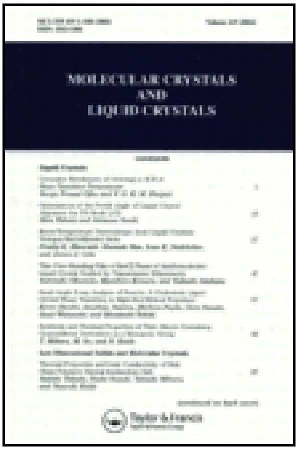

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Comparison of the Dielectric Relaxation Data for the Isotropic and Nematic Phases of Three Homologous Series: nCb, nOCB and nPCH, (n =5÷8)

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Comparison of the Dielectric Relaxation Data for the Isotropic and Nematic Phases of Three Homologous Series: *n*Cb, *n*OCB and *n*PCH, (*n* =5÷8)

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Results of dielectric studies of three homologous series: *n*-alkyl-cyanobiphenyls - *n*CB, *n*-alkyloxy-cyanobiphenyls – *n*OCB, and *trans*-4-(4'-*n*-alkyl-cyclohexyl)-cyanobenzene – *n*PCH, with *n* from 5 to 8, are presented. The parameters characterizing the rotational motions of the molecules around their short axes in the nematic and isotropic phases were derived (dielectric increments, relaxation times, activation enthalpies, retardation factors, nematic potentials, order parameters). Comparative analyses of the parameters in respect to the lengths of the terminal groups and the structures of the molecular cores are given.

Keywords: dielectric properties; nematics; *n*CBs; *n*OCBs; *n*PCHs

INTRODUCTION

Dielectric relaxation method is a powerful tool for studying the rotation motions of polar molecules in condensed phases. This is due to the straightforward relationships between the measured quantity, the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon' - i\,\varepsilon''$, and the parameters characterizing the molecular behavior (dipole moment μ, relaxation time τ, activation enthalpy ΔH). In case of liquid crystalline (LC) substances having usually a complex chemical structure of molecules the polar groups can be placed in different parts of molecules and generally the dielectric spectra might be relatively complex and thus difficult to a unique interpretation. Therefore the substances having a strong dipole moment directed along the symmetry axis of a molecule are especially useful for testing some theoretical models of a mesophase. Their dielectric spectra consist of one dominant band in each phase (including the isotropic phase) which is connected with molecular rotations around the short axes.

Two-rings cyano compounds (with the benzene and/or cyclo-hexyl rings) belong to the best known liquid crystalline substances. They were studied by various experimental methods, including the dielectric spectroscopy [1-13], and many of their properties were well established. However, we did not find in the literature a comparative analysis of the parameters derived from the dielectric relaxation measurements performed for several homologous series. We shall present the results of our dielectric studies of LC substances belonging to three series: alkyl-cyano-biphenyls - *n*CB, alkyloxy-cyanobiphenyls - *n*OCB, and *trans*-4-(4'-alkyl-cyclohexyl)-cyano-benzenes - *n*PCH, with *n* ranging from 5 to 8. Part of the results are taken from recently published papers [6-15] where they were not analysed in that respect, however. Additionally, new measurements with the aid of a time domain spectroscopy (TDS) method [14] were performed for the isotropic phase of several substances. This gives us a possibility to analyse the changes of the rotational dynamics of molecules at the nematic - isotropic phase transition T_{NI}. The influences of the length of the terminal groups and the structure of the molecular cores can be discussed. We shall consider for that purpose the following quantities: the dielectric increment $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, the angle β between the net dipole moment and the symmetry axis of molecules, the relaxation times τ_{is} and $\tau_{\|}$, the retardation factor $g_{\|}$, the nematic potential q, the order parameter S, and the activation enthalpies ΔH_{is} and $\Delta H_{\|}$.

EXPERIMENTAL

All substances studied were obtained from R. Dąbrowski, Military Technical University, Warsaw. Their transition temperatures T_{NI} are shown in Table 1.

The measurements of the dielectric permittivity, $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$, in the nematic phase were performed with the aid of a HP 4192A impedance analyser (1 kHz - 13 MHz) for the samples oriented by a DC electric field of ca. 300 V/cm (nPCH) or a magnetic field of 0.7 T (other substances). The TDS set-up in the Uppsala University was used for measurements $\varepsilon^*(\omega)$ in the isotropic phase. Two time windows were applied, 10 ns and 50 ns, which allow to cover the frequency range 10 MHz - 5 GHz [9-14]. New measurements have been done for 6CB, 7CB, 8CB, 5PCH and 6PCH.

RESULTS AND DISCUSSION

As an example, Fig. 1 presents the TDS spectra for the isotropic phase of nPCH series. The spectra for other substances look similarly [7,11-14]. They show deviations from the symmetrical Cole-Cole plots at high frequencies. This was interpreted as the result of the presence of two main molecular processes: the low frequency (l.f.) process is connected with the molecular rotations around the short axes, and the high frequency (h.f.) process corresponding to the rotations around the long axes. In the nematic phase the l.f. relaxation process was studied only (parallel orientation **E** || **n**). For each substance the dielectric spectra $\varepsilon_{||}^*(\omega)$ can well be described by the Debye theory (corresponding Cole-Cole plots are semicircles).

Taking separately the increments $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ (Figs. 1 and 2a) in both observed relaxation processes in the isotropic phase of particular compounds and the Onsager equation,

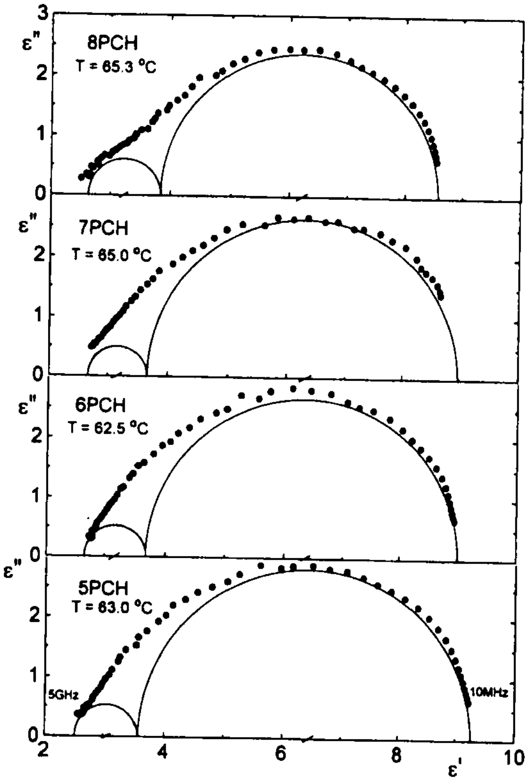

FIGURE 1 Cole-Cole plots from the TDS spectra measured for the isotropic phase of *n*PCH compounds.

$$\mu^2 = \frac{9k_B T\varepsilon_0(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{N\varepsilon_s(\varepsilon_\infty + 2)^2},$$

the angle β between the net dipole moment and the symmetry axes of the molecules could be calculated (tgβ = μ_t/μ_l) [8-10] (Fig. 2b). In Fig. 3 the low frequency relaxation times obtained for the isotropic and nematic phases of *n*PCH substances are presented in the form of Arrhenius plots. All information about the values of parameters characterizing the l.f. relaxation process are quoted in Table 1.

TABLE 1: Parameters of the Arrhenius equation $\tau = \tau_0 \exp(\Delta H/RT)$ for the l. f. relaxation processes in the isotropic and nematic phases of three homologous series (the error in ΔH: ± 2 kJ mol^{-1} in both phases).

Compound	T_{NI} / K	Isotropic phase		Nematic phase	
		$\tau_{0l}\cdot 10^{15}$/s	ΔH_l/kJ mol^{-1}	$\tau_{0\parallel}\cdot 10^{20}$/s	$\Delta H_\parallel$/kJ mol^{-1}
5CB	308.2	13.14	33.2	11.20	66.3
6CB	301.2	3.12	37.1	1.84	70.1
7CB	314.7	8.87	34.5	24.4	65.4
8CB	313.2	3.48	37.4	7.71	68.6
5PCH	328.2	14.70	32.7	3.77	71.7
6PCH	318.2	25.00	31.4	5.80	69.9
7PCH	329.6	5.37	36.1	4.09	72.5
8PCH	327.2	20.70	32.6	2.25	74.0
5OCB	341.2	1.34	42.4	190	63.9
6OCB	348.7	1.82	41.5	22.8	69.9
7OCB	347.2	0.95	43.8	53.7	67.2
8OCB	353.2	0.081	51.4	7.5	74.5

From the obtained data the following quantities could be calculated: the dielectric increments $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ (Fig. 2a); the relaxation times τ_l and $\tau_\parallel$ (Fig. 4 b, c), the activation enthalpies ΔH_l and $\Delta H_\parallel$ (Table 1), the retardation factor $g_\parallel = \tau_\parallel/\tau_l$ at T_{NI} (Fig. 5a) and then the nematic potential q (Fig. 5b) and the order parameter S according to the Kalmykov & Coffey theory ([16a] eq.57) (Fig. 5c).

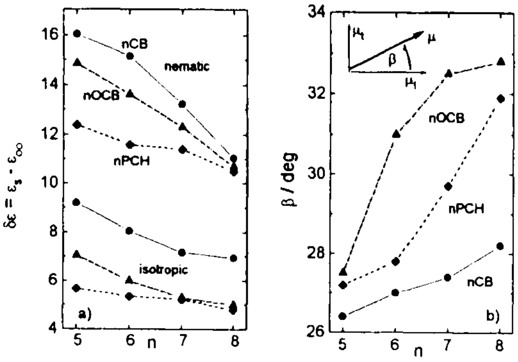

FIGURE 2 Dielectric increments at $T = T_{NI} \pm 10$ K (a) and the inclination angles β, (b) versus *n* for three homologous series studied (l.f. relaxation process).

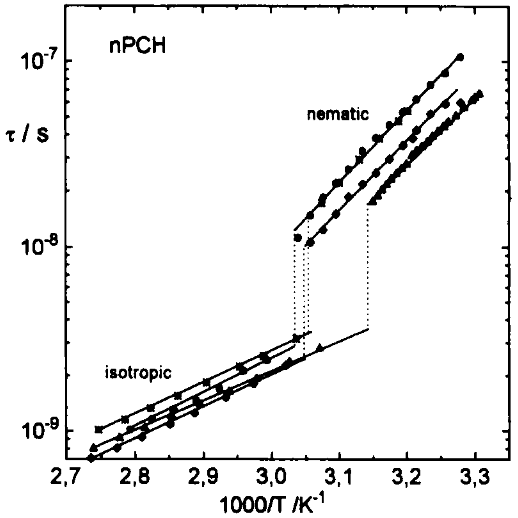

FIGURE 3 Arrhenius plots for the l. f. relaxation process in the isotropic and nematic phases of *n*PCH compounds (◆ 5PCH, ▲ 6PCH, ● 7PCH, ✱ 8PCH).

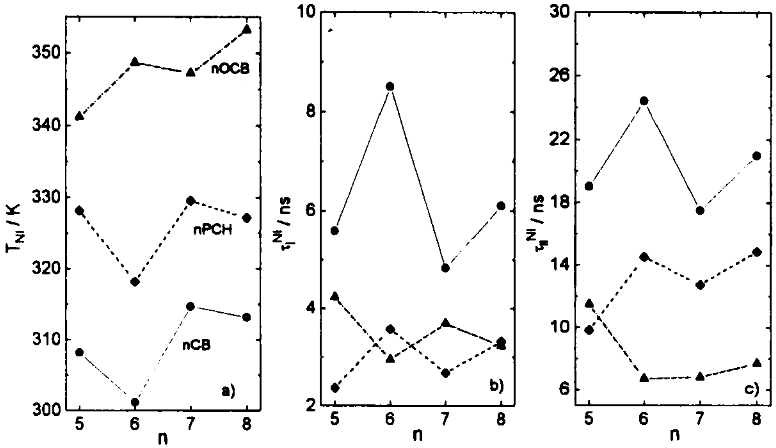

FIGURE 4 Dependencies on *n* of the clearing temperatures T_{NI} (a), the relaxation times $\tau_{\perp}$ at T_{NI} (b), and $\tau_{\parallel}$ at T_{NI} (c) for three homologous series.

The dielectric increments for the l.f. relaxation process $\delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ decrease with increasing *n* in both the nematic and isotropic phases (Fig. 2); this effect can be attributed to a 'solvation' of the dipole moment in the longer alkyl chains and was observed for other homologous series as well [17]. Largest dielectric increments (Fig. 2a) and lowest β - angles (Fig. 2b) indicate that the nCB molecules have most stretched shape and largest longitudinal component of the dipole moments. The influence of the intermolecular motions on the dipole moment of 5CB is discussed in [18]. In case of the *n*OCB series the angle β is enlarged by the dipole moment of the alkoxy group as well. Such inclination of the dipole moments should also be taken into account in discussions of the Fröhlich-Kirkwood dipole correlation factor ($g = \mu_{eff}/\mu_l$, rather than $g = \mu_{eff}/\mu$).

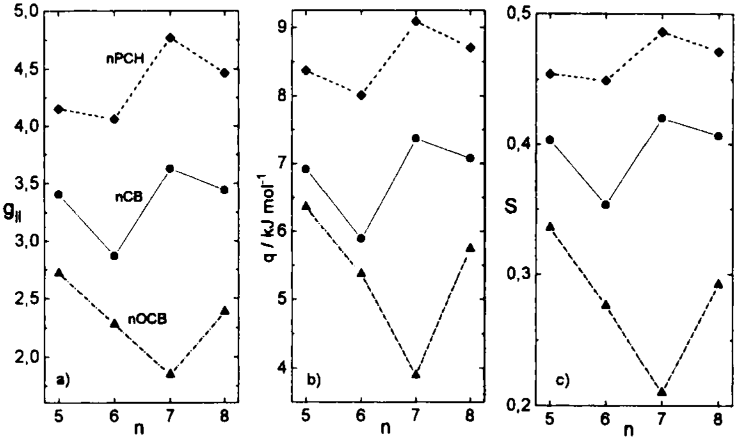

FIGURE 5 Dependencies on *n* of the retardation factor $g_{\parallel}$ (a), the nematic potential q (b), and the order parameter S (all taken at T_{NI}).

Typical odd-even effect (Fig. 4a) is observed for many quantities determined; in the case of the *n*OCB series the O-atom in the alkoxy chains plays the same role as C-atoms in the alkyl chains. It is characteristic that the nPCH molecules having semi-flexible core exhibit largest change at T_{NI} of the parameters characterising the molecular rotations around the short axes (retardation factor, nematic potential and the order parameter, see Fig. 5).

Acknowledgments

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