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Polymer Communication

Dynamic mechanical and dielectric relaxations in poly(dibenzyl itaconate) and poly(diethylphenyl itaconate)

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Abstract

Dynamic mechanical and dielectric behaviour of poly(dibenzyl itaconate), and poly(diethylphenyl itaconate) were studied. The study was performed by determining the components of the complex relaxation modulus E^* and the complex dielectric permittivity ε^*. The results are compared with those previously reported for poly(benzyl methacrylate), poly(monobenzyl itaconate) and poly(monoethylphenyl itaconate). The results are discussed in terms of the effect of flexible spacer groups and of the different steric hindrance between mono and disubstituted polymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric relaxation; Mechanical relaxation; Steric hindrance

1. Introduction

Polymers derived from itaconic acid containing saturated rings as side chains show significant mechanical and dielectric activity when they are affected by force fields [1,2]. This is partly due to the flexibility of the saturated ring which can show flipping between two conformational states (chair-to-chair). On the contrary, in the case of aromatic rings a minor activity would be expected because of the planarity of the unsaturated ring. Monoesterification and diesterification of itaconic acid can be carried out to obtain monomers and polymers having either one or two of the carboxyl groups esterified in each repeated unit [3–5]. From a relaxational point of view the mechanical and dielectric activity should be different for monoester and diesters. In fact, in the case of poly(monoitaconates), the relaxational activity should be higher because of the higher degree of freedom than in poly(diesters) which are more hindered because of the presence of two substituents per repeated unit. Moreover, in many poly(itaconates) the calorimetric glass transition cannot be observed [6]. In previous articles, we have reported the dielectric spectrum of poly(monobenzyl itaconate) (PMBzI) [7] and dynamic mechanical and dielectric behaviour of poly(monoethylphenyl itaconate) (PMEPI) [8]

and several relaxations were detected. It would be interesting to analyse the relaxational behaviour of disubstituted polymer analogues.

The aim of this article is to report the relaxational behaviour of poly(dibenzyl itaconate) (PDBzI) and poly(diethylphenyl itaconate) (PDEPI) (see Scheme 1) by means of dynamic mechanical and dielectric spectroscopy. Further comparison of the relaxational behaviour of these polymers with the data of poly(benzyl methacrylate) (PBzM) [9,10], PMBzI [7] and PMEPI [8] previously reported, will be made.

2. Experimental

2.1. Monomer and polymer preparation

Dibenzyl itaconate (DBzI) and diethylphenyl itaconate (DEPI) were obtained by conventional acid-catalysed esterification of itaconic acid (1 mol) with the corresponding alcohols (3–4 mol) using *p*-toluenesulphonic acid in toluene following procedures previously reported [11–13]. The pure monomers were obtained by repeated distillation of the crude product under reduced pressure. Radical polymerisation of the monomers was carried out in bulk at 330 K using α,α'-azo-bis-isobutyronitrile (0.3–0.4%) as initiator under N_2 (polymerisation time: 48 h, conversion; 65%). The polymer was purified by precipitation in THF with methanol

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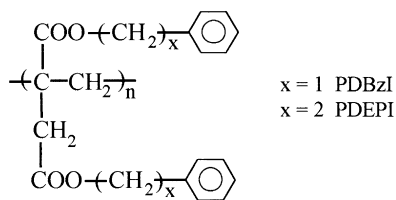
Scheme 1.

and was vacuum dried. The calorimetric glass transitions (T_g) at 10°C/min are 58.9 and 86.7°C, respectively.

2.2. Dynamic mechanical measurements

The components of the complex relaxation modulus E^* were obtained in flexion with a Rheometric DMTA Mark II apparatus in a double cantilever mode. The experiments were carried out at a heating rate of 1°/min from −140°C up to a temperature approximately 30°C below the glass transition temperature (T_g) of each polymer, at 0.3, 1, 3, 10, and 30 Hz. In the vicinity of T_g, the measurements were performed at 0.2, 0.3, 1, 2, 3, 5, 10, 20 and 30 Hz.

2.3. Dielectric measurements

The components of the complex dielectric permittivity, ε^*, were measured in a dry nitrogen atmosphere with a DEA 2970 capacitance apparatus from TA Instruments. The heating history was similar to that used in the mechanical measurements and the range of frequencies was 10^{-1}–10^5 Hz.
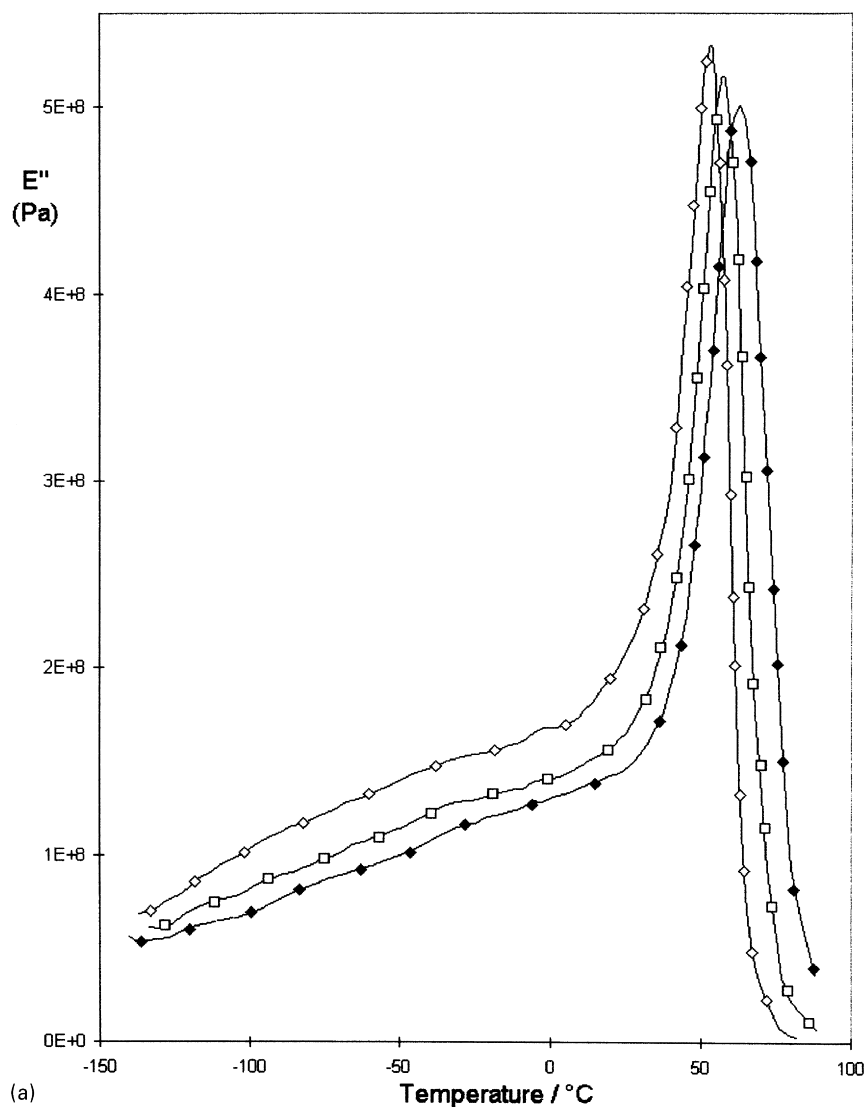

Fig. 1. (a) Experimental mechanical loss modulus E'' as a function of temperature at 30 (◆), 3 (□) and 0.3 (◇) Hz, for PDBzI; (b) temperature dependence of mechanical loss modulus E'' for PDEFI at 30 (◆), 3 (□) and 0.3 (◇) Hz.
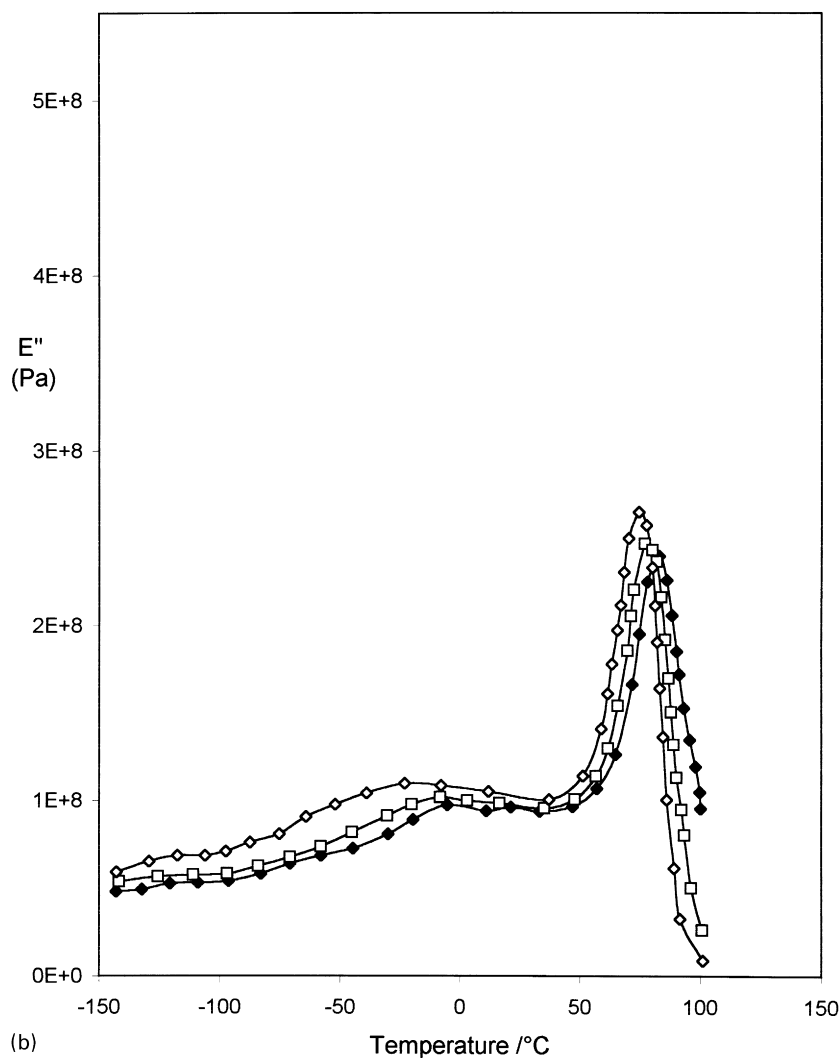
Fig. 1. (*continued*)

3. Results and discussion

The dynamic loss moduli of PDBzI and PDEPI can be seen in Fig. 1(a) and (b). The most relevant feature of this figure is the prominent α-relaxation which can be seen at 50 and 75°C for both polymers, respectively. Moreover, no subglass activity is detected in PDBzI in contrast with PDEPI, where a broad relaxation is observed at about −20°, 1 Hz.

Concerning the subglass mechanical relaxation observed in PDEPI, a rough calculation of the activation energy of $\ln f$ versus $1/T$ Arrhenius plot gives a value of 16 ± 2 kcal/mol. This value is in agreement with the activation energy of the secondary relaxations of polymers found in the same temperature range.

Dielectric loss permittivities of PDBzI and PDEPI are shown in Fig. 2(a) and (b). In this figure, the α-relaxation for both polymers, associated to the glass transition

can be seen at 55 and 75°C for PDBzI and PDEPI, respectively (1 Hz). A detailed plot of the subglass zone of PDEPI reveals the existence of dielectric activity in this region in terms of a broad relaxation. From an Arrhenius plot $\ln f$ versus $1/T$ an activation energy of 15 ± 1 kcal/mol is found.

In order to calculate the temperature dependence of the α-relaxation in the frequency domain a Vogel–Fuecher–Tamman–Hesse (VFTH) equation [14–16] can be used. This equation is formulated empirically by these authors as:

$$\ln f_{\max} = A' - \frac{m'}{T - T_\infty}. \qquad (1)$$

In this equation, T_∞ is an empirical parameter related to the Kauzman temperature or the temperature at which the conformational entropy is zero. The best fit of the dielectric
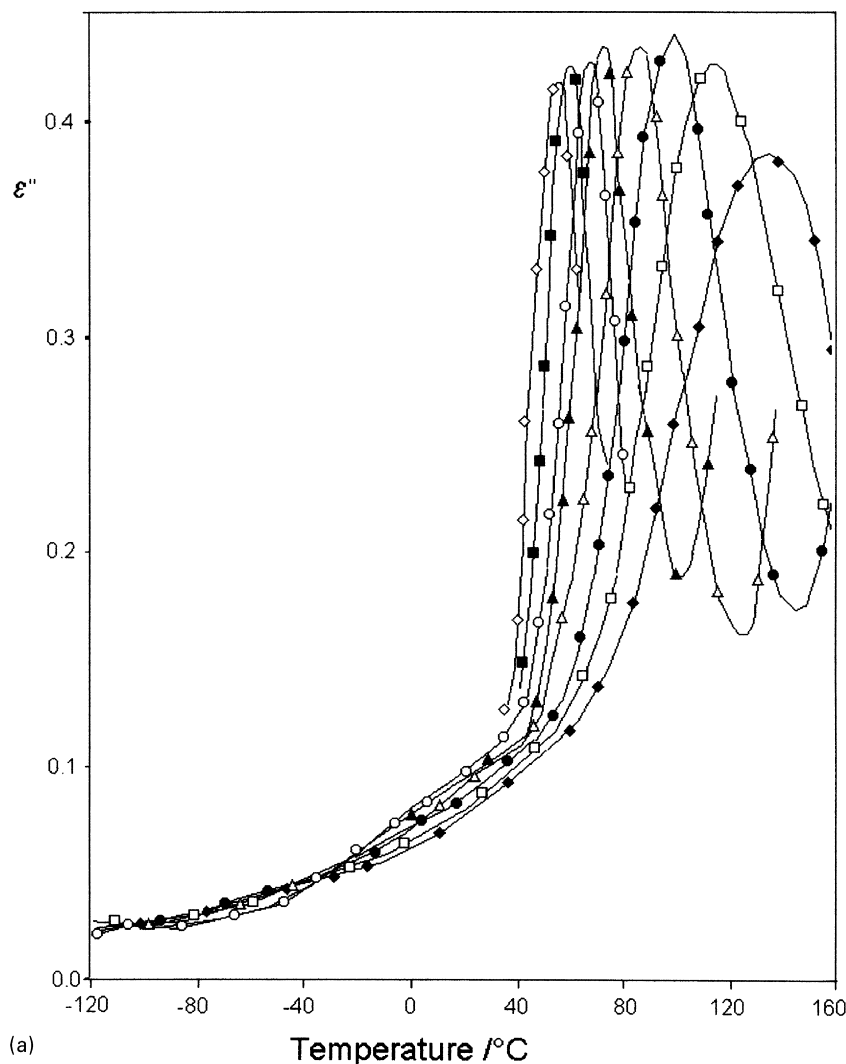
Fig. 2. (a) Experimental loss permittivity for PDBzI at several frequencies as a function of temperature. 10^5 ($\blacklozenge$), 10^4 ($\square$), 10^3 ($\bullet$), 10^2 ($\triangle$), 10^1 ($\blacktriangle$), 10^0 ($\bigcirc$), 10^{-1} ($\blacksquare$) and 10^{-2} ($\diamondsuit$) Hz; (b) experimental loss permittivity for PDEFI at several frequencies as a function of temperature. 10^5 ($\blacklozenge$), 10^4 ($\square$), 10^3 ($\bullet$), 10^2 ($\triangle$), 10^1 ($\blacktriangle$), 10^0 ($\bigcirc$), and 10^{-1} ($\blacksquare$) Hz.

experimental results to Eq. (1) were obtained for values of T_∞ equal to 250 and 290 K for PDBzI and PDEPI, respectively. The values of m' amount to 2428–1898 for PDBzI and PDEPI, respectively.

A comparison of the VFTH equation with the Doolittle equation yields:

$$\frac{\phi}{B} = \frac{T - T_\infty}{m},\tag{2}$$

which relates the free volume that appears in the Doolittle equation with the value of m' in the VFTH relationship. By using the values of m given above, one finds that the relative free volume at T_g, (ϕ_g/B), amounts to 3.4 and 3.7% for PDBzI and PDEFI, respectively. The data corresponding to the α dipolar peak can be represented in a Cole–Cole plot. Because of the skewness of the Cole–Cole plots, the Havriliak–Negami equation can be used to represent the

experimental data.

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (j\omega\tau)^\alpha)^\beta},\tag{3}$$

where

$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty.\tag{4}$$

The parameters of this equation as a function of temperature can be conveniently found by means of an LEVM6 program [14]. The corresponding values are compiled in Table 1. From this table, it can be seen that the intensity of the α-relaxation is higher in PDBzI than in PDEPI.

It is interesting to compare the obtained results with those previously found for PMBzI [5] and PBzM [6,7].

In the case of PMBzI, it is clear that the dielectric activity in the glassy zone is higher in monosubstituted than in disubstituted polymer (see Fig. 3).
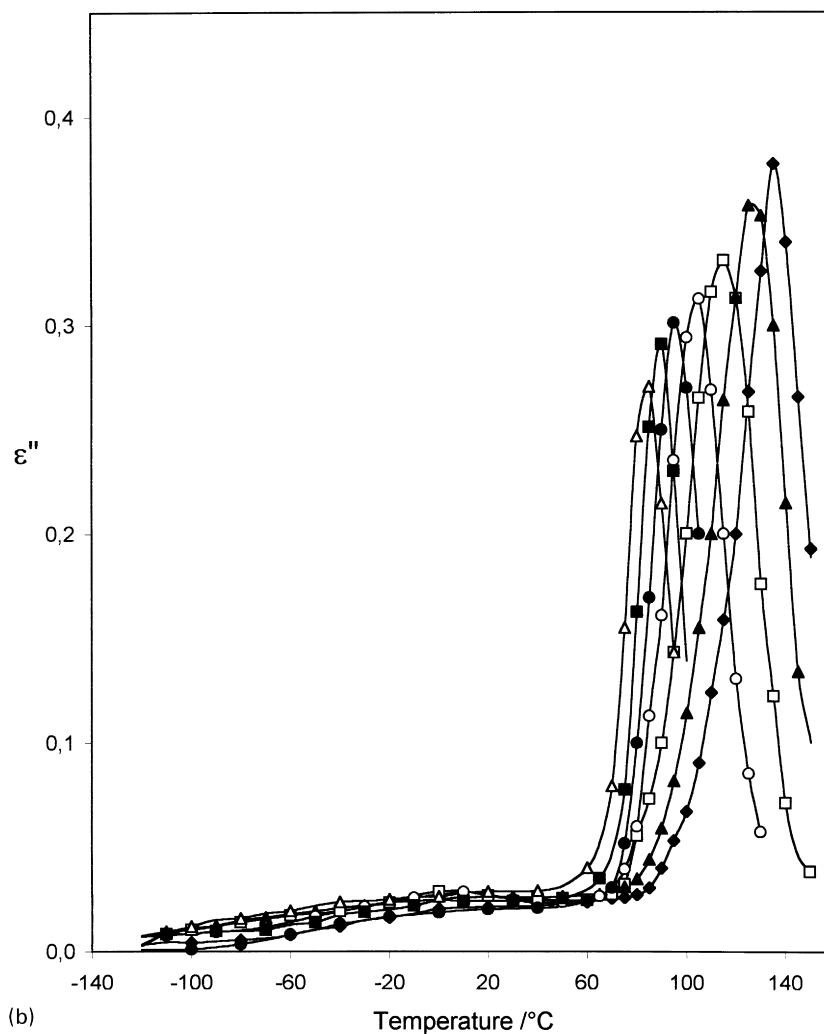
(b)

Fig. 2. (*continued*)

In contrast, a comparison between the dynamic mechanical relaxation of PBzM and PDBzI also shows that in PBzM a remmanent subglass mechanical relaxation can be observed in contrast with the diffuse mechanical activity in the case of PMBzI where no clearly defined subglass relaxations are shown (see Fig. 4). In this figure, the loss modulus for PBzM is corrected relative to the former results. In the previous work [8], the values of the mechanical loss

Table 1
Values of the Havriliak–Negami equation at different temperatures for the polymers under study

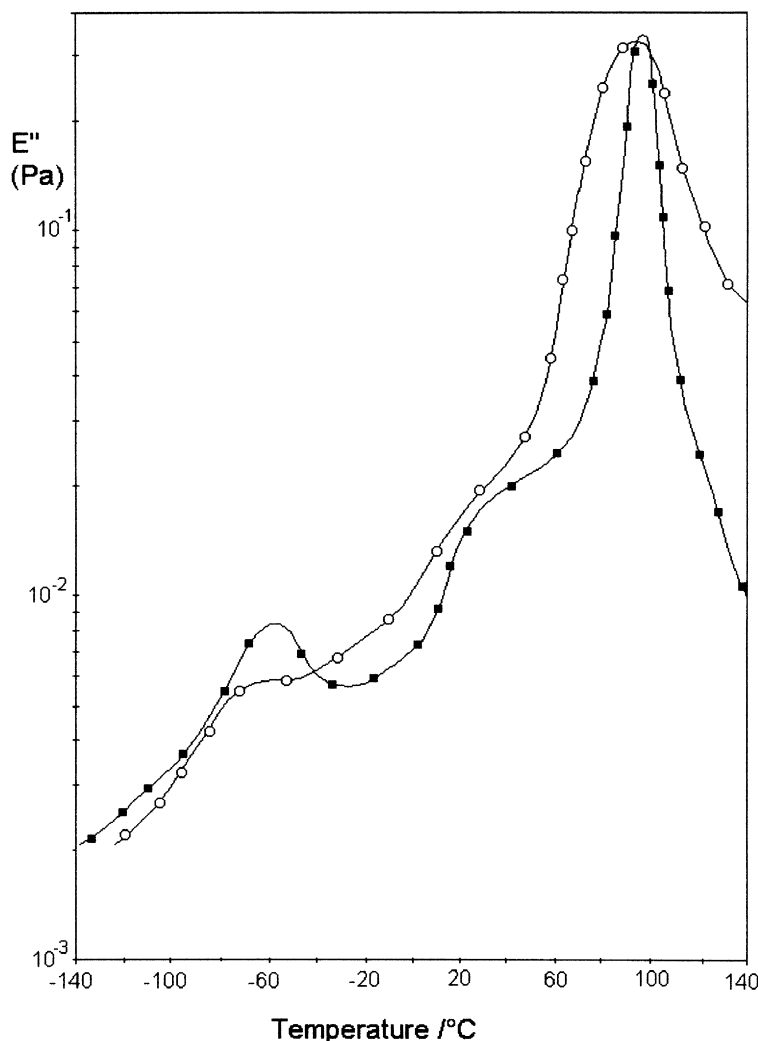| Temperature (K)	τ	α	ε	β	$\Delta\varepsilon$
PDBzI					
70	2.050×10^{-1}	5.255×10^{-1}	2.873	4.752×10^{-1}	2.213
75	2.712×10^{-2}	4.795×10^{-1}	2.985	6.256×10^{-1}	2.130
80	3.093×10^{-3}	3.964×10^{-1}	3.087	9.580×10^{-1}	2.174
85	1.385×10^{-3}	4.374×10^{-1}	3.196	8.434×10^{-1}	2.127
PDEPI					
98	4.972×10^{-3}	0.3552	2.9377	0.9913	1.9773
102	3.052×10^{-3}	0.4146	2.9592	0.8064	1.9010
106	4.793×10^{-4}	0.3896	3.0160	1.0942	1.8589
110	5.851×10^{-4}	0.5308	3.0044	0.6612	1.7746
114	1.708×10^{-4}	0.5128	3.0892	0.8217	1.7249

Fig. 3. Dielectric loss of PMBzI (■) and PDBzI (○) at 200 Hz.

modulus were underestimated because the clamping effect was not taken into account when measuring the free length of the sample. Therefore, the results shown in Fig. 4 are comparable.

Finally, from the comparison of the mechanical loss of PMEPI and PDEPI (Fig. 5), strong differences between both spectra are apparent. The more significant of these differences corresponds to the dynamic glass transition zone where for the monoester only, the α-relaxation appears as a shoulder of the dominant β-peak in contrast with the disubstituted polymer where a well-developed α-relaxation is shown.

4. Conclusions

From the comparison of the relaxational behaviour of the two polymers under study, it can be concluded that the spacer $-CH_2$ group increases the subglass activity. In fact, a broad subglass relaxation is observed in PDEPI but not in PDBzI due to the presence of two side groups per repeat unit. The flexible spacer group gives a greater freedom for rotation of the side group. In contrast, in the case of PMBzI and PBzM which only have one side group per repeat unit subglass activity is also observed. Therefore, small differences in the structure give rise to significant differences in the relaxational behaviour.
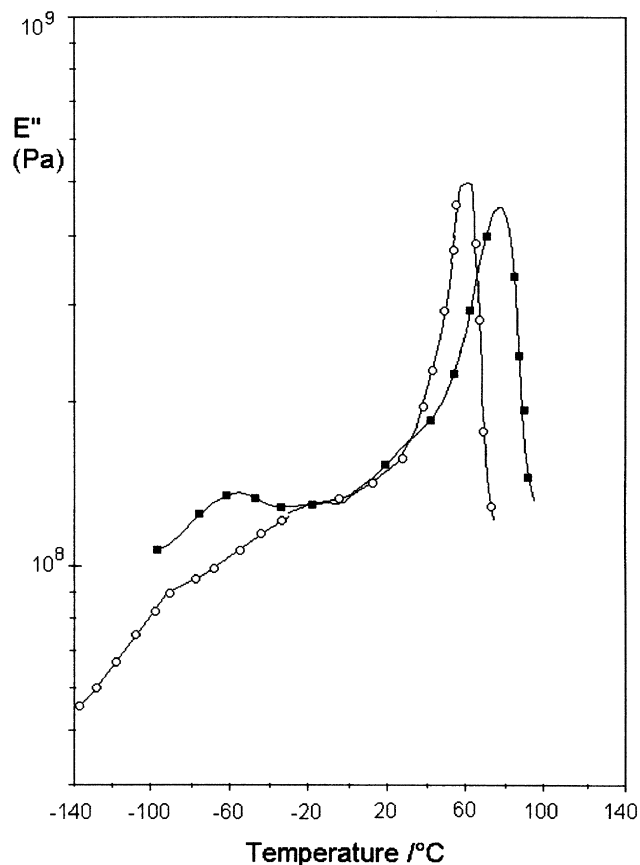
Acknowledgements

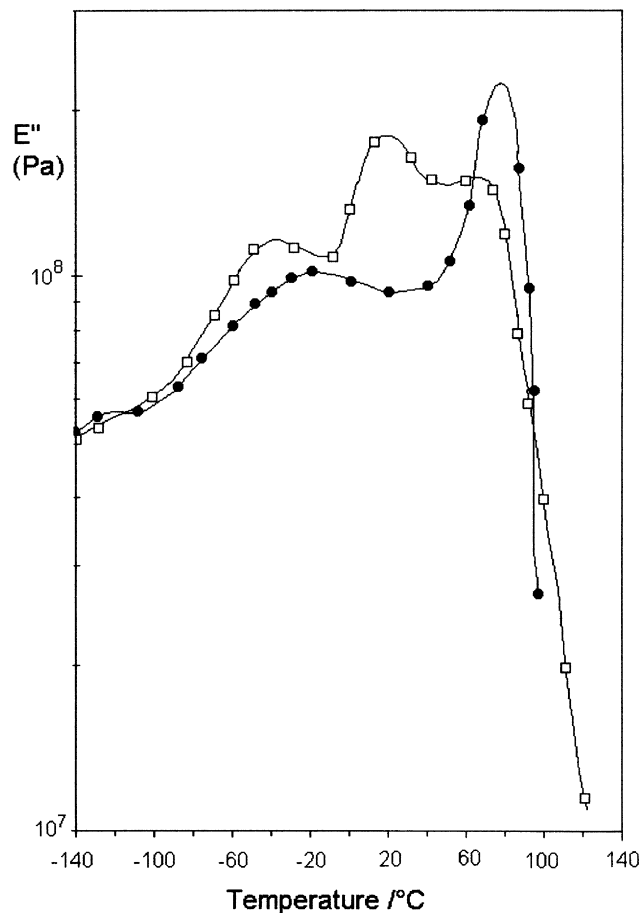Fig. 4. Mechanical loss modulus E'' of PBMA (■) and PDBI (○) at 3 Hz.

Fig. 5. Mechanical loss modulus E'' of PMEPI (□) and PDEPI (●) at 1 Hz.

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