Dynamic mechanical properties of poly(monocyclohexyl itaconate)

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(Received 31 December 1990; revised 22 April 1991; accepted 7 May 1991)

Accurate dynamic mechanical measurements were performed on poly(monocyclohexyl itaconate) at different frequencies over a wide temperature range. Three main relaxations could be observed at different temperatures, which were labelled as γ, β and α relaxations. The γ relaxation was attributed to the motions of the cyclohexyl group, specifically to the chair–chair flipping of the ring; and the β relaxation to the rotation of the side carboxylic groups. In order to analyse α relaxation a mechanical model was used which considered an isotropic continuum containing spherical isotropic non-interacting particles. Qualitative validity of this hypothesis was found and the results were consistent with the dielectric data obtained for the same polymer.

(Keywords: poly(monocyclohexyl itaconate); dynamic mechanical properties; mechanical relaxation)

INTRODUCTION

Viscoelastic and dielectric relaxation spectra of polymers present several absorptions, of which the most prominent is usually that related to the glass transition phenomenon. There are however some exceptions. One of them is the α-dielectric relaxation of poly(methyl methacrylate) (PMMA), in which the β peak is more prominent[1] than the α peak, although the former is associated with the rotation of the lateral group. One explanation of this fact is that the β relaxation is associated with the polar part of the molecule whereas the α relaxation corresponds to a local segmental mode relaxation, in the Stockmayer nomenclature[2], where the polar species are already activated in β absorption. Moreover, molecular mechanics[3] studies seem to have proved that in the β relaxation there is also some type of cooperation of the main chain. For these reasons the dielectric activity to be activated after the β process is small. Nevertheless, the mechanical viscoelastic spectrum does not show the same trend[4]. In this case α relaxation is more prominent than β relaxation. The polar character of the lateral group is insufficient to reach the height of the β loss peak, and the α relaxation is clearly related to cooperative motions of the overall chains of the polymer. This comes back to the classical situation.

Recently[5–7] the present authors have studied the dielectric relaxation spectra of a set of poly(mono-itaconates) containing alkyl[5], benzyl[6] and cyclohexyl[7] groups in the lateral chain. Neither the alkyl- nor the cyclohexyl-substituted polymers show a clear relaxation associated with the glass transition, which would correspond to a prominent peak on the high-temperature side of the spectrum.

The non-occurrence of a T_g phenomenon in these polymers has been checked by a systematic set of d.s.c. measurements[8] in the case of the alkyl-substituted polymers. However, in the case of cyclohexyl-substituted polymers a new dielectric relaxation appears to be hindered for the high conductivity superimposed on the a.c. loss curve in the high-temperature (low-frequency) zone of the spectrum. A transformation of the dielectric permittivity (ε^*) data into polarizability (α^*) by means of

$$\alpha^* = (\varepsilon^* - 1)/(\varepsilon^* + 2) \qquad (1)$$

allows us to show clearly the existence of this new relaxation that can be interpreted as a 'residual T_g', that is due to the dielectric activity of the part of the molecule not activated previously in the β, γ, etc. relaxations.

In this context, mechanical viscoelastic studies confirm these hypotheses and help to explain the complete relaxation behaviour of these types of polymer.

Previous mechanical data obtained on disubstituted poly(itaconates) have been reported by Cowie and co-workers[9–12] but are relative in magnitude, owing to the extreme fragility of these polymers, which are supported on fibreglass or filter paper in a torsion braid apparatus or in a Rheovibron. In contrast, air measurements have been carried out on the pure polymer as described in the Experimental section, and because of this, absolute values are obtained.

EXPERIMENTAL

Monomer and polymer preparation

2-Cyclohexyloxycarbonylmethylacrylic acid (cyclohexyl hydrogen itaconate) was prepared by esterification

0032-3861/92/071406-05

of itaconic acid (1 mol) with cyclohexyl alcohol (3–4 mol) using acetyl chloride as catalyst[13] according to the method previously described[14,15]. Purification of the monomer was achieved by recrystallization from benzene. Radical polymerization of the monomer was carried out in bulk at 67°C under nitrogen using α,α'-azo-bis-isobutyronitrile (AIBN) (0.3 mol%) as initiator. Polymerization time was 24 h and conversion of monomer to polymer was 75%. Purification of the polymer was achieved by repeated dissolution in THF and reprecipitation with diethyl ether before vacuum drying at 40°C[14,15].

Mechanical measurements

A DMTA Mark II apparatus was used at five different frequencies (0.1, 0.3, 1, 3 and 10 Hz) between −100 and +100°C to obtain the real (E') and imaginary (E'') parts of the dynamic viscoelastic spectrum. Single cantilever in flexion was selected as the deformation mode and small strips of 1 × 5.5 mm cross-section were used. Samples were obtained by dissolution of the polymer in a Teflon matrix. Films were removed from the matrix and the remaining solvent was evaporated at room temperature for several days before vacuum drying. Data were scanned at 1°C min^{-1}. Owing to the extreme fragility of the films, several attempts were necessary at different strain values in order to avoid breaking of the sample in measuring from the low temperature and at the same time to obtain reasonable and repeatable values of the moduli and loss tangent.

RESULTS AND DISCUSSION

Figure 1 shows storage and loss moduli of poly(monocyclohexyl itaconate) (PMCHI) between −100 and 100°C at 0.1, 1 and 10 Hz. Peaks in loss are shown at −78°C (1 Hz) and −16°C (1 Hz). A third peak (70°C) is also shown which is overlapped by the high-temperature tail of the second peak. These peaks are labelled as γ, β and α respectively. Evolution of the storage modulus is in accordance with that of the loss modulus, showing inflexions at temperatures approximately similar to those of the corresponding relaxation loss peaks. The three observed relaxations are analysed separately as follows.

γ-Relaxation

This low-temperature relaxation is a narrow mechanical absorption with an activation energy, obtained from an Arrhenius plot, of 13 kcal mol^{-1}. The shape of this relaxation can be characterized by means of the Fuoss–Kirkwood[16] equation, that is:

$$E'' = E''_{\max} \operatorname{sech} mx \qquad (2)$$

with

$$x = (E_a/R)(1/T - 1/T_m)$$

where $E''_{\max}$ is the maximum loss, E_a the activation energy, and m a parameter expressing the width of the peak; m increases for narrow relaxations, and T_m is the temperature at which this maximum is present. A value of $m = 0.29$ (nearly constant with the frequency) is obtained from a $\text{ch}^{-1}E''_{\max}/E''$ vs T^{-1} plot. Constancy of the m value suggests use of the time (frequency)–temperature superposition in the range of frequency studied, and a plot such as that of *Figure 2* (at −80°C) is obtained. This master curve is nearly symmetric although it presents deviations on the low-frequency (high-temperature) side, owing to the β relaxation process. For this reason it is not assimilable to a KWW equation[17], which is obviously asymmetric.

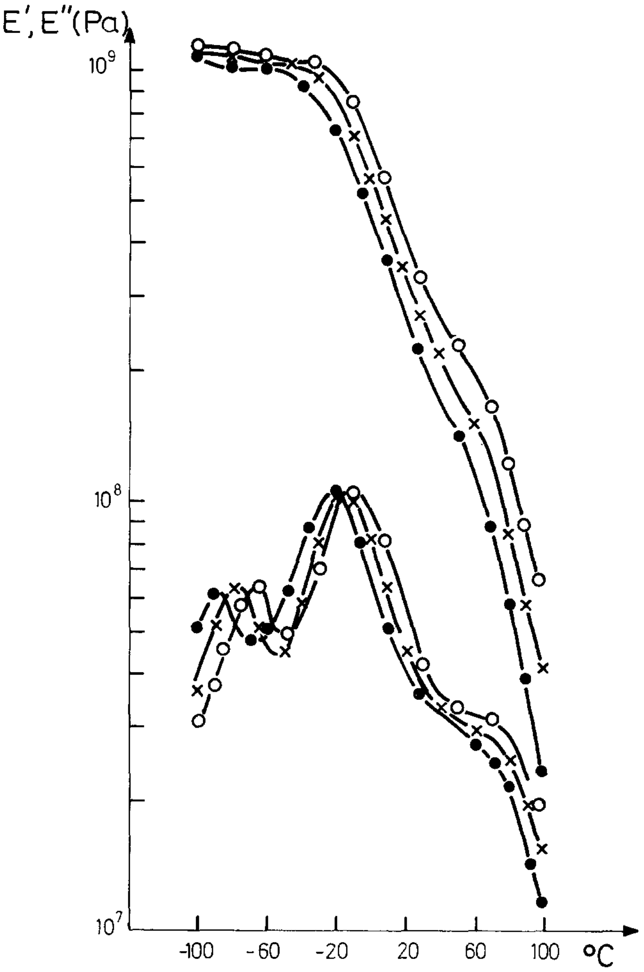

Figure 1 Storage (upper curves) and loss (lower curves) moduli of PMCHI at three frequencies: (●) 0.1, (×) 1, (○) 10 Hz

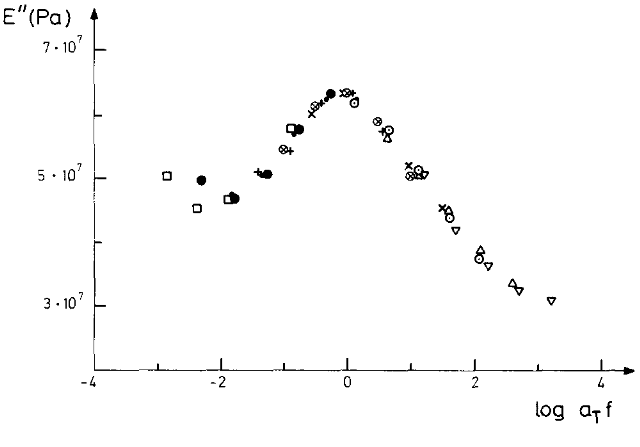

Figure 2 Master curve for the loss modulus of the γ-process at −80°C

The position of the γ loss peak and, to a lesser extent, the calculated activation energy also suggest that the molecular origin of this peak could be due to the chair–chair flipping of the cyclohexyl ring, which has been observed in polymers with cyclohexyl groups in the side chain[18]. In the present case the near-symmetry of the peak is preserved but the height of the loss peak is smaller. (Note that $G''_{\max} \approx \frac{1}{3}E''_{\max}$ in order to compare the present data with those of ref. 15.) At the same time the width of the loss curve is greater. In fact, the m value for poly(cyclohexylmethacrylate) (PCHMA) is about 0.5. These results are in agreement with the variation of the factors governing the relaxation strength $\Delta E'$ ($=E'$(unrelaxed) $-$ E'(relaxed)). It is well known[1] that $\Delta E'$ gives the same information as $E''_{\max}$ with reference to the intensity of the relaxation. The relaxation strength is proportional to the concentration of cyclohexyl units in the molecule. Obviously this concentration is lower in PMHCI than in PCHMA. However, $\Delta E'$ for PCHMA (see Table 7.1 of ref. 18) is about eight times that for PMCHI (≈ 240 MN m^{-2}). The observed difference can be attributed not only to the different concentration of cyclohexyl groups in the molecule, but also to the higher conformational energy for the chair–chair inversion in PMCHI. Thus the height of the loss peak in the polymer under study is smaller than in PCHMA, probably for these two reasons.

β-Relaxation

At higher temperatures a new relaxation process appears. In this case the drop in the storage modulus is higher, by nearly a decade, and from this point of view this mechanical absorption has characteristics intermediate between an absorption associated with a T_g and a secondary relaxation.

The activation energy is also high, 63 kcal mol^{-1}, and in this case the peak is also broader than that of the γ-relaxation. The m parameter has a value varying from 0.24 at 0.1 Hz to 0.23 at 10 Hz. A master curve at -15°C is shown in *Figure 3*. The asymmetric shape of the curve suggests assimilation to an empirical equation governed by a fractional exponential decay function, such as the KWW equation[17], given by[19]

$$\phi = \exp[-(t/\tau)^{\beta}], \qquad 0 < \beta < 1 \tag{3}$$

in which case

$$E'' = (E_0 - E_\infty) \sum_{m=1}^{\infty} \frac{(-1)^{m+1}\Gamma(m\beta + 1)}{m!\, z^{m\beta}} \operatorname{sen}(m\beta\pi/2) \tag{4}$$

In the present case β is 0.12, a low value, indicating perhaps overlapping of two absorptions. Owing to the position of the loss peaks on the temperature axis and to the value of the activation energy, the origin of this relaxation can be assigned to the same molecular motion as causes the high dielectric relaxation in this polymer[7] at 10°C (1 kHz), that is, the rotations of the carboxylic side groups on both sides of the molecule. The dielectric activation energy at higher frequencies is about 56 kcal mol^{-1}, close to the value found here by mechanical measurements.

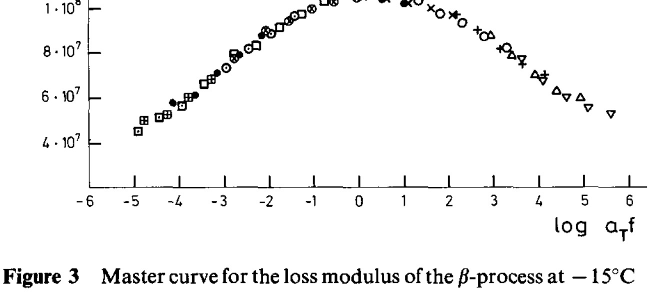

Figure 3 Master curve for the loss modulus of the β-process at -15°C

α-Relaxation

In the high-temperature tail of the β-relaxation and as a shoulder, there is evidence of a new relaxation which can be clearly seen at higher frequencies. As previously reported, dielectric measurements carried out on the same polymer show evidence of a new relaxation which cannot be observed directly, because of the high conductivity in the high-temperature zone of the spectrum. In order to make this phenomenon evident, a transformation from dielectric permittivity data to polarizability has been shown to be useful, according to equation (1). Mechanical relaxation measurements seem to be more clear in this respect, and a shoulder is observed in this case. However, it is necessary to know if there is a transformation similar to equation (1) to transform the inverse of the mechanical modulus, that is, the mechanical tensile compliance $D^* = E^{*-1}$ into a 'deformability', δ^*, function giving evidence of a relaxation peak. In a classical paper by Havriliak and Negami[20], this problem has been discussed and a generalization of equation (1) has been proposed. In fact, the relative vacuum permittivity $\varepsilon = 1$ has been replaced by a tensile compliance of the medium D_∞, where the mechanically active units producing the relaxation are embedded:

$$\delta_1^*(w) = \frac{D^*(w) - D_\infty}{D^*(w) + 2D_\infty} \tag{5}$$

This equation can be considered as a generalization of equation (1) and gives a Cole–Cole plot, δ'' vs δ', having the same trend as the permittivity ε'' vs ε'. In this way the high-temperature compliance effects have been eliminated, as has the loss permittivity due to the conductivity in the dielectric case. However, this attractive model does not have such a physical basis as its dielectric counterpart (equation (1)), and here it is preferred to adopt a more justifiable mechanical model, as presented by Havriliak and Negami[20]. These authors, following the procedures of Uemura and Takayanagi[21], considered a mechanical model in which an isotropic continuum contains spherical isotropic non-interacting particles; by taking a Poisson ratio $\nu = 0.5$ for the medium as well for the particles, they obtained

$$\delta_2^*(w) = \frac{D^*(w) - D_\infty}{D^*(w) + \frac{2}{3}D_\infty} \tag{6}$$

Normally the values for the Poisson ratio change from $\nu = 0.5$ for rubbers and $\nu = 0.4$ for polymers in the glassy state. In order to obtain a simple equation, the same values as those reported in ref. 21 are taken here; they are similar for the matrix as well as for the spherical particles. In this way the error in determining δ_1'' and δ_2'' is similar to that involved in the determination of D_∞. In order to use the directly measured data it is convenient to make $D^*(w) = (E^*(w))^{-1}$ and $D_\infty = E_0^{-1}$ and then to take the corresponding imaginary parts. After some rearrangements,

$$\delta_2'' = \frac{\frac{5}{3}E_0E''}{(E_0 + \frac{2}{3}E')^2 + \frac{4}{9}E''^2} \qquad (7)$$

The corresponding formula for equation (5) would be

$$\delta_1'' = \frac{3E_0E''}{(E_0 + 2E')^2 + 4E''^2} \qquad (8)$$

An estimation for $D_\infty = E_0^{-1}$ appears to be necessary. For this purpose we take $E_\infty\beta = E_0\alpha$, which is the unrelaxed modulus corresponding to β-relaxation equal to the unrelaxed modulus for the α-relaxation. Then obviously $D_\infty\alpha = E_0\alpha^{-1}$ and the estimated values at each frequency are as follows:

f (Hz)	D_∞ (10^9 Pa^{-1})
0.1	7.41
0.3	6.92
1	6.46
3	6.03
10	5.62

Calculated values for δ_2'' are given in *Figure 4*. For comparison, δ_1'' has also been calculated (see *Figure 5*). The trends of both sets of curves are similar, but they are displaced relative to one another on the temperature axis by at least 10°C. This clearly indicates that, contrary to the statements made in ref. 20, significant differences are obtained by using equation (6) instead of equation (5).

Moreover, the hypothesis of the spherical particles moving under a mechanical field, together with the uncertainty in the D_∞ values, makes the present results valid only in a qualitative way. However, despite the rough molecular approach followed, the appearance of a new relaxation peak seems to be out of the question.

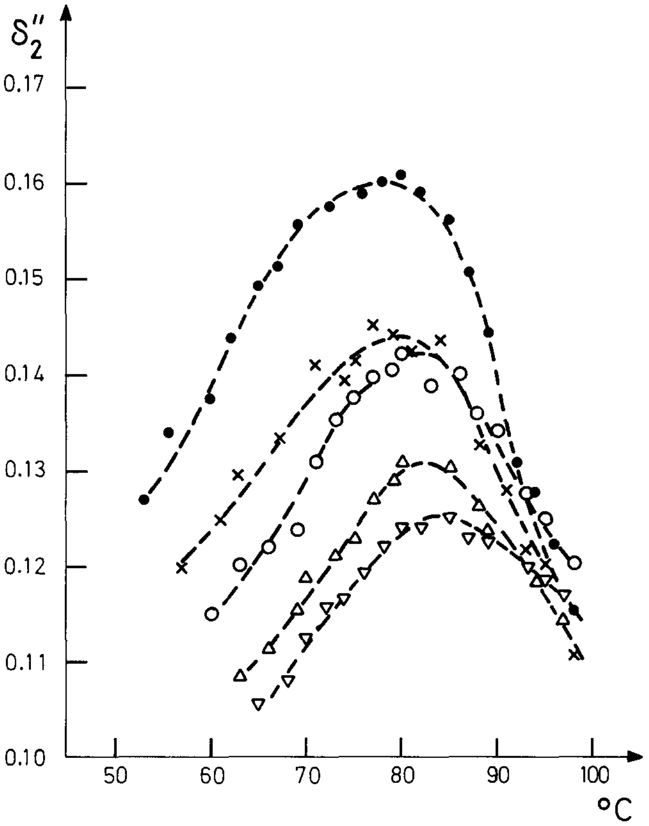

Figure 4 Deformability loss δ_2'' from equation (7) at the five experimental frequencies, showing the relaxation peak

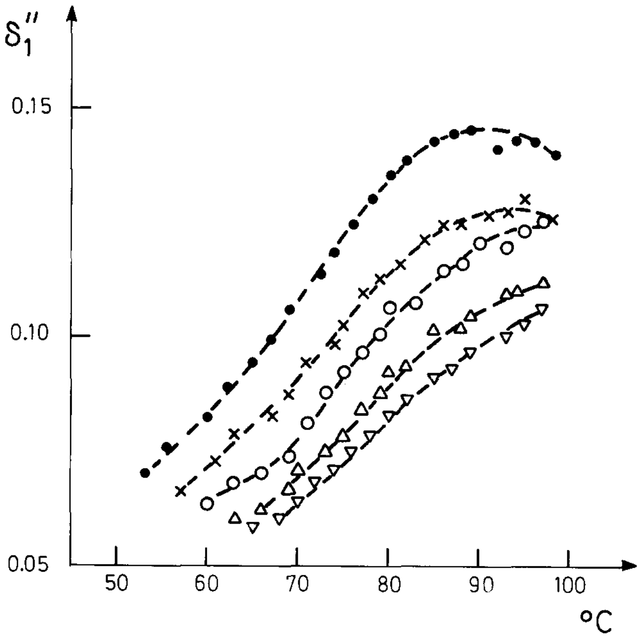

Figure 5 Deformability loss δ_1'' from equation (8) at the five experimental frequencies, showing the relaxation peak at lower frequencies

The results obtained are consistent with dielectric data[7] and with the fact that no glass-transition phenomenon is observed, at least in the range of temperatures studied. This is striking in an amorphous polymer. It is likely that the residual part of the molecule mechanically active above the temperature of the β-relaxation is only a small one, and this is the reason for the low loss observed in the α zone.

ACKNOWLEDGEMENTS

R.D.C. expresses his thanks to CICYT for partial financial support through GRANT MAT/0555. D.R. and L.G. also thank the Dirección de Investigación (DIUC), Pontificia Universidad Católica de Chile and FONDECYT for financial help.

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