

# Detection of Secondary Relaxation in Polyacetal, Polycarbonate and Polyether-Sulfone by Ultrasonic and Dielectric Methods

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## Synopsis

The ultrasonic pulse echo technique in the range of frequencies between 1 and 5.7 MHz and temperatures between 170 and 360 K is used to detect the secondary relaxations in polyacetal, polycarbonate, and polyether-sulfone. The activation energies and the relaxation frequencies were calculated and they were found to be comparable in value. The dielectric permittivity  $\epsilon'$  and loss factor  $\tan \delta$  for such polymers were also studied over a frequency range from  $10^2$  and  $10^6$  Hz and temperatures between 30 and 80°C. At higher temperatures, the polymers possess better dielectric properties.

## INTRODUCTION

Many attempts have been made to systematize the approach to naming of the many observed secondary relaxation processes occurring below the glass transition temperature in polymeric materials.<sup>1,2</sup> These processes are designated by letters of the Greek alphabet,  $\alpha$  representing the highest temperature transition observed at a fixed frequency of observational time, with  $\beta$ ,  $\gamma$ ,  $\delta$ , etc., representing other dispersion regions in decreasing order of temperature. Such processes can be studied over a wide frequency range by dynamic mechanical techniques of various kinds, by dielectric methods or by nuclear magnetic resonance,<sup>3</sup> and recently by ultrasonic technique.<sup>4</sup> The aim of the work is to use the ultrasonic technique to investigate the secondary relaxations of three polymers namely; polyacetal, polycarbonate, and polyether-sulfone. Also, it is aimed to give more information about the dielectric properties of such polymers at a wide range of frequencies and temperatures.

## EXPERIMENTAL

For ultrasonic measurements, flaw detector USM 2 produced by Krautkramer was used.<sup>5</sup> The apparatus is capable of producing high frequency pulses in the frequency range 0.5–12 MHz and usually operates with the same transducer as transmitter and receiver at the same time. If  $l$  is the height of a particular echo on the oscilloscope,  $d$  is the distance traversed,  $l_0$  is the height when  $d = 0$  and  $\alpha$  is the ultrasonic attenuation, so that  $l = l_0 e^{-\alpha d}$ .  $l$  was measured by means of a calibrated scale capable of measuring with an accuracy of  $\pm 0.2$  mm. Usually, in polymers,  $\alpha$  is very high compared with that of metals and only one or two echos are observed

in the oscilloscope. Thus, variation of the ultrasonic attenuation with a certain parameter can be evaluated as seen from the above equation by measuring the change of height of the echo since  $\alpha$  has the dimension of reciprocal height.<sup>4,6</sup> The temperature was achieved by electric furnace.

For dielectric measurements an NF decimeter Schering bridge type in the frequency range between  $10^2$  and  $10^5$  Hz with guard ring capacitor type NFW 5/T was used. Accuracy of measurements in dielectric permittivity  $\epsilon'$  was  $\pm 1\%$  while for the loss factor  $\tan \delta$  was  $\pm 2\%$ . Measurements were carried out at temperatures between 30 and 80°C using an ultrathermostat.

Three different polymers were used in this investigation. Polyacetal and polycarbonate were obtained from Nylonic Engineering Co., (U.K.) while polyether sulfone was obtained from Imperial Chemical Industries (ICI) Ltd. (U.K.). The physical constants of such polymers are illustrated in Table I.

The samples were in the form of circular discs 2.0 cm diameter and 0.7 cm thickness in case of ultrasonic measurements and 5.0 cm diameter and 0.4 cm thickness in case of dielectric measurements.

## RESULTS AND DISCUSSION

Figures 1–3 represent the relation between  $l^{-1}$  ( $\text{cm}^{-1}$ ) and  $T$  (K) at three different frequencies for POM, PC, and PES, respectively.

The observed peaks can be attributed to the movements associated with secondary relaxation processes. These peaks shift to higher temperatures and become higher and sharper with increasing frequency. This trend has been observed before in case of nylon 6 and nylon 6.6.<sup>7</sup> For POM, the peaks are observed in the region of 247 K (2.1 MHz) to 277 K (5.7 MHz). These peaks are considered to be the  $\gamma$ -relaxation when they are compared with those detected dielectrically at lower frequencies.<sup>8</sup> The  $\gamma$ -peak was observed at 10 kHz in the region of 217.5 K and at 320 kHz in the region of 238.8 K.  $\gamma$ -Peaks are considered to be a mechanism associated with the disordered region of the polymer.<sup>8</sup> According to the Arrhenius equation  $f=f_0e^{-E/KT_m}$  (where  $f$  is the operating frequency of the ultrasonic wave,  $f_0$  is the natural frequency of the relaxation process,  $T_m$  is the absolute temperature corresponding to the peak, and  $K$  is the Boltzman constant) and from the relation between  $\log f$  and  $1000/T_m$  (Fig. 4), the apparent activation energy  $E$  associated with the  $\gamma$ -relaxation is calculated and found to be 4.5 kcal/

TABLE I  
Physical Constants of the Different Polymers

Polymer	Grade	Density ( $\text{g}/\text{cm}^3$ )	Melting point (°C)	Moisture absorption (max) (%)	Coefficient of linear thermal expansion ( $10^{-5}/^\circ\text{C}$ )
Polyacetal (POM)	H	1.41	179.1	0.22	4.5
Polycarbonate (PC)	—	1.20	206.9	Low	—
Polyether-sul- fone (PES)	Victrex 200p	1.37	—	—	5.5

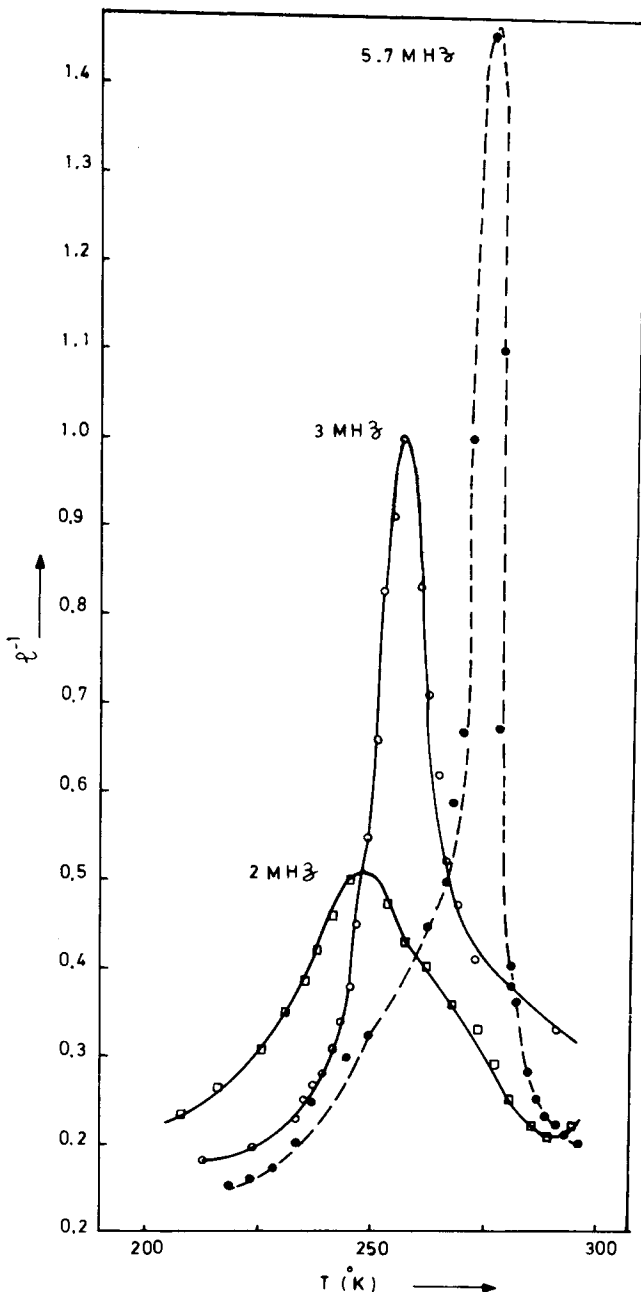


Fig. 1. Relation between  $l^{-1}$  ( $\text{cm}^{-1}$ ) and  $T$  (K) at various frequencies for POM.

mol. The relaxation frequency  $f_0$  is also calculated and found to be  $1.8 \times 10^{10}$  Hz.

The peaks for PC are found in the region of 230 K (1 MHz) to 261 K (3 MHz) while those for PES are found in the region of 265 K (2.1 MHz) to 283 K (4 MHz). The apparent activation energies associated with those relaxations and also the relaxation frequencies in both PC and PES are

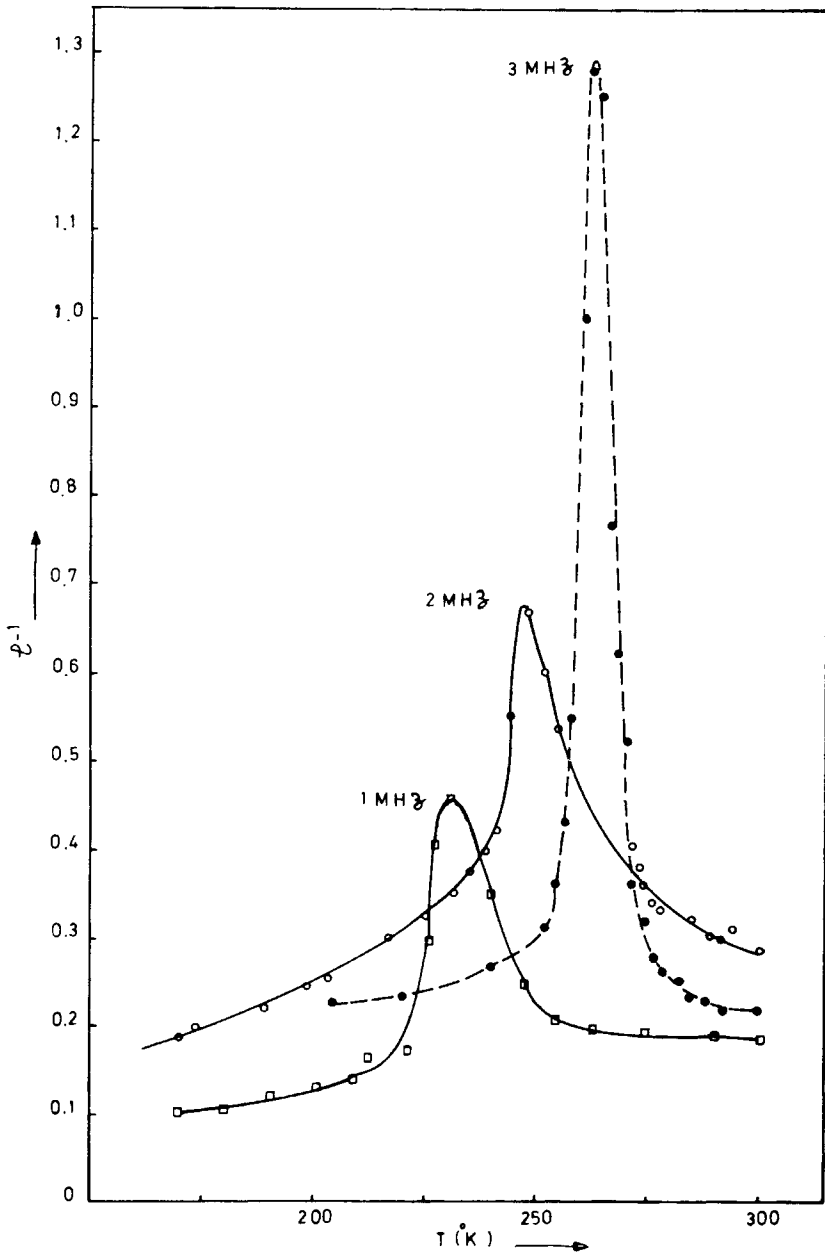


Fig. 2. Relation between  $l^{-1}$  ( $\text{cm}^{-1}$ ) and  $T$  (K) at various frequencies for PC.

calculated and given in Table II. These values are quite comparable, indicating that the secondary relaxation processes in PC and PES are probably similar to that of POM.

The dielectric permittivity  $\epsilon'$  and loss factor  $\tan \delta$  of POM, PC, and PES at frequencies extending from 100 Hz to 100 kHz and at temperatures between 30 and 80°C are shown graphically in Figure 5. These values are comparable with those found in literature<sup>9</sup> at 10<sup>6</sup> Hz and at 20°C (POM:

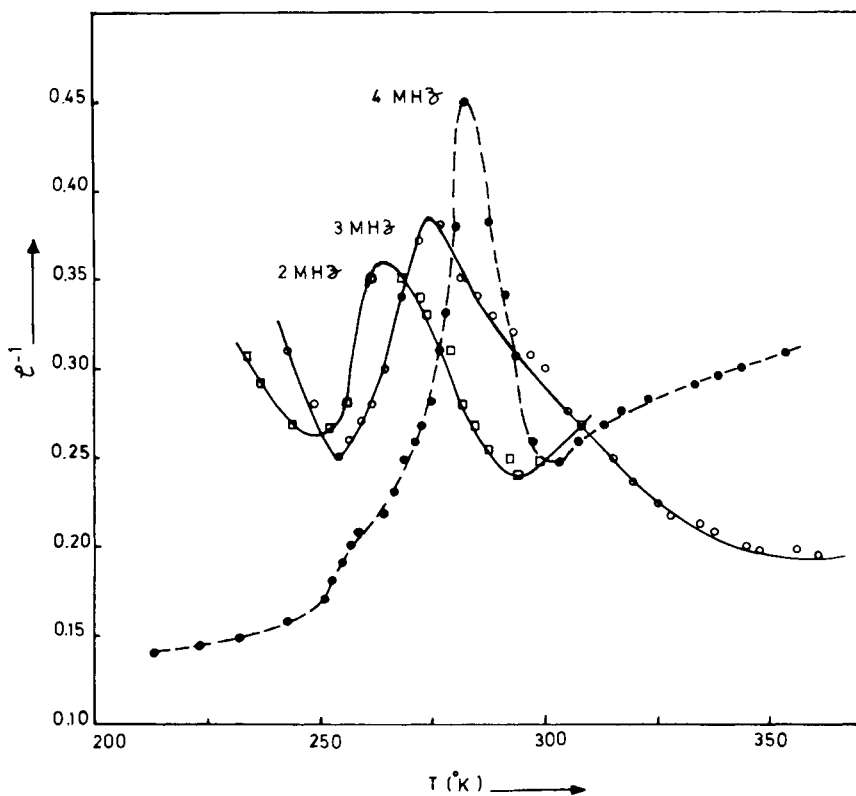


Fig. 3. Relation between  $l^{-1}$  ( $\text{cm}^{-1}$ ) and  $T$  (K) at various frequencies for PES.

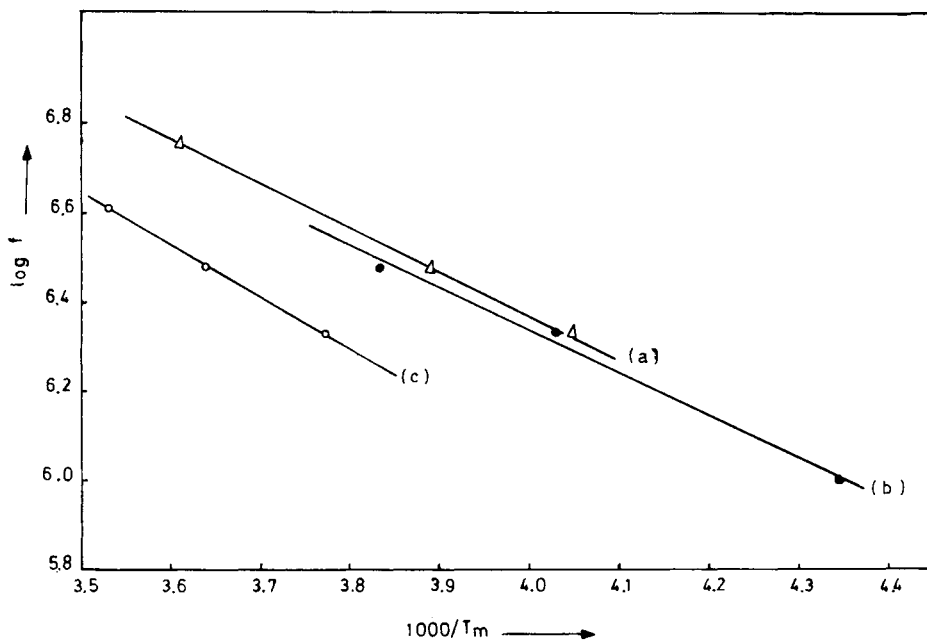


Fig. 4. Relation between  $\log f$  and  $1000/T_m$  ( $\text{K}^{-1}$ ) for: (a) POM; (b) PC; (c) PES.

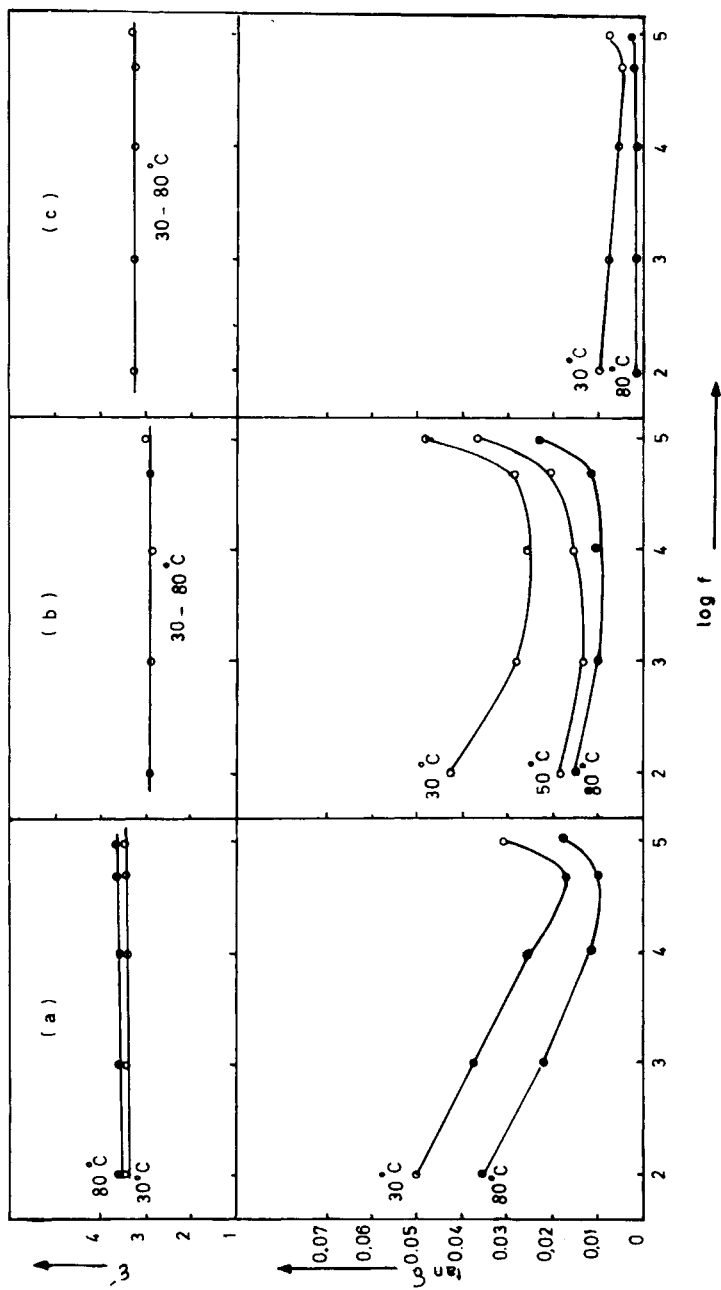


Fig. 5. Frequency dependence of dielectric permittivity  $\epsilon'$  and loss factor  $\tan \delta$  at various temperatures for: (a) POM; (b) PC; (c) PES.

TABLE II  
The Activation Energy  $E$  and Relaxation Frequency  $f_0$  for the Different Polymers

Polymer	$E$ (kcal/mol)	$f_0$ (Hz)
POM	4.5	$1.8 \times 10^{10}$
PC	4.3	$1.2 \times 10^{10}$
PES	5.0	$2.7 \times 10^{10}$

$\epsilon' = 3.7$  and  $\tan \delta = 0.005$ , PC:  $\epsilon' = 2.9$  and  $\tan \delta = 0.01$ , PES:  $\epsilon' = 3.3$  and  $\tan \delta = 0.006$ ). In the case of PC and PES, no change in  $\epsilon'$  either with frequency or with temperature is noticed but in the case of POM a little increase in  $\epsilon'$  with temperature (30–80°C) is noticed while no change with frequency is detected. From the relation between the  $\tan \delta$  and  $\log f$ , it seems that two absorption regions are present in that range of frequencies which are attributed to the secondary relaxations of the polymers. The maxima of these two regions are not reached at the frequency limits of the measurements. From Figure 5 it is also noticed that as the temperature increases,  $\tan \delta$  decreases. Thus, it could be concluded that POM, PC, and PES possess better insulating property at higher temperatures especially PES which is characterized by a very low loss factor (less than 0.01).

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