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Prenematic Self-Assembling of Mesogenic Molecules in Isotropic Liquid and Orientational Order in Nematic Phase

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Dielectric relaxation study of nematogenic 4-n-alkyl-4′-cyanobiphenyls (nCB, n = 5, 6), 4-(trans-4′-n-alkylcyclohexyl)isothiocyanatobenzenes (nCHBT, n = 6, 8), 4-cyanophenyl-4′-n-alkylbenzoates (nCPB, n = 6, 8), 4-cyano-3-fluorophenyl-4′-n-octyloxybenzoate (8OCFPB), and 4-cyanophenyl-4′-n-octyloxy-3′-fluorobenzoate (8OCPFB) was performed in the frequency range from 50 kHz to 100 MHz in the nematic and isotropic phases. The static permittivity and the relaxation process related to the rotation of molecules around their short axis was analyzed. For some of these liquid crystals anomalous temperature dependence of static permittivity in the pretransitional region of the isotropic phase was observed. Based on the Meier–Saupe–Martin model of molecular diffusion in nematics, the orientational order parameter $\langle P_2\rangle$ was determined from dielectric relaxation times and retardation factor. The values of $\langle P_2\rangle$ calculated from the dielectric relaxation data were compared with the results obtained from measurements of polarized electronic absorption. Correlations between the magnitude of the dielectric pretransitional effect and the orientational order in the nematic phase were discussed.

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1. Introduction

Liquid-crystalline materials synthesized for electro-optical applications should be characterized by an appropriate temperature mesophase range, viscosity, and also sufficiently large optical and dielectric anisotropies. The anisotropy of these properties in nematic liquid crystals is a result of long-range orientational order in the mesophase [1]. According to the theories of nematics, the orientational order can be described by a set of expansion coefficients of the distribution function in the Legendre polynomials [2]. It was shown on the ground of the statistical theory that the second coefficient ($\langle P_2\rangle$ order parameter) can be determined experimentally from linear dichroism, optical birefringence or dielectric anisotropy, for example. The $\langle P_2\rangle$ order parameter in the nematic phase is a positive function of temperature, independent of the individuality of molecules creating the mesophase, and vanishing in the isotropic phase. At the phase transition temperature a discontinuity of $\langle P_2\rangle$ is predicted. Unlike the theory predicts, the experiments show that the temperature dependence of $\langle P_2\rangle$ is a characteristic feature of the mesogenic substance.

For many physical effects such as light scattering, nonlinear dielectric effect, Cotton–Mouton, and Kerr effects, for some nematic liquid crystals anomalies can be observed in the isotropic phase near the phase transition. The anomalies are associated with fluctuations of molecular order in this region [1, 3]. The fluctuations occurring just above the nematic-isotropic (N–I) phase transition are usually characterized by a correlation length of several tenth of nanometers. It was also found that for some nematics, when approaching the phase transition from isotropic to nematic phase, the static dielectric permittivity does not satisfy the predictions of the Onsager theory [4, 5]. Bradshaw and Raynes assumed that above the nematic-isotropic (N–I) phase transition there are some domains with nematic-like order (prenematic domains) [5]. Some authors suggested that the magnitude of the pretransitional dielectric permittivity anomaly is correlated with the N–I phase transition type (typical first-order or weakly first-order) [6, 7]. However, the results of calorimetric investigations of the transition enthalpy did not confirm this assumption [8]. Moreover, some experimental results indicate that magnitude of the pretransitional anomaly depends on the value of the longitudinal and transverse components of permanent electric dipole moment of liquid crystal molecules [9–11]. Explicitly, the pretransitional anomaly is larger

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for molecules whose dipole moment has only the component parallel to the main axis of the molecules than for molecules having, in addition, the perpendicular component.

The article presents the results of dielectric relaxation study of some commonly known nematics and two fluoro-substituted nematogens. An attempt to find the correlations between the magnitude of the dielectric pretransitional effect and the orientational order in the nematic phase is done. The order parameter obtained from dielectric spectroscopy is compared to that obtained by the optical absorption method (dye probe method).

2. Experimental

The nematogenic compounds: 4-*n*-alkyl-4′-cyanobiphenyls (*n*CB, $n = 5, 6$), 4-(trans-4′-*n*-alkyl-cyclohexyl)isothiocyanatobenzenes (*n*CHBT, $n = 6, 8$), 4-cyanophenyl-4′-*n*-alkylbenzoates (*n*CPB, $n = 6, 8$), 4-cyano-3-fluorophenyl-4′-*n*-octyloxybenzoate (8OCFPB), and 4-cyanophenyl-4′-*n*-octyloxy-3′-fluorobenzoate (8OCPFB) were synthesized and chromatographically purified at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. Purity of the obtained compounds was greater than 99.5%. The chemical structures of the compounds are given in Fig. 1.

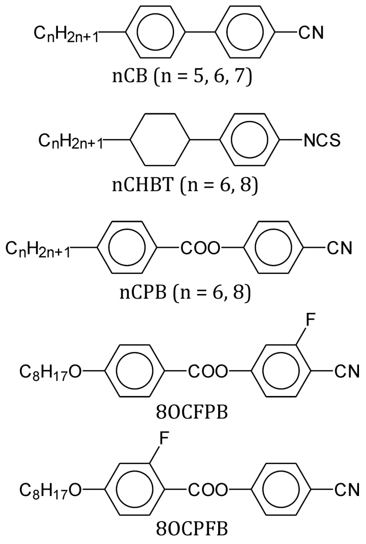

Fig. 1. Chemical structures of the liquid crystals investigated.

The complex dielectric permittivity of the compounds was measured with HP 4194 A impedance/gain phase analyzer in the frequency range from 50 kHz to 100 MHz. The permittivity spectra were registered as a function of temperature in both the nematic and isotropic phases. Measuring capacitor consisted of three plain electrodes, one central and two grounded outside. The distance between the electrodes was approximately 0.5 mm. The probing electric field intensity was equal to 1 V/mm. In the nematic phase a dc biasing electric field of intensity equal to 5 V/mm was applied to the capacitor to obtain homogeneous orientation of the molecules. In this way, it was possible to measure the complex permittivity component parallel to the director $\boldsymbol{n}$ ($\boldsymbol{n} \| \boldsymbol{E}$). The temperature of the sample was adjusted in steps of 0.01 K and stabilized with the same accuracy by using Scientific Instruments 9700 temperature controller. Under these experimental conditions the relative accuracy of the permittivity determination was better than 0.5%.

3. Results and discussion

3.1. Phase transition temperatures

According to the Maier–Saupe theory [2] and the classical Ehrenfest scheme [12], the N–I phase transition is the first-order one. The first-order phase transition is characterized by the finite discontinuity in the mass density and the thermodynamic potentials. In a particular case of nematic liquid crystals, at the transition temperature T_{NI}, one can predict also the discontinuity in the order parameter $\langle P_2 \rangle$. However, the N–I phase transition occurring at a single temperature point is not observed in the experiments. There are, at least, three reasons for such a situation: the chemical impurities in the liquid crystal material, the fluctuations of the thermodynamic parameters (temperature, pressure) in the sample volume, and, finally, some purely physical effects such as the presence of prenematic domains in the isotropic phase. In our current study we used highly purified compounds and ensured a high accuracy of temperature stabilization in the sample volume, and also high measurement precision of the dielectric parameters. Therefore, the first two factors, in our opinion, do not substantially affect the measurement results. Thus, the reasons for the observed weakly first-order nature of the N–I transition must be traced at the level of molecular interactions.

Figure 2 shows the temperature dependence of the logarithm of dielectric relaxation time associated with rotation around the short molecular axis for 6CB (see Sect. 3.2), as an example. Based on the course of the $\ln\tau$ vs. T function it can be concluded that the N–I phase transition for 6CB is not the first-order in the strict sense, but it can be classified as weakly first-order. Such a classification of the phase transition was confirmed by the calorimetric experiments, yielding non-zero values of the transition enthalpy [8].

Since the $\ln\tau$ vs. T curve has clearly marked places of high curvature, it is possible to use this relationship to determine the phase transition interval ΔT_{NI}. The phase transition temperature T_{NI} can then be defined as the lower limit of this interval. The clearing temperature T_{c}, describing the low limit of the isotropic phase, then corresponds to the upper limit of this interval. The dielectric pretransitional effect, which is under consideration, is expected above T_{c} temperature.

For the investigated nematics the T_{NI} and T_{c} temperatures, and also the ΔT_{NI} intervals determined from the

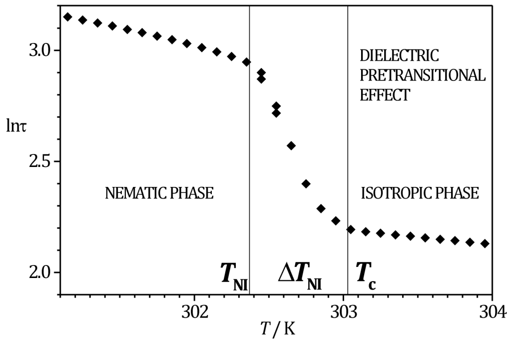

Fig. 2. Logarithm of the dielectric relaxation time related to the rotation around the short molecular axis for 6CB in the vicinity of the N–I phase transition.

$\ln\tau$ vs. T relation, are presented in Table I. The melting temperatures T_m were found earlier by using polarizing microscopy [13, 14]. It should be mentioned here that the considered liquid crystals can be supercooled, so, the nematic phase range available for the experiments can be extended. For the nematogens under consideration the N–I phase transition intervals are found in the range between 0.5 K and 1.2 K. As stated earlier, such large values cannot be explained by the presence of the impurities or by the experimental conditions, and causes must be sought at the molecular level. It is worth mentioning at this point that some non-linear effects, such as the Kerr effect, are also associated with the occurrence in the N–I phase region of a certain interval between the N–I phase transition temperature and the second-order pretransitional temperature [15]. In addition, the size of these intervals are of the same order as our current case, but the correlation in size are not observed.

TABLE I

Melting temperature (T_m) from polarizing microscopy, N–I phase transition temperature (T_{NI}), clearing temperature (T_c), and N–I phase transition interval (ΔT_{NI}) determined from the dielectric relaxation time.

LC	T_m [K]	T_{NI} [K]	T_c [K]	ΔT_{NI} [K]
5CB	297.7[a]	307.85	308.35	0.50
6CB	287.7[a]	302.35	303.05	0.70
6CHBT	285.7[a]	315.75	316.75	1.00
8CHBT	301.2[a]	319.55	320.75	1.20
6CPB	–	320.95	321.55	0.60
8CPB	319.2	325.95	326.95	1.00
8OCFPB	325.7	327.75	328.65	0.90
8OCPFB	329.6	335.55	336.35	0.80

[a] From [13].

In view of the fact that the phase transition is not localized in one temperature point, it can be supposed that the N–I phase transition, by nature, is not exactly the first-order one. Keeping in mind that calorimetric investigations give the evidence for the nonzero values of latent heat one should assume the occurrence of weakly first-order phase transition for the nematogens investigated here [8, 16].

3.2. Dielectric relaxation

In Fig. 3 the spectra of real ε' (dispersion curve) and imaginary ε'' (dielectric loss curve) parts of the dielectric permittivity for the investigated liquid crystals in the nematic (parallel component) and isotropic phases are presented. The spectra for individual mesogenes are chosen at the reduced temperature, $T_{red} = T/T_{NI}$, equal to 0.963 (nematic phase) and 1.050 (isotropic phase). Opportunity to observe the dielectric relaxation in the frequency range available in the measurement is possible due to the presence of polar groups (–CN, –NCS, –COO, –F) in the molecular structure of the nematogens. The permanent electric dipole moment associated with the polar groups can be decomposed into two components: parallel and perpendicular to the long molecular axis. The relaxation process observed in the spectra of the liquid crystals studied is related to the parallel component of the electric dipole moment and the rotation of the molecules around their short axis. Maximum of the second relaxation process associated with the perpendicular component of the dipole moment and the rotation of molecules around their long axis is not observed in the discussed frequency range. However, this process must be taken into account when the dielectric spectra are decomposed into bands corresponding to the individual processes. Therefore, in fitting procedure two Cole–Cole functions are used, each with the individual dielectric strength, relaxation time τ, and exponent α describing the deviation of the dielectric loss curve with respect to the Debye function [17]. The Cole–Cole function selection resulted from the fact that this function has successfully been used previously, and currently studied spectra of liquid crystals also have obtained a good fit with the use of such function [18].

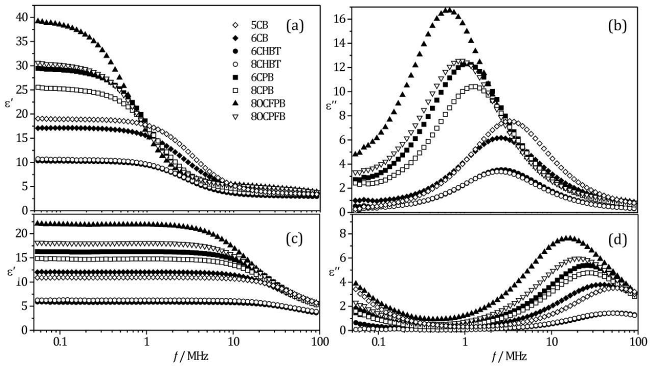

Fig. 3. Dielectric relaxation spectra of nCBs (n = 5, 6), nCHBTs ($n = 6$, 8), nCPBs ($n = 6$, 8), 8OCFPB, and 8OCPFB, in the nematic phase at $T_{red} = 0.963$ [(a) ε', (b) ε''] and in the isotropic phase at $T_{red} = 1.050$ [(c) ε', (d) ε''].

In our consideration only the process associated with the rotation of molecules around their short axis is taken into account. For the considered liquid crystals, the frequency corresponding to the maximum of the dielectric loss for this process is less than 100 MHz. This frequency is markedly greater for nCBs and nCHBTs than for the other liquid crystals. For the investigated mesogenes the second process, related to the perpendicular component of the dipole moment, is hardly seen or practically unobserved in the parallel component of ε'' in this frequency range [19]. This is a direct consequence of the fact that this process has a maximum above 100 MHz [20].

Values of electric dipole moments, taken from the literature, and static dielectric constants for the studied liquid crystals in the nematic and isotropic phases are collected in Table II. Because of axial symmetry of the rigid part of the cyanobiphenyls, one can assume that the electric dipole moment is directed along the long axis of the molecule. That is not the case with the other studied liquid crystals. For example, the components of the electric dipole moment for 8OCFPB in the ground state are equal to 6.45 D (μ_l) and 1.3 D (μ_t), in accordance with the vector addition model [21–23]. As a result, the angle between the vector of the dipole moment and the long axis of this molecule is about 12°.

TABLE II

Electric dipole moment (μ) and static permittivity in nematic ($\varepsilon_{\mathrm{s}\|}$, $T_{\mathrm{red}} = 0.963$) and isotropic ($\varepsilon_{\mathrm{s\,I}}$, $T_{\mathrm{red}} = 1.050$) phases.

LC	μ [D]	$\varepsilon_{\mathrm{s}\|}$	$\varepsilon_{\mathrm{s\,I}}$
5CB	5^a	19.0	10.9
6CB	5^a	17.1	12.0
6CHBT	2.5^a	10.3	5.9
8CHBT	2.5^a	10.7	6.2
6CPB	6.5^b	29.4	16.3
8CPB	6.5^b	25.6	14.9
8OCFPB	6.6^c	39.2	22.1
8OCPFB	6.6^c	30.6	18.1

[a] From [8]. [b] From [7]. [c] From [21].

A cursory overview of the data allows one to find out the sequence correlation between the values of the dipole moments and the static permittivity, both in the nematic and isotropic phases. In substance, when knowing the optical refractive indices for the investigated liquid crystals, and thus ε_∞, it is possible to calculate the Kirkwood correlation factor g (e.g. from the Kirkwood–Froehlich equation) [4].

3.3. Dielectric pretransitional effect

According to the Onsager theory, the static permittivity ε_{s} should increase proportionally to the inverse temperature ($\varepsilon_{\mathrm{s}} \sim \mu^2/kT$) [4]. This means that when the temperature is decreased in the isotropic phase, approaching the N–I phase transition, the static permittivity should increase, presenting linear dependence on the reciprocal temperature. In fact, such the temperature dependence is not common for liquid crystals. Apart from this linear behaviour, two types of pretransitional anomaly can be observed: a decrease in permittivity after passing its maximum value and the slowing down the increase of ε_{s} with decreasing temperature.

In Fig. 4 the dielectric pretransitional effect is presented for the representatives of the investigated compounds. For convenience, the values of the dielectric constant ε_{c} at the clearing temperature, T_{c}, taken for the probing electric field of a frequency equal to 200 kHz, are subtracted from the static values of permittivity in the isotropic phase. As it is seen, two types of the temperature dependence of permittivity (the bent curves without and with the evident maximum) are found for the investigated liquid crystals. The anomalous behaviour of static permittivity near the N–I phase transition in the isotropic phase was explained earlier as caused by the decrease of an effective dipole moment, resulting from the increase of the share of antiparallel associations between the molecules and the creation of the prenematic domains [5]. The pretransitional anomalies in ε_{s} are possible only for compounds with permanent dipole moment but some other conditions enabling the molecular associations could be discussed simultaneously. As it was suggested earlier [7], the magnitude of the pretransitional effect in ε_{s} can be characterized by the difference between the temperature corresponding to the permittivity maximum and the clearing temperature, $\delta T = T_{\max} - T_{\mathrm{c}}$. This definition is somewhat confusing in the case when a curvature but no maximum is observed in ε_{s}. In such a case, one can give only a qualitative description of the pretransitional effect. The δT values for all the investigated compounds are given in Table III (see Sect. 3.4). Based on the presented results, one can find that the magnitude of the pretransitional effect is the largest for the representatives of nCB homologous series, which do not have the perpendicular component of the electric dipole moment. The dielectric pretransitional effect is practically not observed for 6CHBT and 8CHBT with a relatively small electric dipole moment. This may indicate that for the latter liquid crystals the prenematic domain size is probably much smaller than for the other compounds. Intermediate pretransitional anomalies are found for the fluoro-substituted compounds and nCPB liquid crystals with relatively high value of the dipole moment, μ, and a nonzero value of the perpendicular component, μ_t.

As it was said in above, the anomalous dielectric behaviour of the investigated liquid crystals can be explained by the increase of the number of molecules participating in antiparallel associations. When the antiparallel associations predominate then the Kirkwood correlation factor g is smaller than 1. For the lack or the balanced antiparallel and parallel associations $g = 1$. Usually, for a given nematogen, the g factor is almost con-

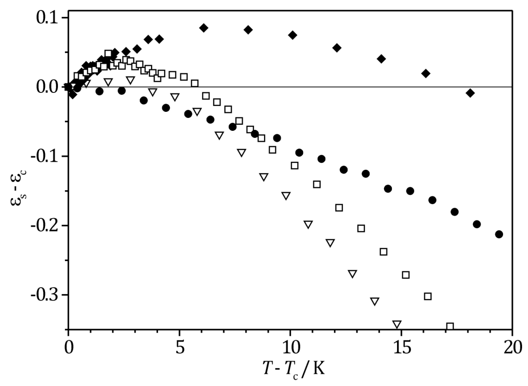

Fig. 4. Static permittivity ($\varepsilon_s - \varepsilon_c$) of 6CB, 6CHBT, 8CPB, and 8OCPFB in the isotropic phase (data points as described in Fig. 3).

stant within the isotropic phase beyond the vicinity of the phase transition. Constant values of g are also expected in the temperature range of the nematic phase. When approaching the phase transition in the isotropic phase, if $g < 1$, one can observe the decrease of the g factor as a result of the antiparallel associations increase [24]. The prenematic fluctuations in the isotropic phase near the phase transition seem to be correlated with the changes in molecular associations, as it was found earlier [5]. According to this supposition, it is possible to conclude that the greatest increase of the antiparallel associations is found for nCBs, in agreement with previous results [8]. For nCHBTs $g = 1$ [24] which indicates the lack of molecular associations, and, as a consequence, the dielectric pretransitional effect is not observed in this case.

TABLE III

Dielectric pretransitional effect characteristics δT and orientational order parameter $\langle P_2 \rangle$ determined from retardation factor G and from optical absorption of DANS probe.

LC	δT [K]	$\langle P_2 \rangle$ at $T_{\text{red}} = 0.963$		$\langle P_2 \rangle$ at $T_{\text{red}} = 0.991$	
		from G factor	from opt. abs.	from G factor	from opt. abs.
5CB	5	0.46	–	0.36	0.40[a]
6CB	8	0.42	–	0.33	0.37[a]
6CHBT	0	0.55	0.59[a]	0.45	0.46[a]
8CHBT	0	0.54	0.57[a]	0.44	0.44[a]
6CPB	1	0.52	0.56[a]	0.42	0.44[a]
8CPB	3	0.51	0.56[a]	0.42	0.45[a]
8OCFPB	1	0.40	0.51[b]	0.30	0.41[b]
8OCPFB	2	0.40	0.56[b]	0.30	0.47[b]

[a] From [13]. [b] From [14].

3.4. Order parameter

In Fig. 5, $\ln \tau$ as a function of T^{-1} is presented for the investigated liquid crystals. This relation is strongly nonlinear at the phase transition and presents almost linear dependence outside the phase transition region. In fact, as it was shown experimentally, this relationship is non-linear well outside the transition [25]. In our case we have assumed that outside the phase transition, at the temperature at which the measurements were performed, both in the nematic and isotropic phases, this dependence can be treated as linear.

According to the Meier–Saupe–Martin model [26], the observed shift between hypothetical isotropic-like temperature dependence of τ and the values of the dielectric relaxation time in the nematic phase is related to the additional hindering of the molecules in the mesophase by the nematic potential. The nematic potential, unequivocally defined by the potential barrier q, is closely related to the orientational order parameter $\langle P_2 \rangle$ of a liquid crystal. The $\langle P_2 \rangle$ order parameter is temperature dependent and defined as:

$$\langle P_2 \rangle = \int_0^{\pi} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) f(\theta) \sin \theta \, \mathrm{d}\theta \,, \tag{1}$$

where $f(\theta)$ is the distribution function and θ is the angle between the long axis of a molecule and the direction of the macroscopic orientation of liquid crystal.

Meier and Saupe [27] introduced the retardation factor G defined as a ratio of the relaxation time $\tau_{\parallel}$ in the presence of nematic potential and the hypothetical relaxation time τ_0 for $q = 0$,

$$G = \frac{\tau_{\parallel}}{\tau_0} \,. \tag{2}$$

As it was shown by Coffey et al. [28], the retardation factor G is related to the nematic potential barrier q by the following equation:

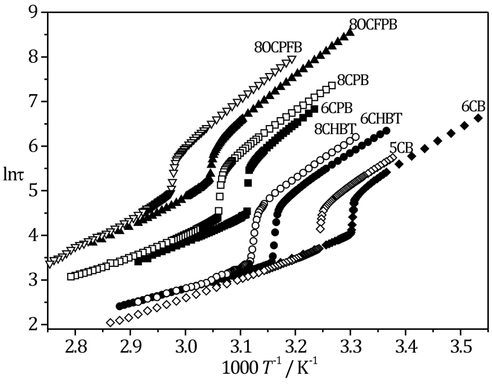

Fig. 5. Plots of $\ln\tau$ as a function of T^{-1} for the dielectric relaxation processes related to the rotation of the molecules around their short axes.

$$G = \frac{e^{\sigma} - 1}{\sigma}\left(\frac{2}{1 + 1/\sigma}\sqrt{\frac{\sigma}{\pi}} + 2^{-\sigma}\right)^{-1}, \tag{3}$$

where $\sigma = q/k_{\mathrm{B}}T$.

The retardation factor G as a function of reduced temperature for the investigated liquid crystals is presented in Fig. 6 whereas the calculated $\langle P_2\rangle$ orientational order parameter in the nematic phase is shown in Fig. 7. The order parameters for the investigated liquid crystals at T_{red} equal to 0.963 and 0.991, obtained from the retardation factor G, are also collected in Table III. Because the G factor is related to the nematic potential barrier q, the temperature dependence of the order parameter is unequivocally determined by the $G(T)$ function. The smallest values of $\langle P_2\rangle$, equal to 0.40 at $T_{\mathrm{red}} = 0.963$, are found for the fluoro-substituted compounds whereas the greatest, $\langle P_2\rangle = 0.55$, at the same reduced temperature, are characteristic of the nCHBT series. This indicates that the degree of orientational order in the mesophase determined from G is not correlated with the δT values for these compounds (the lowest values of δT in both cases). Moreover, it is also very characteristic for the nCB series with the largest δT values that the $\langle P_2\rangle$ parameters are not significantly greater (especially in the case of 6CB) than the order parameters of 8OCFPB and 8OCPFB. Comparing the nCPB series to the fluoro-substituted compounds, one can find that the values of the order parameter differ from each other significantly in the nematic phase, despite of the similarities in the molecular structure. The difference in $\langle P_2\rangle$ for 8CPB and 8OCPFB at $T_{\mathrm{red}} = 0.963$ is equal to 0.11 and is the consequence of substitution of one hydrogen atom by fluorine. The relatively small values of $\langle P_2\rangle$ for 8OCFPB and 8OCPFB nematogens, obtained from the dielectric relaxation, can be a result of short-range interactions related to the additional, perpendicular to the main molecular axis, component of electric dipole moment associated with the fluorinated part of the molecules.

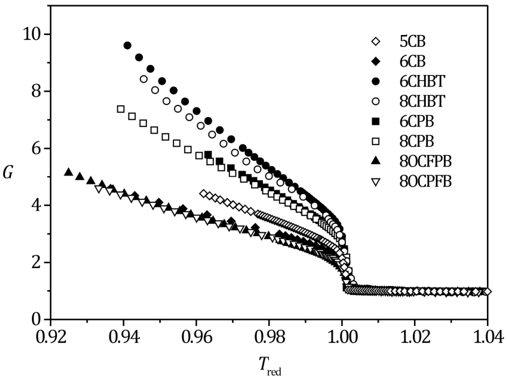

Fig. 6. Retardation factor G as a function of reduced temperature for the liquid crystals investigated.

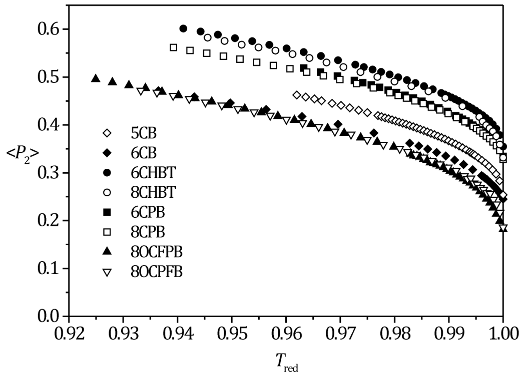

Fig. 7. Orientational order parameter $\langle P_2\rangle$ in the nematic phase for the liquid crystals investigated.

The dielectric method of $\langle P_2\rangle$ determination seems to be more sensitive to the short-range molecular interactions than, for example, the method based on the electronic absorption spectroscopy. This second method allows to determine the order parameter $\langle P_2\rangle$ of nematic liquid crystal from the anisotropic absorbance of a dichroic dye probe dissolved in it. In particular, $\langle P_2\rangle$ is calculated from the absorbances of the light polarized parallel ($A_{\parallel}$) and perpendicularly ($A_{\perp}$) to the direction of the macroscopic orientation of liquid crystal using the following formula [29]:

$$\langle P_2\rangle = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}\frac{2}{3\cos^2\beta - 1}, \tag{4}$$

where β is the angle between the absorption transition moment of dye molecule and the long molecular axis.

For comparison with the results of the dielectric experiments, the order parameters for the liquid crystals investigated at T_{red} equal to 0.963 and 0.991, obtained from the optical absorption (taken from [13, 14]), are also collected in Table III. In the case of the investigated liquid crystals, 4-dimethylamino-4′-nitrostilbene (DANS) was used as the light absorbing probe, for which, in a good approximation, $\beta = 0°$. As it is seen, the $\langle P_2\rangle$ values for 8OCFPB and 8OCPFB obtained from the optical spectroscopy are significantly greater than those calculated from the retardation factor. Such a result was also obtained earlier for 8CB [24], and it is common for a lot of liquid crystals for which some different methods yielded distinct values of $\langle P_2 \rangle$ [30, 31]. It is also evident that, on contrary to the dielectric method, the position of the fluorine atom in the investigated molecules influences the values of $\langle P_2 \rangle$ determined from the optical absorption. Moreover, the $\langle P_2 \rangle$ values from the optical absorption for the fluoro-substituted compounds are comparable to the order parameters of nCPBs. Taking into account the similar chemical structure of these compounds, it is reasonable to say that the $\langle P_2 \rangle$ values from the optical absorption method are more realistic than those calculated from the retardation factor. It should be mentioned that at $T_{\text{red}} = 0.991$ a relatively great difference in $\langle P_2 \rangle$ from both methods is observed not only for 8OCFPB and 8OCPFB but also for the representatives of nCB series.

Based on the data in Table III, a general observation is that the order parameters obtained from optical absorption of the DANS probe are better correlated with the δT values than the $\langle P_2 \rangle$ values calculated from G factor. Namely, the greatest values of δT correspond to the smallest values of $\langle P_2 \rangle$ (nCB series) and, vice versa, the smallest δT values are linked to the greatest values of the order parameter (nCHBT series). Although such kind of correlation seems to be compliant with intuitive predictions, the problem requires further investigations.

4. Conclusions

In the paper the dielectric relaxation in the nCBs, nCHBTs, nCPBs, 8OCFPB, 8OCPFB nematogens was discussed. From the temperature dependence of the relaxation time, related to the rotation around the short molecular axis, the N–I phase transition range ΔT_{NI} was determined. Because ΔT_{NI} values were considerably greater than zero, the weakly first-order type of the N–I phase transition was supposed. For the most of the liquid crystals investigated the dielectric pretransitional effect in the isotropic phase was observed. The magnitude of this effect was characterized by the difference δT between the temperature corresponding to maximum of ε_{s} in the isotropic phase and the clearing temperature. Extremely large values of δT were found for the representatives of nCB series which suggested the presence of domains with the nematic-like order in the isotropic phase for these liquid crystals. The δT values were compared with the orientational order parameters $\langle P_2 \rangle$ in the nematic phase calculated from the retardation factor G and obtained by using the optical absorption method (DANS probe). The dielectric relaxation method gave relatively small values of $\langle P_2 \rangle$ for both the nCBs and the fluoro-substituted liquid crystals. For the nematogens characterized by $g < 1$ the values of the order parameter obtained from optical absorption were substantially greater than those resulting from dielectric spectroscopy. Especially large differences in $\langle P_2 \rangle$ obtained from both methods were found for 8OCFPB and 8OCPFB. Comparison of the δT values with the $\langle P_2 \rangle$ values determined from the optical absorption showed regular correlation between these parameters, in contrary to the results obtained for $\langle P_2 \rangle$ determined from the dielectric spectroscopy. Regular correlation was also found between the δT values and the g data: the decrease in g was in the coincidence with the increase of δT.

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