Dielectric and mechanical–dynamical studies on poly(cyclohexyl methacrylate)

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The relaxation processes in poly(cyclohexyl methacrylate) have been studied by transient and dynamic dielectric means as well as by viscoelastic techniques. The study embraces also the effect of the thermal treatment on the α and β relaxations. The α relaxation has been fitted into the empirical model of Havriliak and Negami, and the functional relation between the mean relaxation times and the temperature has been adjusted to the equation of Vogel. The β relaxation is strongly hindered, so it is scarcely perceivable. The secondary γ relaxation was studied mainly by dielectric means. Its apparent activation energy does not depend on the temperature and amounts to 11.2 ± 0.2 kcal mol^{-1}. It allows an application of the time–temperature superposition principle and its behaviour is thermorheologically simple. A δ relaxation with a temperature-independent apparent activation energy of 8.5 kcal mol^{-1} has been obtained

(Keywords: polycyclohexyl metacrylate; dielectric relaxations; mechanical relaxations; apparent activation energy; master curve; Fuoss–Kirkwoods' parameter)

INTRODUCTION

Poly(cyclohexyl methacrylate)—PCHMA—shows four relaxation processes which have been labelled α, β, γ and δ in order of decreasing temperature.

The α-relaxation has been studied by Ishida[1] with dielectric means and by Heijboer[2] with mainly mechanical means, who have associated its origin to the glass transition of the polymer.

The β-relaxation, scarcely perceivable on these measurements, was analysed by Heijboer[3–5], and the intra- or intermolecular nature of the potential barrier to be overcome is still a matter of query.

Frosini[6], and above all Heijboer[7], have studied the mechanical γ relaxation assigning its molecular origin to be the transition between the two conformational saddle-forms of the cyclohexyl ring. They also characterized this relaxation as a well defined process, so as to allow the curves of it to be superposed according to the time–temperature superposition principle following an Arrhenius-like equation, and giving rise to a well defined master curve. The hypothesis can be made that the mechanical relaxation that appears in the same zone is due to the same molecular process, i.e. it is almost thermorheologically simple. The testing of this hypothesis is part of the present work.

The above mentioned authors[6,7] noted that the values of tan δ tended to increase at temperatures below that of the γ relaxation, a fact that led them to suppose the existence of a new relaxation process below the mentioned temperature.

The purpose of this work is to present a complete spectrum of the four relaxations of PCHMA at low and high temperatures and frequencies chiefly by dielectric means, although some viscoelastic results are included which have allowed us to complete the analysis of the relaxations and the effect of the thermal treatment on the α- and β-relaxations.

EXPERIMENTAL

Preparation of samples

Samples of PCHMA were obtained by polymerization of commercial cyclohexyl methacrylate monomer from Fluka (98 GC, $d_4^{20} = 0.964$, $n_D^{20} = 1.458$ and stabilized with 0.006% hydroquinone), which had been previously distilled at 4 mmHg and $T = 75.5°\text{C} \pm 0.1°\text{C}$.

Bulk polymerization via free radical took place at 50°C or 60°C for 68 h, with $0.050 \pm 0.001\%$ AZBN as initiator, the prepolymer being poured into a cuvette formed by glass plates. The polymer so obtained was vacuum-dried at 50°C for 30 days. The procedure is analogous to that of Heijboer[7].

The PCHMA plates thus obtained were characterized by determination of the mean molecular weight through dynamic viscosity measurements ($\bar{M}_w = 4 \times 10$ to 6×10).

After polymerization the samples were subjected to different thermal treatments (accordingly different letters have been assigned to the samples):

Samples of type *Q* were maintained at 125°C for 15 h and quenched afterwards;

Samples of type *S* were maintained at 125°C for 15 h and then cooled slowly at a rate of 5°C h^{-1}.

The temperature of 125°C was chosen because it lies above the T_g and in the temperature range which leads to the lowest concentration of free monomer[8].

Measurements

Dielectric and viscoelastic measurements have been done on the samples of PCHMA. For the first group two methods were employed:

Alternative: the real and imaginary parts of the complex dielectric permittivity $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ are measured with a capacitor bridge (General Radio 1615 A) and a Balsbaugh LD3 cell with a guard electrode.

Transient: the dielectric permittivity $\varepsilon(t)$ is obtained from measurements of isothermal polarization and de-

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polarization currents, and transformed to values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ through the methods of Hamon and Brather[9-13]. A HP 4329 A electrometer, a HP 6516 High Voltage DC power supply and the same cell as above was employed.

The viscoelastic results were obtained with the Dynamic Mechanical Thermal Analyser of Polymer Laboratories Ltd. The apparatus gives directly the values of the storage modulus E' and of $\tan\delta(\omega)$ in the range of frequencies 0.033–90 Hz and of temperatures −150°C to 300°C.

RESULTS

PCHMA shows four relaxation zones (*Figure 1*).

α *Relaxation*

As previously stated the relaxation has been ascribed to the glass transition of the polymer. Its molecular origin is retraced to the microBrownian movement of segments of the chain backbone.

Alternative dielectric measurements in a range of 60–10^5 Hz and of 40°C–180°C have been undertaken to study the dielectric relaxation on samples of types Q and S (*Figures 2* and *3*).

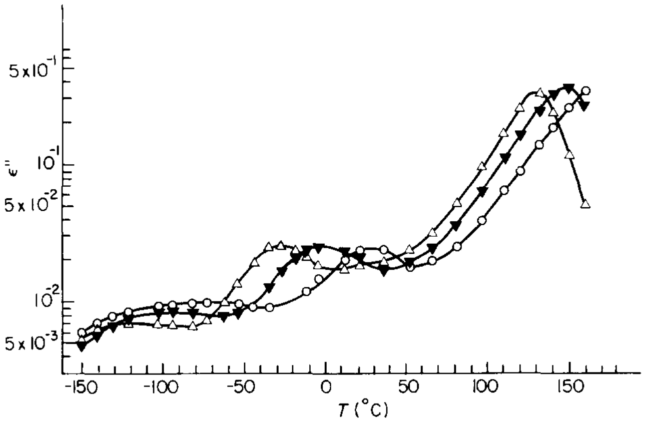

Figure 1 Values of ε'' vs. T for frequencies of 5 × 10 Hz (△), 5 × 10 Hz (▼), 5 × 10 Hz (○)

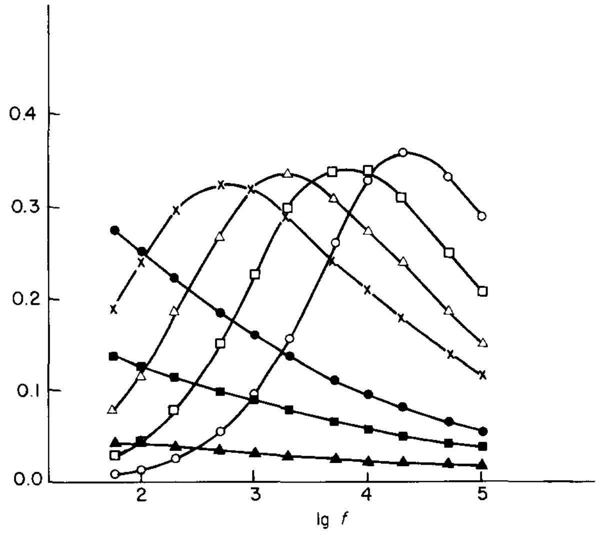

Figure 2 Values of ε'' vs. log f for Q sample at temperatures of 65.9°C (▲), 96.5°C (■), 110.6°C (●), 131.7°C (×), 140.5°C (△), 149.9°C (□), 159.4°C (○)

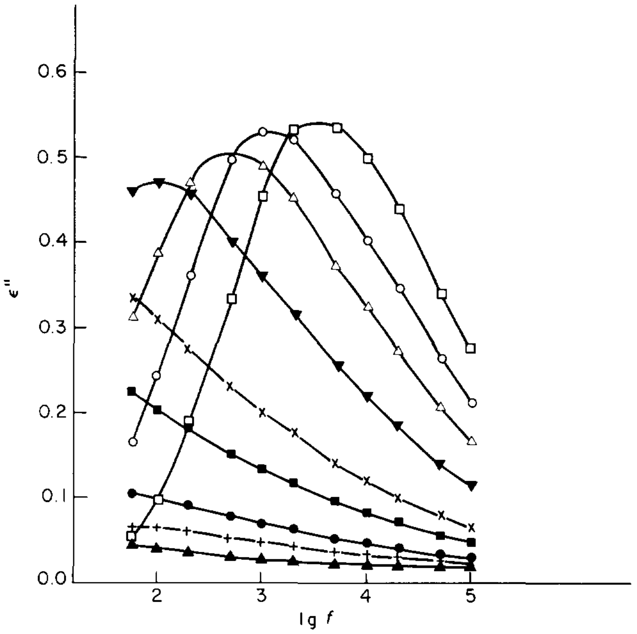

Figure 3 Values of ε'' vs log f *for* S sample at temperatures of 59.9°C (▲), 74.9°C (+), 84.7°C (●), 100.0°C (■), 109.7°C (×), 118.8°C (▼), 129.3°C (△), 137.4°C (○), 145.0°C (□)

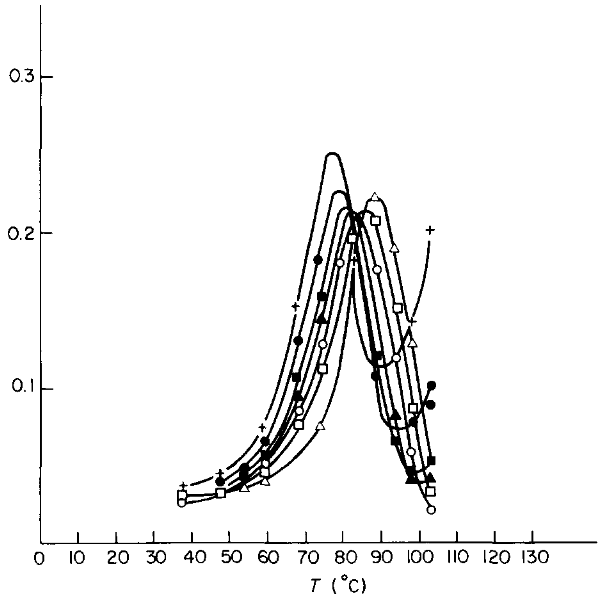

Figure 4 Values of ε'' vs. T obtained from isothermal depolarization measurements for frequencies of 7.8 × 10 Hz (+), 1.6 × 10 Hz (●), 3.1 × 10 Hz (■), 6.8 × 10 Hz (▲), 1.25 × 10 Hz (○), 2.5 × 10 Hz (□), 5 × 10 Hz (△)

Also, transient measurements have been applied to the study of this relaxation; they were not carried out on the other relaxations because of the necessity to maintain low temperatures for a long time. The frequency range thus obtained is of 4.9×10^{-5} to 5×10^{-2} Hz when the transformation method of Hamon is applied, and of 6.2×10^{-4} to 7.9×10^{-2} Hz when the applied method is the one of Brather (*Figure 4*). The mechanical α relaxation has been obtained with the DMTA at 10 Hz also on samples of types S and Q (Figure 5).

The dielectric relaxation has been fitted to the empirical model of Havriliak and Negami[14]:

$$\varepsilon^* = \varepsilon + \frac{\varepsilon_\infty - \varepsilon_0}{[1+(i\omega\tau)^{1-h}]^m} \qquad (1)$$

Figures 6 and *7* show the representation of the Cole–Cole arcs for *S* and *Q* samples. As an example, three temperatures have been considered. The parameters obtained are given in *Tables 1* and *2*. The parameter *h* in equation (1) is equal to zero for both kinds of samples, which means that the relaxation could have been fitted to the more simple model of Davidson and Cole.

The width of the relaxation, represented by the parameter '*m*' of equation (1), does not change at all with temperature in samples of type *S* and increases only slightly in samples of type *Q*, which suggests that the temperature has little influence on the form of the relaxation.

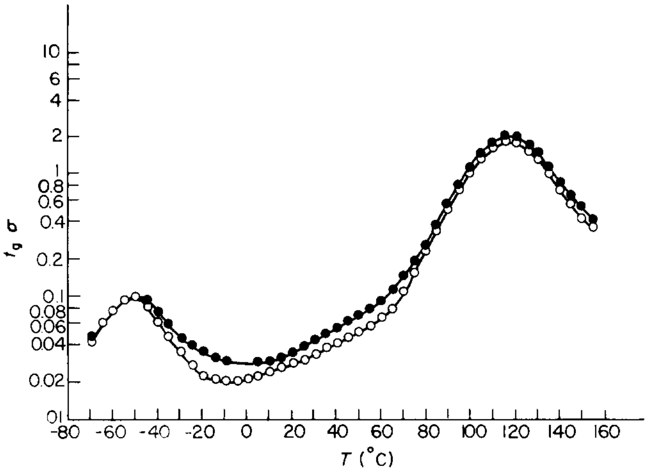

Figure 5 Values of mechanical $t_g\ \delta$ vs. *T* at frequiencies of 10 Hz for samples of type *Q* (●) and *S* (○)

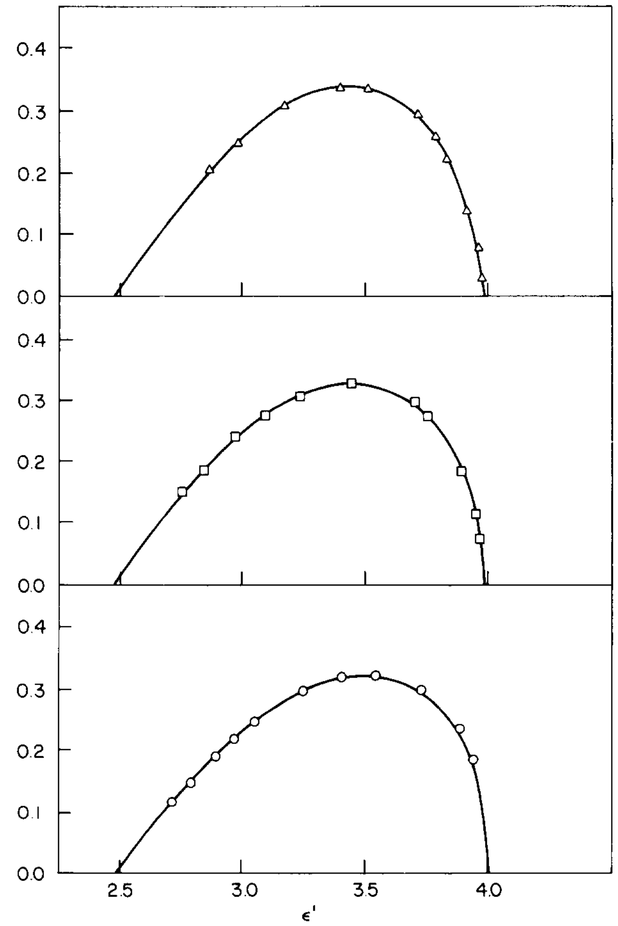

Figure 6 Cole–Cole arcs at temperatures of 131.7°C (○), 140.5°C (□) and 149.9°C (△) for *Q* sample

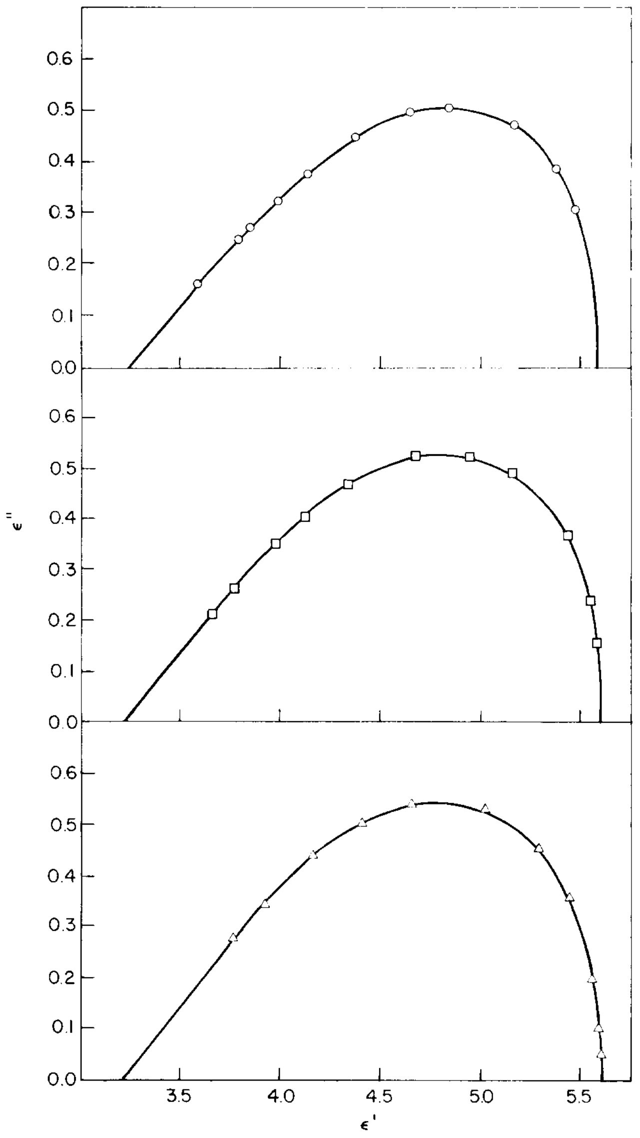

Figure 7 Cole–Cole arcs for *S* sample at temperatures of 129.3°C (○), 137.4°C (□) and 145.0°C (△)

Table 1 Parameters of the equation of Havriliak and Negami for samples of type *Q*

t	$\varepsilon-\varepsilon_\infty$	$1-h$	*m*	$\varepsilon'(\omega\tau_0)$
131.7	1.50	1	0.57	3.82
140.5	1.55	1	0.58	3.80
149.9	1.60	1	0.59	3.78

Table 2 Parameters of the equation of Navriliak and Negami for samples of type *S*

t	$\varepsilon-\varepsilon_\infty$	$1-h$	*m*	$\varepsilon'(\omega\tau_0)$
129.3	2.35	1	0.58	5.35
137.4	2.40	1	0.58	5.35
145.0	2.45	1	0.58	5.35

The logarithm of the frequency of the maxima of ε'' has been plotted against the inverse of the temperature (*Figure 8*) in order to study the dependence of the mean relaxation times on temperature. This relaxation has been adjusted to a Vogel equation,

$$\lg f_{\max} = A - \frac{B}{T - T_{\infty}} \tag{2}$$

The parameters A, B and T_{∞} for samples Q and S are shown in *Table 3*.

The apparent activation energy depends on temperature for both kinds of samples and is related to the parameters of B and T_{∞} through:

$$E_a = -RB\left(\frac{T}{T - T_{\infty}}\right)^2 \tag{3}$$

These parameters are slightly different for the two kinds of samples. Thus, the apparent activation energy is, at 25°C, of 89 kcal mol^{-1} for the type Q sample and of 97 kcal mol^{-1} for sample S.

β Relaxation

The β relaxation in PCHMA was attributed by Heijboer[3-5] to the partial rotation of the carboxyl group; the hypothesis has been laid down that the potential barrier that hinders the rotation is of intramolecular origin, caused by the methyl groups in the α position in the monomeric unit of the chain backbone.

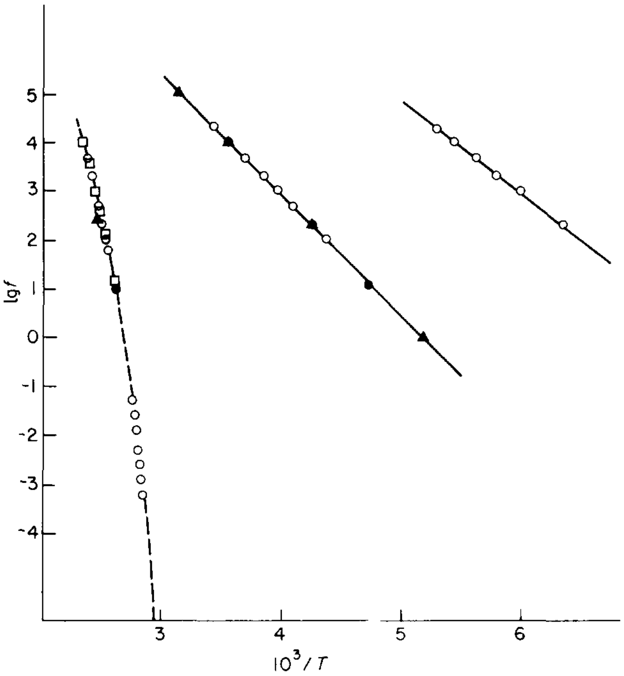

Figure 8 Arrhenius diagram showing the agreement between our results and those of other authors. (▲) mechanic dynamical results of Heijboer[2,7]; (□) dielectric results of Ishida and Yamafuji[1]; (○) our dielectric results; (●) our dynamic mechanical results on samples Q

Table 3 Parameters of the Vogel equation for the α relaxation of PCHMA

Sample	A	B (K)	T_{∞} (K)
Q	10.4	−994.6	342.5
S	11.6	−1138.9	343.6

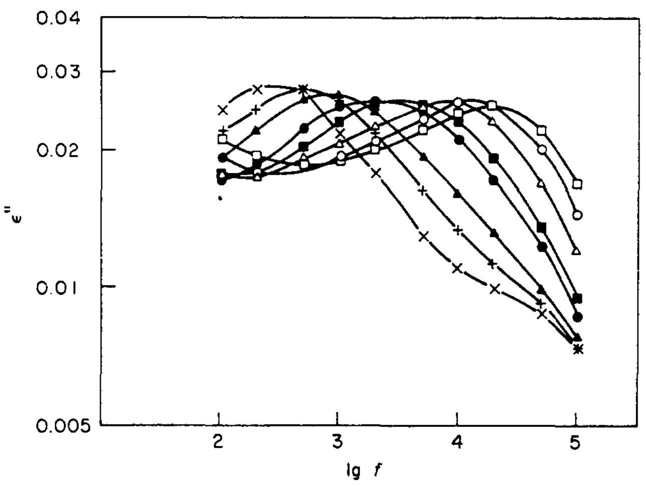

Figure 9 Values of ε'' vs. log f at temperatures 19.9°C (□), 12.7°C (○), 3.7°C (△), −5.4°C (■), −9.8°C (●), −21.5°C (▲), −27.6°C (+), −34.4°C (×)

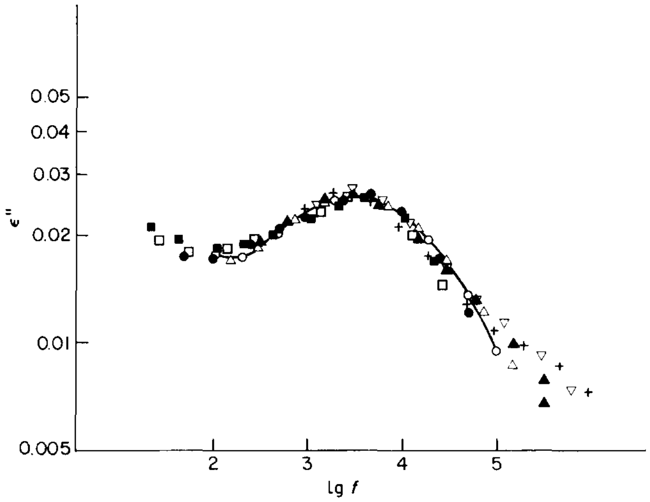

Figure 10 Master curve obtained by horizontal shift of isotherms 19.9°C (■), 12.7°C (□), 3.7°C (●), −9.8°C (△), −21.5°C (▲), −27.6°C (▽), −34.4°C (+), superposed on the −5.4°C (○) isotherm

This relaxation has been studied on samples Q and S by alternative and transient dielectric means and, mainly, by viscoelastic analysis at 10 Hz. These results, *Figures 1* and *5*, show, in agreement with other researches, that there is little evidence of a well defined β relaxation. Because of the volume of the cyclohexyl radical this relaxation is stongly hindered, thus explaining its weak intensity.

γ Relaxation

The γ relaxation has been studied by viscoelastic techniques on samples Q and S, *Figure 5*, and mainly by alternative dielectric means in the range of 10 to 10 Hz and of −50°C to 25°C on samples of type Q, *Figure 9*.

The dependence of the logarithm of the frequency of the maxima of $\varepsilon''(\omega)$ with the inverse of the temperature (*Figure 8*) has been adjusted to an Arrhenius equation:

$$\ln f = \ln f_0 + \exp(E_a/RT) \tag{4}$$

The apparent activation energy is practically constant with temperature and its value is 11.2 ± 0.2 kcal mol^{-1}.

A master curve (*Figure 10*) has been drawn by application of the time–temperature superposition principle, shifting horizontally (a_T) the isothermal curves of ε'' vs. log f with the isotherm of −5.4°C as base curve.

The shift factor is related with the temperature through:

$$E_a = R \; \mathrm{d} \ln a_T/\mathrm{d}(T^{-1}) \qquad (5)$$

Thus, plotting log a_T vs. $1/T$ the apparent activation energy is obtained as 11.7 kcal mol^{-1}. This means that the heights of the peaks do not appreciably depend on temperature, and the γ dielectric relaxation is then thermorheologically simple, according to the definition of Staverman and Schwarzl[15], the same behaviour as shown by the mechanical γ relaxation[16].

The dielectric γ relaxation has been adjusted to the model of Fuoss and Kirkwood[17]

$$\varepsilon(\omega) = \varepsilon(\omega_{\mathrm{max}})\mathrm{sech}(m.\ln\omega) \qquad (6)$$

The dependence of 'm' on temperature and frequency is shown in *Figures 11* and *12*.

The secondary δ relaxation

The study has been carried out by alternative dielectric means in a range of 10 to 10 Hz and of −150°C to −70°C on samples of type Q, *Figure 13*.

We have determined the relation between the mean relaxation times and temperature by means of an Arrhenius-like equation (4).

The apparent activation energy, almost constant with temperature, has the value of 8.5 kcal mol^{-1}.

We have fitted this relaxation to the model (6) of Fuoss and Kirkwood. The relationship between the marameter 'm' and frequency is shown in *Figure 14*. The low values of m mean that it is a very broad relaxation.

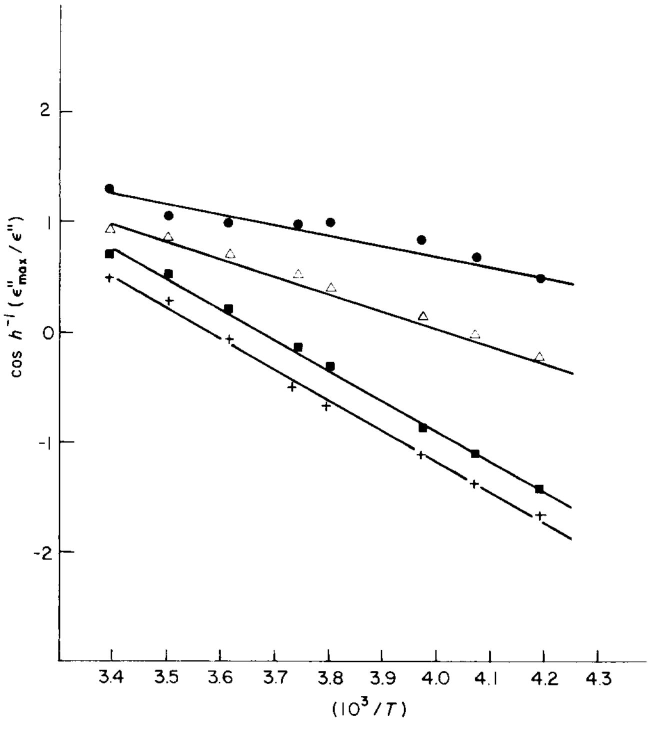

Figure 11 Relationship between the parameter m of the Fuoss–Kirkwood equation and temperature for the frequencies 10Hz (+), 5×10Hz (■), 5×10Hz (△), 10Hz (●)

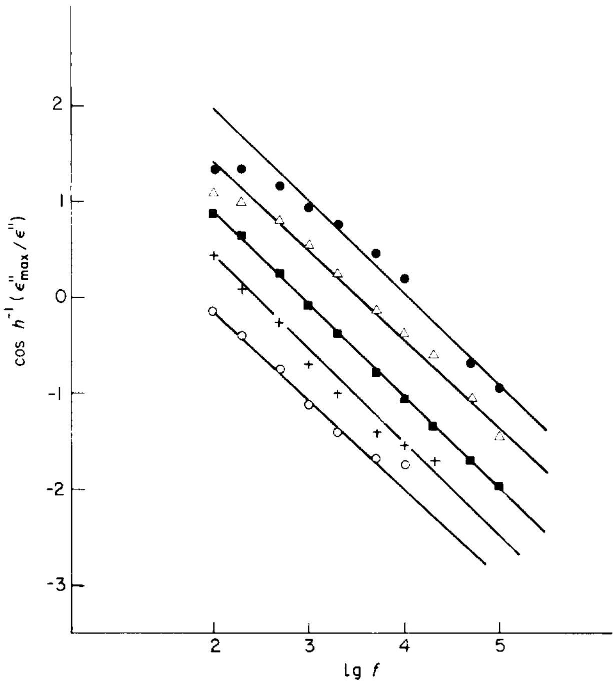

Figure 12 Relationship between the parameter m of the Fuoss–Kirkwood equation and log f for temperatures of 19.9°C (●), 3.7°C (△), −21.2°C (■), −34.4°C (+), −44.2°C (○)

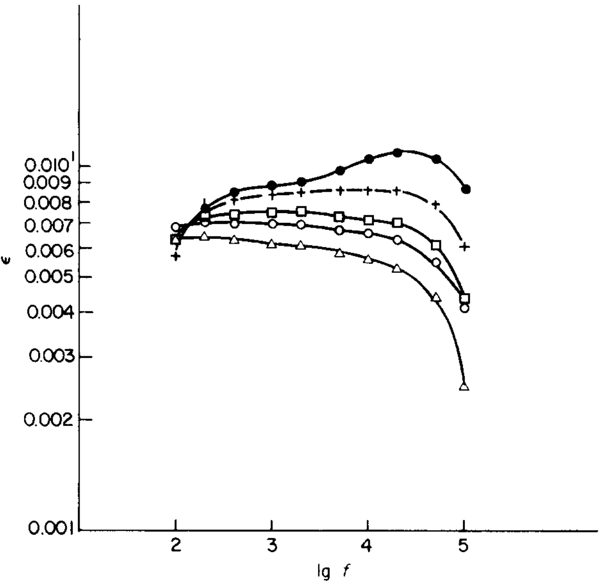

Figure 13 Values of ε'' vs. log f for temperatures of −94.5°C (●), −115.1°C (+), −130.7°C (□), −137.1°C (○), −152.1°C (△)

DISCUSSION

The experimental results obtained in this work agree with previous ones from other authors, as *Figure 8* shows.

Greater values of tan δ on plate Q than on plate S can be observed in dynamic mechanical measurements from the γ relaxation maximum till 80°C, because of the greater free volume induced in the first by the quenching process[18].

These differences in free volume are thought to affect in the first place the mobility of the chain backbones at $T < T_g$; the extent to which the motion of the groups responsible for the β and α relaxations is affected by the free volume cannot be known[19,20].

In dielectric measurements there is no significant difference in tan δ and ε'' between plates Q and S at temperatures below T_g. For temperatures above T_g the

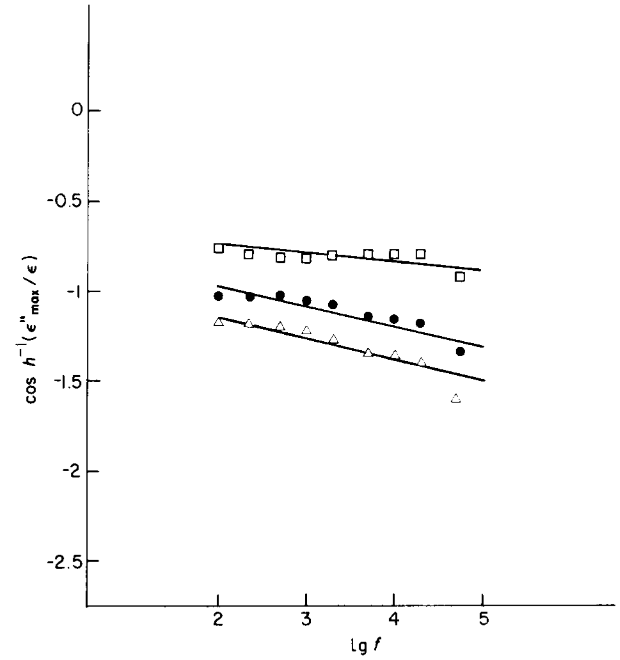

Figure 14 Relationship between the parameter *m* of the Fuoss–Kirkwood equation and log *f* for temperatures of −152°C (△), −137.1°C (●), −130.7°C (□)

values of tan δ and ε'' are higher for plate *S* than for plate *Q*. These differences should be ascribed in the main to the measuring method (air gap). In it, an air layer is left between the electrodes and the sample; as the sample is introduced at one temperature and the tests are carried out at different ones, the material's dilatation can provoke changes in the thickness of the air layer impossible to evaluate. At temperatures below T_g the errors due to this cause are very small because of the low dilatation of the material. Nevertheless, when results on samples *Q* and *S* are compared the error at temperatures above T_g can be significant. The sample *S*, more contracted, suffers a dilatation greater than sample *Q* as it passes through temperature above T_g, even occupying completely the volume left between electrodes. Thus, the values of tan δ and ε'' of the material as calculated from the capacity and tan δ measured considering that the air gap is the same as initially are higher than the real ones. This means that in our case the values of ε'' ($\varepsilon'' = \varepsilon' \tan \delta$) have very significant excess errors. The differences in tan δ between samples *Q* and *S* are about 15% while those in ε'' amount to 50%. This fact has also been observed on other amorphous polymers in similar conditions[19,20].

Other methods of measurements will produce similar effects, because if the electrodes were tightened against the sample the free expansion accompanying the increase of temperature would not be allowed and the pressure exerted would alter the results. If the plate is metallized and left free to expand it would be necessary to measure its thickness at each temperature.

Given the important study of Heijboer on the molecular origin and chararacterization of the mechanical γ relaxation[7], we have thought it convenient to carry out a comparison between our results and his.

Figure 8 shows an Arrhenius representation of the dielectric γ results together with those obtained by Heijboer on the mechanical γ relaxation[7]. The apparent activation energy (E_a) as calculated from this representation is of 11.2 ± 0.2 kcal mol^{-1}, very similar to the value of 11.3 kcal mol^{-1} of Heijboer. When calculated from the shift factor a_T we find a mean value of 11.7 kcal mol^{-1}, whereas Heijboer obtains a mean value of 11.6 kcal mol^{-1}.

The half width of the dielectric γ relaxation Δ (1000/*T*) K[7] is 0.97 and 0.90 for the frequencies of 5×10^3 and 10^4 Hz respectively, similar to those obtained by Heijboer (0.87, 0.90, 0.79, 0.84) at 1 Hz.

The dielectric γ relaxation appears in the same temperature and frequency zone as the mechanical γ relaxation; it has an apparent activation energy constant with temperature of practically the same value and a very close rheological behaviour. We can thus lay down the assumption that the dielectric γ relaxation has the same molecular origin as that proposed by Heijboer for the mechanical γ relaxtion, i.e., the motion of the cyclohexyl ring between its two chair form conformations.

A dielectric δ relaxation has been obtained, whose existence had been previously predicted by other authors[6,7].

ACKNOWLEDGEMENT

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