Dielectric and dynamic–mechanical relaxations in methyl methacrylate and methyl isopropenyl ketone copolymers

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Dynamic–mechanical and dielectric (alternative and thermally stimulated depolarization currents) tests have been carried out on methyl methacrylate and methyl isopropenyl ketone copolymers. Results indicate that the α relaxation, which has been related to the cooperative motions of the main chain, shifts to lower temperatures when the content of methyl isopropenyl ketone is increased. However, the position in the temperature axis and the magnitude of activation energy of the β relaxation is the same in the poly(methyl methacrylate) and in all the copolymers. These facts reinforce the classical hypothesis that there is an intramolecular barrier which hinders the rotational motion of the alkoxy carbonyl group contributing to the secondary loss peak of poly(methyl methacrylate).

(Keywords: α and β dielectrical and mechanical relaxations; methyl methacrylate and methyl isopropenyl ketone copolymers; side group motions; glass transition)

INTRODUCTION

Recently methyl methacrylate (MMA)–methyl isopropenyl ketone (MIK) has been prepared by radical copolymerization, and the degradation by exposure to sunlight and under environmental conditions[1] has been studied. It is interesting to know the mechanical and dielectric behaviour of these copolymers as a main aspect of the physical properties of these new materials.

Moreover, there is a subtle question concerning the mechanical and dielectric properties of polymers; in most cases it is the detailed molecular processes causing the loss peaks (α, β, γ,...) which have not been ascribed unequivocally. In the case of the α and β relaxations of PMMA many attempts have been made to interpret these dielectric and mechanical relaxations as seen from the review of McCrum *et al.*[2]. The α relaxation has been considered as the principal relaxation and associated with the onset of long range segmental motion of the polymer backbone, and the β relaxation is usually assigned to a local motion of the side groups with a specific intramolecular barrier[2–6]. However, it has been claimed[7] that the molecular motions associated with secondary peaks do not have a specific intramolecular barrier, and some investigators[8] even assign the β peak of PMMA to the main chain and the α peak to the side chain. They have based their theory on the relative magnitude of dielectric relaxations which are larger in the β peak than in the α one.

The systematic variation of the chemical structure of PMMA has been used to obtain information about the groups responsible for the α and β peaks, and there are several reasons favouring the assignment of the molecular origin of these peaks proposed by Heijboer[4]. One reason is that when the α-methyl group, which hinders the backbone mobility and the rotation of the lateral chain, is substituted by hydrogen atoms, the α and β peaks shift to lower temperatures[9]. When the substituent of the carboxyl group is replaced by a bulky group, the α peak shifts to lower temperatures while the position of the β peak does not change although its intensity decreases[2,10–12]. Also, the prominency of the β dielectrical relaxation over the α relaxation constitutes evidence of the motion of a polar ester group, whereas the converse is true for the mechanical relaxations where the mobility of the chains is more important. Nevertheless, the relative intensity of the α and β peaks is a function of polymer tacticity[13,14]. The α peak of isotactic samples is somewhat taller and narrower and located about 40°C lower in temperature than the α peak of the syndiotactic and atactic samples, and the β peak of isotactic samples is perhaps a small peak submerged in the low-temperature tail because the isotactic chain is considerably more mobile than the syndiotactic and atactic chains.

Heijboer *et al.*[6] have recently carried out a theoretical molecular mechanics study on rotational motions of side groups in PMMA, and have partly confirmed that the β-maximum is due to reorientation of the ester side group. They also revealed the existence of a significant contribution of the main chain units to the intramolecular barrier. Our present results support this conclusion, because the α peak shifts to lower temperatures and the position of the β peak does not change with the addition of methyl isopropenyl ketone. Furthermore, we find that the apparent activation energy of the β relaxation has a smooth energy distribution which may be associated with

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intermolecular interactions that contribute to this relaxation.

EXPERIMENTAL

Preparation and molecular weight evaluation of MMA–MIK copolymers (PMIK) with approximately 0, 4, 7, 10 and 15% MIK content have been reported elsewhere. These copolymers have been designated as PMIK.00, PMIK.04, PMIK.07, PMIK.10 and PMIK.15. All the samples were characterized with respect to microtacticity content and there were negligible differences between the copolymers. The samples had a high degree of syndiotactic character[15] (60% of syndiotactic triad and 78% of syndiotactic dyad). Before each measurement the samples were maintained at 130°C for 10 min and quenched afterwards.

Dielectric and viscoelastic measurements were done on the samples of PMIK copolymer.

The real and imaginary parts of the complex dielectric permittivity $\varepsilon'(w)$, $\varepsilon''(w)$ were measured with a capacitor bridge (General Radio 1615 A) and a Balsbaugh LD3 cell with a guard electrode, in the temperature range of 20–140°C and for frequencies between $2\cdot10^2$ Hz and 10^5 Hz.

Thermally stimulated depolarization currents (t.s.d.c.)

Experimental equipment with standard characteristics[16] for t.s.d.c. was employed. The measurements were carried out in the temperature range −100 to 140°C. The t.s.d.c. apparatus employed was formed by a Keithley 642 electrometer, which can measure values of intensity of current in the range 10^{-16}–10^{-8} A, a d.c. power supply HP5616A, and a cell with aluminium electrodes, which was cooled with liquid N_2. The rate of heating was controlled by a thermal control Eurotherm 211. The parameters of all t.s.d.c. measurements were the following: polarization temperature 120.8°C, polarizing field, $E_p = 20\,\mathrm{KV\,cm^{-1}}$, polarization time, $t_p = 120$ min and heating scan $2°\mathrm{C\,min^{-1}}$.

Viscoelastic measurements

The viscoelastic results were obtained with the Dynamic Mechanical Thermal Analyser of Polymer Laboratories Ltd. The apparatus directly yields the storage modulus, E', and damping factor, $\tan\delta$, values. The measurements were carried out in the temperature range −40 to 140°C and for frequencies between 0.3 Hz and 30 Hz on the PMIK.00, PMIK.04 and PMIK.07 samples (suitable samples of the other copolymers were not available).

RESULTS

Average molecular weights M_v, M_n, M_w are shown in *Table 1* for PMIK.00, PMIK.04, PMIK.07, PMIK.10 and PMIK.15 and *Figures 1–5* show their respective ε'' calculated values.

Figure 6 shows t.s.d.c. spectra for PMIK.00, PMIK.04, PMIK.07, PMIK.10 and PMIK.15 in the temperature range −100 to 140°C.

The dynamic-mechanical spectra have been represented as the values of E'' *versus* temperature for the PMIK.00, PMIK.04 and PMIK.07 copolymers, respectively, in *Figures 7–9*.

Table 1 Chemical characterization of copolymers

Sample	PMIK.00	PMIK.04	PMIK.07	PMIK.10	PMIK.15
Composition (MMA)	1.000	0.960	0.930	0.901	0.857
$M_v\cdot10^{-5}$	6.02	3.73	5.89	5.64	5.20
$M_w\cdot10^{-5}$	6.40	7.15	6.29	6.01	5.55
$M_n\cdot10^{-5}$	3.48	4.18	3.38	3.02	2.98

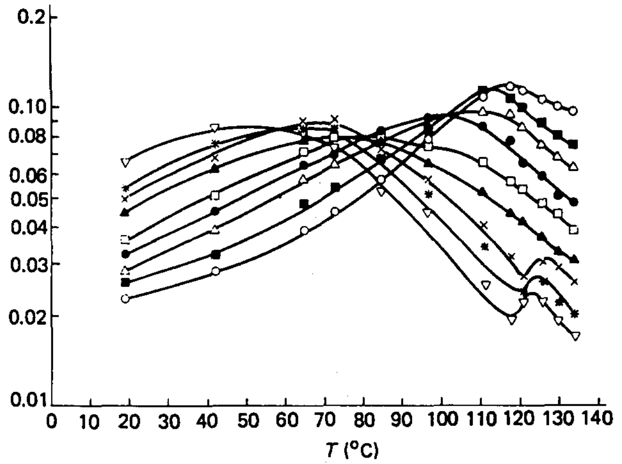

Figure 1 Imaginary parts of the complex dielectric permittivity ε'' *versus* temperature plots of PMIK.00 at the following frequencies (Hz): $2\cdot10^2$ (▽), $5\cdot10^2$ (*), 10^3 (×), $2\cdot10^3$ (▲), $5\cdot10^3$ (□), 10^4 (●), $2\cdot10^4$ (△), $5\cdot10^4$ (■), 10^5 (○)

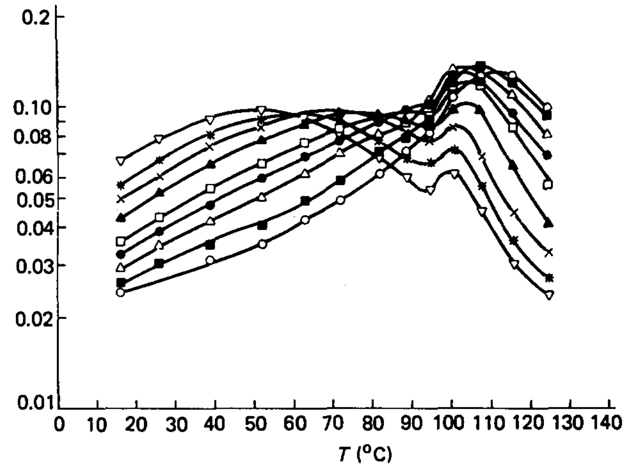

Figure 2 Imaginary parts of the complex dielectric permittivity ε'' *versus* temperature plots of PMIK.04. Symbols as in *Figure 1*

The more important results obtained for each relaxation zone are analysed separately.

α Dielectric and mechanical relaxation

Because the α dielectric relaxation obtained overlaps with the β dielectric relaxation, especially at higher frequencies ($5\cdot10^3$–10^5), we were not able to get much information about the former. However, at lower frequencies ($2\cdot10^2$–$2\cdot10^3$) it can be seen in *Figures 1–5* that the α peaks shift to lower temperatures when MIK content increases.

The t.s.d.c. measurements, which are plotted in *Figure 6*, show the α relaxation clearly separated from the β relaxation, and it can be seen that the position of α peak shifts to lower temperatures with increasing MIK content.

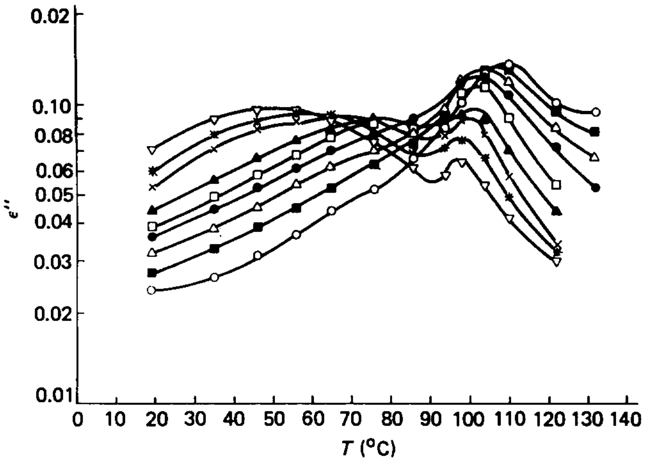

Figure 3 Imaginary parts of the complex dielectric permittivity ε″ *versus* temperature plots of PMIK.07. Symbols as in *Figure 1*

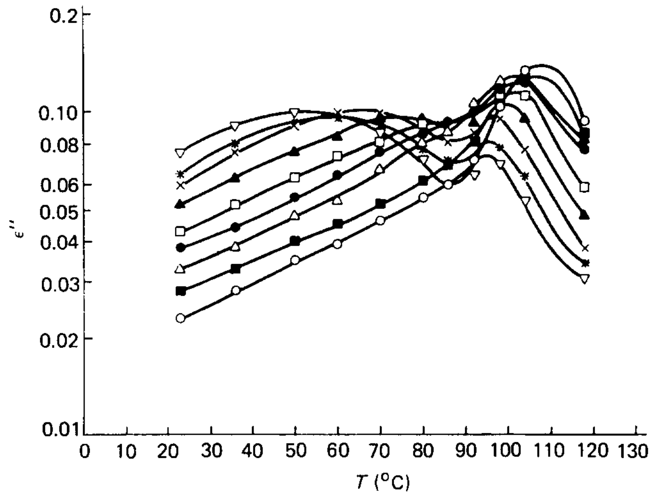

Figure 4 Imaginary parts of the complex permittivity ε″ *versus* temperature plots of PMIK.10. Symbols as in *Figure 1*

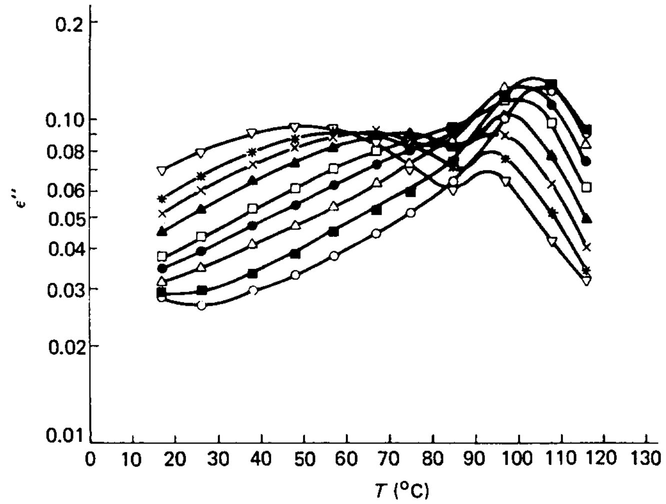

Figure 5 Imaginary parts of the complex dielectric permittivity ε″ *versus* temperature plots of PMIK.15. Symbols as in *Figure 1*

Viscoelastic measurements have also been applied to the study of this relaxation. In this case, the α relaxation is separated from the β relaxation and its study is possible. *Figure 10* shows the plot of the logarithm of the frequency of the maxima E″ against the inverse of the temperature. The curve obtained has the characteristic form of the glass transition and has been adjusted to a Vogel equation:

$$\log f_{\max} = A - B/(T - T_{\infty}) \qquad (1)$$

where the A, B, and T_{∞} parameters are shown in *Table 2*.

The apparent activation energy depends on the temperature and is related to B and T_{∞} through:

$$E_{a} = -RB(T/(T - T_{\infty}))^{2} \qquad (2)$$

These parameters are different for each copolymer but, at the same temperature, the apparent activation energy is

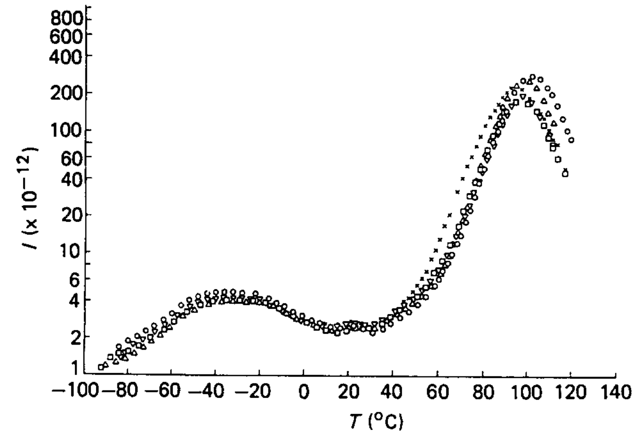

Figure 6 T.s.d.c. spectra of PMIK.00 (○), PMIK.04 (△), PMIK.07 (□), PMIK.10 (▽) and PMIK.15 (×)

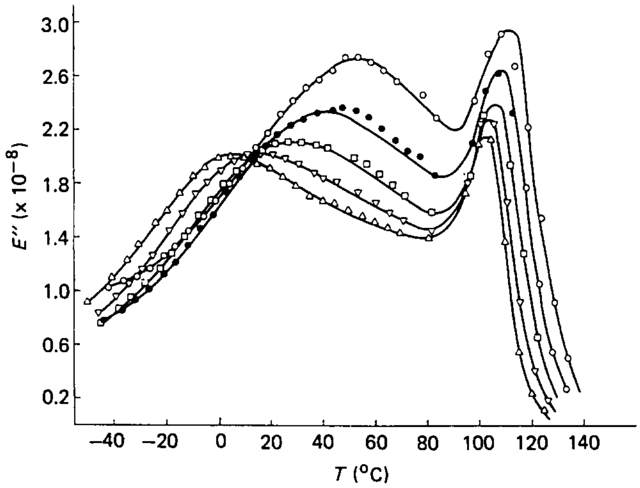

Figure 7 Dynamic loss modulus E″ *versus* temperature plots of PMIK.00 at the following frequencies (Hz): $0.3 \cdot 10^{-1}$ (△), 1 (▽), 3 (□), 10 (●), 30 (○)

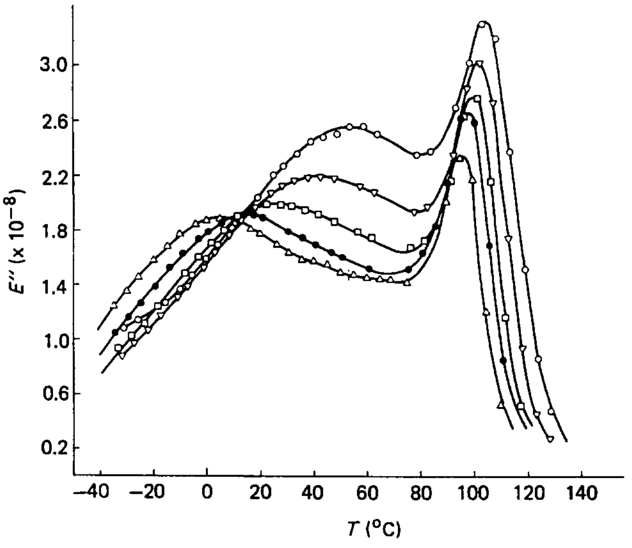

Figure 8 Dynamic loss modulus E″ *versus* temperature plots of PMIK.04. Symbols as in *Figure 7*

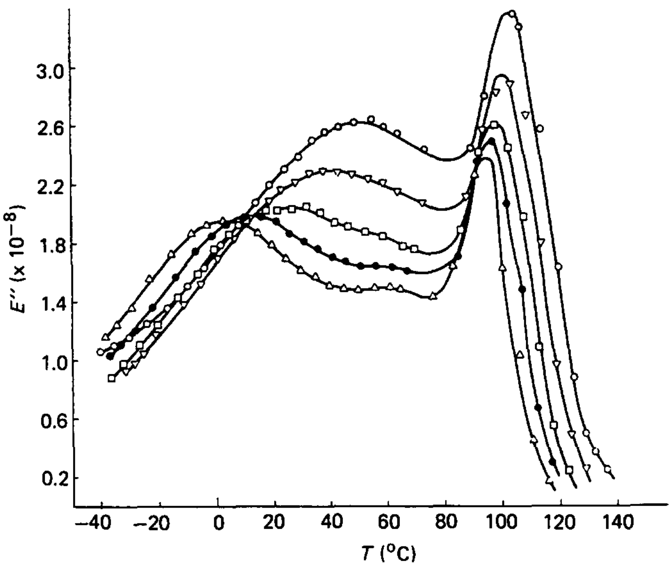

Figure 9 Dynamic loss modulus E'' *versus* temperature plots of PMIK.07. Symbols as in *Figure 7*

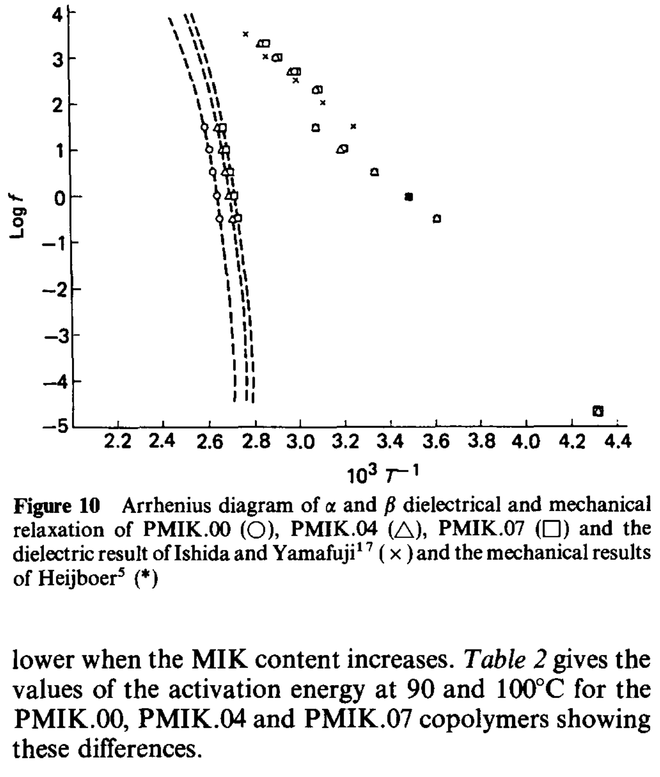

Figure 10 Arrhenius diagram of α and β dielectrical and mechanical relaxation of PMIK.00 (○), PMIK.04 (△), PMIK.07 (□) and the dielectric result of Ishida and Yamafuji[17] (×) and the mechanical results of Heijboer[5] (*)

lower when the MIK content increases. *Table 2* gives the values of the activation energy at 90 and 100°C for the PMIK.00, PMIK.04 and PMIK.07 copolymers showing these differences.

β Dielectric and mechanical relaxation

The β dielectric relaxation obtained by alternative dielectric measurements is more predominant than the α one, as previously stated, and we were able to analyse it. Thus, the β dielectric relaxation has been fitted to the empirical model of Fuoss–Kirkwood:

$$\varepsilon'' = \varepsilon''_{\max} \cdot \operatorname{sech} m \ln \omega\tau_0 \tag{3}$$

The mean Fuoss–Kirkwood parameter of the β dielectric relaxation represents the width of the relaxation. It is possible to obtain this parameter from the curves of ε'' *versus* temperature at different constant frequencies when the relaxation strength was constant with temperature[11]. In this case, the slope of the curve of $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ *versus* $10^3\,T^{-1}$ at constant frequency is:

$$\mathrm{d}(\cosh^{-1}(\varepsilon''_{\max}/\varepsilon''))/\mathrm{d}(T^{-1}) = mE_a/R \tag{4}$$

We calculated the '*m*' parameter values from the slope of the curve of $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ *versus* $10^3\,T^{-1}$ at a constant frequency of 10^3 Hz (*Figure 11*). The '*m*' parameter values for each sample are given in *Table 3*. These values do not change appreciably, which suggests that the different percentage of MIK has little influence on the form of the β dielectric relaxation.

Furthermore, the relationship between the mean relaxation time and the temperature has been adjusted to an Arrhenius equation:

$$f_m = f_0 \exp(-E_a/RT) \tag{5}$$

The logarithm of the frequency, for which the value of ε'' is maximum has been plotted against the inverse of the temperature (*Figure 10*). The apparent activation energy for each sample is given in *Table 3*. These values are also practically constant with the percentage of MIK and agree with the ones for poly(methyl methacrylate) from the results of Ishida *et al.*[17].

The t.s.d.c. results show that the position and the intensity of the peak reveal only slight differences between the copolymers. We have verified by successive measurements that this is mainly due to the dispersion of the results inherent to the experimental technique and not to the addition of MIK. The results obtained for all the copolymers agree with the results obtained by other authors[18] for poly(methyl methacrylate).

For symmetrical distributions Van Turnhout[16] has shown by means of model calculations that up to the

Table 2 Dynamic–mechanical analysis of α mechanical relaxation

	A	B	T_∞	E_a (90°C) (kcal mol^{-1})	E_a (100°C) (kcal mol^{-1})
PMIK.00	7.85	−235.80	75.9	310.5	112.2
PMIK.04	9.69	−377.96	59.0	102.0	62.2
PMIK.07	11.20	−527.19	49.0	82.1	56.0

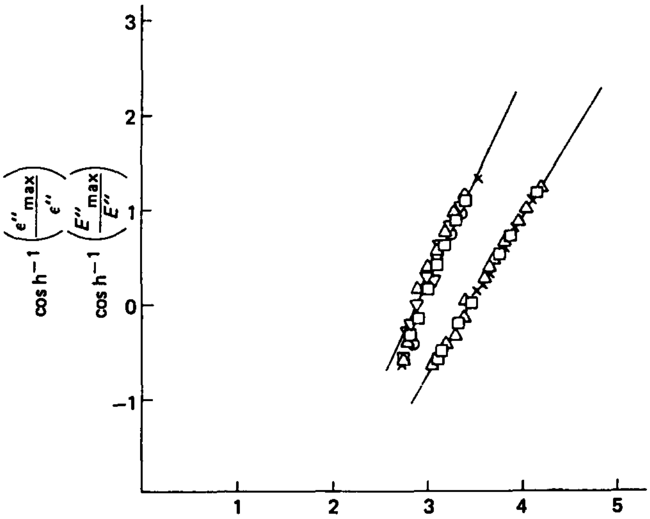

Figure 11 Relationship between $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ and the temperature for β mechanical relaxation at a frequency of 1 Hz for PMIK.00 (×), PMIK.04 (△), PMIK.07 (□), and dielectrical relaxation at 1 kHz for PMIK.00 (○), PMIK.04 (△), PMIK.07 (□), PMIK.10 (▽) and PMIK.15 (×)

Table 3 Dielectric and dynamic–mechanical analysis of β relaxation

	Alternative		T.s.d.c.		Dynamic–mechanical	
Sample	m	E_a (kcal mol^{-1})	f_{eq} ($\cdot 10^5$)	E_a (kcal mol^{-1})	m	E_a (kcal mol^{-1})
PMIK.00	0.25	19.3	1.7	15	0.20	16.8
PMIK.04	0.25	19.2	1.7	15	0.22	16.7
PMIK.07	0.26	19.5	1.7	15	0.21	16.8
PMIK.10	0.25	19.8	1.7	15	–	–
PMIK.15	0.26	18.8	1.7	15	–	–

lower half-width temperature, the initial current rise takes the form:

$$\ln I = \text{constant} - mE_a/RT \qquad (6)$$

where 'm' is the Fuoss–Kirkwood parameter, I is the intensity of depolarization currents, R is the perfect gas constant and E_a is the mean activation energy. We have considered as a first approximation that the β peak has a symmetrical distribution, and have calculated the values of mean activation energy from the initial slope of the curve represented by the equation (6). In order to calculate the value of the Fuoss–Kirkwood parameter 'm', we have taken the parameter calculated from the alternative dielectric measurements and have considered the dependence of this parameter on temperature[11], which is ($\mathrm{d}m/\mathrm{d}T = 8 \cdot 8 \times 10^{-4}$). The value obtained for the mean Fuoss–Kirkwood parameter around -40°C is approximately 0.2. The values obtained for the mean activation energy are shown in *Table 3*.

The equivalent frequency[19] corresponding to the maximum of the β peak of t.d.s.c. measurements (f_{eq}), i.e. the frequency at which the alternative experiments should be performed in order to obtain a loss peak having the same maximal temperature as the t.d.s.c. peak, can be estimated by relating the heating rate 'q' and the angular frequency $\omega = 1/\tau$. For an Arrhenius relationship between the relaxation times and the temperature:

$$f_{eq} = \omega/2\pi = qE_a/2\pi RTm^2 \qquad (7)$$

We have calculated the equivalent frequency from equation (7). The values are shown in *Table 3* for each copolymer. In the Arrhenius diagram are shown both the dielectric and t.s.d.c. results (*Figure 10*).

The mechanical β relaxation has also been fitted to the empirical model of Fuoss–Kirkwood. The mean Fuoss–Kirkwood parameter 'm' of mechanical relaxation is obtained from the slope of the curve of $\cosh^{-1}(E''_{\mathrm{max}}/E'')$ *versus* $10^3\,T^{-1}$ at 1 Hz (*Figure 11*). The 'm' values for each sample are given in *Table 3*.

The relationship between the mean relaxation time and the temperature has also been adjusted to an Arrhenius equation. The logarithm at the frequency of the maxima of E'' has been plotted against the inverse of the temperature (*Figure 10*). The apparent activation energy for each sample is given in *Table 3*. These values are practically constant with the percentage of MIK and agree with the previous values for poly(methyl methacrylate) from other authors[3–5].

DISCUSSION

The dynamic–mechanical and dielectric spectra of PMIK copolymers are mainly formed by the α and β relaxation in the temperature and frequency range studied.

The α relaxation of PMMA has been ascribed[2–5,17] to the glass transition of the polymer. Its molecular origin is related to the rotational or translational microbrownian motions of the segments of the chain backbone. Alexandrov and Lazurkin[20] and McLoughlin and Tobolsky[21] have studied the plasticizer effect and observed a decrease in the temperature of the relaxation at constant frequency. Ishida and Yamafuji[17] studied the dielectric behaviour in a series of poly(alkyl methacrylates) and found a decrease of the α peak with increasing length of the n-alkyl group. The same results were obtained by Rogers and Mandelkern[22] with mechanical measurements. The explanation given for this observation is that when the length of the side groups increases the hindrance to chain backbone motion decreases, an effect similar to that produced by the addition of plasticizer.

We have studied the α relaxation by dielectric, t.d.s.c. and dynamic–mechanical methods, and we can see that in all the cases the relaxation shifts to lower temperatures when the MIK content in the samples is increased. We think that the molecular origin of the α peak in the PMIK copolymers is due to the motion of the main chain as for PMMA. The addition of MIK produced an effect similar to the addition of plasticizer, because the copolymer inserts at random a shorter side chain, increasing the free volume, decreasing the hindrance to the chain backbone motions and making the microbrownian motion of the segments of the chain backbone easier. This has been confirmed by the fact that the apparent activation energy of the peak decreases when the MIK content increases.

The β dielectric and mechanical relaxation in PMMA has been assigned to the hindered rotation of the side group. The hindrance to this rotation mainly arises from interaction with the main chain methyl groups of the adjacent units[2]. The β dielectric and mechanical relaxation in PMIK copolymers can be attributed to the same molecular movement as in PMMA, because we have found the same apparent activation energy, Fuoss–Kirkwood parameter and height for the β relaxation in all the copolymers. These results agree with those obtained by other authors[2–5,11,16–18].

On the other hand, these results allow us to clarify which is the side group that produces the β peak. In a recent paper, Heijboer *et al.*[6] calculated the energy barrier for rotational motions of C–C in the alkyl side group of poly(alkyl methacrylates). Heijboer argues that the alkoxy group cannot be responsible for the β maximum of PMMA although the calculated value of the barrier to the rotation of the alkoxy group is not far from the activation energy observed experimentally. It also affirms that the β relaxation is due to the rotation of the alkoxy carbonyl group, in spite of the fact that there is a serious discrepancy between the calculated height of the barrier and the activation energy of the process observed experimentally because matrix effects have been neglected in the calculations.

The results obtained in this work agree with those of Heijboer. We exclude the rotation of the alkoxy group as the molecular motion associated with the β relaxation in favour of the rotation of the alkoxy carbonyl group because the height of the β peak does not decrease significantly with the addition of MIK. Also, we found that the apparent activation energy of the β peak increased with the frequency:

$$f_{\text{t.s.d.c.}} < f_{\text{mech.}} < f_{\text{dielec.}}$$

$$E_{\text{t.s.d.c.}}\ (15\ \text{Kcal mol}^{-1}) < E_{\text{mech.}}\ (17\ \text{Kcal mol}^{-1}) < E_{\text{dielec.}}\ (20\ \text{Kcal mol}^{-1})$$

This probably means that there is a smooth distribution of the activation energies associated with the process, which is due to the matrix effect of the intermolecular interactions.

By a careful check of the t.d.s.c. and mechanical–dynamic spectra we observe low peaks at 0–10 and 10–20°C, respectively. We think that these are due to the physical ageing produced by the heat treatment (quenching) that the samples are subjected to before each measurement. The free volume induced by the quenching affects the mobility of the chain backbones at $T < T_g$, as observed for PVC[23–25].

REFERENCES

1 Soria, V., Celda, B., Tejero, R. and Figueruelo, J. E. *Polym. Degrad. Stab.* 1985, **10**, 287

2 McCrum, N. G., Read, E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967

3 Heijboer, J., Dekking, P. and Staverman, A. J. Proc. 2nd Int. Congr. Rheology, Oxford, 1953

4 Heijboer, J. J. Proc. Int. Congr. Physics Non Cryst. Solids, Delft, 1964

5 Heijboer, J. *J. Ann. NY Acad. Sci.* 1976, **279**, 104

6 Heijboer, J., Baas, J. M. A., Van der Graaf, B. and Hoefnagel, M. a. *Polymer* 1987, **28**, 509

7 Johari, G. P. and Goldstein, M. *J. Chem. Phys.* 1970, **53**, 2372; 1971, **55**, 4245

8 Havriliak, S. and Roman, N. *Polymer* 1966, **7**, 387

9 Mikhailov, G. P., Borisova, T. L., Ivanov, N. N. and Nigmankhodzhaev, A. S. *Polym. Sci. USSR* 1967, **9**, 869

10 Heijboer, J. *J. Macromol. Chem.* 1960, **35**, 86

11 Gomez Ribelles, J. L. and Diaz-Calleja, R. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 1297

12 Ribes-Greus, A., Gomez Ribelles, J. L. and Diaz-Calleja, R. *Polymer* 1985, **26**, 1849

13 Williams, G. *Adv. Polym. Sci.* 1979, **33**, 59

14 Shindo, H., Murakami, I. and Yamamura, H. *J. Polym. Sci.* 1969, **A-1(7)**, 297

15 Ribes-Greus, A., Soria, V., Figueruelo, J. E. and Diaz-Calleja, R. *Macromol. Chem.* in press

16 Van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier, Amsterdam, 1975

17 Ishida, Y. and Yamafuji, H. *Kolloid Z.* 1961, **177**, 97

18 Lamarre, L., Schreiber, H. P., Wertheimer, M. R., Chantain, D. and Lacabanne, C. *J. Macromol. Sci. Phys.* 1980, **B18**(2), 195

19 Vanderschueren, J. and Gasiot, J. 'Thermally Stimulated Relaxations in Solids' (Ed. P. Braunlich), Springer-Verlag, Berlin, 1979

20 Alexandrov, A. P. and Lazurkin, J. S. *Acta Phys. Chem. USSR* 1940, **12**, 647

21 McLoughlin, J. R. and Tobolsky, A. V. *J. Colloid Sci.* 1952, **7**, 555

22 Rogers, S. S. and Mandelkern, L. *J. Phys. Chem.* 1957, **61**, 985

23 Gomez-Ribelles, J. L. and Diaz-Calleja, R. *Anales Fisica* 1985, **B81**, 99

24 Gomez-Ribelles, J. L. and Diaz-Calleja, R. *Polym. Eng. Sci.* 1984, **24**, 1202

25 Gomez-Ribelles, J. L., Diaz-Calleja, R., Ferguson, R. and Cowie, J. M. G. *Polymer* 1987, **28**, 2262