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THERMAL EFFECTS ON THE STRUCTURE AND RELAXATION PROPERTIES OF POLY(MONOCYCLOPENTYL ITACONATE)

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Summary

A study has been carried out of the effect of thermal treatment and subsequent chemical structural modifications on the viscoelastic and dielectric properties of PMCPI (poly(monocyclopentyl itaconate)). The low temperature relaxation (γ relaxation) is unnafected by the thermal history or chemical changes. The intermediate relaxation (β relaxation) is shifted about 40° C to higher temperature after thermal treatment. The α relaxation (related to Tg, that is the glass transition temperature) suffer the more stricking changes moving to higher temperatures

Introduction

It is a well known fact that the relaxation spectra of poly(mono and dicyclohexyl itaconates) gives indications of a variety of processes[1-8)]. In general, it is commonly considered[9] that the shape and the size of the secondary glassy relaxations are not disturbed in a significant way either by the presence of plasticizer or low molecular weight substances, and thermal treatment, excepting when changes in the structural unit take place. This behaviour can be explained in terms of the intramolecular character of the barriers governing molecular motions that produces the absorptions. However, the α relaxations associated to the glass transition is very sensitive to the formerly mentioned modifications. For

example, plasticizers and chemical degradation usually reduce the temperature of the α relaxation. It is also well known that structural modifications due to temperature effects, are produced in poly(mono-n-alkyl itaconates). Specifically it has been described[10] a primary degradation by dehydration or des-esterification reaction. As a result a poly(anhydride) structure can be proposed[10]. In the study of mechanical and dielectric relaxation properties of poly(monocyclopentyl itaconate) we have observed significant modifications of the spectra when different thermal treatment are applied to the polymer. Accordingly it is our purpose to report such results and to stablish a relationship between structural modifications and the relaxation spectra of this polymer.

Experimental part

Preparation of Polymers

The polymer was synthesized and characterized according to the procedures reported previously[11].

Measurements

Dynamic mechanical viscoelastic measurements were carried out by means of DMTA-MARK II on samples of 10 mm width and from 0.5-1.0 mm thickness obtained by compression moulding. A flexural single cantilever mode was used at frequencies of 0.1, 0.3, 1.0, 3.0, 10.0 Hz from about -120 °C to temperatures of 140°C to 250°C depending of the experiment.

Dielectric measurements were carried out by means of a Dielectric analyzer DEA 2970 from TA Instruments. Measurements were performed from -140°C to 140 °C at frequencies ranging from 0.1 Hz to 30 kHz, three frequencies each decade. Samples were also molded in a disk shape of 27 mm diameter and thicknes from 0.5 to 1.0 mm. In any case the rate of measurements was 1° min^{-1}.

Mechanical measurements were carried out on three types of samples each one with different thermal treatment. a) Molded samples at 120 °C

with the polymer as without previous treatment. b) with molded samples at 140°C after drying about three weeks in a vacuum oven at 130 °C; c) with molded samples at 160 °C after drying in the same conditions than in b). Dielectric measurements were carried out with samples corresponding to the thermal treatment type a) and b). Samples will be labelled as a), b) and c) refering to the different thermal treatments.

The experimental error for E' and ε' are typically 2% and for tanδ about 5%.

Results

Figure 1 shows the loss modulus E" at 3Hz for the polymer under study after the three thermal treatment indicated above. In the samples a) and b) we can observe three relaxation peaks labelled as γ, β and α in increasing temperature sense. In sample c) we observe four relaxations labelled as γ, β, α_1 and α_2 in increasing temperature sense. We do not observe significant modifications in the γ relaxation at -75°C in the three spectra.

With reference to the following relaxation observed in the spectra, labelled as β relaxation, it is observed that for probe a) the temperature of the relaxation peak is 0°C and for b) and c) probes the temperature is 40°C. Moreover, we observe in samples b) and c) a broadening of the relaxation peak showing at the same time indications of structure.Relaxation map for β and γ relaxations is shown in Figure 2 where a Lnf_m vs T^{-1} corresponding to the Arrhenius plot is presented for the both mechanical and dielectric processes.

Concerning the α relaxation we observe that for the a) sample the relaxation peak is present at 100 °C while in the b) sample this peak is present a 120°C and the more stricking fact is that in the sample c) we found two peaks at about 170°C and 230°C. After a further scanning until 250°C all the viscoelastic activity above 120° C disappears and a black sample is observed indicating degradation.

Figure 3 shows the loss permittivity at 2Hz in samples a) and b). A γ relaxation at -100°C is also observed, which remains unaltered by the drying process. Moreover, in the dielectric measurements the temperature of the γ peaks is lower than in the mechanical ones.

A prominent β peak is observed in the sample a) also at nearly 0°C but in the dry sample this relaxation is shifted to higher temperatures like in the mechanical case. However, only the low temperature side of this peak is observed due to the fact that at higher temperatures, important conductive effects that overlaps this relaxation appears. Although this conductive effect is also present in the wet sample at lower temperatures, not overlapping is observed in this sample. This is more clearly seen when we represent the dielectric loss modulus against temperature. In this context dielectric loss modulus is defined as $Im[(\varepsilon^*)^{-1}]$. Using dielectric loss modulus in stead of loss permittivity allow us the better splitting of the relaxation peaks (Figure 4).

Although the peak corresponding to conductive effects is shifted about 50°C there is not indication in any case of the α relaxation, as in the mechanical case.

In a previous paper[12] we have proposed a strategy to split the dipolar α relaxation from the conductive and interfacial phenomena. In the case of the dry sample the maxima of M" are shifted at higher temperatures. For this reason it is not possible to follow the same strategy without modifying the thermal treatment of the sample.

Table I summarizes the activation energies for the β and γ relaxations for samples a) and b) in the mechanical as well as in the dielectric case. The dryness increases the activation energy in all cases. We can also observe that the activation energy is higher in the mechanical case in comparison with the dielectric one. This is consistent with the highest temperature at which the mechanical relaxation peaks are seen in comparison with the dielectric ones. The effect of an increase of forthy degrees in the mechanical β relaxation implies nearly a fifty per cent of increase in the activation energy.

A Fuoss-Kirkwood[13] equation was used to fit experimental data for the γ and β relaxation according to:

$$\lambda'' = \lambda''_{max} \text{ sech } mx \qquad (1)$$

λ'' E'' (for mechanical measurements)

ε'' (for dielectric measurements)

where

$$x = \frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_{max}}\right] = \text{Ln } \frac{f_{max}}{f} \qquad (2)$$

and m indicate the broadness of the relaxation peak; m = 1 for a single Debye peak. The values of m for the dry sample b) are given in Table II.

As can be seen the broadness of the relaxation increases with the frequency. In the mechanical case the values for the β relaxation are about one half than those for the γ relaxation indicating that the β relaxation is broader than γ in good agreement with the results obtained by us for the corresponding peak of poly(dicyclohexyl itaconate)[4]. The γ dielectric relaxation peak is two times narrower than the mechanical one in terms of the m parameter.

Discussion

The relaxation behaviour of the PMCPI are close to the other mono and disubstituted poly(itaconic esters)[6-8]. Although it has been postulated pseudorotational or geminal sites exchange motions for the cyclopentyl ring, this type of molecular motions would be present at very low temperatures, below our experimental range of measurements. We note that in the poly(cyclopentyl methacrylate) it has been observed[14] a prominent peak near 212°C (0.64Hz), that has not counterpart in the corresponding poly(itaconates). On the other hand,

Cowie et al[15] have studied molecular motions in poly(dicyclopentyl itaconate) . They found a weak mechanical activity near -150 °C and a pronounced relaxation about -52°C (1Hz). These authors have assigned the last relaxation peak to the restricted oscillation of the cyclopentyl ring as a whole around the COO bond. It is possible that the relaxation that we labell as γ observed a -75°C in the mechanical measurements would be due to the same molecular motion. The lower temperature observed for the peak in our case could be due to a decrease of the potential barrier opposing to the motion because in our case we have only a cyclopentyl ring for structural unit. The fact that the activation energy is higher in the mechanical case than in the dielectric can be due to a higher intermolecular cooperattivity in the former case.

As it was indicated in previous papers[1-8] the β relaxation could be due to motions in which ester groups are involved. It is a surprising fact that this relaxation peak is shifted forty degrees higher when we dry the sample at 130°C in a vacuum oven. This can be explained in terms of deplastization phenomenon. For the polymer c) the relaxation broadens and this can be indication of some structural modification in the lateral chain of the polymer. Accordingly a water molecule could be eliminated following the dehydration scheme reported by Cowie et al[10]. Moreover we observe swelling and a more intense colour in the sample. In order to analyze this problem we have carried out I.R. spectra. In fact, I.R. spectra for the sample heated to 170°C shows the presence of a new peak at 1650 cm^{-1} corresponding to the vibration of the -C=0 for an anhydride type structure.

It is possible that in sample b) the β relaxation could be due to molecular motions of the lateral chain affecting esters as well as anhydride groups after elimination of one water molecule from two acid neighbour groups. This can be an explanation for the high value observed in the activation energy.

The shift of the α relaxation peak to higher temperatures from 100°C to 120°C can be due to the elimination of the solvent that in the sample a) promoves plasticization. Moreover, the missing of the mechanical activity and the appearance of two new relaxations around 170°C and 230°C after heating the polymers at 160°C can be due to the appearance of new structures in the main backbone giving as a result a more much rigid chain. In this main backbone now

can appear the two anhydride groups predicted by Cowie et al[10]. One of them is produced by elimination of a water molecule and the second one by elimination of an alcohol molecule. This is consistent with a typical smell when the polymer is molded at 160°C also would be possible the break of the chain giving two incompatible structures with different glass transition temperatures. It is interesting to note that a further heating to 250°C do not gives indication of mechanical activity, starting probably the degradation of the polymer.

Dielectric results are consistent with the mechanically observed. But in any case activation energy of the dielectric relaxation are lower than mechanical ones in the γ relaxation as well as in the β relaxation zone.

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TABLE I. Activation energies (kcalmol^{-1}) for the γ and β relaxation in samples a) and b)

Dielectric	γ	β
a)	7.3± 0.5	22.9± 0.5
b)	8.5 ± 0.5	-
Mechanical		
a)	13.4 ± 0.5	27.2± 0.5
b)	13.7± 0.5	39.6± 0.5

TABLE II. Parameter m appearing in the Fuoss-Kirkwood equation for the sample b)

Dielectric γ relaxation					
Frequency (Hz)	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}
m	0.225	0.248	0.250	0.247	0.263
Mechanical relaxations					
Frequency (Hz)	10^{-1}	$3x10^{-1}$	10^{0}	$3x10^{0}$	10^{1}
m (γ)	0.099	0.111	0.120	0.123	0.127
m (β)	0.049	0.053	0.056	0.058	0.065

FIGURE CAPTIONS

Figure 1. Loss modulus E" ast 3Hz for PMCPI for the samples a) (o), b) (●) and c) (x).

Figure 2. Activation energy plot for the γ and β relaxation of PMCPI. γ dielectric: (o) , (◆); β dielectric (Δ). γ mechanical: (◇), (●); β Mechanical: (Δ), (■).

Figure 3. Loss permittivity at 2 Hz for samples a) (o), b) (●) and c) (x).

Figure 4. Dielectric Loss Moduli for a) non-dried; b) dried sample of PMCPI as function of Temperature at (▲) 10^{-1} Hz, (Δ) 10^{0} Hz, (■)10^{1} Hz, (□)10^{2} Hz, (●)10^{3} Hz, (O) 10^{4} Hz.

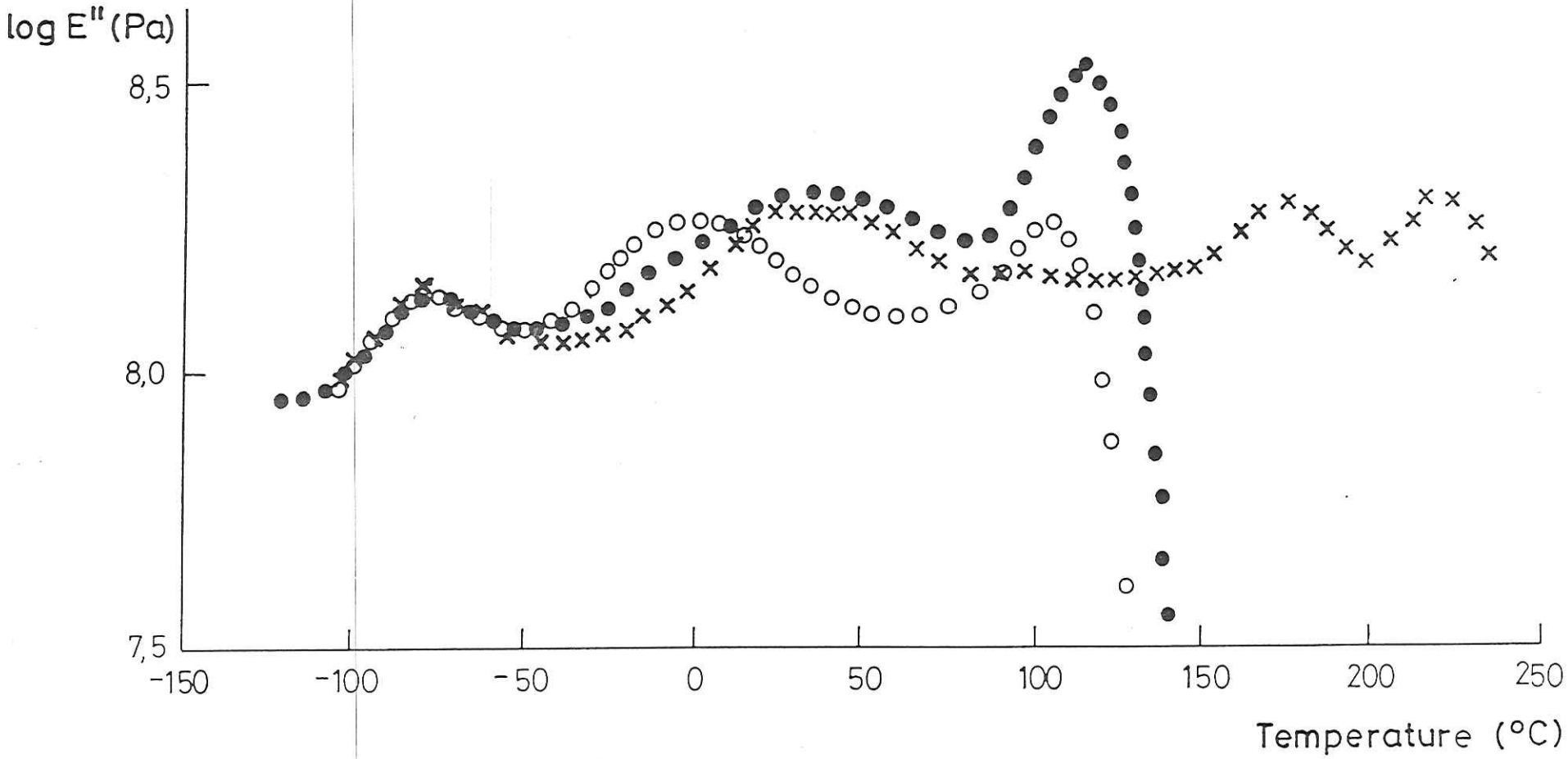
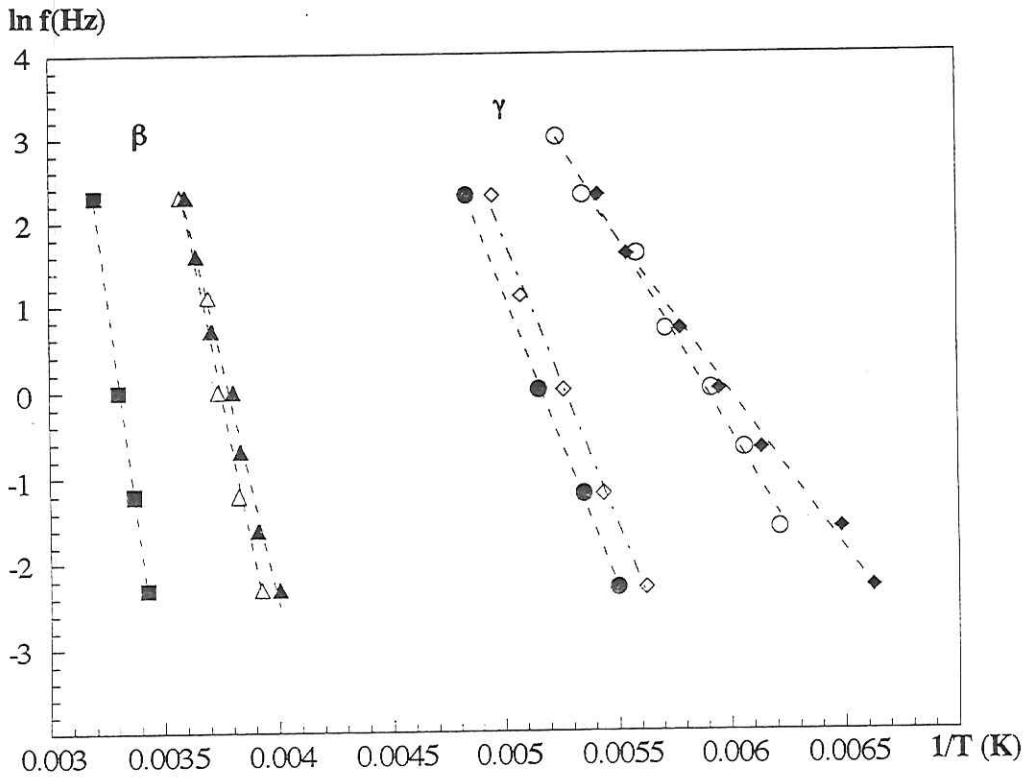
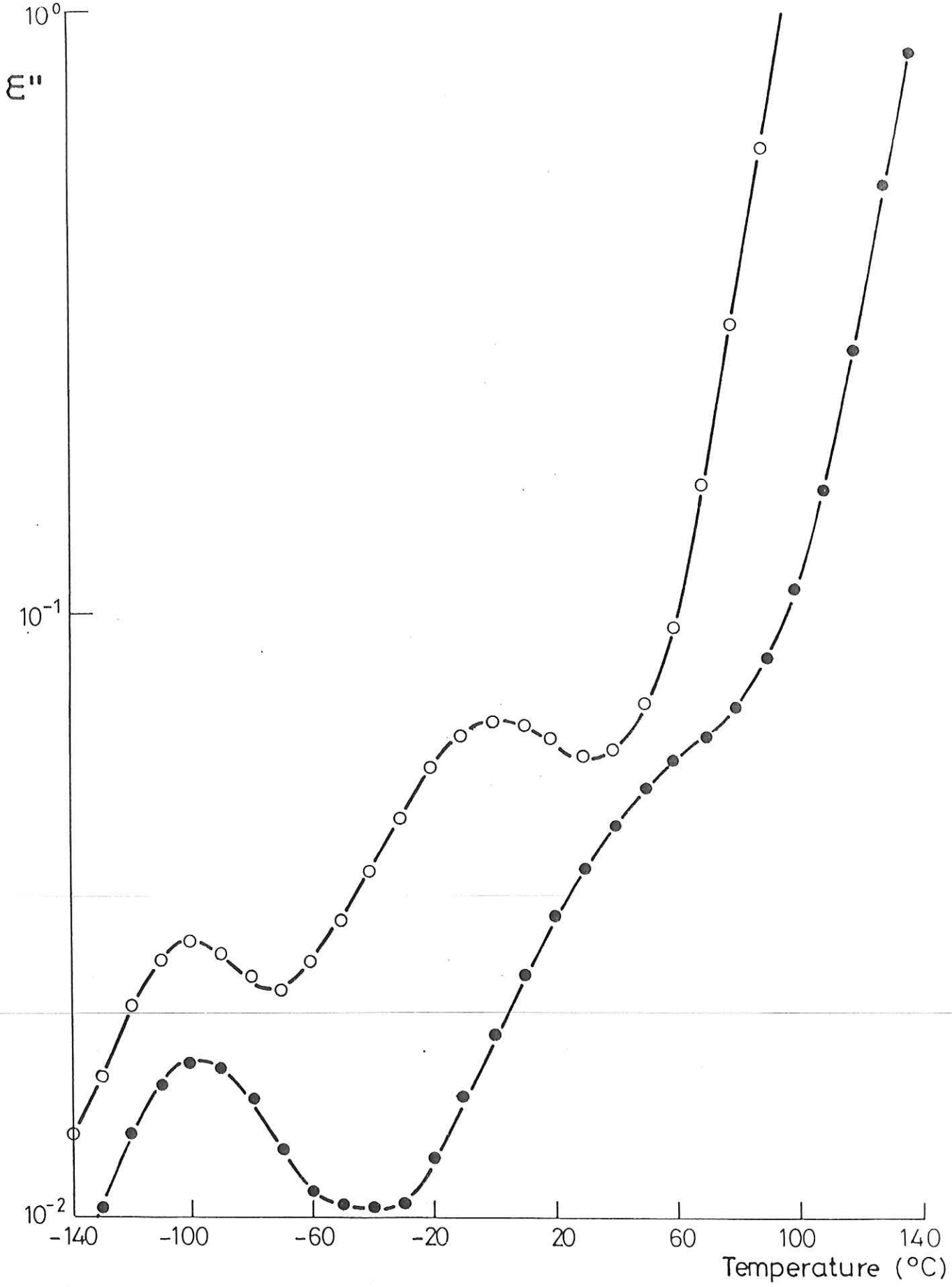
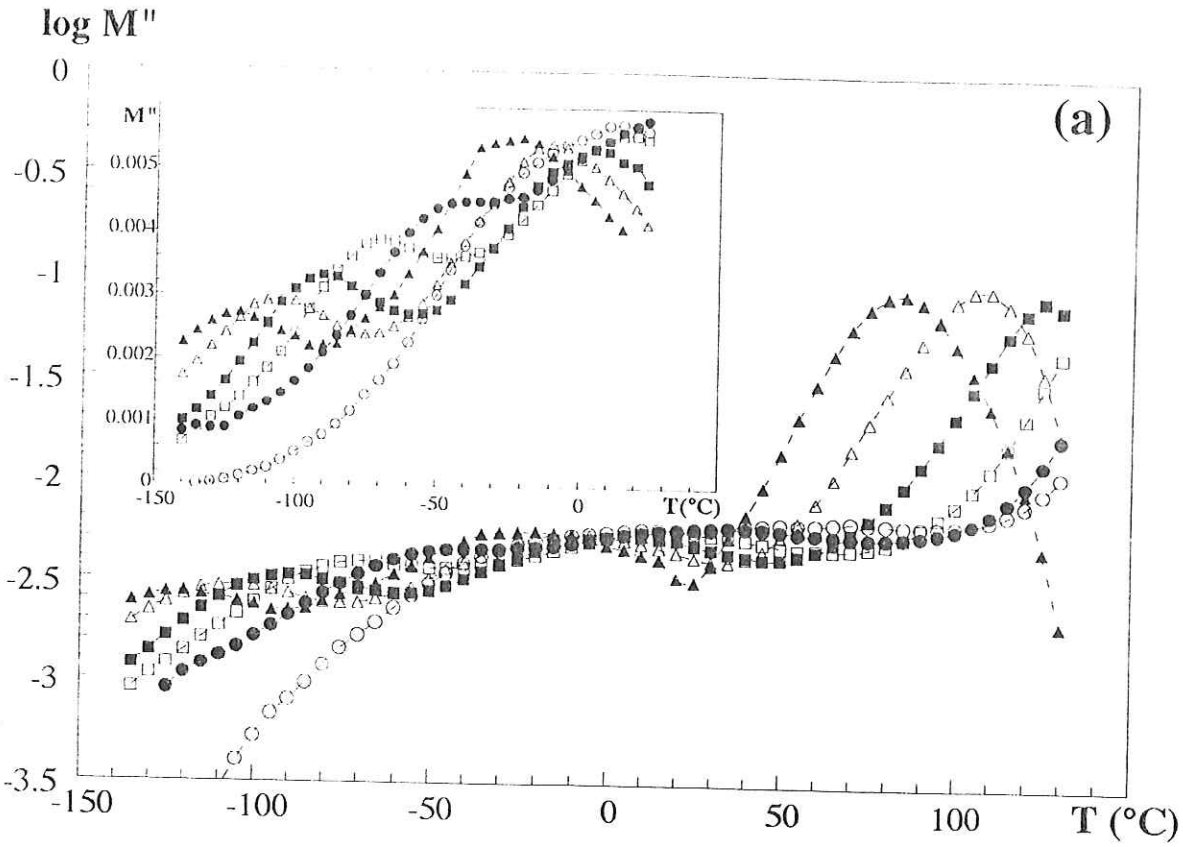
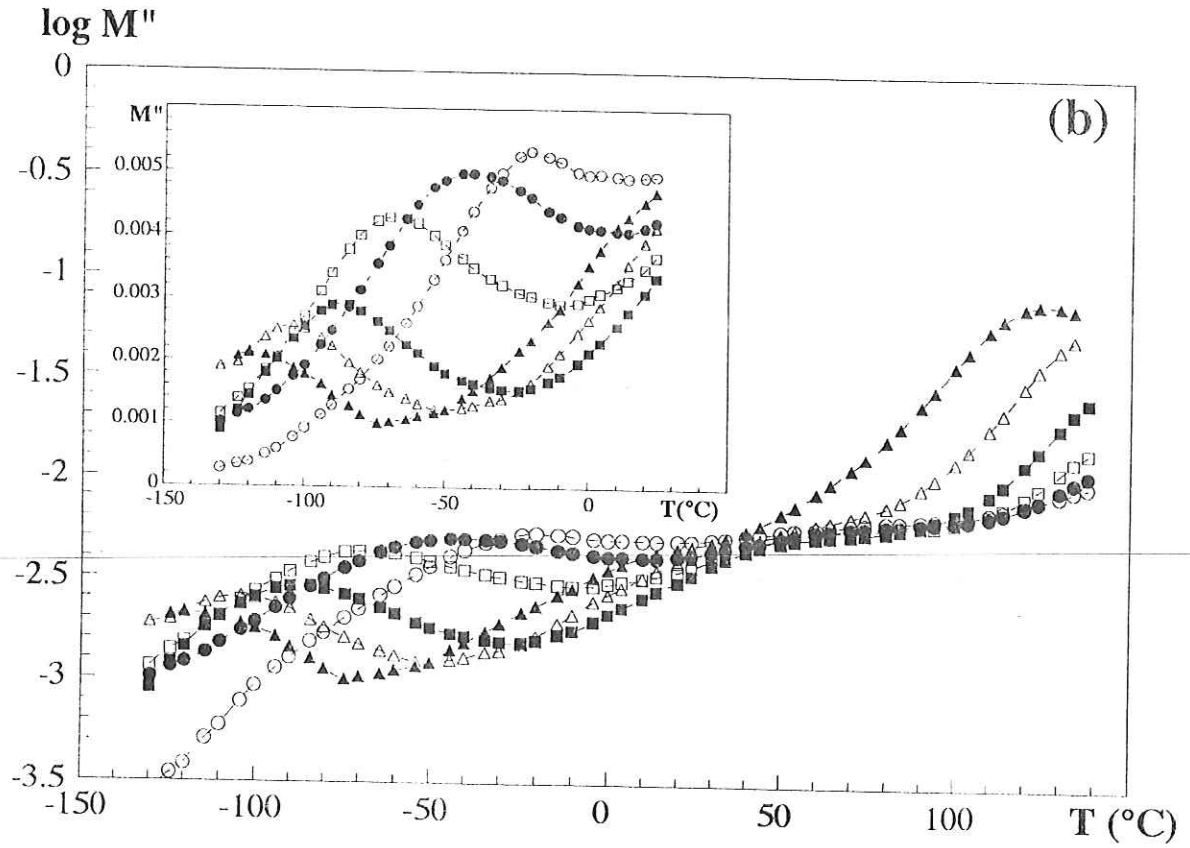


Figure 1


ln f(Hz)
4
3
2
1
0
-1
-2
-3
β
γ
0.003
0.0035
0.004
0.0045
0.005
0.0055
0.006
0.0065
1/T (K)


10⁰
ε"
10⁻¹
10⁻²
-140
-100
-60
-20
20
60
100
140
Temperature (°C)


log M"
(a)
M"
T(°C)
T (°C)


log M"
(b)
M"
T(°C)
T (°C)