Dielectric relaxation in poly(monobenzyl itaconate)

Ricardo Díaz-Calleja and Amparo Ribes-Greus
Laboratorio de Termodinámica y Fisicoquímica, ETSIIV, Universidad Politécnica de Valencia, Apartado 22012, 46071 Valencia, Spain

Ligia Gargallo and Deodato Radić
*Laboratorio de Fisicoquímica Molecular, Facultad de Química,
Pontificia Universidad Católica de Chile, Casilla 6177, Santiago, Chile*

The dielectric relaxation properties of poly(monobenzyl itaconate) have been studied and four relaxation processes (α, β, γ and δ) have been found. These processes respectively appear in the decreasing order of temperatures 100, 20, -42 and $-110°C$ at 2 kHz. The best defined relaxations, α and γ, have been described in terms of semiempirical models. Different molecular origins for each relaxation have been proposed by comparison with other polymers of similar structures, particularly with poly(benzyl methacrylate). In the general case, the higher complexity of the side chains in poly(methacrylates) as well as in poly(itaconates) involves the possibility of multiple relaxation mechanisms that are not always easy to interpret.

INTRODUCTION

Polymers derived from methacrylic and itaconic acids can be obtained with a great variety of structures in the side chains, and these are interesting from different points of view[1-3]. Particularly interesting are the different rotations and motions of the side groups. For these reasons, several dielectric relaxations below the glass transition temperature (T_g) have been observed[4-7]. The influence of spacer groups in the side chains is a factor that should be taken into account in this kind of study. If the side groups are fixed to the main chain via a flexible spacer, the motions of the main chain and the side chains might be decoupled, and this should be reflected in the dielectric relaxations. The aim of this work is to obtain information on the dielectric relaxations in poly(monobenzyl itaconate) (PMBzI) [poly(1-carboxy-1-benzyl-oxycarbonylmethylethene)], which is a monoester derived from itaconic acid containing a double spacer group $-CH_2-$ before and after the ester group. The dielectric relaxation behaviour of this polymer has also been compared with that of poly(benzyl methacrylate).

$$-(CH_2-C)_n-$$

CH_2-COO-CH_2-⟨benzene ring⟩ / COOH

PMBzI
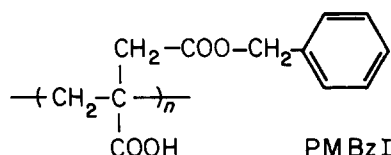
EXPERIMENTAL

Monomer and polymer preparation

2-Benzyloxycarbonylmethacrylic acid (benzyl hydrogen itaconate) was prepared by esterification of itaconic acid (1 mol) with benzyl alcohol (3–4 mol) using acetyl chloride as catalyst[8] according to the method previously described[9,10]. Purification of the monomer was achieved by recrystallization from benzene[9,10]. Radical polymerization of the monomer was carried out in bulk at 350 K in nitrogen using α,α'-azobisisobutyronitrile (AIBN) (0.1 mol) as initiator. Polymerization time was 48 h and the conversion of monomer to polymer was 34.5%. Purification of the polymer was achieved by repeated dissolution in tetrahydrofuran (THF) and reprecipitation with diethyl ether before vacuum drying at 313 K[9,10].

Dielectric measurements

High-frequency dielectric measurements were carried out by means of a Genrad 1620AP capacitance bridge equipped with a three-terminal cell and stainless-steel electrodes over which a polymer solution was deposited after evaporation drying. The thickness of the polymer film was 0.16 mm. This was the best procedure for sample preparation owing to the brittleness of the dry polymer film. Measurements were carried out between -140 and 140°C in the frequency range from 0.2 to 100 kHz.

RESULTS AND DISCUSSION

Figure 1 shows the imaginary part of the dielectric permittivity (loss permittivity ε'') for poly(monobenzyl itaconate) at three different frequencies. As can be seen in the temperature range studied, four relaxations labelled α, β, γ and δ can be observed in the order of decreasing temperature. Let us analyse each one separately.

δ relaxation

A small dielectric absorption can be observed in the temperature range -120 to $-100°C$ with an activation energy of 7 ± 0.5 kcal mol^{-1}. A similar relaxation has been observed (see *Figure 2*) in poly(benzyl methacrylate) in the same temperature range and with a similar activation energy. The only common group in the structural unit of this polymer compared with that of poly(monobenzyl itaconate) is the benzyl group linked to the oxygen of the ester. Therefore, it is possible to
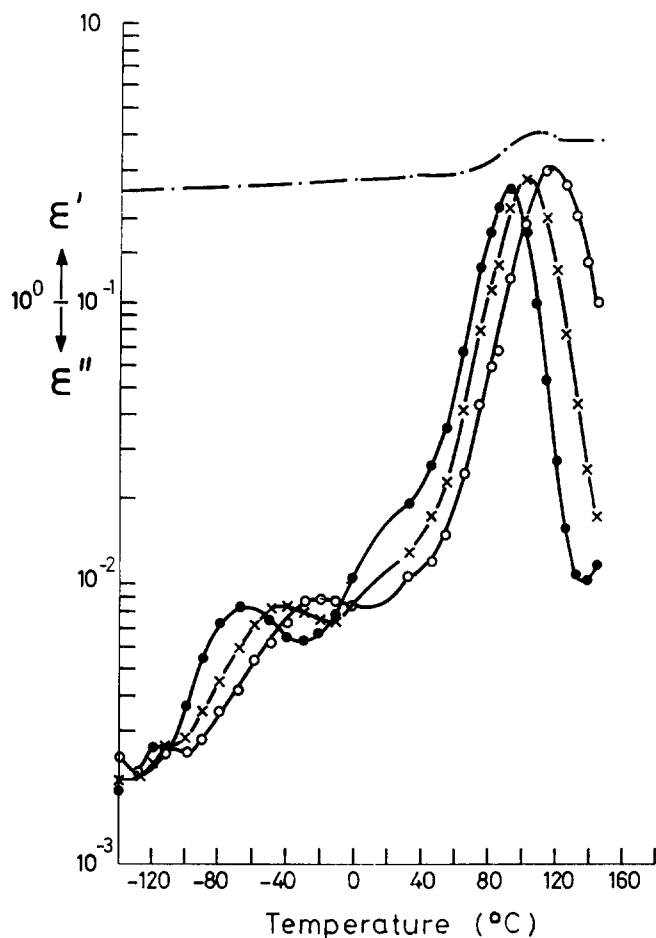
Figure 1 Permittivity (0.2 kHz) and loss permittivity against temperature at 0.2 kHz (●), 2 kHz (×) and 20 kHz (○) for poly(monobenzyl itaconate)

assume that the molecular origin of this relaxation is due to the rotation of the benzyl group with a small participation of the oxygen, taking into account the slow intensity of this relaxation as a consequence of a low dipolar activity. This relaxation is not observed in poly(phenyl methacrylate)[11] and presumably is not observed in the corresponding poly(monophenyl itaconate), because of the absence of the flexible spacer group $-CH_2-$, which would diminish the flexibility of the group directly linked to the ester.

γ relaxation

A well defined relaxation process is observed in the temperature range -70 to $-20°C$ with an activation energy of 10.5 kcal mol^{-1}. In order to quantify the main characteristics of this relaxation, we have used the Fuoss–Kirkwood[12] model, according to the equation:

$$\varepsilon'' = \varepsilon''_{max} \operatorname{sech}(mx) \tag{1}$$

Here $x = (E_a/R)(1/T - 1/T_m)$, where E_a is the activation energy, R is the universal gas constant and T_m is the temperature where $\varepsilon'' = \varepsilon''_{max}$. At a frequency of 0.5 kHz, $m = 0.28$ and is indicative of a relatively small distributed process.

The intensity of the relaxation (strength) $\Delta\varepsilon$ can be calculated with the equation:

$$\Delta\varepsilon = 2\varepsilon''_{max}/m \tag{2}$$

giving a value of 0.060, which is very close to the value

0.062 obtained from the Cole–Cole arc for this relaxation at $-40.5°C$ (see *Figure 3a*). An alternative representation is that corresponding to a non-exponential relaxation function, which is known as the KWW[13] model:

$$\Phi(t) = \exp[-(t/\tau)^{\beta}] \tag{3}$$

with $0 \leqslant \beta < 1$.

The imaginary part of the permittivity (loss permittivity) is a non-symmetric function in the frequency axis according to the asymptotic development[14]:

$$\varepsilon''/\varepsilon_0 - e_\infty = \sum[(-1)^{n-1}/(\omega\tau)^{n\beta}][\Gamma(n\beta+1)/\Gamma(n+1)]$$

$$\sin(n\beta\pi/2) \tag{4}$$

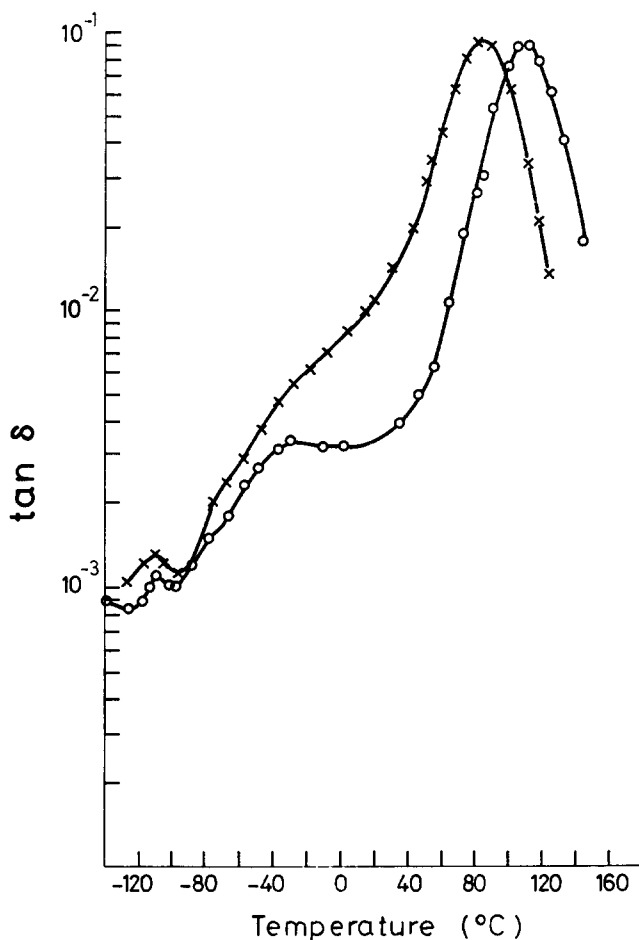where Γ is the Euler gamma function.

Figure 2 Dielectric loss tangent against temperature at 10 kHz for poly(benzyl methacrylate) (×) and poly(monobenzyl itaconate) (○)
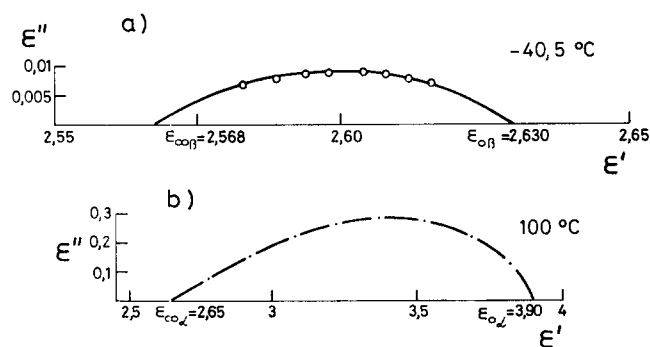

Figure 3 Cole–Cole arcs for poly(monobenzyl itaconate): (a) for γ relaxation at $-40.5°C$ and (b) for α relaxation at 100°C. The characteristic parameters are $\varepsilon_{0\alpha} = 3.90$, $\varepsilon_{\infty\alpha} = 2.65$, $\varepsilon_{0\beta} = 2.63$, $\varepsilon_{\infty\beta} = 2.568$
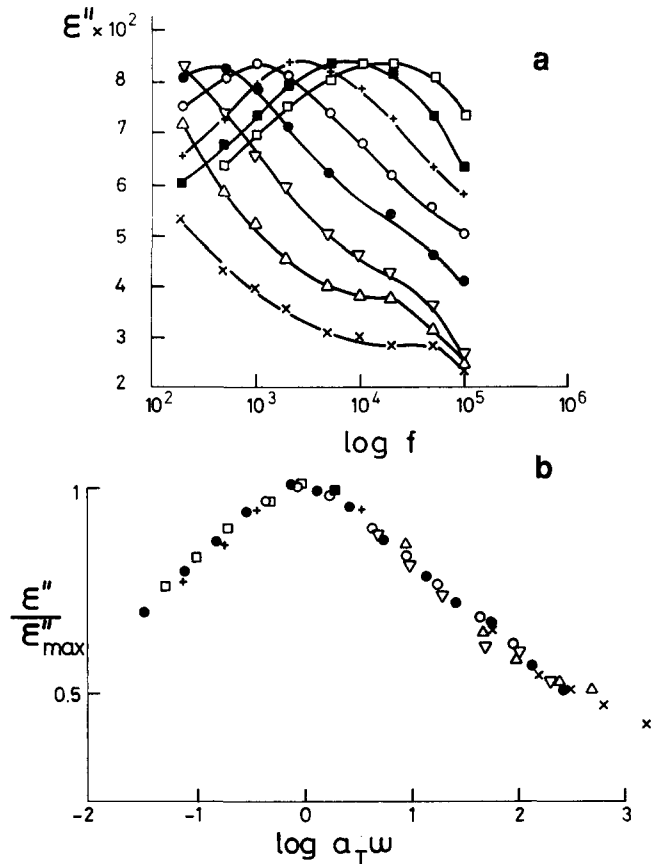
Figure 4 (a) Variation of the loss permittivity ε'' in the γ region with the frequency at several temperatures: $-90.5°C$ ($\times$), $-81°C$ ($\triangle$), $-69°C$ ($\triangledown$), $-60.5°C$ ($\bullet$), $-51°C$ ($\bigcirc$), $-40.5°C$ ($+$), $-30.7°C$ ($\blacksquare$), $-21.9°C$ ($\square$). (b) Master curve for the γ relaxation (symbols represent the different temperatures of (a)). The high-frequency region for low temperatures has been omitted because of the scattering of the points

The fitting procedure supposes the previous construction of a master curve (normalized for ε'', that is to say $\varepsilon''/\varepsilon''_{max}$ against frequency) from a longitudinal shift of the corresponding isotherms on the frequency axis (see *Figures 4a* and *4b*). The β value found is 0.32 ± 0.01 at the reference temperature, $-40.5°C$.

The molecular origin of this relaxation can be attributed to the rotation of the carboxylic group, as for poly(n-alkyl itaconates)[7], although in this case the temperature and the activation energy would be lower and no overlapping with the rotation of the other ester group of the molecule should be observed.

β relaxation

In the curves of ε'' against temperature at low frequencies, a shoulder that is overlapped at the beginning of the α relaxation can be observed. This shoulder is not observed in tan δ because of its right shift on the temperature axis. Clearly this phenomenon indicates a specific dielectric activity, which could be associated with the ester group linked to the benzyl group. In fact, only partial rotations of the bulky side group are possible as a whole, but it is evident that this kind of motion should require a higher activation energy than those analysed. This is the reason that β and γ do not appear to overlap as in the case of the poly(n-alkyl itaconates)[7]. From *Figure 2* it is possible to assume that γ and β absorptions would be reciprocally overlapped and also overlapped with the α peak in poly(benzyl

methacrylate)[6]. Naturally this is only a speculative explanation.

α relaxation

This relaxation is observed at temperatures close to but higher than the calorimetric T_g. Therefore, this relaxation is associated with the cooperative motions of the chains, which also produce a dielectric activity because of the motions of the dipoles related to the chains.

The application of the free-volume theory[15,16] to this relaxation gives a value of 6.4×10^{-2} for ϕ_g/B, which is of the same order of magnitude as those values observed for other related polymers[7], although this value is slightly higher than that predicted by this theory. *Figure 3b* shows the Cole–Cole arc (ε'' against ε') at 100°C for the α relaxation zone. Because of the oblique shape of the arc, in this figure it is possible to fit equation (5) according to the Havriliak–Negami[17] model:

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (i\omega\tau)^\alpha]^\beta \tag{5}$$

where τ_0 is the characteristic relaxation time for which $\omega\tau_0 = 1$ (ε^* has been normalized for ε'', i.e. $\varepsilon''/\varepsilon''_{max}$ against frequency) and α and β are related to the intersection angles ϕ_1 and ϕ_2, respectively, for the Cole–Cole arc at low and high frequencies, according to:

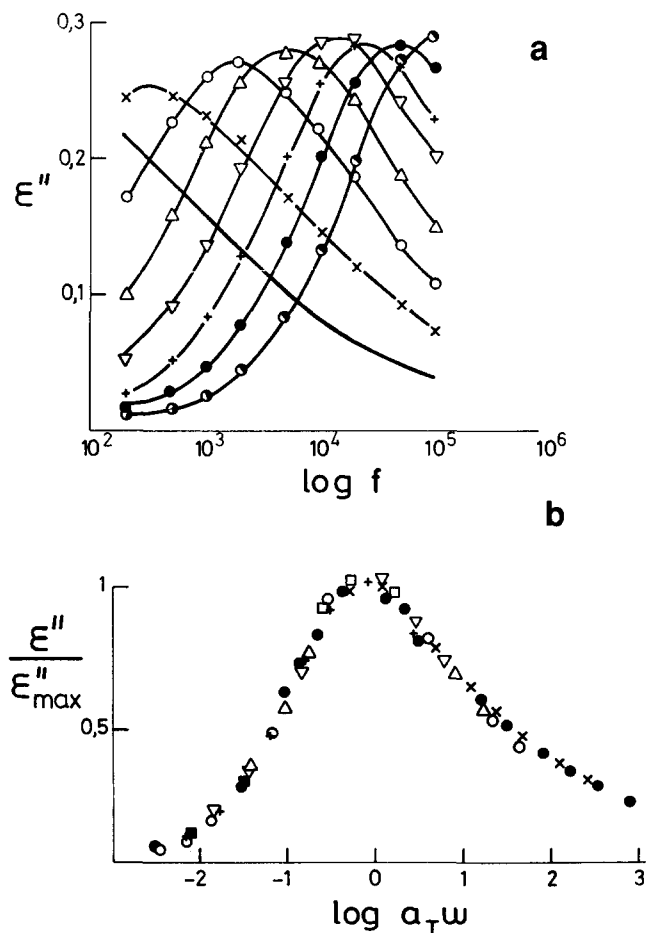$$\alpha = 2/\pi\phi_1 \qquad \beta = \phi_2/\phi_1 \tag{6}$$

Figure 5 (a) Variation of the loss permittivity ε'' in the α region with the frequency at several temperatures: 83.4°C ($-$), 90.7°C ($\times$), 100°C ($\bigcirc$), 106°C ($\triangle$), 112°C ($\triangledown$), 118°C ($+$), 124°C ($\bullet$), 130°C ($\ominus$). (b) Master curve for α relaxation (symbols represent the different temperatures of (a))

In our case the following values have been found: $\tau_0 = 2.65 \times 10^{-4}$ s, $\alpha = 0.75$, $\beta = 0.43$, $\phi_1 = 64.0°$, $\phi_2 = 27.8°$.

Following a similar procedure as in the case of the γ relaxation, it is possible, with the aid of the corresponding master curve for $\varepsilon''/\varepsilon''_{max}$, to find the β exponent of equation (3) for this relaxation (see *Figures 5a* and *5b*). A higher β value is to be expected because of the narrow peak for the α relaxation, compared with the other secondary relaxations β, γ, and δ. This is indicative of a minor correlation between the molecular motions associated with the α relaxation. In fact, the value obtained for β is 0.46 ± 0.01.

Finally, it is interesting to note that the T_g value, and the corresponding α relaxation, are about 20°C higher in poly(monobenzyl itaconate) than in poly(benzyl methacrylate), which reflects the fact that the lower flexibility of the side group will dominate over T_g, and it is only compensated by the higher influence of the intermolecular interactions, due to the bigger concentration of dipoles in poly(monobenzyl itaconate).

ACKNOWLEDGEMENTS

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