Dielectric and viscoelastic relaxation of poly(2-chloroethyl methacrylate) and poly(3-chloropropyl methacrylate)

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Dielectric and viscoelastic relaxation measurements have been performed on poly(2-chloroethyl methacrylate) and poly(3-chloropropyl methacrylate) between −140°C and the glass transition temperatures. The splitting of the dipolar relaxations from those of conductive origin in the dielectric spectra was performed.

(Keywords: viscoelastic relaxation; dielectric relaxation; poly(chloroalkyl methacrylate))

INTRODUCTION

The dielectric and viscoelastic properties of poly(methacrylates) have been extensively studied in the past decades[1–7]. However, it is difficult to find in the literature works in which viscoelastic and dielectric properties of a family of polymers have been studied in a systematic and comparative way. By extending the experimental range of measurements at lower frequencies, new phenomena are detected in the dielectric spectrum. These phenomena are located at temperatures higher than the glass transition temperature, T_g.

The aim of the present work is to perform a comparative study of the relaxation properties of poly(2-chloroethyl methacrylate) (poly[1-(2-chloroethyloxycarbonyl)-1-methylethylene]) (PCEMA) and poly(3-chloropropyl methacrylate) (poly[1-(3-chloropropyloxycarbonyl)-1-methylethylene]) (PCPMA). Special effort will be devoted to the splitting of the conductive and dipolar components in the dielectric spectrum, improving a procedure for this purpose.

EXPERIMENTAL

Monomer and polymer preparation

Chloroalkyl methacrylates were prepared by reaction of methacryloyl chloride with the corresponding alcohols in benzene solution and *N*,*N*-dimethylaniline at reflux temperature for 24 h, as previously reported[8]. Polymerization of the monomers was achieved in vacuum in benzene solution using azobisisobutyronitrile (AIBN) as initiator[8].

Dynamic measurements

Films of 0.6 mm were obtained after moulding PCEMA and PCPMA polymers. These films were dried for 2 days in vacuum at 60°C for PCEMA and 50°C for PCPMA before viscoelastic and dielectric experiments.

Dynamic dielectric measurements were carried out in a TA 2970 dielectric analyzer between −140 and +140°C with frequency ranging from 1 Hz to 30 kHz at a scan rate of 1°C min^{-1}.

Dynamic mechanical measurements were performed on a DMTA Mark II apparatus from Polymer Labs, in a single cantilever flexure mode. Samples 0.6 mm thick and 10 mm wide were used, with a span-to-depth ratio of 8. Because these polymers are very fragile at room temperature, clamping was carried out at 60°C (45°C for PCPMA) before the experiment. Five frequencies were used (0.3, 1, 3, 10 and 30 Hz) between −140 and +100°C (80°C for PCPMA) at a scan rate of 1°C min^{-1}.

RESULTS AND DISCUSSION

The whole dielectric spectra, permittivity ε' and loss ε'' *versus* temperature at 1 kHz, are plotted on *Figure 1* for both polymers. Viscoelastic spectra are represented in the same way, real modulus E' and imaginary one E'', at 1 Hz, on *Figure 2*.

The presence of three relaxation phenomena is deduced from the observation of both dielectric and viscoelastic spectra. At high temperature, a relaxation α attributed to the glass transition process clearly appears in viscoelastic measurements, but is partially covered in dielectric experiments by the increase of dielectric loss ε'' at high temperature. This increase is related to a conduction process. Around 0°C a shoulder on all spectra reveals the presence of a β process of low intensity. At

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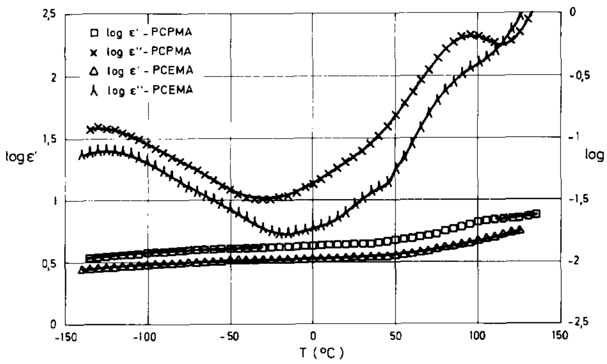

Figure 1 Permittivity ε′ and dielectric loss ε″ of PCEMA and PCPMA at 1 kHz against temperature

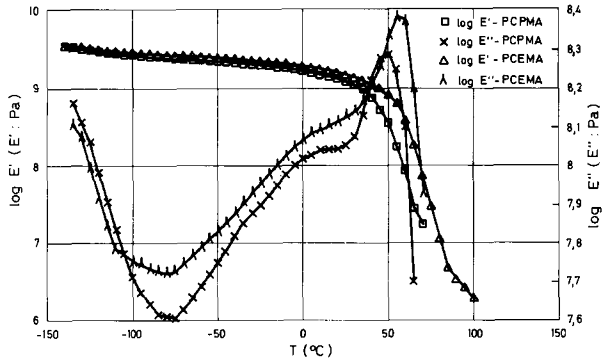

Figure 2 Storage E' and loss modulus E'' of PCEMA and PCPMA at 1 Hz against temperature

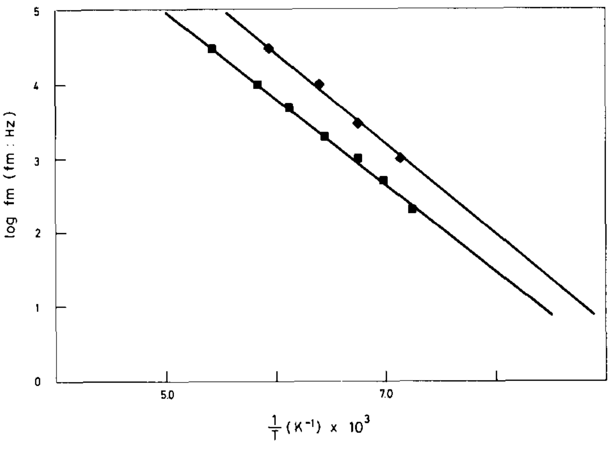

Figure 3 Arrhenius plot for γ dielectric relaxation (maximum for ε″ spectra): (■) PCEMA, activation energy $E_a = 5.4$ kcal mol^{-1}; (◆) PCPMA, $E_a = 5.8$ kcal mol^{-1}

low temperature, dielectric spectra show the presence of a γ relaxation. Only the high-temperature side of this process appears in mechanical measurements owing to the low frequencies used during these experiments.

The γ relaxation

The positions of the γ dielectric relaxation at 1 Hz, i.e. maximum of ε″ at −125°C for PCEMA and −133°C for PCPMA, are in good agreement with the results of Mikhailov[1] on the same polymers. However, the activation energies calculated by Mikhailov[2] are significantly higher than the 5.4 and 5.8 kcal mol^{-1} values we have obtained for PCEMA and PCPMA, by means of an Arrhenius-type plot (*Figure 3*).

It is worth comparing these results to the γ dielectric relaxation in similar poly(alkyl methacrylate) series. It has been observed that polymers containing the n-propyl group, or longer alkyl groups, in the side chain exhibit a relaxation process around 120 K, unlike poly(chloroethyl methacrylate) (PCEMA) or poly(isopropyl methacrylate) (PiPMA), for which this process is absent. Shimizu[3] attributes the 120 K relaxation peak to the internal rotation of the alkyl group, whereas the low-temperature relaxation peak of PCEMA or PiPMA is related to the rotation of the whole alkyl group attached to the COO group. The common steric analogy between the chlorine atom and a methyl group may therefore be supported by the presence of a clear γ relaxation in the PCEMA spectra. Indeed PCEMA and PCPMA relaxation peaks appear in the same temperature range as poly(n-butyl methacrylate) (PBMA) and poly(n-propyl methacrylate) (PPMA), and the activation energy is 5.5 kcal mol^{-1} for both polymers[3,4], comparable to our values. Moreover, the hypothesis of internal chloroalkyl chain motion supports the attribution of the lower-temperature maximum and wider γ peak of PCPMA over PCEMA to the internal mobility of the chloropropyl group. However, the higher dipolar moment of the side chain induced by the presence of the chlorine atom, in comparison with a CH_3 group, would give rise to a higher relaxation strength as observed for example in fluoroalkyl methacrylate polymers[9].

A viscoelastic γ relaxation was also observed by Heijboer[6] on PPMA, PBMA and larger poly(alkyl methacrylate) polymers. The characteristics of that relaxation are similar to the dielectric one, but fall in lower temperature zone, around 100 K because of the low frequencies used in dynamic mechanical experiments. The analogy between poly(chloroalkyl methacrylates) and poly(alkyl methacrylates) may justify the fact that at −140°C and 1 Hz our viscoelastic spectra only show the high-temperature side of the γ process. Indeed, an extrapolation of the Arrhenius plot, based on tan(δ(ε*)) maximum, would predict a 1 Hz peak around 100 K.

High-temperature dielectric behaviour

Analysis. The high-temperature dielectric behaviour of PCEMA and PCPMA is characterized by a strong increase of dielectric loss ε″ and permittivity ε′ at low frequency. This increase overlaps the α process, specially in the case of PCEMA, and may be due to the contribution of conduction processes, mainly d.c. conduction. This contribution is expressed by:

$$\varepsilon''_\sigma = \sigma / \varepsilon_0 \omega \qquad (1)$$

where ε_0 is the permittivity of vacuum and σ the conductivity of the polymer.

In the absence of other loss mechanisms, σ is taken as a constant d.c. conductivity σ_{dc}. As a consequence, the frequency dependence of the conductivity contribution is inversely proportional to ω. In a log(ε″) *versus* log(*f*) plot, conductivity gives rise to a straight line of slope −1. The fitting of this line is a commonly used method to subtract the conductivity contribution of the spectra[10]. But this method is very sensitive to the fitting procedure and the slope of the low-fequency side of the peak usually deviates slightly from −1 behaviour.

Another way for describing the conductivity contribution consists in using the electrical modulus M^* defined by:

$$M^* = (\varepsilon^*)^{-1} \qquad (2)$$

This method has been used with efficiency by Pathmanathan and Johari[11]. The real and imaginary parts of electrical modulus were therefore calculated and the corresponding spectra are shown in *Figure 4*, together with the high-temperature dielectric spectra of PCPMA. The striking consequence of this transformation is that the $M''(T)$ spectra exhibit two families of peaks: low-amplitude peaks corresponding to the α process at high frequency, on the low-temperature side of the spectra; and high-amplitude and narrow peaks, corresponding to the conduction process, at high temperature. It must be noted that the maximum of these latter peaks is almost temperature-independent, whereas their width increases with temperature. At low frequencies ($f < 100$ Hz), these two families completely overlap, and the α maximum disappears. However, we must point out that, in the dielectric loss spectra, the overlapping of the α process by the conductivity contribution was observed up to 1000 Hz. As a first result of the modulus calculation, a gain in the resolution on the α process of one frequency decade is obtained. The two-step decays of the real electrical modulus M' are associated with the two families of peaks of the M'' spectra. The first decay, corresponding to the α process, is followed by a larger one, due to the conduction process, the final relaxed modulus of which is almost zero.

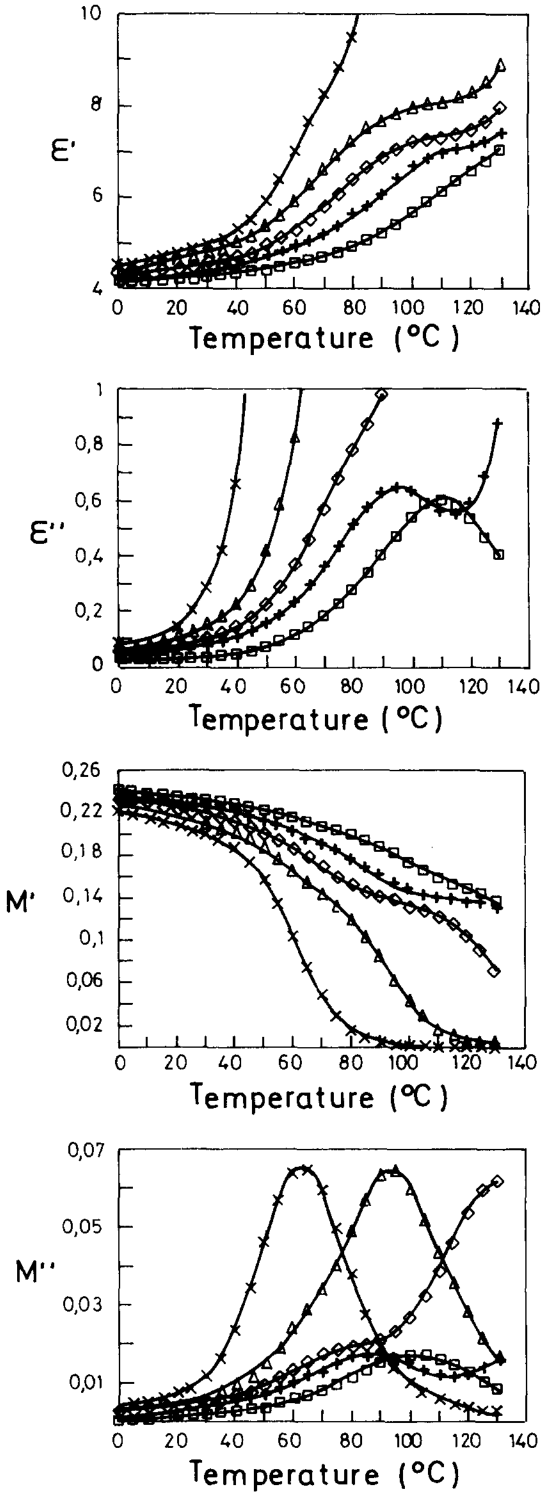

Figure 4 Dielectric loss ε'' and permittivity ε' and dielectric modulus M' and M'' for PCPMA at (×) 1, (△) 10, (◇) 100, (+) 1000, (□) 10000 Hz

We assume, like Cole and Tombari[12] do, that this additive contribution results from a complex impedance (Z_σ^*) in series with the dipolar properties of polymer (Z_d^*) (*Figure 5*). That representation supposes a complex interference between dipolar and conduction contributions. According to that scheme, the conduction contribution (M_σ^*) will be directly subtracted from the whole electrical modulus by:

$$M'_d = M' - (M'_\sigma - M_{\sigma\infty}) \qquad (3)$$

and

$$M''_d = M'' - M''_\sigma \qquad (4)$$

Finally, after subtraction of the conduction contribution, electrical modulus (M_d^*) is back-transformed to dielectric complex permittivity (ε_d^*) in order to obtain more information about the α process.

Conduction fitting. The Cole–Cole diagram of electrical modulus for PCPMA is shown on *Figure 6*. This diagram exhibits two well separated zones: a semi-circular shape

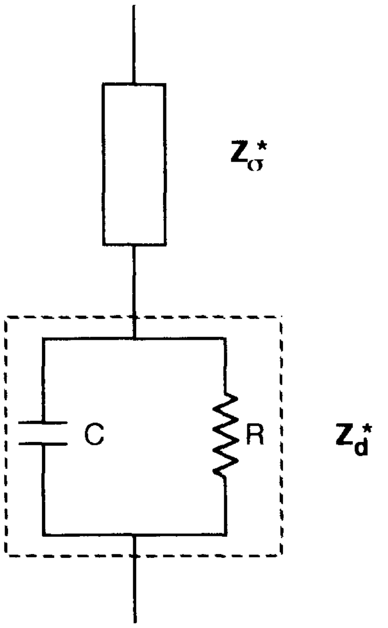

Figure 5 Equivalent electrical circuit

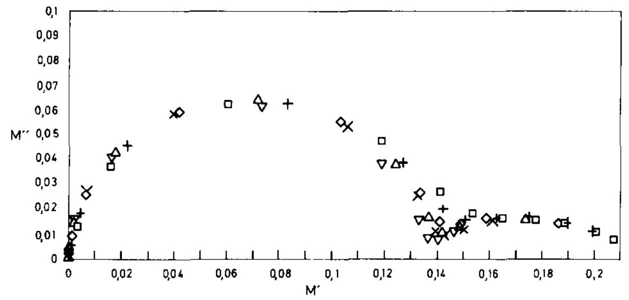

Figure 6 High-temperature Cole–Cole plot for PCPMA in terms of dielectric modulus at (□) 80, (+) 90, (◇) 100, (△) 110, (×) 120, (▽) 130°C

corresponding to the conduction process, and a skewed arc associated with the α process.

It can easily be shown that a simple Maxwellian conductivity process results in an electrical modulus behaviour similar to a Debye process, with one relaxation time, which is equal to the product of capacity and resistance. Indeed the semi-circular shape of the conductivity contribution in *Figure 6* suggests its modelling through a simple Debye function. Moreover, because the final relaxed modulus ($M_{\sigma0}$) is nearly zero (*Figure 4*), the Debye function reduces to:

$$M_\sigma^* = M_{\sigma\infty} - \frac{M_{\sigma\infty}}{1+i\omega\tau_{\sigma0}} \tag{5}$$

with only two parameters, the unrelaxed modulus $M_{\sigma\infty}$ and the characteristic time $\tau_{\sigma0}$. The conductivity contribution was fitted to a Debye semi-circle centred on the (Ox) axis with a radius of $M_{\sigma\infty}/2$ (*Figure 7*). The temperature dependence being negligible, the same fit was performed for all temperatures. We can, however, see from *Figure 7* that the quality of the fitting, high at 130°C, rapidly decreases with temperature. The relaxation time was then determined by shifting the Debye peak:

$$M''_\sigma = \frac{M_{\sigma\infty}\omega\tau_{\sigma0}}{1+\omega^2\tau_{\sigma0}^2} \tag{6}$$

in the $M''/\log(f)$ plane. Again it is seen that the accuracy of fitting is better at high than at low temperature. Finally, the conductivity contribution was subtracted from the original M' and M'' spectra, and a new transformation $M_d^* \rightarrow \varepsilon_d^*$ gives the corrected ε'_d and ε''_d spectra. These spectra will be discussed later in the analysis of the α relaxation.

The decreasing accuracy of the fitting of a conduction process by a Debye model when temperature decreases, and the fact that this model does not foresee the contribution of conductivity to ε', leads us to look for an alternative model. The Cole–Cole function:

$$M_\sigma^* = M_{\sigma\infty} + \frac{M_{\sigma0} - M_{\sigma\infty}}{1+(i\omega\tau_{\sigma0})^{1-\alpha}} \tag{7}$$

with only one supplementary parameter (α) is proposed as the simplest way to solve the limitations of the Debye approach. This function supposes a distribution of relaxation times, which may be interpreted in terms of a conduction process altered by a blocking electrode phenomenon as a consequence of using non-metallized samples. Again $M_{\sigma0}$ is reduced to zero and $M_{\sigma\infty}$ and α were determined from the Cole–Cole diagram at different temperatures (*Figure 7*). M_∞ is seen to decrease slightly with temperature. The α decay with temperature is more significant, and shows that the difference between the Cole–Cole and Debye fits diminishes when the temperature goes up. Relaxation times were also determined from $M''/\log(f)$ representation. The accuracy of the fitting procedure is obviously improved by the use of the Cole–Cole function.

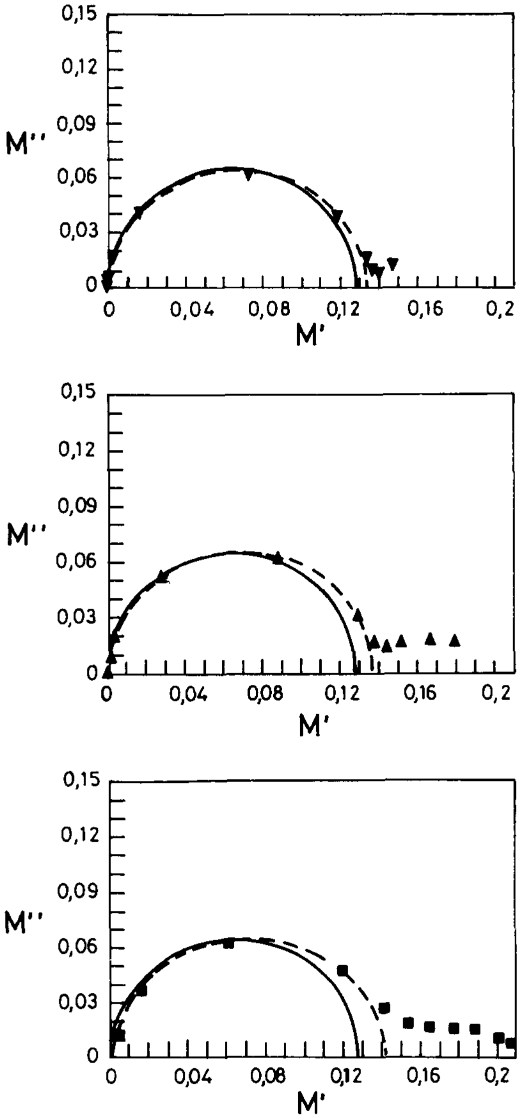

Figure 7 Cole–Cole plot for PCPMA showing Debye semi-circle (full curve) and Cole circular arc (broken curve) at (▼) 130, (△) 105, (■) 80°C

Similar treatment was done on the spectra corresponding to PCEMA, though, in that case, the accuracy of the adjustment procedure was not so good, because of a greater overlap between α and conduction processes. Debye and Cole–Cole parameters are summarized in *Table 1*.

Temperature dependence of d.c. conductivity. As mentioned before, the modelling of the conduction contribution by a Debye function (in terms of electrical modulus) is equivalent to a simple d.c. conduction process. Indeed, the calculation of the inverse of equation (5) gives:

$$(M_\sigma^*)^{-1} = \frac{1}{M_{\sigma\infty}}\left(1 - \frac{1}{i\omega\tau_{\sigma0}}\right) \tag{8}$$

Table 1 Parameters of Debye and Cole functions for the conduction process in PCEMA and PCPMA in terms of dielectric modulus

		PCEMA		PCPMA	
Model	T (°C)	M_∞	α	M_∞	α
Debye	–	0.120	0	0.128	0
Cole	80	0.174	0.18	0.144	0.07
	90	0.169	0.12	0.142	0.05
	100	0.164	0.10	0.138	0.04
	110	0.159	0.09	0.138	0.04
	120	0.157	0.08	0.138	0.04
	130	0.153	0.08	0.134	0.04
	140	0.150	0.07	–	–

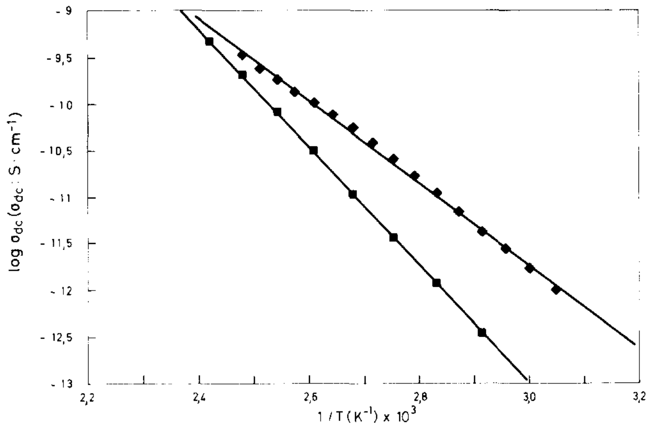

Figure 8 Temperature dependence of d.c. conductivity: (■) PCEMA, activation energy $E_a = 29.2$ kcal mol^{-1}; (◆) PCPMA, $E_a = 20.4$ kcal mol^{-1}

Then, from (1), we deduce:

$$\sigma_{dc} = \varepsilon_0 / M_{\sigma\infty} \tau_{\sigma 0} \tag{9}$$

Therefore we may evaluate the d.c. conductivity from the Debye parameters calculated before. Their dependence with temperature is plotted on *Figure 8*. For both polymers, an Arrhenius-like temperature behaviour was observed. Low apparent activation energies are obtained: 29.2 kcal mol^{-1} for PCEMA and 20.4 kcal mol^{-1} for PCPMA. This result is of the same order as previous estimations made by other authors on different polymers[13,14]. It is worth mentioning that d.c. resistance measurements[15] lead to similar activation values (27.9 kcal mol^{-1} for PCEMA and 20.0 kcal mol^{-1} for PCPMA). Such results show the consistency of considering that the high-temperature dielectric behaviour is dominated by a d.c. conduction effect.

The α relaxation

Corrected dielectric spectra. Figure 9 is a comparison of the original and corrected dielectric spectra of PCEMA and PCPMA at 100 Hz. The correction corresponds to a conduction contribution modelled by a Cole–Cole function. The correction is shown to be satisfactory, in terms of both imaginary and real parts of electrical modulus. However, in the case of PCEMA the accuracy of the correction rapidly decreases at low frequencies. This is due to a higher degree of overlapping of α and conduction processes that may invalidate the basic assumption of our data treatment (see equation (3)). More generally, the maxima that were apparent in the original $M''(T)$ and $\varepsilon''(T)$ spectra are slightly shifted to low temperature as a result of the correction procedure. These results are coherent if we refer to the very first measurements made by Mead and Fuoss[5] and then by Mikhailov[1] on similar polymers, who obtained α maxima at somewhat lower temperature than in our original data. Finally, we give an example of a Cole–Cole plot of original and corrected complex permittivity for PCPMA (*Figure 10*). The shape of the corrected data can be fitted

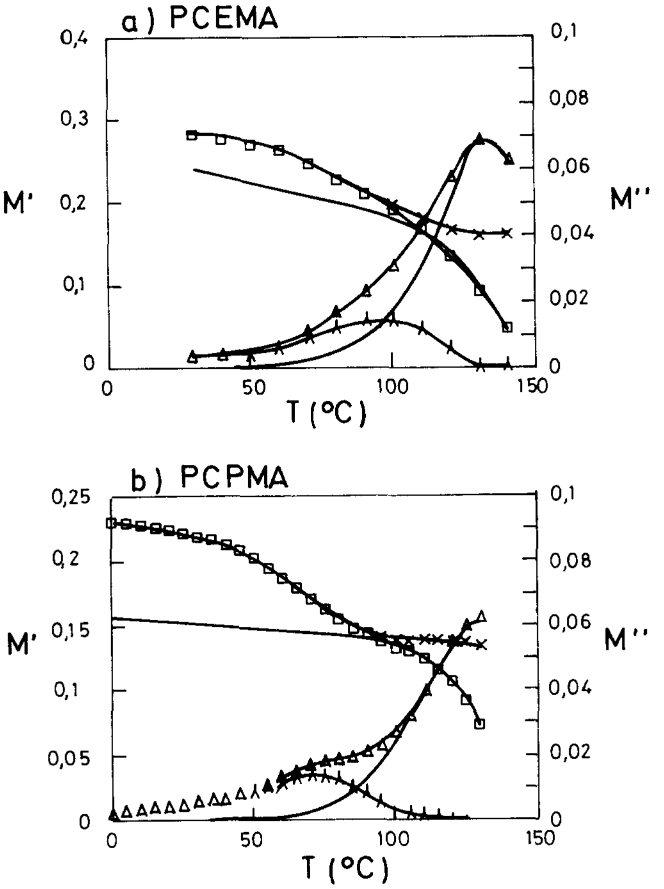

Figure 9 Original and corrected spectra of real M' and imaginary M'' parts of dielectric modulus at 100 Hz for (a) PCEMA and (b) PCPMA: (□) original M' values; (×) corrected M' values; (△) original M'' values; (∧) corrected M'' values; full curves correspond to the Cole function calculated with parameters extrapolated from *Table 1*

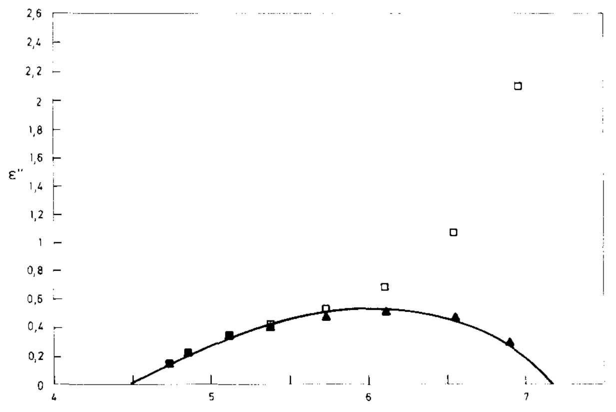

Figure 10 Cole–Cole plot of original (□) and corrected (▲) complex permittivity for PCPMA at 75°C; full curve corresponds to Havriliak–Negami function with the following fitted parameters: $\alpha = 0.395$, $\beta = 0.533$, $\tau_{d0} = 3.5 \times 10^{-3}$ s, $\varepsilon_{d0} = 7.18$ and $\varepsilon_{d\infty} = 4.46$

by a skewed arc of Havriliak–Negami[16]:

$$\varepsilon_d^* = \varepsilon_{d\infty} + \frac{\varepsilon_{d0} - \varepsilon_{d\infty}}{[1 + (i\omega\tau_{d0})^{1-\alpha}]^{\beta}} \qquad (10)$$

The values of the parameters α, β, τ_{d0}, ε_{d0} and $\varepsilon_{d\infty}$ are given in *Figure 10* at 75°C. Note that such fitting would not have been possible with the original values.

Viscoelastic relaxation. From the viscoelastic $E''(T)$ spectra of both polymers (*Figure 2*) arises a clear peak at high temperature, associated with a pronounced decrease of the real modulus. This phenomenon presents the characteristics of the relaxation associated with a glass transition process. E'' spectra on *Figure 2* give somewhat low values of mechanical transition temperature at 1 Hz (57°C for PCEMA and 50°C for PCPMA). No significant reference is found in the literature concerning viscoelastic measurements on both polymers. The sensitivity of methacrylate polymers to residual solvent or humidity may explain the low mechanical transition temperature of PCEMA. On the other hand, tan(δ) spectra of PCEMA give a peak at quite high temperature (84°C at 1 Hz). However, this peak is abnormally large and high for a simple α process and the 27°C difference between E'' peak and tan(δ) peak is exaggerated. Díaz Calleja[17] has already mentioned that, in parallel to conduction effects in dielectric measurements, a viscoelastic effect due to high viscosity could perturb high-temperature mechanical relaxation. This hypothesis may work in the case of PCEMA as far as it justifies a shifting of tan(δ) peak towards high temperature and its widening.

Temperature dependence of α relaxation. Temperature dependences of frequency maximum of ε'' and M'' for α relaxation of PCPMA are plotted in *Figure 11*. In this diagram the original and Cole-corrected values of $\varepsilon''(T)$ and $M''(T)$ spectra are reported. Williams–Landel–Ferry (WLF) parameters, C_1 and C_2, for corrected values are directly deduced from the fitting of WLF equation[18]:

$$\log f = \frac{C_1(T - T_g)}{C_2 + T - T_g} + \log f_g \qquad (11)$$

where f_g is a fitting parameter representing the relaxation frequency at the glass transition temperature. The fitted curves are plotted on *Figure 11*. Within the free-volume theory, these parameters are related to the free-volume coefficient Φ_g/B and the expansion coefficient α, by:

$$\Phi_g/B = 0.434/C_1 \qquad (12)$$

and

$$\alpha_f = (\Phi_g/B)/C_2 \qquad (13)$$

(B is a constant whose value is believed to be close to unity). These parameters are summarized in *Table 2*. Fitted parameters on M_d'' and ε_d'' are coherently similar. The agreement with 'universal' values of 0.025 for Φ_g/B and 4.8×10^{-4} K^{-1} for α_f is correct and within the range of values effectively obtained from dielectric measurements[13,19].

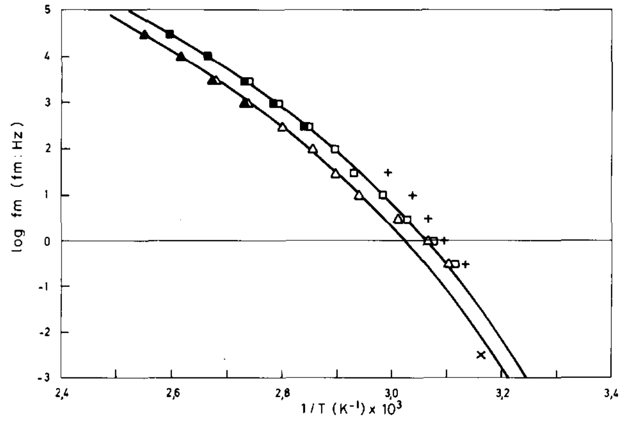

Figure 11 WLF fits to the frequency shift of the dielectric α relaxation. Data are from: (▲) ε'' spectra, (△) ε'' spectra corrected for conductivity, (+) E'' spectra, (□) M'' spectra, (■) M'' spectra corrected for conductivity, (×) t.s.c. experiments

Table 2 WLF parameters for α process of PCPMA

Spectra	T_∞ (K)	Φ_g/B	α_f (K^{-1})	C_1	C_2 (K)
ε''	−35	0.033	4.2×10^{-4}	13.0	80
M''	−34	0.035	4.4×10^{-4}	12.4	79

Frequency maxima of E'' spectra are also added on the diagram. These values can be compared to equivalent dielectric maxima. Viscoelastic relaxation shows similar temperature dependence to dielectric one, but its maxima are slightly shifted towards low temperature. This difference is clearly reduced through the coherent comparison of viscoelastic and electrical modulus, and falls within the precision of isochronous measurements.

The lowest frequency point in *Figure 11* is a result of thermally stimulated discharge current experiments, which are in progress at present. The equivalent frequency f_{eq} for dynamic experiment was deduced from WLF parameters by:

$$f_{eq} = \frac{qC_1C_2}{2\pi(C_2 + T_m - T_g)} \qquad (14)$$

where q is the heating rate and T_m the temperature maximum of the peak corresponding to α relaxation (7°C min^{-1} and 43°C respectively). The remarkable correlation between this value and the extrapolated curve from dielectric loss maxima gives some support to the WLF scheme used to describe the temperature dependence of the α process.

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