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W. Otowski[a]; R. Nozaki[ab]; T. K. Bose[a]
[a] Groupe de Recherche sur les Dielectriques, Departement de Physique, Universite du Quebec a Trois-Rivieres, Quebec, Canada [b] Department of Physics, Faculty of Science, Hokkaido University, Sapporo, Japan

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Broadband dielectric relaxation study on a diluted solution of a ferroelectric liquid crystal by time domain reflectometry

by W. OTOWSKI*, R. NOZAKI† and T. K. BOSE

Groupe de Recherche sur les Dielectriques, Departement de Physique, Universite du Quebec a Trois-Rivieres, C.P. 500, Trois-Rivieres, Quebec G9A 5HZ, Canada

In this work, complex permittivity measurements on a diluted solution of the ferroelectric liquid crystal, 4-[(*S*,*S*)-2,3-epoxyhexyloxy]-phenyl 4-(decyloxy)-benzoate, which shows ferroelectric smectic C phase (S_C^*), have been performed. Using time domain reflectometry, at frequencies between 10 MHz and 10 GHz, in the temperature range from 50°C down to 10°C for every 10°C, at 5, 10 and 30 wt.% in benzene we observe two independent relaxation processes around 150 MHz and 2 GHz. It is shown that the high frequency process is due to the internal molecular reorientations while the low frequency one is due to molecular orientation around the long molecular axis. It is concluded that the reorientation around the long axis is hindered and leads to a resultant macroscopic polarization.

1. Introduction

Recently, we have reported [1] that for the ferrolectric liquid crystal, 4-[(*S*,*S*)-2,3-epoxyhexyloxy]-phenyl 4-(decyloxy)-benzoate, relaxation curves in the high frequency region are somewhat broad, indicating the presence of more than one relaxation mechanism. Based on multiple Debye relaxations and analysis of the experimental data we have proposed that the distribution of relaxation times τ was due to two processes: internal molecular reorientation (intra) and rotation around the molecular long axis. The purpose of this paper is study the dielectric spectra of the mixture 4-[(*S*,*S*)-2,3-epoxyhexyloxy]-phenyl 4-(decyloxy)-benzoate-benzene as a function of concentration and temperature in order to be able to differentiate between intra-reorientation and intermolecular rotation of the ferroelectric liquid crystal molecules. It is expected that the concentration dependence of τ_{intra} would be simpler than the intermolecular rotation which may be affected by the dipole–dipole interaction [2–4]. For example one possible manifestation of dipole–dipole interactions can be molecular association. This phenomenon which is best studied by measuring the dielectric properties of dilute solutions has been suggested by Dunmur and Toriyama [3].

2. Experimental

Time domain reflectometry (TDR) is an important technique for the measurement of the complex permittivity of materials over a wide frequency band. A step-like pulse produced by a pulse generator propagates through the coaxial line and is reflected from the sample section placed at the end of the line. The reflected pulse also propagates through the same line. The difference between the reflected and the incident pulses recorded in the time domain contains the information on the dielectric properties of the sample.

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* Author for correspondence.

† Present address: Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

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Since the dielectric response is recorded in the time domain, one measurement covers a wide frequency range. In this paper we have carried out time domain measurement over the frequency range 10 MHz to 10 GHz. A detailed description of the measurement system has been reported elsewhere [5]. In the present case, we have used a bilinear coefficient method to obtain the complex permittivity. Using the Fourier transform of the reflected signal from the dielectric cell with the sample placed at the end of the coaxial line $V_x(\omega)$, and $V_O(\omega)$ for the empty cell, the complex permittivity of the sample $\varepsilon^*(\omega)$, is given in bilinear form by

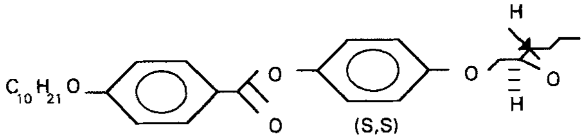
$$\varepsilon^* = (1 - A^*)\Omega/(1 + B^*\Omega) \tag{1}$$

and

$$\Omega = (c/j\omega d)(V_O - V_x)/(V_O + V_x), \tag{2}$$

where c is the speed of light, ω is the angular frequency and d is the effective electrical length of the cell. The complex coefficients A^* and B^* are determined by measuring standard samples with known permittivity. Acetone and toluene were used in this work as references.

The ferroelectric liquid sample 4-[(*S*,*S*)-2,3-epoxyhexyloxy]-phenyl 4-(decyloxy)-benzoate which shows a ferroelectric smectic C phase (S_C^*) was purchased from the Aldrich Chemical Company. The chemical structure of the sample and its phase transition temperatures are shown in figure 1. The cell temperature is stabilized by use of a liquid flow jacket with circulating polyethylene glycol controlled by a refrigerated bath unit (NESLAB model RTE-210). In order to change the temperature, the setpoint for the bath is controlled by a 16-bit personal computer through a 12-bit D/A converter.



$$C \xleftarrow{60^\circ C} S_3 \xleftarrow{64^\circ C} S_C^* \xleftarrow{80^\circ C} S_A \xleftarrow{81^\circ C} N \xleftarrow{97^\circ C} I$$

Figure 1. Chemical structure and the phase transition temperatures of the pure sample.

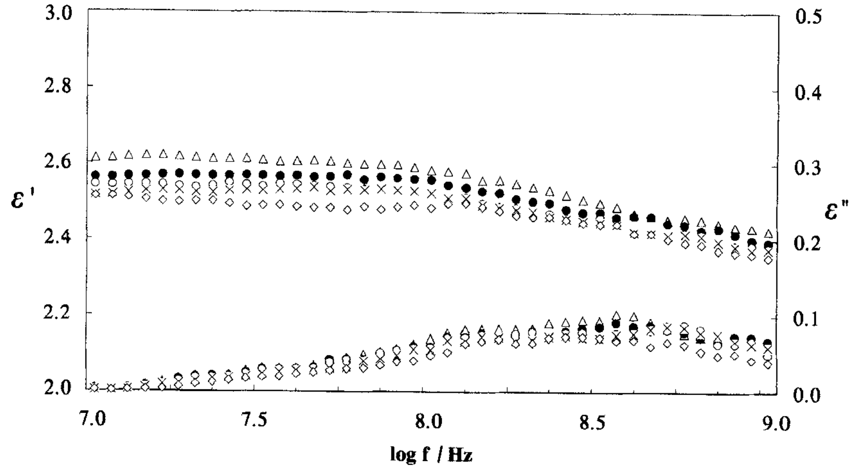


Figure 2. The temperature dependence of the permittivity and loss curves at 10 wt.% solute concentration (△, 10°C; ●, 20°C; ○, 30°C; ×, 40°C; ◇, 50°C).

3. Results and discussion

In figure 2, the temperature dependence of the permittivity and loss at 10 wt.% solute concentration are shown. As we can see in the case of the gigahertz frequency mode, the position of the maximum of the loss curves is not strongly affected by the temperature.

Figure 3 shows the frequency dependence of the complex permittivity at 20°C for three different concentrations. The strong solute concentration dependence of the position of the loss curve maximum is clearly visible. The decomposition of the dispersion and the loss curves in figures 2 and 3 show the presence of two independent relaxation processes. The lower relaxation frequency is around 150 MHz and the higher relaxation frequency is around 2 GHz. The frequency dependence of the complex dielectric constant can therefore be written as:

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_l}{1 + j\omega\tau_l} + \frac{\Delta\varepsilon_h}{1 + j\omega\tau_h}, \tag{3}$$

where ε^* is the measured complex permittivity, ω is the angular frequency, $\Delta\varepsilon_i$ and τ_ith are the dielectric relaxation strength and relaxation time for the *i*th process, and ε_∞ is the permittivity at limiting high frequency. Symbols l and h stand for low and high frequency processes, respectively.

It has been pointed out that two relaxation processes have been observed also for benzene solutions of 7CB and 8CB by Shin Yagihara *et al.* [6]. It is considered that the low frequency relaxation process reflects the overall rotation around the short molecular axis while the high frequency one reflects that around the long molecular axis.

It is well-known from dielectric studies of large molecules that the intramolecular rotation causes a distribution of the dielectric relaxation times [4, 7, 8]. In principle, the internal reorientation can substantially affect the observed relaxation spectra because this motion takes place on the same scale as the reorientation about the long molecular axis. This intramolecular rotation has been observed in quasielastic neutron scattering (QNS) experiments [9].

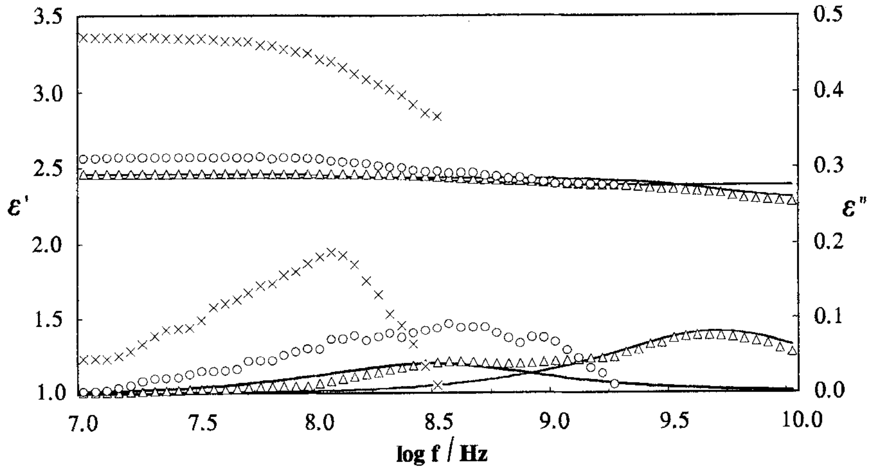


Figure 3. The frequency dependence of the complex permittivity at 20°C for 5 wt.% (△), 10 wt.% (○) and 30 wt.% (×) solute concentration. Solid curves show the result of decomposition.

In figure 4 it is seen that τ_h is almost temperature independent at 5 and 10 wt.% solute concentration. At 30 wt.% solute concentration we can see the decrease of τ_h with increasing temperature. It was suggested [4, 9] that the potential barrier to reorientation of two halves of the molecules was low enough to allow them to rotate independently around the weak bond. Taking into account the above information it seems probably that this kind of reorientation also takes place in the present case (reorientation around the single O–C bond between the benzene ring and the bridging

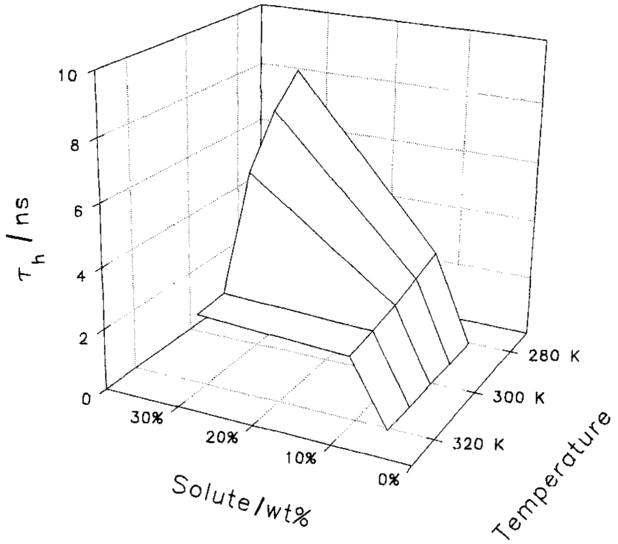


Figure 4. The temperature and solute concentration dependence of the high frequency relaxation time.

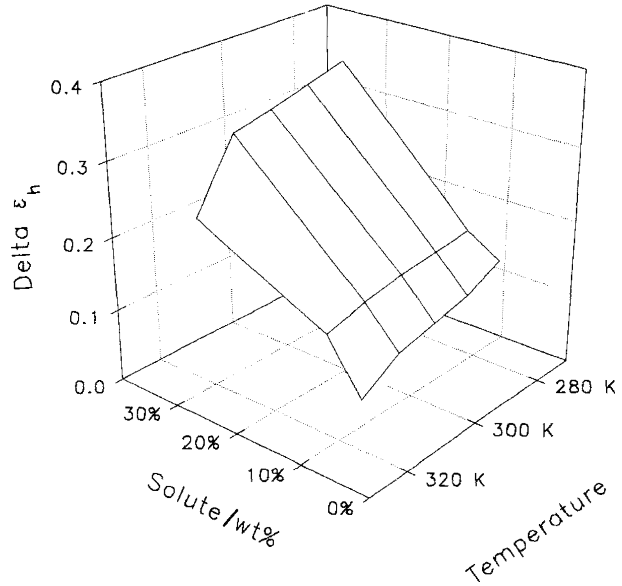


Figure 5. The temperature and solute concentration dependence of the high frequency dielectric strength.

group). At low concentration the intramolecular rotation occurs with relatively low disturbance from the surrounding molecules [8]. It is seen that at 5 and 10 wt.% solute concentration, τ_h is almost temperature independent which agrees with the above conclusion. However, at higher solute concentration (30 wt.%) the decrease of τ_h with increasing temperature is probably due to the viscosity of the solution. The temperature dependence of the viscosity is given by:

$$\eta = B(\exp E/k_B T), \tag{4}$$

where η is the viscosity, B is a constant, E is the energy barrier, k_B is the Boltzmann constant and T is the temperature. We notice (see figure 5) that the dielectric strength $\Delta\varepsilon_h$ for this process increases with increasing solute concentration. This means that $\Delta\varepsilon$ is proportional to the effective dipole moment which increases with increasing solute concentration (i.e. an increase of the number of molecules per unit volume). Because of the very high relaxation frequencies and the weak temperature dependence of τ_h, we can assume them to be due to internal molecular motions.

In figures 6 and 7 the temperature and the solute concentration dependence of the relaxation time τ_l and the low frequency dielectric strength $\Delta\varepsilon_l$ are seen, respectively. We see that the low frequency relaxation time decreases with increasing temperature at 5 wt.% and 30 wt.% solute concentration. At 10 wt.% solute concentration the temperature dependence of τ_l is rather complex. However, Dunmur and Toriyama [3] have suggested that even in the absence of a nematic ordering potential, the solute prolate molecules tended to form dimers with parallel and/or antiparallel molecular axes. Moreover, for dimers in which there is some internal rotation of dipole components the Fröhlich–Kirkwood dipole correlation factors g_i may be a complex function of the temperature. We see that using the relation [4],

$$\tau_{DR}/\tau_l \propto g_l, \tag{5}$$

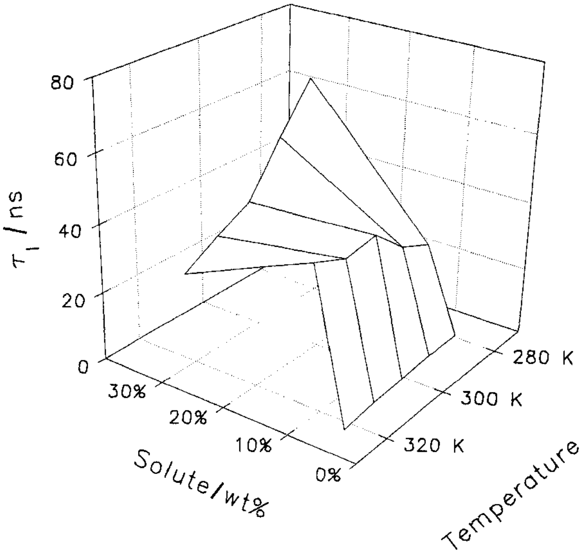


Figure 6. The temperature and solute concentration dependence of the low frequency relaxation time.

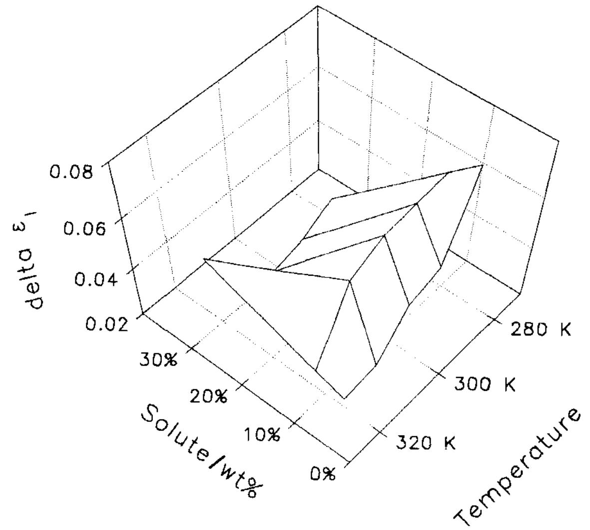


Figure 7. The temperature and solute concentration dependence of the low frequency dielectric strength.

where τ_{DR} is the polymolecular dielectric relaxation time and τ_l is the monomolecular correlation time, our results can be explained in terms of an internal rotation dimer model [3].

In figure 7 it is seen that the dielectric strength $\Delta\varepsilon_l$ decreases with increasing temperature at 5 wt.% solute concentation. As mentioned above, for prolate molecules the molecular interactions responsible for self-organization in liquid crystals will also cause the organization of solute molecules and align them into parallel order. Thus a decrease in the effective dipole moment with increased concentration can be interpreted as an anti-parallel association. The depolarizing field will promote this anti-parallel ordering. We observe the same tendency at 10 wt.% solute concentration. However, a different situation occurs at 30 wt.% solute concentration. An increase in the temperature causes an increase in the mobility of molecules and finally allows them to create a new state above 30°C. In this state the effective dipole moment increases rapidly. It seems that the rapid increase in $\Delta\varepsilon$ is caused by the formation of dimers with parallel association. This tendency has been observed for molecules with large transverse dipole moments [3]. The previously mentioned suggestion can be supported by the data presented in our earlier paper [1] which showed that the pure (100 wt.%) ferroelectric liquid crystal had a negative dielectric anisotropy. Based on the above observations, it may be assumed that the origin of the low frequency mode is due to reorientation around the molecular long axis. The rapid increase in $\Delta\varepsilon$ at 30 wt.% solute concentration can be related to a ferroelectric dynamic ordering of the transverse dipole components. This state leads to a resultant macroscopic polarization as suggested in an earlier paper [1].

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