Dynamic mechanical behaviour of poly(benzyl methacrylate) and poly(cyclohexylmethyl methacrylate)

R. Díaz Calleja*

Departamento de Termodinámica Aplicada, ETSII, Universidad Politécnica de Valencia (UPV), Valencia, Spain

and Ligia Gargallo and Deodato Radic

Facultad de Química (502), Departamento de Química Física, Pontificia Universidad Católica de Chile, Casilla 306 – Correo 22, Santiago, Chile

(Received 22 July 1991; revised 15 February 1993)

The dynamic mechanical properties of poly(benzyl methacrylate) (PBzMA), and poly(cyclohexylmethyl methacrylate) (PCHMMA) were studied. In order to show the β relaxation in both polymers and the γ relaxation in PBzMA, the derivative of the real part of the complex modulus dE'/dT was calculated, which is proportional to $T^{-2}E''$. A detailed study of the γ relaxation spectra of PCHMMA in terms of activation free energy distribution was performed.

(Keywords: poly(benzyl methacrylate); poly(cyclohexylmethyl-methacrylate); dynamic mechanical relaxations; secondary relaxations; Gibbs free energy distribution)

INTRODUCTION

The dynamic mechanical properties of polymers are strongly dependent upon their structure. Flexibility of the lateral chains can give rise to secondary loss maxima but, on the other hand, intramolecular hindrance produced by other lateral groups can prevent mobility and consequently impede the appearance of these secondary relaxations. In a very important contribution to the analysis of secondary relaxations in polymers containing cyclohexyl rings, Heijboer[1] has reported the dynamic mechanical properties of poly(cyclohexyl methacrylate) (PCHMA) in a broad range of frequencies. The main finding of this research was that flipping (chair-to-chair) of the pendant cyclohexyl group was the molecular origin of a typical dynamic mechanical relaxation near $-80°C$ (1 Hz), having an activation energy of 11.4 kcal mol^{-1}. On the contrary, in phenyl-substituted polymers there is no indication of such a relaxation, probably due to the rigid structure of the unsaturated ring.

Many other polymers were studied in ref. 1 but in many cases the results have been reported only at one frequency (1 Hz). Among them, poly(benzyl methacrylate) (PBzMA) and poly(cyclohexylmethyl methacrylate) (PCHMMA) are suitable for analysing the effect of the presence of a spacer $-CH_2-$ in the lateral chain containing the cyclohexyl ring. In fact, if the side groups are fixed via a flexible spacer to the main chain, the motions of the main chain and the side chains might be decoupled[2]. On the other hand, if the side groups are fixed directly to the main chain, the ability to move and orient is changed drastically[3,4].

The aim of this work is to study the viscoelastic relaxation spectrum by dynamic methods in both polymers covering a range of frequencies from 0.3 to 30 Hz.

EXPERIMENTAL

The preparation of monomers and polymers as well as the molecular characterization of the corresponding polymers have been reported previously[5]. Films of both polymers, PBzMA and PCHMMA, were obtained by dissolution and subsequent evaporation from tetrahydrofuran (THF) solutions. The dried polymers are very fragile. A Polymer Laboratories dynamic mechanical thermal analysis (d.m.t.a.) instrument in flexure single cantilever mode was used at frequencies of 0.3, 1, 3, 10 and 30 Hz, using samples of 0.25 mm × 5 mm × 5 mm. In order to obtain a better description of the relaxation process of PCHMMA at low temperatures, it would be preferable to use higher frequencies, i.e. 50, 100 and 200 Hz. However, at those frequencies, due to the resonance of the instrument and the fragility of the samples at low temperatures, it is very difficult to prevent the samples from breaking. Measurements were performed between -100 and $+90°C$ for PBzMA and from -130 to $+100°C$ for PCHMMA at $1°\,min^{-1}$ in both cases.

---

*To whom correspondence should be addressed

0032-3861/93/204247-05

RESULTS

Figures 1 and *2* show the storage and loss moduli for PBzMA and PCHMMA, respectively. In PBzMA, a viscoelastic relaxation between 60 and 80°C is observed, which can presumably be associated with the glass transition temperature T_g, while the remainder of the spectrum is relatively plain. Slight viscoelastic activity is observed around −60 and 20°C. The appearance of this new relaxation is the main difference between the dynamic mechanical spectrum of this polymer and that of PCHMA, as reported in ref. 1. On the contrary, in the case of PCHMMA there are at least three relaxations. The first is that associated with T_g, but there are two relaxations at low temperatures, the first at −124°C (30 Hz) which is labelled δ and the other at −60°C (30 Hz) which we call γ. Besides the two relaxations, part of a β relaxation at ~20°C (30 Hz) is observed. Because of the experimental reasons mentioned above, it is difficult to calculate the energy of activation of the δ relaxation because the relaxation peak only appears at the highest frequency (30 Hz).

For the γ relaxation, the energy of activation, calculated by an Arrhenius-type equation ($\ln f_{\max}$ *versus* T^{-1}) is 12.5 ± 0.5 kcal mol^{-1}. Considering the frequency and position of these relaxations it is possible to conclude that all the parameters characterizing the relaxations found in this study are in good agreement with those reported by dielectric measurements in ref. 1.

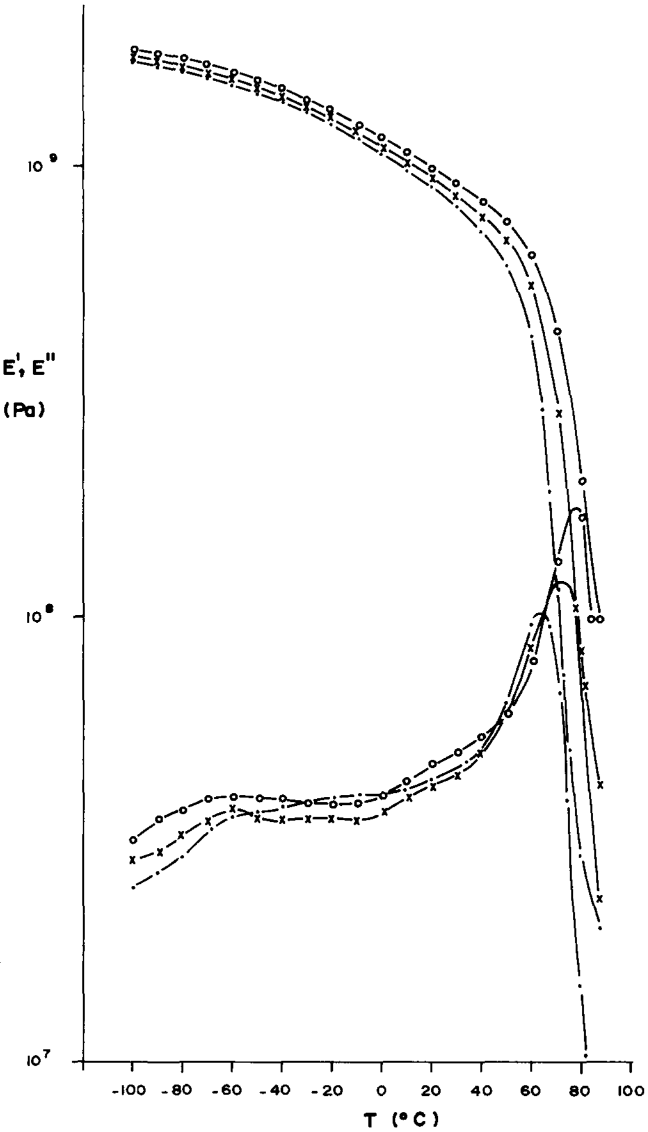

Figure 1 Storage and loss moduli of PBzMA. Frequency: •, 0.3 Hz; ×, 3 Hz; ○, 10 Hz

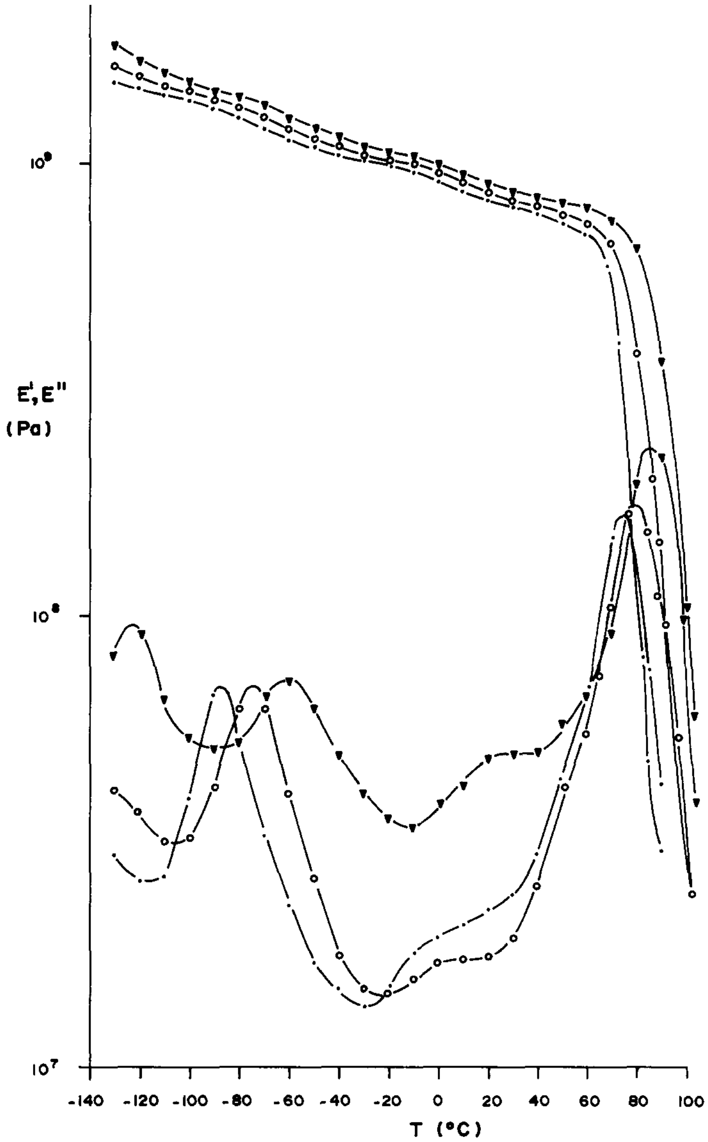

Figure 2 Storage and loss moduli of PCHMMA. Frequency: •, 0.3 Hz; ○, 3 Hz; ▼, 30 Hz

DISCUSSION

As mentioned above, there is evidence of mechanical absorptions at −60°C for PBzMA which will be labelled γ and another absorption at about 20°C for both polymers which will be labelled β. In order to visualize these relaxations clearly, we have followed the procedure used in previous papers[5,6].

Starting from the thermodynamic relationships between the storage modulus (E'), the angular frequency (ω) and the absolute temperature (T):

$$\left.\frac{\partial E'}{\partial T}\right|_{\omega} \left.\frac{\partial T}{\partial \ln \omega}\right|_{E'} \left.\frac{\partial \ln \omega}{\partial E'}\right|_{T} = -1 \qquad (1)$$

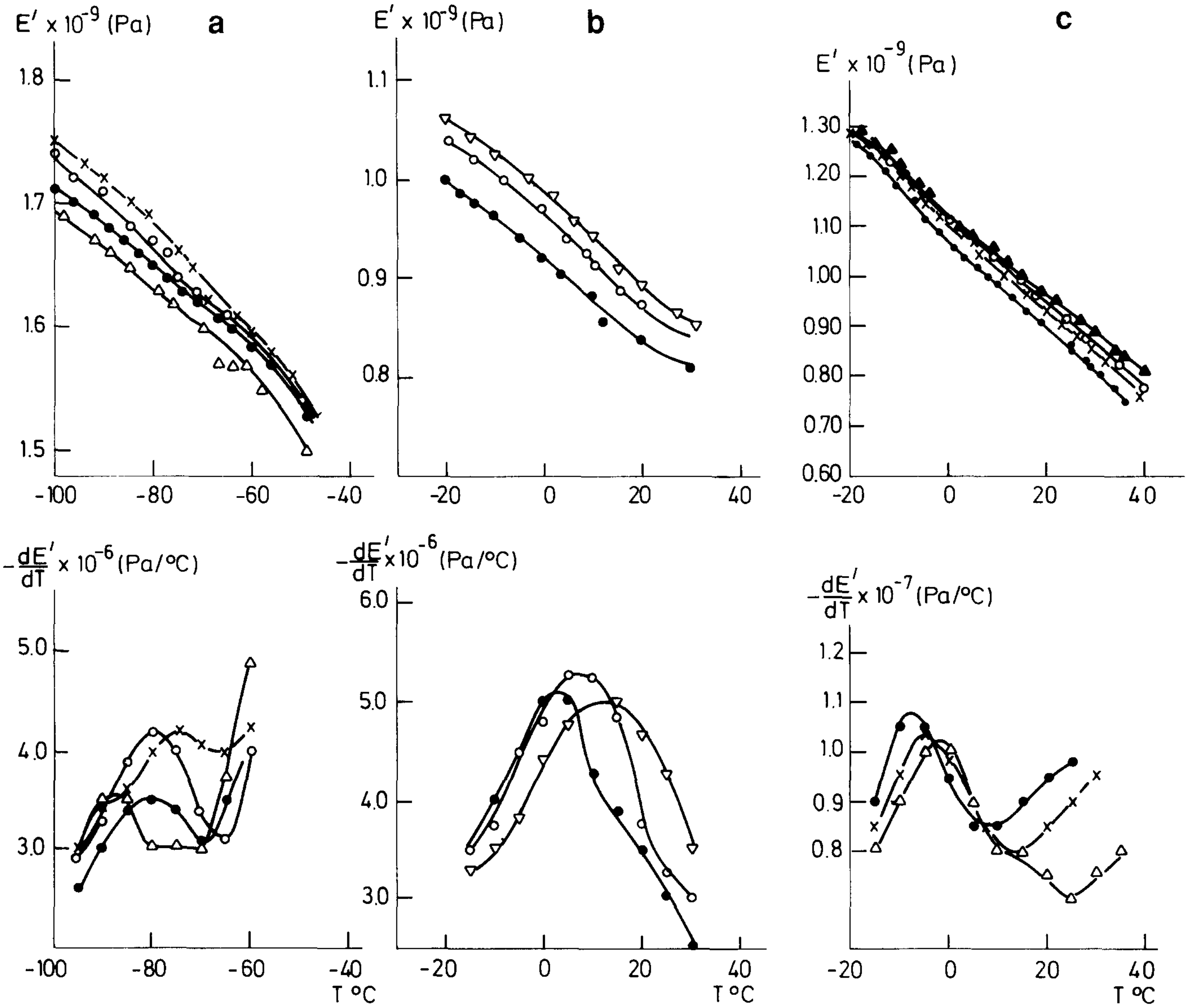

Figure 3 Storage moduli and their temperature derivatives. (a) PBzMA (γ relaxation): △, 0.3 Hz; ●, 1 Hz; ○, 3 Hz; ×, 10 Hz. (b) PCHMMA (β relaxation): ●, 0.3 Hz; ○, 3 Hz; ▽, 3.0 Hz. (c) PBzMA (β relaxation): ●, 0.3 Hz; ×, 1 Hz; ○, 3 Hz; △, 10 Hz

we obtain:

$$\left.\frac{\partial E'}{\partial T}\right|_{\omega} = -\left.\frac{\partial E'}{\partial \ln \omega}\right|_{T} \left.\frac{\partial \ln \omega}{\partial T}\right|_{E'} \tag{2}$$

On the other hand, since

$$\left.\frac{\partial E'}{\partial \ln \omega}\right|_{T} \equiv \frac{2}{\pi} E' \quad \text{and} \quad \frac{\partial \ln \omega}{\partial T} = \frac{E_a}{RT^2} \tag{3}$$

where E_a is the activation energy, it is possible to obtain:

$$\left.\frac{\partial E'}{\partial T}\right|_{\omega} \equiv \frac{2E_a}{\pi R T^2} E'' \tag{4}$$

where E'' is the loss modulus. If E_a is considered to be constant, the effect of T^{-2} on the left-hand side of equation (4) is to diminish its value in the high-temperature side of the spectrum, more than in the left-hand side of the same spectrum, giving rise to a peak in $\left.\frac{\partial E'}{\partial T}\right|_{\omega}$.

Figure 3 shows the variation of E' and of its derivative with respect to T. This figure shows maxima corresponding to the small inflections observed in E'. This reflects the existence of true viscoelastic relaxations. These results are in good agreement with the dielectric relaxations found in the case of PBzMA[5,7]. These results are satisfactory, taking into account the experimental error arising from d.m.t.a. measurements.

β relaxations can be tentatively attributed to the whole rotation of the ester group of the side chains. γ relaxation in PBzMA can be attributed to motions of the phenyl or benzyl group in those lateral chains.

It is not possible to make a more detailed analysis of the δ relaxation in PCHMMA because the presence of this relaxation is only apparent on the isochrone of 30 Hz. In this polymer and in poly(ethylcyclohexyl methacrylate) a relaxation was observed by Heijboer[1] at −160°C only at a frequency of 1 Hz. Assuming an activation energy of 5.5 kcal mol^{-1} for this relaxation, which corresponds to the value found by previous dielectric measurements[5], then at 30 Hz the relaxation should be detected at about −140°C, near the value of −124°C found by us from viscoelastic measurements. This would therefore be the relaxation previously reported by Heijboer[1]. The γ relaxation in PCHMMA is clearly defined at all

Table 1 Frequency dependence of parameter m, the loss maximum and the strength of the relaxation

f (Hz)	m	$E''_{max}\times 10^{-7}$ (Pa)	$\Delta E\times 10^{-9}$ (Pa)
0.3	0.50	6.8	0.27
1	0.41	7.0	0.34
3	0.43	6.9	0.32
10	0.41	6.9	0.34

Table 2 Temperature dependence of the relaxation spectrum as a function of the frequency, loss modulus and Gibbs free energy

Temperature (°C)	ϕ^a	f (Hz)	$E''\times 10^{-7}$ (Pa)	ΔG^b (kcal mol^{-1})
−90	0.127	0.3	6.85	10.37
	0.114	1	6.10	9.93
	0.089	3	4.75	9.53
	0.068	10	3.65	9.09
−80	0.107	0.3	5.20	10.96
	0.131	1	6.90	10.49
	0.199	3	6.35	10.07
	0.095	10	5.10	9.60
−70	0.064	0.3	3.40	11.55
	0.095	1	5.10	11.06
	0.122	3	6.50	10.61
	0.129	10	6.90	10.12
	0.108	30	5.75	9.68
−60	0.043	0.3	2.30	12.14
	0.062	1	3.30	11.62
	0.079	3	4.20	11.15
	0.109	10	5.80	10.64
	0.130	3	6.95	10.17
−50	0.031	0.3	1.65	12.72
	0.041	1	2.20	12.19
	0.056	3	3.00	11.70
	0.075	10	4.00	11.16
	0.118	30	6.30	10.67

[a] $\phi=2E''/\pi\Delta E$ and $\Delta E=34\times 10^7$ Pa
[b] $\Delta G=RT(21.922+\ln T/f)$

frequencies. It is therefore possible to perform a detailed study of this relaxation. Using the empirical equation of Fuoss and Kirkwood[8], it is possible to model the relaxation according to:

$$E''=E''_{max}\mathrm{Sech}\; mx \tag{5}$$

where m is a parameter dealing with the broadening of the relaxation, and

$$x=\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{max}}\right) \tag{6}$$

where T_{max} is the temperature of the maximum in E''.

From equation (5) it is possible to estimate m for the different isochrones. *Table 1* summarizes these values. Although, strictly, m depends on temperature, for our purposes it is enough to take an average value.

Starting from the well known equation[9]:

$$\Delta E=\frac{2E''_{max}}{m} \tag{7}$$

it is possible to estimate ΔE, i.e. the intensity of the relaxation. The values found are also summarized in *Table 1*. We will take $\Delta E=34\times 10^7$ Pa. Equation (5) is a very simple model but has the advantage that it is possible to estimate the intensity of the relaxation, which will be useful for our purposes. Nevertheless, it corresponds to motions due to small molecular groups. In fact it is well known that secondary relaxations show a very broad distribution of the relaxation time. There are several ways to represent the relaxation time spectra starting from experimental data; one of the simplest and most useful methods for secondary relaxations is to use the following equation:

$$\phi=\frac{2E''(f)}{\pi\Delta E} \tag{8}$$

with $f=(1/2\pi)\tau$, where ϕ is the distribution of the relaxation times, $E''(f)$ is the frequency dependent loss and ΔE is the strength of the relaxation, which in terms of an empirical equation such as equation (5) can be written as:

$$\phi=\frac{m}{\pi}\mathrm{Sech}\; mx \tag{9}$$

In order to draw the relaxation spectrum according to equation (8) it is necessary to obtain an isothermal master curve. In this case it is not difficult to obtain such a master curve, for instance at a reference temperature of −70°C. From this, ϕ can be calculated (see *Table 2*), which is directly proportional to a curve corresponding to equation (9) (see *Figure 4*). A distribution of relaxation times can be the consequence of a distribution of activation energy E_a or pre-exponential factors τ_0, or both, in the equation:

$$\tau=\tau_0\exp\frac{E_a}{RT} \tag{10}$$

Because of the difficulties in studying a distribution

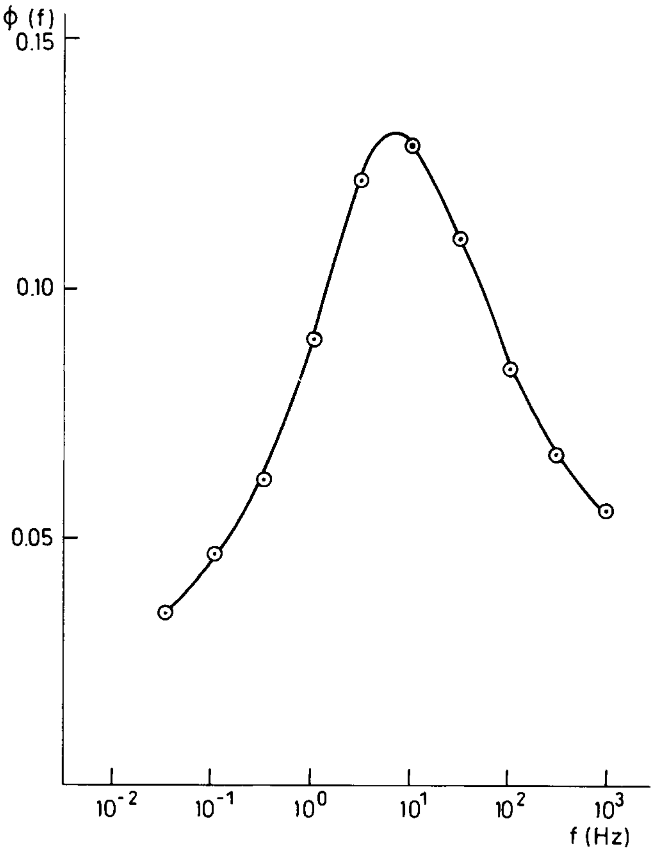

Figure 4 Frequency-dependent relaxation spectrum for the γ relaxation of PCHMMA

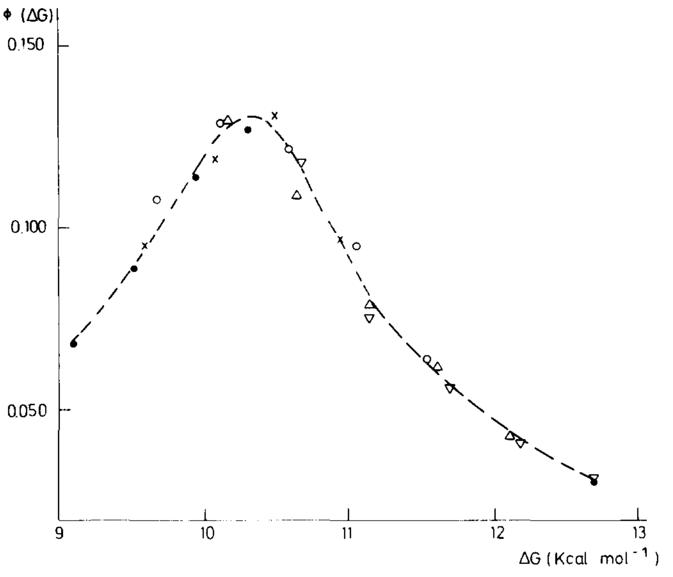

Figure 5 Distribution of Gibbs free energy at five temperatures: ●, −90°C; ×, −80°C; ○, −70°C; △, −60°C; ▽, −50°C

in τ_0, we will interpret the results about the γ relaxation of PCHMMA in terms of an energy distribution. We will follow a procedure similar to that described by Starkweather[10]. We start our analysis by assuming a model more sophisticated than the Arrhenius equation for the dependence of frequency on temperature. According to the Eyring equation:

$$f=\frac{kT}{2\pi h}\exp-\frac{\Delta G}{RT} \qquad (11)$$

where k and h are the Boltzmann and Planck constants, respectively. Here it is assumed that the potential barrier, which is opposite to the relaxation, is governed by a Gibbs free energy ΔG given by:

$$\Delta G=\Delta H-T\Delta S \qquad (12)$$

where ΔH and ΔS are the activation enthalpy and entropy, respectively. For this case, the values found are $\Delta H=12.4\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S=9.5\ \mathrm{cal\,mol^{-1}\,K^{-1}}$.

It is well known[11] that ΔH and the activation energy E_a given by the Arrhenius equation are related by:

$$E_a=\Delta H+RT \qquad (13)$$

Most of the secondary relaxations show a slightly cooperative character that is reflected by a very small value of ΔS. These are the so-called simple relaxations[11,12].

For the case when $\Delta S\cong 0$ it is easy to see from equations (11) and (13) that:

$$E_a=RT\left(1+\ln\frac{kT}{2\pi hf}\right) \qquad (14)$$

with $\ln(k/2\pi h)=21.922$. From this equation the minimum of the activation energy at a given temperature for a secondary relaxation process can be obtained at a frequency $f=f_0$.

The basic objective is to characterize the whole relaxation, not only the maximum, with the aid of equation (11). In fact, from equation (11) it is easy to see that:

$$\Delta G=\Delta H-T\Delta S=RT\left(21.922+\ln\frac{T}{f}\right) \qquad (15)$$

There is a distribution of ΔG in the range of frequencies studied for each temperature and at the same time a spectrum $\phi(f)$ (*Table 2*). Consequently, by using f and T as parameters it is possible to obtain a distribution $\phi(\Delta G)$. If the points lie on the same curve, i.e. the shape of the spectrum is independent of the temperature, $\Delta S\equiv 0$ and $\Delta G\equiv\Delta H$ and therefore there is a distribution of enthalpies. In *Figure 5* it is observed that this is the case, despite a small scattering.

In fact, if the γ relaxation in PCHMMA is attributed[1] to the chair-to-chair inversion of the cyclohexyl ring, it is clear that it is a molecular motion governed by a predominantly intramolecular barrier. Therefore, there is a small cooperativity which is in good agreement with the obtained results.

It should be noted that our analyses have been carried out on data obtained from dynamic experiments at 1°C min^{-1}, that is, in non-equilibrium from a thermodynamic point of view, whereas the parameters ΔH, ΔG and ΔS must of course be considered in equilibrium. Although 1°C min^{-1} is a relatively low rate, this can be a source of discrepancy between the results obtained from our data and those obtained in equilibrium conditions.

ACKNOWLEDGEMENTS

This work was supported by Grant MAT 91/0695 of the Cicyt. L. G. and D. R. express their thanks to Dirección de Investigación (DIUC), Pontificia Universidad Católica de Chile, and Fondo Nacional de Desarrollo Científico y Tecnológico (FONDECYT) for partial financial support.

REFERENCES

1 Heijboer, J. PhD thesis, Leiden, 1972, p. 109
2 Gargallo, L., Méndez, I. and Radic', D. *Makromol. Chem.* 1983, **184**, 1053
3 Finkelman, H., Happ, M., Portugal, M., Ringsdorf, H. and Wendorff, J. *Makromol. Chem.* 1978, **179**, 2541
4 Finkelman, H., Ringsdorf, H. and Wendorff, J. *Makromol. Chem.* 1978, **179**, 273
5 Ribes Greus, A., Díaz Calleja, R., Gargallo, L. and Radic', D. *Polymer* 1989, **30**, 1685
6 Banhegyi, G., Hedvig, P. and Karasz, F. E. *J. Appl. Polym. Sci.* 1988, **35**, 679
7 Kihira, Y., Ichidayama, K. and Takagi, S. *Makromol. Chem.* 1990, **191**, 2609
8 Fuoss, R. M. and Kirkwood, J. G. *J. Am. Chem. Soc.* 1941, **63**, 385
9 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967
10 Starkweather, H. W. *Macromolecules* 1990, **23**, 328
11 Starkweather, H. W. *Macromolecules* 1981, **14**, 1277
12 Starkweather, H. W. *Macromolecules* 1988, **21**, 1798