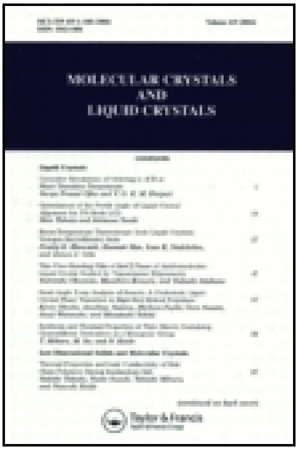

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Dielectric Relaxation Studies in OBT al Low Temperatures

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Dielectric measurements have been made in the stable and metastable solid modifications of *n*(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) in the frequency range 0.5 to 100 KHz and in the temperature range −180 to +40°C. While cooling rapidly for metastable modification, the OBT first attained glassy phase I and thereafter changed to glassy phase II at a temperature of about −45°C. On heating, the metastable phase converts to stable crystalline phase at a characteristic temperature of about +23°C. The dielectric dispersion was absent in the stable phase while in the metastable modification an asymmetrical distribution of relaxation times was seen. The dispersion mechanism for glassy phase II and I identified as β and α relaxation processes have been attributed due to the group orientation and free orientation of the molecules about their long axes respectively.

INTRODUCTION

In recent years there has been considerable interest[1–5] on the study of the dielectric properties of solid phase liquid crystals. The two monotropic modifications of solid phase liquid crystals have been identified:[6,7] a stable and a metastable one, which are obtained depending on the thermal history

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of the sample. Metastable phase of a system represents the thermodynamically non-equilibrium state and which is acquiring, at a very slow rate, thermodynamic equilibrium. Studies in solid phase liquid crystals indicated the absence of dielectric dispersion in the stable modification, while in the metastable modification a clear dielectric dispersion[1–5] arising from the partial reorientation of active dipoles has been observed. In the metastable solid phase of a few nematic liquid crystals[3] two dielectric relaxation processes have been identified, termed as α and β relaxations above and below the glass transition temperature t_g, similar to those observed in a large number of glasses.[8,9] However, there has been relatively little study to understand the character of α and β relaxations in the metastable solid modifications of liquid crystals. In the present paper we report the results of our dielectric relaxation measurements in the stable and metastable solid modifications of *n*(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) in the temperature range −180 to +40°C. The present study has been carried out to characterize the dielectric behaviour of solid phase of OBT and to identify the nature of α and β relaxations which will help to understand the mechanism of dielectric dispersion in the solid phase liquid crystals.

EXPERIMENTAL

A General Radio Schering bridge type 716 CS was used with a Hewlett-Packard 209A oscillator and GR tuned amplifier/null detector to measure the capacitance and loss factor in the frequency range 0.5 to 100 KHz. A gold plated cylinderical cell (effective capacitance 30.8 pF) was used for two terminal measurements. The measuring techniques were the same as described earlier.[2] The slow and fast coolings at the rate of about 0.5°C/min and 8°C/min, using liquid nitrogen, yielded stable and metastable solid modifications respectively of the sample. When −180°C temperature was reached, the cell was kept at this temperature for more than 40 minutes. The measurements for both the stable as well as metastable solid forms were taken during heating cycle only. It took about 8 hours to complete each run.

The error in the measurements of the electric permittivity (ε') and dielectric loss (ε'') was about $\pm 1\%$ and $\pm 2\%$ respectively. At low frequencies there was a significant increase in the dielectric loss, probably caused by the ionic conductivity and this was taken into account in deriving the values of ε''.

RESULTS AND DISCUSSION

The variation of dielectric permittivity (ε') and loss (ε'') with temperature for both the stable and metastable solid forms of OBT are shown in Figures

1 and 2 at three typical frequencies. The substantial difference between the dielectric properties of both phases is evident. In the metastable form there appears a clear dielectric dispersion and absorption which do not appear in

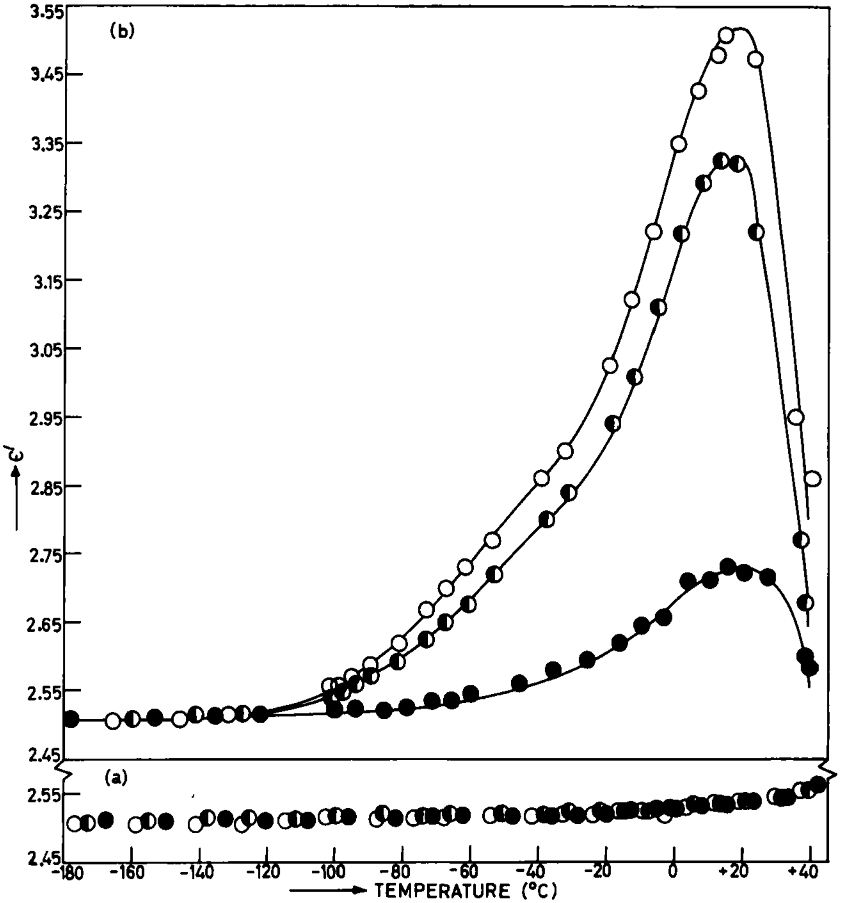

FIGURE 1 Temperature dependence of dielectric permittivity (ε') at 500 Hz (○), 1 KHz (◐) and 50 KHz (●) for the stable (a), and metastable (b), solid phase OBT.

the stable modification. A similar difference in the dielectric behaviour of stable and metastable forms of other liquid crystals has also been observed.[1,3,5]

It may be noticed from Figure 1(b) that the dielectric permittivity (ε') in the metastable phase of OBT increases with the increase in temperature, which reaches finally to a high value and then suddenly drops to a low value at about +23°C. At this critical temperature (t_c) of +23°C the metastable

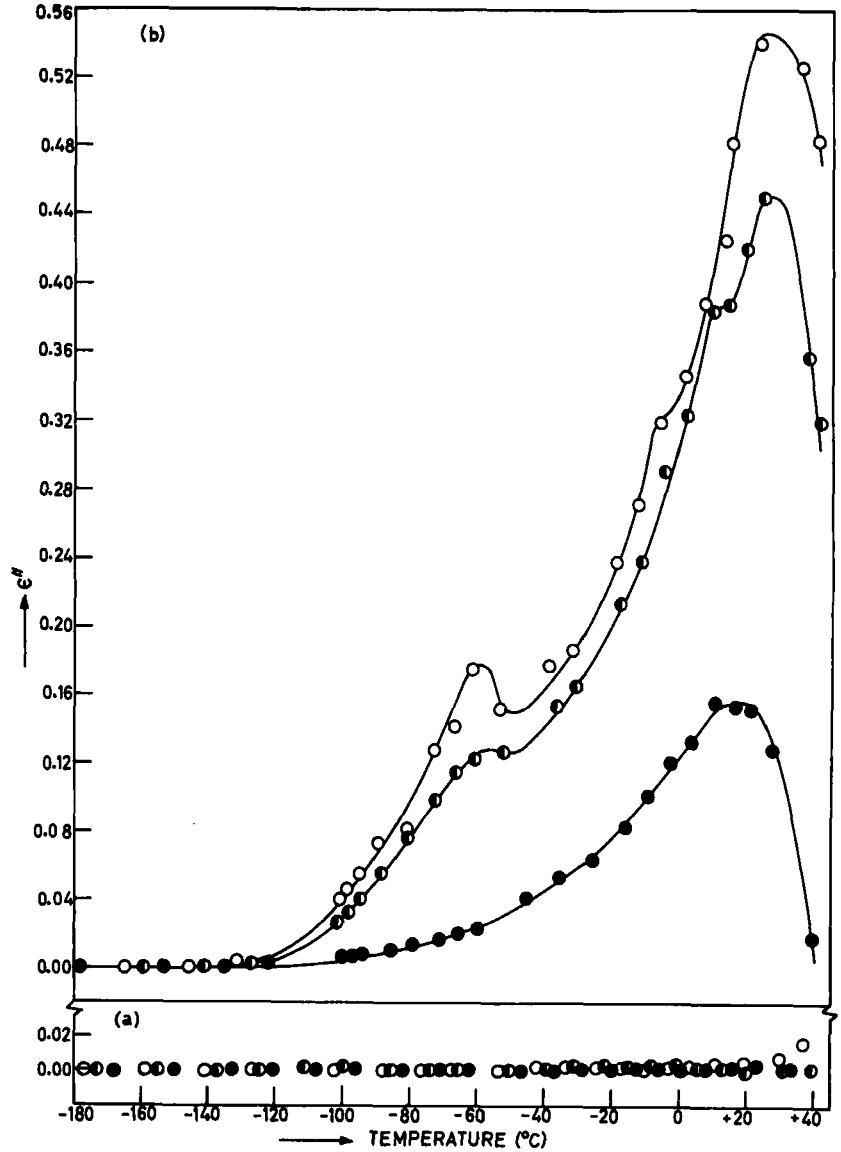

FIGURE 2 Temperature dependence of dielectric loss (ε″) at 500 Hz (○), 1 KHz (◐) and 50 KHz (●) for the stable (a), and metastable (b), solid phase OBT.

phase is converted into a stable crystalline phase, where no dielectric dispersion occurs. The rate of falling off of ε′ at t_c depends upon the rate of heating the sample.

From Figure 2(b) it may be seen that in the metastable solid phase OBT, a clear peak in ε'' for low frequencies exists below about $-45°$ which is probably due to β relaxation. The ε'' peak at 500 Hz, is well defined, while at 1 KHz just a hump is noted. At 50 KHz, no peak is observed below $-45°$C. This behavior of ε'' peak is characteristic of β-relaxation, as has been observed in several glasses.[8–14] The difference in the temperatures of peaks in ε'' for 500 Hz and 1 KHz, below $-45°$C, suggest that if these peaks were due to α-relaxation a clear peak at 50 KHz should also have been observed. The characteristic temperature ($-45°$C) where a dip in ε'' is obtained at the lowest frequency of measurements may be indicative of a glass transition temperature t_g. In the metastable phase the peaks in ε'' appear at almost the same temperature for all frequencies at $+23°$C. These peaks are due to sudden fall in ε'' value on transition from metastable to stable crystalline phase. However, if one notices carefully, a slight hump at 500 Hz and 1 KHz are observed, before the peaks in ε''. These humps, we believe, are due to α-relaxation and the well defined loss peaks are not observed due to large contribution of dc conductivity on measured ε''. Our results suggest that as the sample is cooled at a fast rate, it goes first to an amorphous glassy phase I where molecular aggregates are formed that allow completely free orientation of the molecules about their long axes, and this phase changes at a glass transition temperature t_g ($\sim -45°$C) to glassy phase II where only group rotations are possible. On heating, the glassy phase II changes to glassy phase *I* at t_g. The metastable state is a glassy state and the lifetime of this metastable state depends on the temperature. At a critical temperature t_c at which the viscosity becomes low enough to permit rapid crystallization, the amorphous phase changes to the crystalline phase, as indicated by the sharp drop in ε' and ε'' at $+23°$C in Figures 1 and 2 and this temperature is the same at all frequencies. Such a behaviour of metastable form converting into stable form has also been observed in the solid phase studies of some solutions of rigid polar molecules.[15]

In order to investigate the dielectric relaxation behaviour of metastable phase OBT we have analysed our results above t_g. The ionic losses due to the conductivity of impurities have been separated out using the following relations.

$$\begin{aligned}\varepsilon''(\text{total}) &= \varepsilon''(\text{dielectric}) + \varepsilon''(\text{conductance})\\ &= sf + \frac{1.80\sigma \times 10^{12}}{f} \qquad (1)\end{aligned}$$

where σ, the d.c. conductivity, is evaluated from the straight line plot of $\varepsilon''(\text{total}) \times f$ against f^2. The plots of ε' and $\varepsilon''(\text{dielectric})$ as functions of frequency and at different temperatures are shown in Figure 3. The two peaks

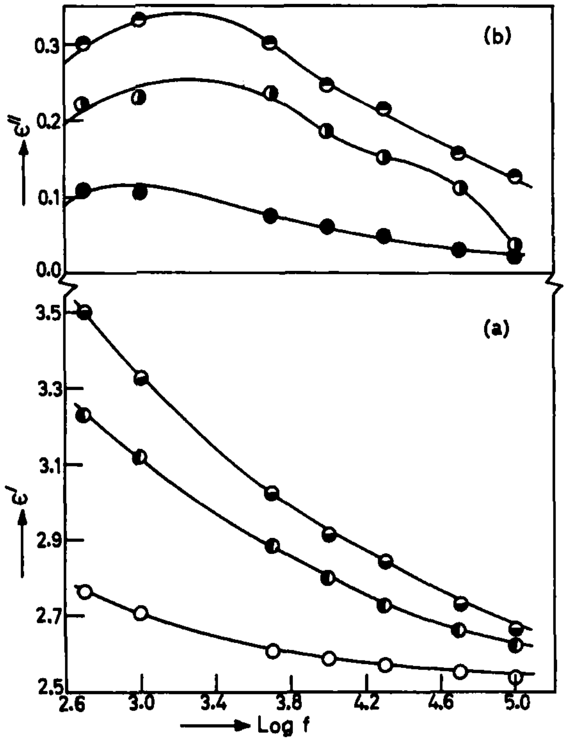

FIGURE 3 Frequency dependence of the dielectric permittivity ε′ (a) at −55°C (○), −5°C (◐) and +15°C (◒) and dielectric loss ε″ (b) at −55°C (●), −5°C (◑) and +15°C (◓) for the solid phase OBT.

corresponding to α relaxation (at low frequencies) and β relaxation (at high frequencies) are clearly seen in the loss curve.

The present data indicate an asymmetrical distribution of relaxation times according to an empirical equation developed by Cole–Davidson.[16]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)^\beta} \tag{2}$$

Rationalizing it to find ε′ and ε″ yields

$$\begin{aligned} \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} &= \cos^\beta \varnothing . \quad \cos \beta\varnothing \\ \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} &= \cos^\beta \varnothing . \quad \sin \beta\varnothing \end{aligned} \tag{3}$$

where $\tan \varnothing = \omega\tau_0$.

With the known experimental data, the best fit of Cole–Davidson curve is drawn. Representative curves at two temperatures are shown in Figure 4.

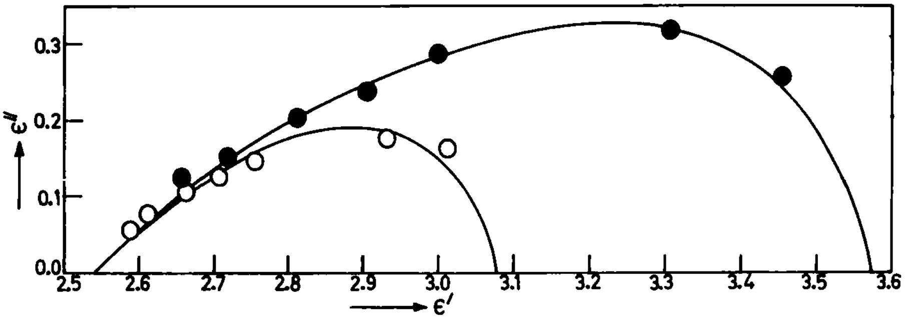

FIGURE 4 Cole–Davidson plots at −20°C (○) and +10°C (●).

This dispersion behaviour is in contrast to that observed in the mesomorphic phase of nematogens[17–19] where there is no distribution of relaxation times. Our earlier studies on metastable solid phase EBBA[3] also indicated the existence of secondary relaxation in addition to primary relaxation, but with a symmetrical distribution of relaxation times. However, Johari and Goldstein[8] have obtained asymmetrical distribution of relaxation times in glasses of rigid molecules.

The relaxation times at different temperatures have been obtained from the straight line plot of the following equation:

$$\log\omega + \log\tau_0 = \log\left[\tan\left\{\beta^{-1}\tan^{-1}\left(\frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty}\right)\right\}\right] \tag{4}$$

The plot of $\log\tau_0$ vs. $1/T$ is shown in Figure 5 from which an activation energy of 0.71 Kcal/mol is obtained for the α relaxation.

CONCLUSION

The dielectric studies indicate the existence of two monotropic modifications of solid OBT: stable and metastable. The metastable phase on heating converts to stable phase at a characteristic temperature t_c, similar to that observed in the solid phase of the solutions of rigid polar molecules. While cooling for metastable modification, the liquid crystal first goes to an amorphous or glassy phase I, which changes to glassy phase II at about −45°C. The dispersion mechanism for the glassy phase II and I, have been characterized due to the group rotation and the free orientation of the

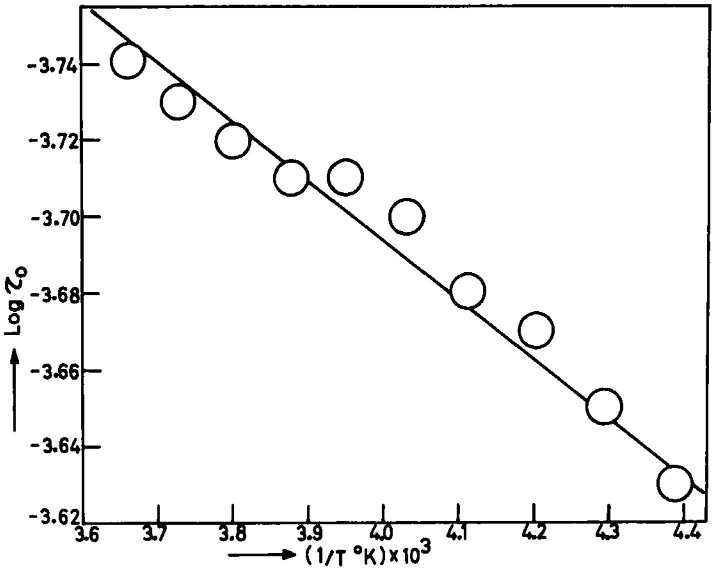

FIGURE 5 Temperature dependence of the dielectric relaxation time in the solid phase OBT.

molecule as a whole about its long axis respectively. The exact glass transition temperature t_g could not be precisely determined by the present measurements as the relaxation frequency at t_g appears to be much lower than the lowest frequency of measurements (500 Hz).

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