

Dielectric relaxation behaviour of poly(cyclohexylmethyl methacrylate) and poly(benzyl methacrylate)

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The relaxation processes in poly(cyclohexylmethyl methacrylate) (PCMMA) and poly(benzyl methacrylate) (PBzMA) have been studied by dynamic dielectric techniques. The study includes the α -, γ - and δ -relaxations in the first polymer and the α -relaxation in the second one. The α -relaxation has been fitted to 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. In the case of PCMMA two new relaxations labelled δ and γ in order of increasing temperature have been observed. The apparent activation energy of these relaxations are 5.5 and 11.8 kcal mol⁻¹ respectively. The dielectric relaxation behaviours of PCMMA and PBzMA are discussed in relation to that of poly(cyclohexyl methacrylate) previously studied.

(Keywords: poly(cyclohexylmethyl methacrylate); dielectric relaxations; apparent activation energy; loss permittivity; Cole-Cole arcs; isochrone difference)

INTRODUCTION

The dynamic mechanical properties of amorphous polymers containing saturated rings in the side-chains have been exhaustively investigated by Heijboer¹. He demonstrated that the origin of the molecular γ -relaxation (-80°C at 1 Hz) in poly(cyclohexyl methacrylate) (PCMA) is due to a transition between the two chair conformations in the cyclohexyl ring. However, this type of internal motion is hindered by rather high intramolecular barriers, which can reach about 11 kcal mol⁻¹.

All previous work on this subject was specifically on the mechanical relaxation behaviour. We considered that it was important to study this kind of polymer from the dielectric relaxation point of view, and have recently reported dielectric and dynamic mechanical studies on PCMA². The aim of the present study is to obtain information on the dielectric relaxation behaviour on the same polymer but with a spacer group inserted between the main chain and the cyclohexyl group: poly(cyclohexylmethyl methacrylate) (PCMMA). 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. In order to compare the influence of the spacer group $-\text{CH}_2-$ in PCMMA and in poly(benzyl methacrylate) (PBzMA), we have also analysed this latter polymer in this work.

EXPERIMENTAL

Monomer and polymer preparation

The monomers, cyclohexylmethyl methacrylate and benzyl methacrylate, were prepared by reaction of methacryloyl chloride (0.12 mol) with cyclohexylmethanol and benzyl alcohol (0.10 mol) respectively, in benzene solution, and *N,N*-dimethylaniline (0.10 mol) at reflux temperature for 52 h³⁻⁵.

The monomers were polymerized at 50°C in bulk *in vacuo*, in the presence of 2,2'-azobisisobutyronitrile (AIBN), 3×10^{-3} to 7×10^{-2} mol l⁻¹.

The polymers were fractionated by standard precipitation procedures using benzene as solvent and methanol as non-solvent. The polymers were characterized by osmometric and size exclusion chromatography (s.e.c.) measurements. The films were prepared by dissolution of the polymer in tetrahydrofuran (THF) and evaporated directly onto the measuring electrode, because of the brittleness of the films.

Measurements

The number-average molecular weight M_n of the PCMMA sample³ studied was 4.84×10^5 with a polydispersity $M_w/M_n = 1.20$. For PBzMA M_n was 4.62×10^5 and polydispersity 1.10.

High-frequency dielectric measurements were carried out by means of a GENRAD 162OAP capacitance bridge and three-terminal cell. The measurements were carried out in the frequency range from 100 Hz to 100 kHz, although at lower temperatures (-120°C) it was not

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always possible to perform the measurements at the extreme frequencies.

The range of measurements for $\tan \delta$ was between -150°C and 130°C for PCMMA and from -100°C to 100°C for PBzMA. The glass transition temperatures T_g were measured using a Dupont Mechanical Thermal Analyzer. The T_g values found were 90°C for PCMMA and 76°C for PBzMA.

RESULTS AND DISCUSSION

Figure 1 shows the loss permittivity (ϵ'') for poly(cyclohexylmethyl methacrylate) (PCMMA) and poly(benzyl methacrylate) (PBzMA). In the same figure are also shown the values for poly(cyclohexyl methacrylate) (PCMA) for comparison². PCMMA shows α -, γ - and δ -relaxations as the temperature decreases and a shoulder between the α - and γ -relaxations, which is present in all the polymers. In the case of PBzMA a continuous increase of ϵ'' with temperature from about -90°C to 70°C was observed. At this last temperature (70°C) the main relaxation was observed, which we will call α because of the analogy with the other two polymers. The relaxation map corresponding to the polymers studied in this work is shown in Figure 2.

The region of the α -relaxation is represented for both polymers in Figures 3 and 4 in terms of the isotherm curves of ϵ'' in the range of frequencies studied. These relaxations can be related to the glass transitions for both polymers because they are in the same range of temperature. The α -relaxation can be characterized better

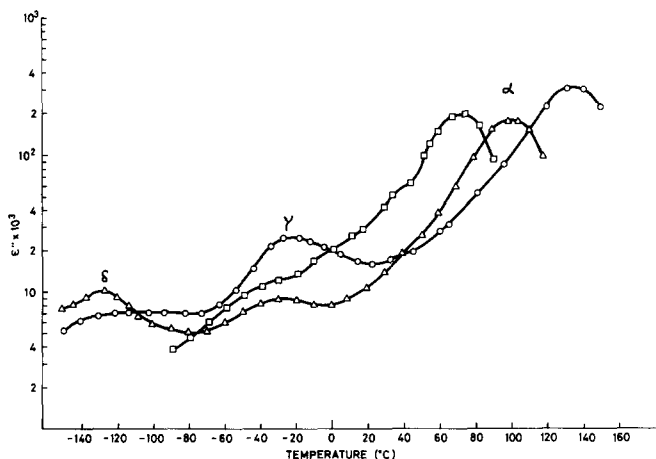


Figure 1 Values of ϵ'' vs. T at a frequency of 1 kHz for PCMA (O), PCMMA (Δ) and PBzMA (\square)

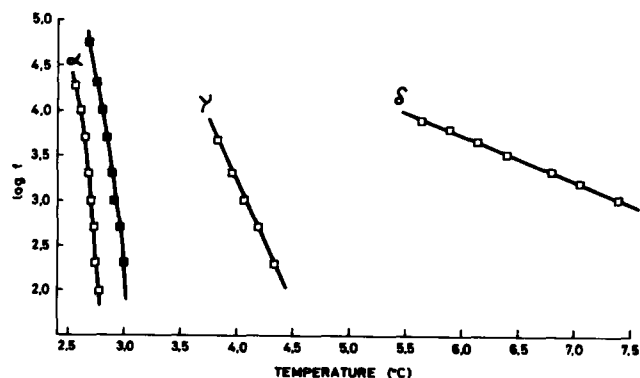


Figure 2 Arrhenius plots for PCMMA (\square) and PBzMA (\blacksquare)

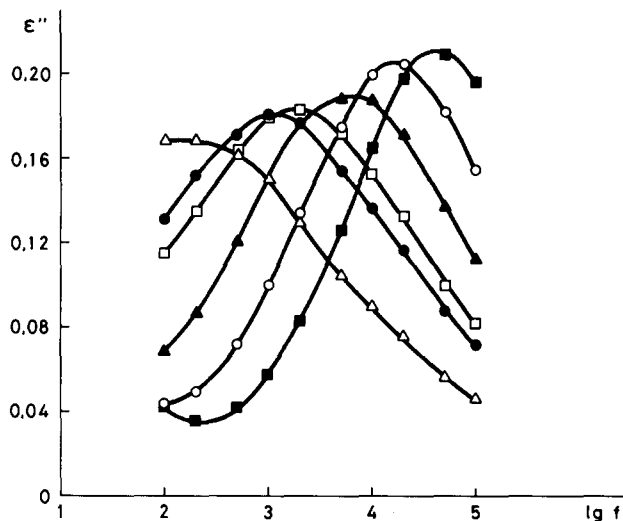


Figure 3 Values of ϵ'' vs. $\log f$ for PCMMA at temperatures of 88.9°C (Δ), 98.3°C (\bullet), 102.5°C (\square), 109°C (\blacktriangle), 118°C (\circ) and 127.1°C (\blacksquare)

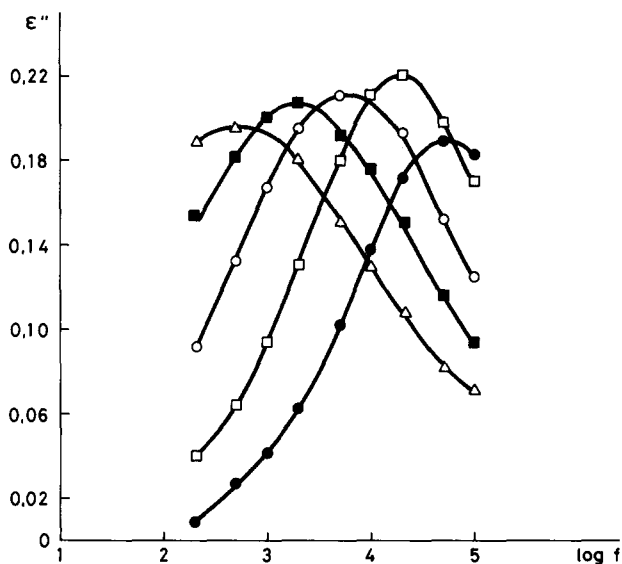


Figure 4 Values of ϵ'' vs. $\log f$ for PBzMA at temperatures of 67.1°C (Δ), 74°C (\blacksquare), 81.4°C (\circ), 90°C (\square) and 99.2°C (\bullet)

by calculating ϵ_0 and ϵ_∞ from Cole-Cole arcs (ϵ'' vs. ϵ'), as illustrated in Figures 5 and 6 in the range of temperatures corresponding to the α -relaxation. The results have been fitted to the empirical model of Havriliak and Negami⁶:

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega\tau)^\alpha]^b \quad (1)$$

The best fits for the three chosen temperatures are listed in Table 1 for PCMMA and in Table 2 for PBzMA. The results were also analysed as the α -relaxation behaviour in relation to the free-volume theory according to the WLF equation or its equivalent version given by Vogel⁷:

$$\log \tau_i = A + m / [2.303(T - T_\infty)] \quad (2)$$

By assuming that all the relaxation times have the same temperature dependence, the shift factor a_T ($a_T = \tau_i / \tau_{i,0}$ where $\tau_{i,0}$ is the relaxation time at the reference temperature T_0) is given by:

$$\log a_T = A' + (m/2.303)(T - T_\infty)^{-1} \quad (3)$$

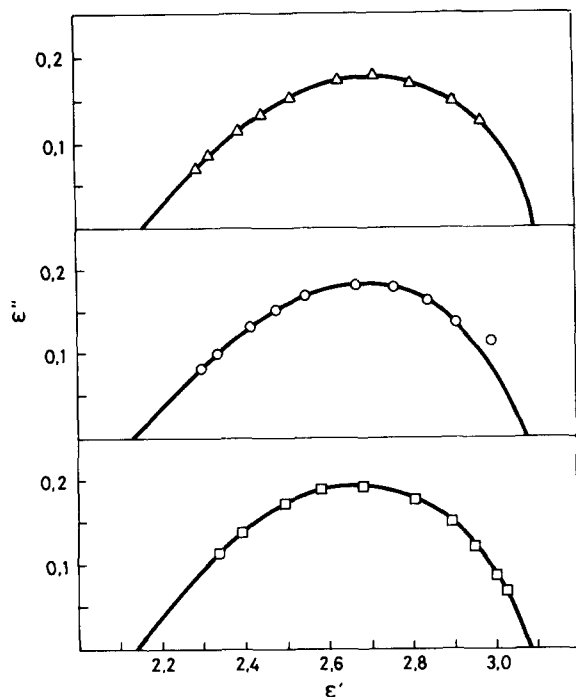


Figure 5 Cole-Cole arcs for PCMMA at temperatures of 98.3°C (Δ), 102.5°C (\circ) and 109°C (\square)

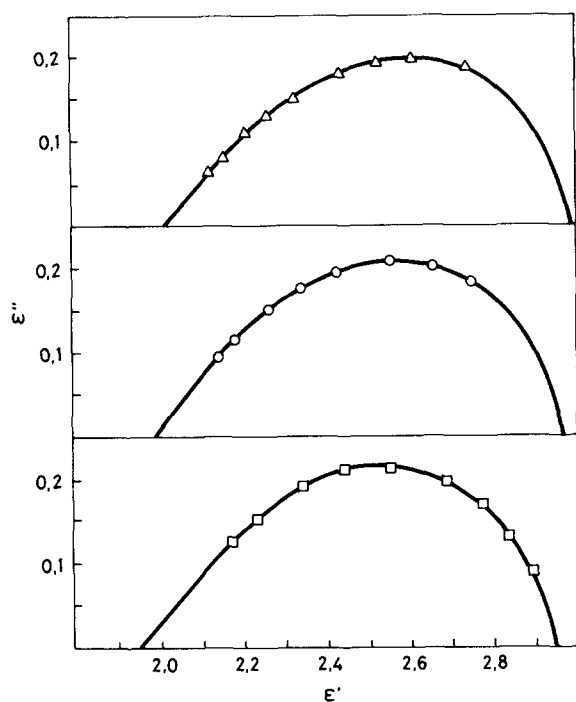


Figure 6 Cole-Cole arcs for PBzMA at temperatures of 67.1°C (Δ), 74°C (\circ) and 81.4°C (\square)

Table 1 Parameters of the equation of Havriliak and Negami⁶ for PCMMA

T (°C)	98.3	102.5	109.0
$\epsilon_0 - \epsilon_\infty$	0.95	0.95	0.93
a	0.336	0.378	0.365
b	0.337	0.387	0.369
$\epsilon'(\omega\tau_0)$	2.925	2.885	2.920

Table 2 Parameters of the equations of Havriliak and Negami⁶ for PBzMA

T (°C)	67.1	74.0	81.4
$\epsilon_0 - \epsilon_\infty$	0.99	0.98	1.02
a	0.293	0.256	0.263
b	0.345	0.337	0.321
$\epsilon'(\omega\tau_0)$	2.830	2.810	2.800

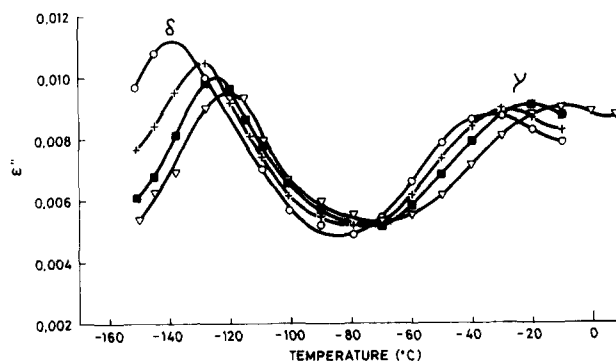


Figure 7 Values of ϵ'' vs. temperature at frequencies of 0.5 kHz (\circ), 1 kHz ($+$), 2 kHz (\blacksquare) and 5 kHz (∇)

where

$$A' = (-m/2.303)(T_0 - T_\infty)^{-1}$$

and

$$m = Bv/\alpha_f$$

Here B is an empirical constant, v is the specific volume and α_f is the thermal expansivity coefficient.

By comparison with the Doolittle⁸ equation:

$$m = (T - T_\infty)B/\phi = (T_g - T_\infty)B/\phi_g \quad (4)$$

and

$$\alpha_g = (T_g - T_\infty)^{-1} \phi_g/B \quad (5)$$

where ϕ is the relative free volume and ϕ_g is taken as unity.

The best fit gave $\phi_g = 0.04$ and $\alpha_f = 3.8 \times 10^{-4}$ and $\phi_g = 0.1$ and $\alpha_f = 3.15 \times 10^{-3}$ for PCMMA and PBzMA respectively. The values found in the case of PBzMA are slightly higher than those predicted by the theory.

In the case of PCMMA two new relaxations, δ and γ , were observed, as commented before. These relaxations are shown as a function of temperature and at different frequencies in Figure 7.

The energy of activation corresponding to the γ -relaxation at about -30°C (1 kHz) is $11.8 \text{ kcal mol}^{-1}$. The position as well as the activation energy E_a for this relaxation, but not the height, can be related to the dielectric γ -relaxation of PCMA², which was described as a transition between the two chair conformations according to Heijboer¹.

The differences in the height found for the γ -peak in PCMMA relative to the γ -peak in PCMA can be explained by taking into account the number of groups participating in the relaxation. It has also been observed that the dynamic loss modulus decreases when the conformational energy ΔF associated with the motion increases but not with increase in the volume of the group in motion. In our case we found that $\Delta F = 0.7$ and $1.7 \text{ kcal mol}^{-1}$ for PCMA and PCMMA respectively. Therefore, it is possible to associate the decrease of the

loss permittivity with two effects: first, increase of the conformational energy, and secondly, decrease of the cyclohexyl group concentration due to the incorporation of methylene group $-\text{CH}_2-$ into the side-chain in PCMA.

The analysis of the dielectric γ -relaxation can be performed, by assuming that this relaxation follows the Fuoss-Kirkwood model⁹:

$$\varepsilon'' = \varepsilon''_{\max} \operatorname{sech} m\tau \quad (6)$$

where

$$\tau = E_a(T^{-1} - T_{\max}^{-1})/R$$

and m is a parameter that generally depends on the temperature and frequency, and its values are related to the width of the relaxation.

From the plot of $\cosh^{-1}(\varepsilon''_{\max}/\varepsilon'')$ vs. $10^3/T$ for the frequencies 0.5–5 kHz, we found m values from 0.23 to 0.16 respectively. These m values are lower than those reported for PCMA, the difference being about 50%.

On the other hand, we have used the well known equation:

$$\varepsilon_0 - \varepsilon_{\infty} = 2\varepsilon''_{\max}/m \quad (7)$$

and if, in this expression, the ε'' and m values decrease by 3/8 and 1/2 respectively in relation to the values corresponding to PCMA, then $(\varepsilon_0 - \varepsilon_{\infty})$ should diminish by about 3/4 from polymer to polymer. On the other hand, we have calculated the area under the curve $\varepsilon''_{\text{corr}}$ according to the equation:

$$(\varepsilon_0 - \varepsilon_{\infty})_{\gamma} = \Delta\varepsilon'_{\text{calc}} = (2E_a/\pi R) \int_{1/T_1}^{1/T_2} \varepsilon''_{\text{corr}} d(1/T) \quad (8)$$

We found that $\varepsilon''_{\text{calc,PCMA}}/\varepsilon''_{\text{calc,PCMA}} = 0.74$, which is in good agreement with the 3/4 relation expected. This good agreement may be fortuitous, if we take into account that when our results are compared, the error in using equation (8) ($\varepsilon''_{\text{corr}}$ and the limits $1/T_1$, $1/T_2$ instead $+\infty$ to $-\infty$) can be significant (about 10%). We can conclude that the decrease of ε''_{\max} in PCMA in relation to PCMA is important but not as important as the decrease of the intensity of the relaxation, represented by $(\varepsilon_0 - \varepsilon_{\infty})$.

The relaxation at lower temperature appears at -125°C at 1 kHz and is designated as δ -relaxation. The activation energy of this relaxation is $5.5 \text{ kcal mol}^{-1}$. The height of this relaxation is larger than that observed for PCMA (Figure 1). In PCMA the δ -relaxation is rather diffuse. According to these results, it is possible to suggest that the molecular motions that give rise to both relaxations were not necessarily the same. In the case of PBzMA the γ - and δ -relaxations are not observed, and therefore we can conclude that the molecular origin of the δ -relaxation can be attributed to the motion of the cyclohexyl group, which is absent in PBzMA.

The application of the Fuoss and Kirkwood⁹ model (equation (6)) leads to values of 0.29 and 0.20 for frequencies of 0.5 and 5 kHz. These values indicate that this relaxation is narrower than the γ -relaxation.

We have observed a small β -relaxation between the α - and γ -relaxations for the polymers studied here and also the existence of a slight dielectric activity about -40°C (see Figure 1) for PBzMA.

In order to verify the presence of the new relaxations hidden under another, and appearing as shoulders, different treatments based on the analysis of the relaxation curves in terms of $\tan \delta$ and ε' have been proposed. In fact, on the one hand Johari *et al.*¹⁰ have proposed an analysis of the relaxations at high

frequencies, using the differences between the values of the curves of $\tan \delta$ at two fixed well separated frequencies (greater than a decade) as a function of temperature. This is called the isochrone difference. This kind of study requires very precise results. On the other hand, Bánhegyi *et al.*¹¹ have proposed to use the difference between the ε' values at two given frequencies as a function of temperature or $d\varepsilon'(T)/dT$ at constant frequency.

To prove the existence of peaks in the loss curve it has been proposed to use the derivative of the real part of the complex dielectric permittivity. This treatment is based on the following equations. It is well known that:

$$\left(\frac{\partial \varepsilon'}{\partial T}\right)_{\omega} \left(\frac{\partial T}{\partial \ln \omega}\right)_{\varepsilon'} \left(\frac{\partial \ln \omega}{\partial \varepsilon''}\right)_T = -1 \quad (9)$$

from which we obtain:

$$\left(\frac{\partial \varepsilon'}{\partial T}\right)_{\omega} = -\left(\frac{\partial \varepsilon'}{\partial \ln \omega}\right)_T \left(\frac{\partial \ln \omega}{\partial T}\right)_{\varepsilon'} \quad (10)$$

On the other hand:

$$\left(\frac{\partial \varepsilon'}{\partial \ln \omega}\right)_T \approx \frac{2}{\pi} \varepsilon''(\omega)$$

and

$$\left(\frac{\partial \ln \omega}{\partial T}\right)_{\varepsilon'} \approx \frac{E_a}{RT^2} \quad (11)$$

Consequently:

$$\frac{\partial \varepsilon'(T)}{\partial (1/T)} \approx \frac{T^2}{\partial T} \frac{\partial \varepsilon'(T)}{\partial T} = \frac{2E_a}{\pi R} \varepsilon''(T, \omega) \quad (12)$$

If equation (12) is rigorously exact and E_a is noticeably constant, the first term of equation (12) is proportional to ε'' and therefore the first term would not show a maximum if ε'' does not show such a maximum. From this analysis we conclude that to have a peak in a $d\varepsilon'(T)/d(1/T)$ curve the activation energy E_a should decrease with temperature. Moreover equation (12) is only approximate, and as a consequence of these arguments the derivative $-d\varepsilon'(T)/d(1/T)$ can show in relation to ε'' an enhancement in the zone at low temperatures relative to that at high temperatures. This should be the origin of the peaks in this function. As a matter of fact, the difference in using $d\varepsilon'/dT$ or $-d\varepsilon'(T)/d(1/T)$ is only the modification of the relaxation height relative to the peak; probably, it will also appear in $d\varepsilon'/dT$.

Figure 8 shows the four functions, i.e. $\Delta \tan \delta(\omega, T)$, $\Delta \varepsilon'$, $d\varepsilon'/dT$ and $d\varepsilon'/d(1/T)$, for PBzMA. We can observe a better resolution in the third and fourth functions where two new peaks appear.

The first peak appears at about 0°C and can be identified, due to its position, with the β -relaxation of the poly(methacrylates), which is associated with the rotation of the carboxy-cyclohexyl group of the side-chain. This relaxation does not appear so clearly as in the case of poly(methyl methacrylate) (PMMA), probably due to the larger volume of cyclohexyl group than methyl group.

The second peak was observed at about -45°C , which is consistent with the small shoulder found from dynamic mechanical measurements to represent G'' (at 1 Hz and -90°C) for the same polymer¹ (see figures 6 and 7 of ref. 1, p. 109).

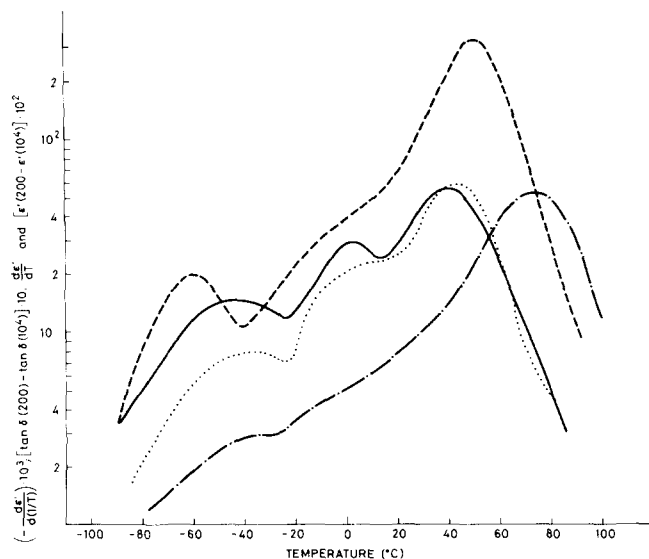


Figure 8 Values of $\epsilon'(200 \text{ Hz}) - \epsilon'(10^4 \text{ Hz})$ (---), $\tan \delta(200 \text{ Hz}) - \tan \delta(10^4 \text{ Hz})$ (-·-·-), $d\epsilon'/dT$ (—) and $d\epsilon'/d(1/T)$ (·····)

Accordingly it follows that the procedure proposed by Bánhegyi *et al.*¹¹ should be appropriate to resolve secondary relaxations when they are overlapped by other near relaxations.

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