad 1620 capacitance bridge between 133 and 343 K. The measurements were determined in the frequency range 0.1 to 10^2 kHz and a three-terminal cell was used.

RESULTS AND DISCUSSION

The real part of the complex permittivity (ε') and the loss tangent ($\tan\delta$) have been calculated for PMOI, PMDI, PMDoI and PMTDI and are shown in *Figure 1*. In this figure in every case two well defined relaxation zones can be observed. The first is at about 153 K with a small intensity, and is labelled the γ relaxation. The other is at over 233 K, with an intensity, in terms of $\tan\delta$, ten times higher than the former, and is labelled the β relaxation. The β relaxation broadens progressively when the frequency increases, and in the particular case of PMTDI, a splitting into two peaks can be found (*Figure 1d*). Let us analyse each one separately.

γ relaxation

The dielectric γ relaxation for these polymers agrees well with the corresponding mechanical relaxation reported by Cowie *et al.*[10] for poly(monoesters) derived from itaconic acid, labelled by these authors as ε. This type of relaxation has also been observed in poly(n-alkyl methacrylates)[7], by dynamic mechanical methods. A similar relaxation has been observed by Mikhailov and Borisova[11] in a series of poly(chloroalkyl methacrylates) and by Kawamura *et al.*[8] in a series of poly(alkyl methacrylates) by dielectric methods. These findings could be explained in terms of motions of sequences of $-CH_2-$ in the lateral chain with an additional contribution of the ester group in the case of the dielectric relaxation.

In order to characterize this relaxation in a more detailed form, we have analysed the dielectric absorption (ε'') against temperature in this relaxation zone at different frequencies. *Figure 2* illustrates these results. From this figure the activation energy (E_a) has been calculated by means of a typical Arrhenius equation for the dependence of $\ln f$ vs. $1/T$.

Table 2 collects the activation energy values for the polymers studied and the corresponding temperatures for the maxima in ε''. From this table we can observe that the activation energy and the temperature increase when the length of the side-chain increases. This behaviour could be explained in terms of a more complicated motion of the segment when the lateral chain lengthens, giving rise to an increase of the barrier opposed to that motion.

According to Wada *et al.*[12] the intensity of the dielectric relaxation is given by:

$$\varepsilon = \frac{4\pi N(\Delta\mu)^2}{3RT}\left(\frac{\varepsilon_\infty + 2}{3}\right)^2\left(\frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty}\right)\frac{K}{(1+K)^2} \qquad (1)$$

where N is the molar number of the units that participate in the relaxation, $\Delta\mu$ is the change of the dipole moment vector in vacuum induced by the transition, R is the gas constant, and K is the equilibrium constant of the transition, being related to the energy difference of the two states (ΔG) by:

$$K = \exp(-\Delta G/RT) \qquad (2)$$

A small ΔG value implies a large value of the intensity of the relaxation $\Delta\varepsilon$ according to equation (2), while the activation energy E_a is also related to the height of the barrier between the two states where the transition takes place.

An accurate ΔG value should be calculated from a conformational analysis. However for $\Delta G > 4$ kJ mol^{-1}, the K value (equation (2)) at 150 K is small relative to unity and ΔG should be calculated by equation (2), by means of a plot of $\ln(T\Delta\varepsilon)$ vs. $1/T$. *Table 3* summarizes the calculated $\Delta\varepsilon$ values in two ways, one from a plot of ε'' vs. ε' (Cole–Cole plot) and the second a Fuoss–Kirkwood[13] plot for ε'' according to the equation:

$$\begin{aligned} &\varepsilon'' = \varepsilon''_{\max} \operatorname{sech} mx \\ &x = \ln(\omega_{\max}/\omega) = (E_a/R)(T^{-1} - T_m^{-1}) \qquad (3) \\ &\Delta\varepsilon = 2\varepsilon''_{\max}/m \end{aligned}$$

where m is a parameter that reflects the broadening of the relaxation, for a Debye process controlled by only one relaxation time $m = 1$, while m varies between 0.15 and 0.30 for secondary relaxation[14]. The ΔG values were estimated by the method mentioned above and using the data collected in *Table 3*.

The values found for ΔG lie between 2.5 and 4 kJ mol^{-1} but there is no clear relationship between ΔG and the length of the lateral chain. The errors induced by this approximation are no bigger than 10%.

In *Table 3* we can also observe that the values of the m parameter decrease as the length of the lateral chain increases, which indicates a more complicated motion, according to the results previously reported by Wada[12].

We can explain our results in terms of several possibilities. First, polymers with a long side-chain containing sequences of the type C–C–C–C or O–C–C–C exhibit typical γ relaxation. The second possibility is to attribute the relaxation to a crankshaft-type motion involving from three to five bonds, as has been reported by Boyd[15]. In every case from *Table 2* we can observe that the strength of the relaxation is close to that found by Kawamura *et al.*[8], who give a value of $\Delta\varepsilon = 0.042$. By comparing our results with those of Kawamura[8], we can assume that small variations of the angles involving the ester group are enough to give rise to a small γ relaxation peak.

β relaxation

This relaxation is observed in all the polymers studied, and this process is more prominent than the γ relaxation. PMOI and PMDI show β relaxation at about 233 K (1 kHz) and a broadening is found as the frequency increases. In PMDoI and PMTDI, the β relaxation is practically split into two peaks, especially at higher frequencies.

Table 4 summarizes the activation energy for the polymers studied, but for PMTDI it was not possible to calculate E_a owing to the slope of the curve. In order to characterize the broadening of the peak, the m parameter was calculated (equation (3)) by the procedure mentioned before.

The results are also shown in *Table 4*. According to these results the activation energy of the process is almost the same for all the polymers in which the alkyloxycarbonyl group is directly linked to the main chain.

It is very well known[16,17] that the relaxation in these types of polymers with the activation energy shown in

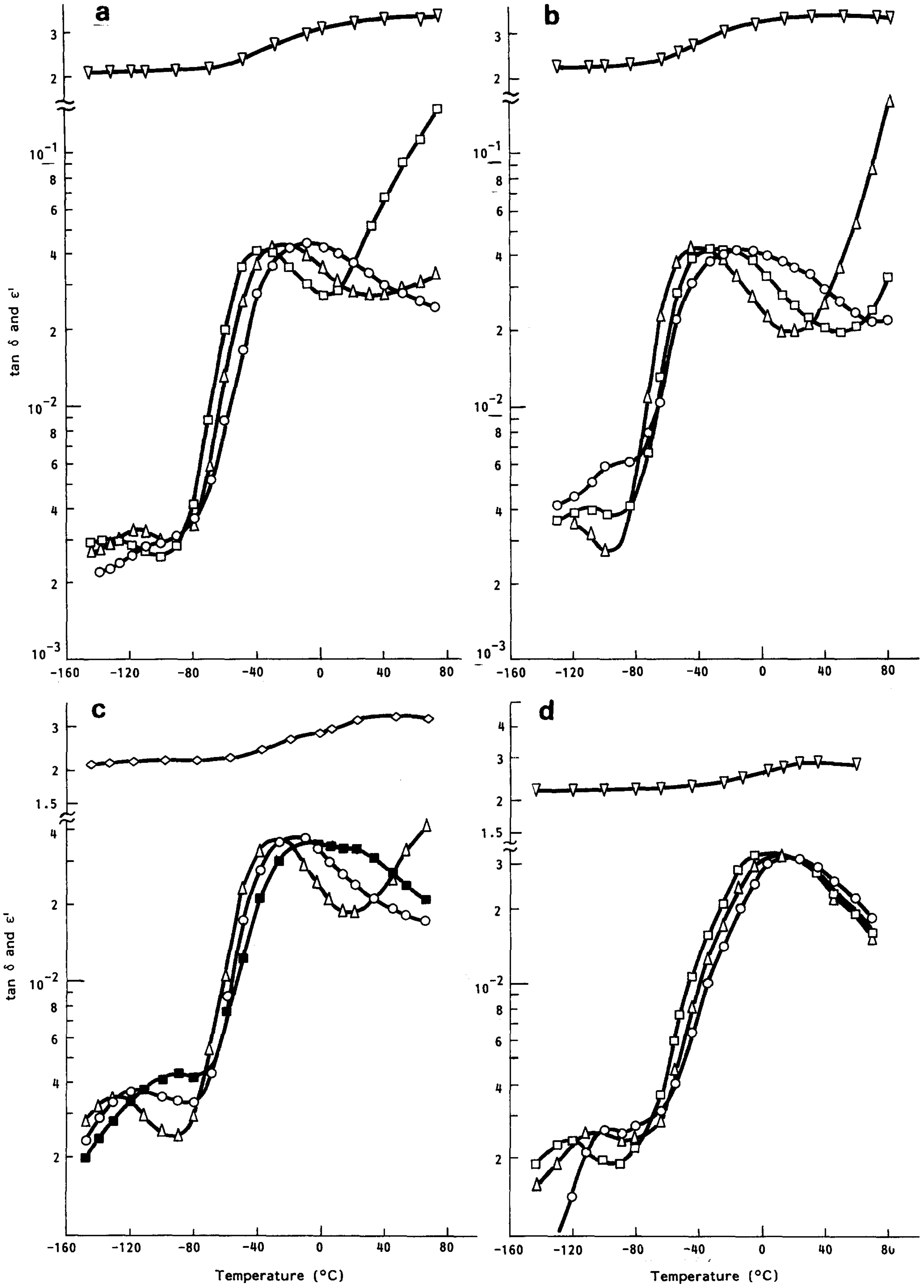

Figure 1 The real part of the complex permittivity (ε') at a frequency of 10 kHz and the loss tangent (tan δ) *versus* temperature calculated for: (a) PMOI at frequencies of 1 kHz (□), 10 kHz (△) and 100 kHz (○); (b) PMDI at frequencies of 1 kHz (△), 10 kHz and 100 kHz (○); (c) PMDoI at frequencies of 1 kHz (△), 10 kHz (○) and 100 kHz (■); (d) PMTDI at frequencies of 1 kHz (□), 10 kHz (△) and 100 kHz (○)

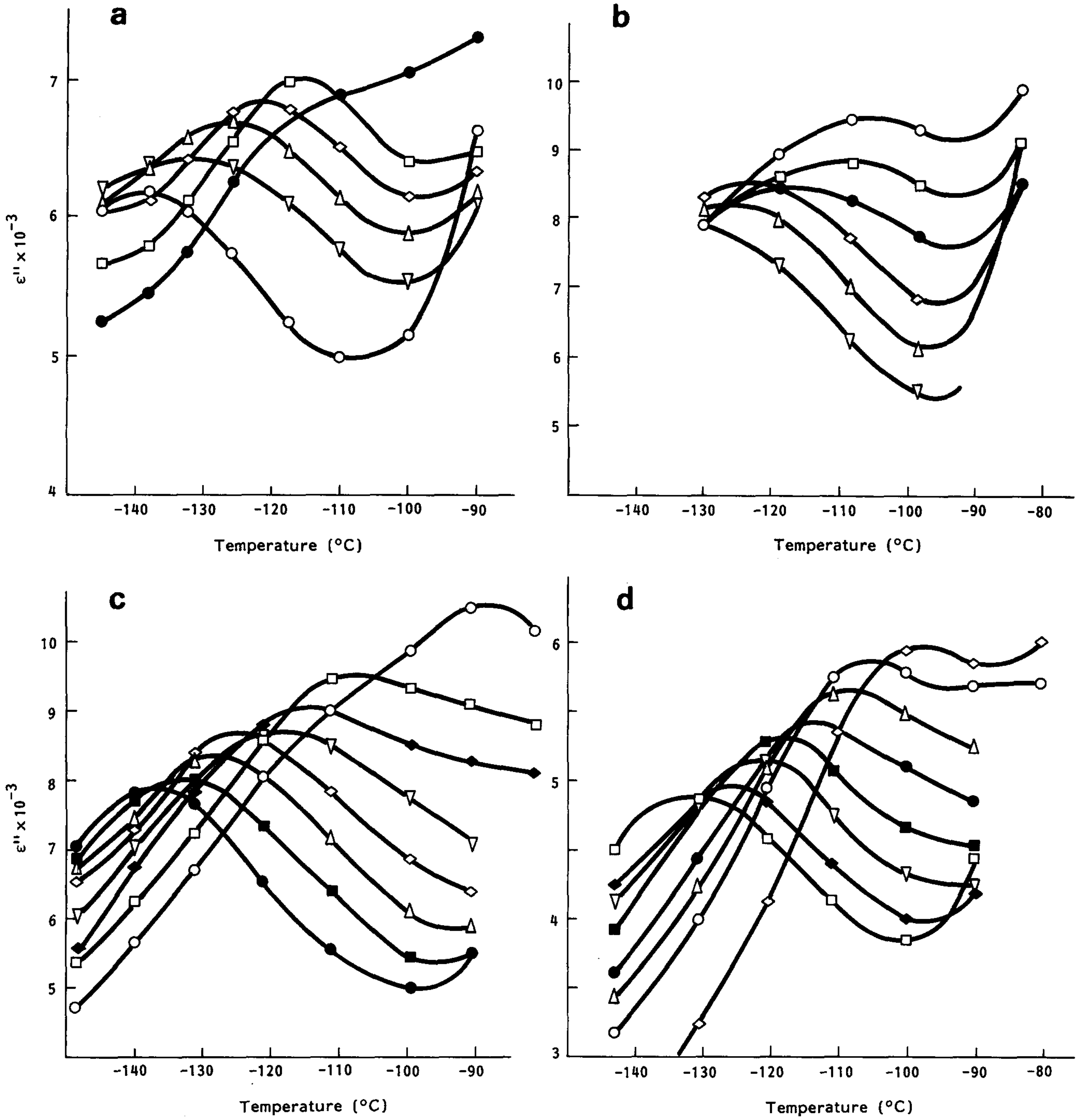

Figure 2 The loss permittivity ε'' *versus* temperature calculated for: (a) PMOI at freqencies of 0.5 kHz (○), 1 kHz (▽), 2 kHz (△), 5 kHz (◇), 10 kHz (□) and 20 kHz (●); (b) PMDI at frequencies of 0.5 kHz (▽), 1 kHz (△), 2 kHz (◇), 5 kHz (●), 10 kHz (□) and 20 kHz (○); (c) PMDoI at frequencies of 0.2 kHz (●), 0.5 kHz (■), 1 kHz (△), 2 kHz (◇), 5 kHz (▽), 10 kHz (◆), 20 kHz (□) and 50 kHz (○); (d) PMTDI at frequencies of 0.2 kHz (□), 0.5 kHz (◆), 1 kHz (▽), 2 kHz (■), 5 kHz (●), 10 kHz (△), 20 kHz (○) and 50 kHz (◇)

Table 2 Dielectric characterization of γ relaxation

Sample	Activation energy (kcal mol^{-1})	T (K) (ε''_{max} at 1 kHz)
PMOI	5.8	140
PMDI	6.0	144
PMDoI	6.8	146
PMTDI	7.4	151

Table 4 can be attributed to partial rotation of the carboxyalkyl group around the main chain. However, poly(itaconates) have two –COO– groups (one acid and one ester), and therefore it is possible to think that the broadening of the peak could be due to an overlapping of two independent rotations of each –COO– group. According to these results, both relaxations would be similar to the mechanical relaxations observed by Cowie *et al.*[10] (and labelled by them as δ and γ) at approximately 200 and 250 K.

In the case of the poly(itaconates) studied in this work, the overlapping of both phenomena could be due to the fact that higher frequencies have been used than in the dynamic mechanical methods. This may be the reason for the observed diminishing of m due to a large broadening of the curve. Then the activation energy of the first relaxation should correspond to the COOH group, and the second to the –CH_2–COOR group.

Table 3 Dielectric analysis of γ relaxation

		Fuoss–Kirkwood				Cole–Cole			
Sample	T (K)	m	$\Delta\varepsilon$	$\ln(T\Delta\varepsilon)$	G (kJ mol^{-1})	ε_0	ε_∞	$\ln(T\Delta\varepsilon)$	G kJ mol^{-1})
PMOI	135.0	–	–	–	2.72	2.134	2.095	1.661	3.47
	140.5	0.280	0.046	1.866		2.138	2.096	1.775	
	147.0	0.290	0.048	1.954		2.143	2.097	1.911	
	155.8	0.270	0.052	2.092		2.149	2.098	2.073	
	163.0	–	–	–		2.154	2.099	2.193	
PMDI	143.0	0.321	0.052	2.006	2.42	2.234	2.184	1.967	2.63
	154.0	0.309	0.052	2.137		2.242	2.188	2.118	
	164.5	0.298	0.059	2.273		2.250	2.192	2.256	
PMDoI	124.5	–	–	–	2.72	2.309	2.247	2.044	2.51
	133.0	–	–	–		2.312	2.249	2.126	
	142.0	0.243	0.069	2.282		2.320	2.251	2.282	
	152.0	0.234	0.076	2.447		2.327	2.252	2.434	
	162.0	0.238	0.080	2.562		2.335	2.253	2.587	
PMTDI	130.0	–	–	–	3.97	2.213	2.171	1.697	2.63
	142.5	–	–	–		2.216	2.173	1.813	
	152.5	0.230	0.043	1.813		2.221	2.173	1.949	
	162.0	0.227	0.047	1.970		2.227	2.172	2.111	
	173.0	0.203	0.057	2.218		2.233	2.171	2.306	

Table 4 Dielectric analysis of β relaxation

	PMOI	PMDI	PMDoI
Fuoss–Kirkwood parameter, m			
$f=200$ Hz	0.17 (9)	0.21 (9)	0.24 (8)
$f=2$ kHz	0.15 (6)	0.21 (8)	0.24 (1)
$f=20$ kHz	0.15 (3)	0.19 (2)	0.20 (5)
Activation energy, E_a (kcal mol^{-1})	21	19	21

However, participation of the main chain could not be excluded as in poly(methyl methacrylate)[18].

On the other hand, in this family of polymers, the relaxation phenomena take place at lower temperature than in polymethacrylates. This behaviour could be attributed to a flexibilization of the whole system because of the presence of the flexible spacer group $-CH_2-$ between the lateral group and the main chain. This relaxation should be independent of the length of the lateral chain.

In the case of PMTDI a particular behaviour was found, in the sense that at 293 K this polymer in addition shows a clear peak separated from the β peak and practically independent of the frequency (*Figure 1d*).

It is known[19] that in a family of poly(itaconates) containing more than 12 carbon atoms in the side-chain, some degree of crystalline content has been observed by differential scanning calorimetry. This phenomenon was also observed in PMTDI at about 273 K, and can be related to the dielectric relaxation peak at about 293 K, on the basis that this peak has not been shifted with the frequency.

As the activation energy and the position of the γ relaxation in the case of PMTDI follow the sequence shown in *Table 2*, it seems to indicate that this γ relaxation should take place essentially in the amorphous phase. However a possible crystallization process in the side-chains would produce an inhibition of the whole lateral chain, giving rise to the new reported relaxation peak on the right-hand side of the β relaxation. We are at present working on the crystalline content in this family of polymers.

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