

# Dielectric Properties of Mesomorphic *n*-TPEB's in Isotropic Phase

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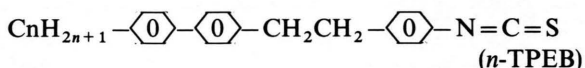
Dielectric relaxation studies have been performed for the isotropic phase of a series of mesogenic molecules of 1-[3-*n*-alkyl-biphenyl]-2-[4-isothiocyanatophenyl]ethane,  $\text{CnH}_{2n+1}-\phi-\phi-\text{CH}_2\text{CH}_2-\phi-\text{NCS}$  (*n*-TPEB), for *n*=7, 8 and 9. Two Debye-type dielectric absorption bands have been interpreted as corresponding to the rotation around the short and long molecular axis.

**Key words:** Dielectric relaxation; Molecular dynamics; Mesomorphic molecules; Relaxation time; Activation energy.

## Introduction

Dielectric relaxation studies provide essential data on molecular dynamics in liquids crystals [1–6]. Such data are very actual because of the increasing number of computer simulations of the molecular dynamics of such substances.

In this paper we present the results of dynamic electric measurements performed for a new class of mesomorphic molecules:



For  $n \geq 4$ , the compounds show the following sequence of phases: isotropic ( $\sim 130^\circ\text{C}$ ) nematic ( $\sim 100^\circ\text{C}$ ) smectic B. For  $n=4$  and 5 the smectic phase appears as the *monotropic* one.

The measurements have been performed for three members of *n*-TPEB's:  $n=7, 8$  and 9 in their *isotropic phase*.

Molecular dynamics studies in the isotropic phase of mesomorphic molecules are important for many reasons. First of all, the data can be considered as a reference for the dynamics of molecules in the presence of a nematic potential. Besides, an interpretation of the dielectric behaviour of liquid crystalline materials requires the data on the interactions and dynamics of individual molecules.

## Experimental

The dielectric relaxation measurement devices are two Hewlett-Packard impedance analyzers HP 4192 A (5 Hz to 13 MHz) and HP 4191 A (1 MHz to 1 GHz), piloted by an HP 87 computer. They allow automatic measurements of the complex permittivity,  $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ , of the sample [7, 8]. The measuring cell is a parallel plate capacitor located at the end of a coaxial line.

## Results and Discussion

Figure 1 shows the variation of the electric permittivity  $\varepsilon'$  and the dielectric loss factor  $\varepsilon''$  of *n*-TPEB's as a function of frequency of the measuring electric field at

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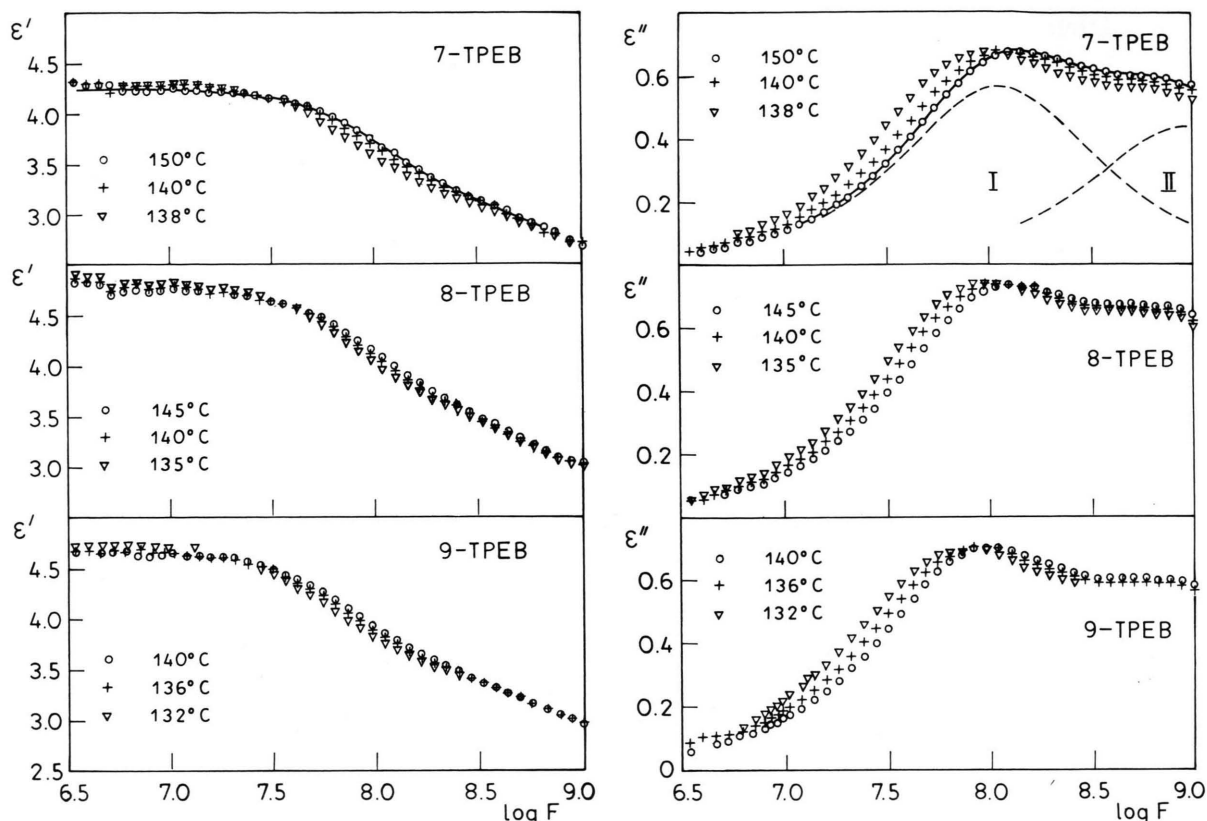


Fig. 1. Real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex permittivity of isotropic *n*-TPEB's against the frequency of the measuring electric field.

$t, ^\circ\text{C}$	7-TPEB			8-TPEB			9-TPEB		
	138°	145°	150°	135°	140°	145°	132°	136°	140°
$s_1$	1.18	1.15	1.13	1.28	1.25	1.22	1.24	1.23	1.22
$s_2$	0.858	0.870	0.877	1.01	1.02	1.03	0.954	0.948	0.960
$\tau_1$ , ns	12.6	10.1	8.83	12.9	11.3	9.73	16.4	13.9	12.2
$\tau_2$ , ns	1.28	1.14	1.06	1.27	1.19	1.11	1.37	1.25	1.16

Table 1. The amplitude ( $s_i$ ) and relaxation time ( $\tau_i$ ) of dielectric relaxation in isotropic *n*-TPEB's.

different temperatures. Figure 2 presents the results at 140 °C as the Cole-Cole diagram.

Two bands of the dielectric absorption can be distinguished for all studied TPEB's. The dotted lines in Figs. 1 and 2 denote the result of the decomposition of the measured dielectric absorption into two Debye-type bands:

$$\epsilon'(\omega) = \epsilon_\infty + \sum_{i=1}^2 s_i \frac{1}{1 + \omega^2 \tau_i^2},$$

$$\epsilon''(\omega) = \sum_{i=1}^2 s_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}, \quad (1)$$

where  $s_i$  and  $\tau_i$  denote, respectively, the amplitude and the dielectric relaxation time for the corresponding Debye-type absorption band (I or II). The amplitude  $s_i$  is the difference between the static and high frequency values of the permittivity,  $\epsilon'_{0i} - \epsilon'_{\infty i}$ , related to a given relaxation process. The relaxation time,  $\tau_i$ , is related to the critical frequency  $f_{ci}$ , i.e. to the frequency which corresponds to a maximum of the dielectric loss:  $2\pi f_{ci} \tau_i = 1$ .

Solid lines in Figs. 1 and 2 are the best fittings of the theoretical dependences described by (1) to the experimental data. The values of the parameters  $s_i$  and  $\tau_i$  resulting from the fitting are given in Table 1.

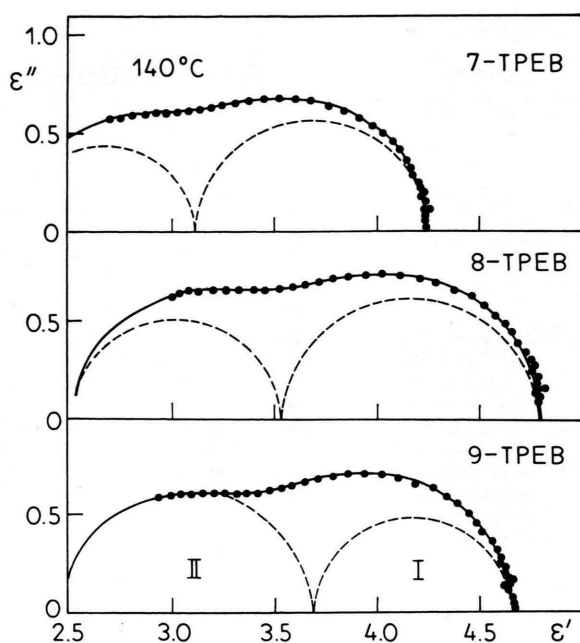
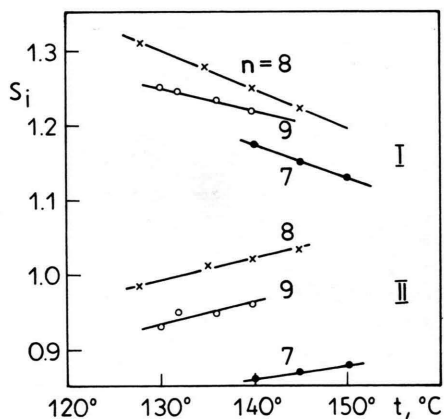
Fig. 2. The Cole-Cole diagrams for *n*-TPEB's at 140 °C.

Fig. 3. The amplitude of the two absorption bands vs. temperature.

Figure 3 shows the temperature dependence of the amplitude  $s_i$  of the two bands of absorption. The dependencies are quite different in character: the amplitude of the band I (lower frequency band) increases with decreasing temperature while the amplitude of the band II (higher frequency band) decreases with decreasing temperature.

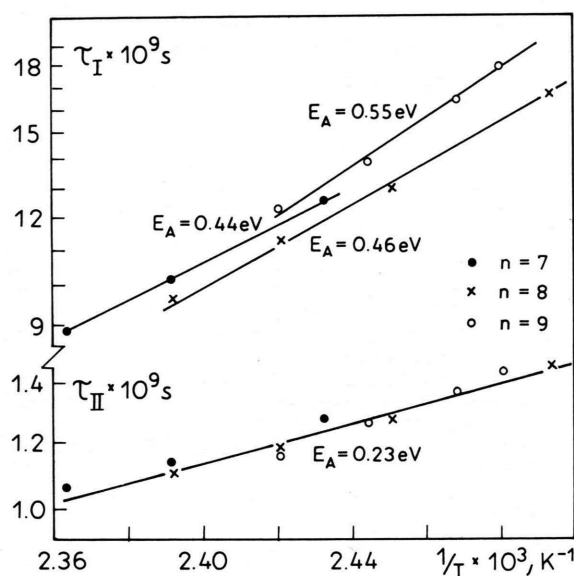
Fig. 4. Arrhenius plots of dielectric relaxation times in isotropic *n*-TPEB's.

Figure 4 presents the temperature dependence of the values of the dielectric relaxation times in form of Arrhenius plots, i.e.  $\log \tau_i$  versus the reciprocal of absolute temperature. The values of the activation energy,  $E_A$ , calculated from the slopes of these dependencies, are presented in the figure.

The quite different dependence of  $\tau_1$  and  $\tau_2$  on the molecular length and the important difference in the values of the activation energy can be the base for an interpretation of the two bands of dielectric absorption in the isotropic phase of *n*-TPEB's. It seems to be reasonable that these bands correspond to the different molecular rotations: around the short and long molecular axis [9]. The band II corresponds to the rotation around the long axis: both  $\tau_2$  and  $E_A$  within our experimental errors do not depend on the length of the TPEB molecules. This can be expected for this kind of the rotation.

This absorption band can also be considered as corresponding to the intramolecular rotation of the  $\phi$ -NCS group. However, our calculations made by a quantum mechanical semi-empirical method [10] show that this internal rotation involves only a small change in the dipole moment and can not be detected in the dielectric absorption.

For the rotation around the short molecular axis (band I), both the values of the relaxation time  $\tau_1$  and the activation energy  $E_A$  depend on the molecular length. The value of the activation energy is here about twice that obtained for rotation around long molecular axis.

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