Study of Condensed Matter by Neutron Scattering and Complementary Methods

Dynamics and Phase Transitions of 4-Bromobenzylidene-4′-pentyloxyaniline and 4-Bromobenzylidene-4′-hexyloxyaniline as Studied by Dielectric Spectroscopy

N. Osiecka[a], M. Massalska-Arodź[a], Z. Galewski[b], K. Chłędowska[c], S. Wróbel[d], T. Morito[e], Y. Yamamura[e] and K. Saito[e]

[a]The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences
E. Radzikowskiego 152, 31-342 Kraków, Poland

[b]The Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

[c]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology
al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

[d]Institute of Physics, Jagiellonian University, W.S. Reymonta 4, 30-059 Kraków, Poland

[e]Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan

Significant differences in phase sequence and dynamics between 4-bromobenzylidene-4′-pentyloxyaniline (5BBA) and -bromobenzylidene-4′-heksyloxyaniline (6BBA) substances were detected by broadband dielectric spectroscopy. In the smectic A (6BBA), the smectic B (found in both substances) and the smectic E (5BBA) phases the relaxation was ascribed to reorientations of the molecules around the short axes. Slow dynamics detected in the smectic E and in two crystalline phases of 5BBA was ascribed to conformational changes of molecular chains. Coexistence of Cr(I) and Cr(II) conformationally disordered crystal (CONDIS) phases was observed and vitrification of Cr(II) was identified with help of polarizing microscopy.

1. Introduction

Details of the phase diagram for a given substance are the result of interplay between structure, interactions and dynamics of molecules. Studies performed for sequence of liquid crystalline substances belonging to the same homologous series are helpful to get insight into that problem. For the Schiff bases 4-bromobenzylidene--4′-alkyloxyaniline, nBBA ($n = 4$–12), with the bromine atom as a lateral substitution and –CH=N– and –COC– additional dipolar groups, we performed recently systematic investigations using polarizing microscopy, X-ray diffraction [1] and IR spectroscopy. Interestingly, for all nBBA substances a highly ordered SmB phase exists and molecular dynamics can be expected [2]. It was found that behaviour of substances with $n = 4$ and 5 differs from those of $n = 6$–12. In this paper, our goal is to compare the dynamic features of two substances belonging to these groups, i.e. 5BBA and 6BBA, which differ in a CH_2 molecular segment only.

2. Experimental section

5BBA and 6BBA ($BrC_6H_4CHNC_6H_4OC_nH_{2n+1}$) were synthesised by Prof. Galewski [1]. Liquid crystal textures of mesophases were investigated using Biolar PI

polarised microscope (PZO Warsaw). The temperature was stabilised by Linkam THM 600 silver heating/cooling stage and TMS 90 temperature controller. Substances were placed between two glass plates at the temperature above melting point. Thickness of samples was of about 50 μm and the length 1 cm. Temperature was measured by platinum resistance thermometer with 0.1 K accuracy. The observation was carried out with the temperature cooling rate 20 °C/min. Differential scanning calorimetry (DSC) measurements were carried out using T Instruments, Q200 at ±5 K/min. The weight of sample was equal to 3.776 mg.

The real and imaginary parts of the electric permittivity of 6BBA and 5BBA substances were recorded using a high precision Novocontrol LPH analyser at the Jagiellonian University (6BBA) and at the Rzeszów University of Technology (5BBA). ll measurements were carried out in the temperature range between −50 °C and 120 °C, in the frequency range from 10^{-2} Hz to 10^7 Hz. Measurements were performed in cooling and heating runs. Measurement of each experimental point lasted about 20 min. The temperature was stabilized with 0.2 °C. 5BBA was sandwiched between two disc-shaped plates, covered with gold layers. In case of 6BBA the gold planar cell (u-HG) was used (2 cm — diameter, 50 μm — thickness).

The mean relaxation time of the observed processes

was determined by fitting to the loss spectra the Havriliak–Negami function [3, 4]:

$$\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{(1-\alpha)}]^\gamma} \qquad (1)$$

where $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, ε_0 and ε_∞ are the low and high frequency limits of dielectric permittivity, τ is a characteristic relaxation time, $(\omega)/\omega$ describes electric conductivity, α and γ are the Havriliak–Negami shape parameters ranging between 0 and 1.

3. Results and discussion

To illustrate the phase transitions for 6BBA and 5BBA, sequence of textures was observed for each substance on cooling using polarizing microscopy [5] as shown in Figs. 1 and 2, respectively.
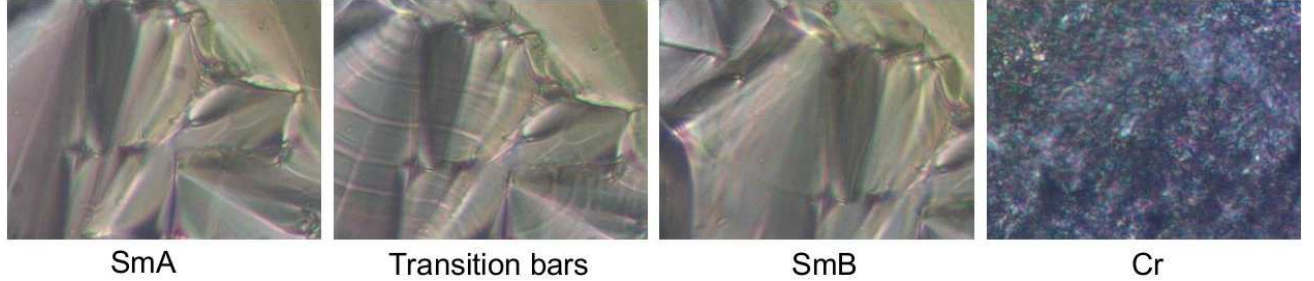

SmA   Transition bars   SmB   Cr

Fig. 1. Textures of 6BBA during cooling.

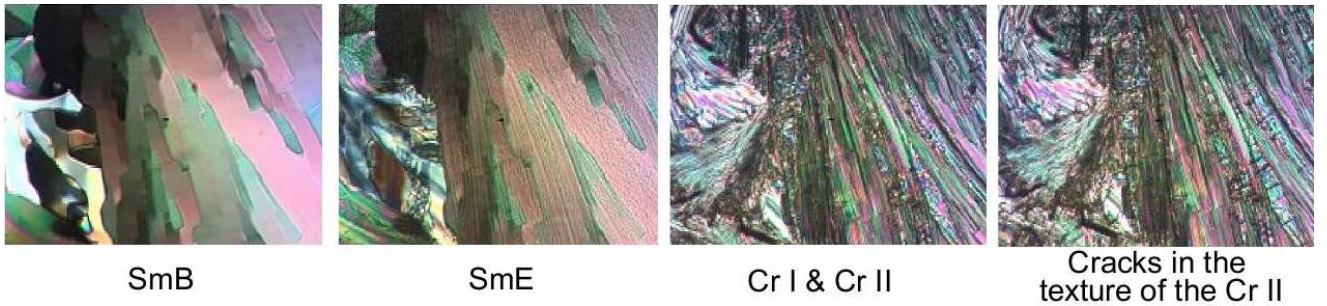SmB   SmE   Cr I & Cr II   Cracks in the texture of the Cr II

Fig. 2. Textures of 5BBA during cooling.

TABLE

Best fit values of fitting parameters for the 6BBA and 5BBA in selected temperatures.

Substance	Phase	Temperature	α	γ	τ [s]	$\Delta\varepsilon$		ε_∞
6BBA	Sm	393.15 K	0.02 ± 0.01	0.90 ± 0.01	$2.22\times10^{-6} \pm 6.7\times10^{-7}$	0.25 ± 0.01	20 ± 2	3.75
	SmB	377.15 K	0.01 ± 0.01	0.95 ± 0.01	$8.92\times10^{-6} \pm 3.1\times10^{-5}$	0.20 ± 0.01	28 ± 2	3.83
5BBA	SmB	363.15 K	0.03 ± 0.01	0.98 ± 0.01	$4.43\times10^{-5} \pm 5.7\times10^{-6}$	3.46 ± 0.01	50 ± 1	6.43
	SmE	355.15 K	0.32 ± 0.01	0.72 ± 0.01	$1.18\times10^{-4} \pm 2\times10^{-6}$	1.49 ± 0.01	76 ± 2	5.97
			0.05 ± 0.01	0.99 ± 0.01	$1.55\times10^{-8} \pm 7.8\times10^{-9}$	0.29 ± 0.01		5.65
	Cr(I) and Cr(II)	308.15 K	0.12 ± 0.01	0.98 ± 0.01	$7.87\times10^{-8} \pm 7.2\times10^{-9}$	0.19 ± 0.01	89 ± 3	5.20
	Cr(I) and glass of Cr(II)	263.15 K	0.33 ± 0.01	0.70 ± 0.01	$1.11\times10^{-6} \pm 6.9\times10^{-7}$	0.11 ± 0.01	45 ± 5	5.21

One can see that for 6BBA the phase diagram reveals Sm and SmB liquid crystalline phases and one crystalline phase. This phase transition pattern is characteristic for derivatives with longer alkyloxy chain. For 5BBA, a smectic A phase is absent (as was established also for 4BBA) while a phase transition to another unknown smectic phase was detected at temperature 343.13 K. This phase was identified as SmE phase on the basis of textures during another cooling run. While the domain structure was kept, the black region in SmB phase became mosaic due to the biaxiality within the layer. This transition sequence was also observed in DSC as shown in Fig. 3. On further cooling under optical observation, at 338.05 K coexistence of Cr(I) and Cr (II) started. One

can say that it is due to slow kinetics of crystallisation of crystal I. Below 293 K, a process of cracking of some areas of the sample evidenced vitrification of the crystal Cr(II) [6].

In Fig. 4 one can see the temperature dependence of the real part of electric permittivity measured at 1 kHz on cooling and heating of the 5BBA and 6BBA samples. Values of ε' indicate that in all phases some forms of dynamics are present. In 6BBA, a nearly single, rather weak MHz-relaxation process has been found in Sm and SmB phases, as one can see in Fig. 5. Due to the narrow range of the Sm phase, we were not able to estimate activation enthalpy ΔH for this phase. Unexpectedly, at the Sm –SmB transition on cooling a dynamics becomes
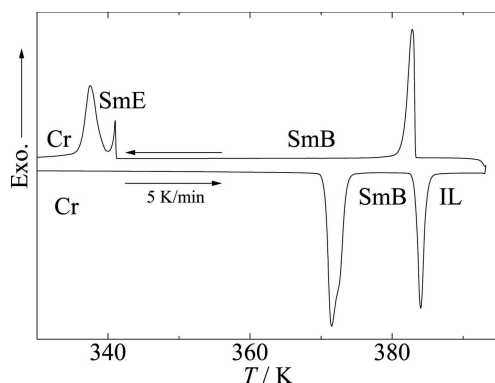
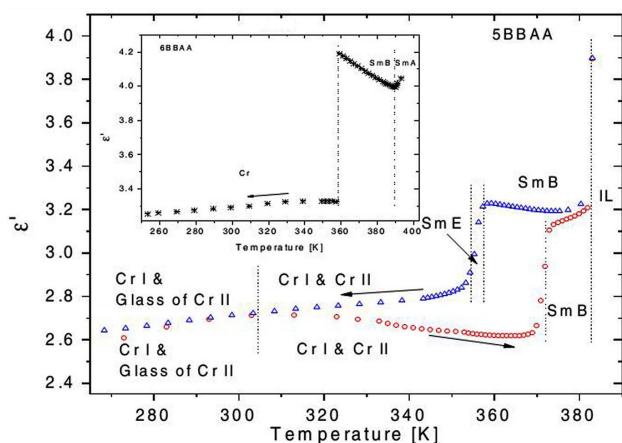Fig. 3.   DSC trace of 5BBA obtained at ± 5 K/min.

Fig. 4.   Real part of the dielectric permittivity of 5BBA and 6BBA (inset) observed vs. temperature at 1 kHz. Triangles and circles correspond to the 5BBA's data, while stars to the 6BBA's data. Dotted lines indicate the phase transition temperatures observed on cooling.
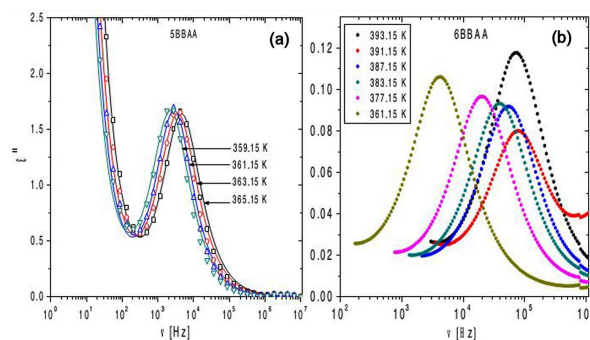

Fig. 5.   Dielectric loss spectra in the smectic B phase of 5BBA (a) and 6BBA (b). Data was collected during cooling.

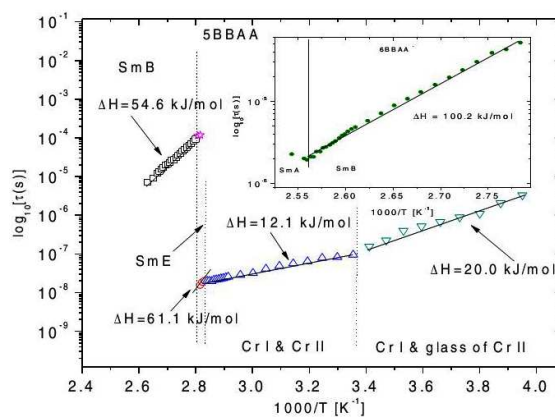Fig. 6.   Temperature dependence of relaxation time of 5BBA and 6BBA (inset).

faster. In the smectic B phase, long-range fluctuations of centres of mass create enough space for the reorientation of molecules around short axes [1]. The temperature dependence of the relaxation time τ, estimated with help of Eq. (1), can be seen in the inset of Fig. 6, while the values of α and γ parameters are collected in Table. The relaxation process is close to the Debye one ($\alpha \approx 0$ and $\gamma \approx 1$) and follows the Arrhenius behaviour. It was ascribed to the molecular reorientations around the short axes (flip-flop motions), hindered by the activation enthalpy ΔH equalling to 100.2 kJ/mol. Usually, the value of ΔH for SmB is between 50 and 100 kJ/mol [7].

As it is presented in Fig. 6, in the smectic B phase of 5BBA dynamics was observed at the same frequency range as in case of 6BBA. The motions of the 5BBA molecules are hindered by enthalpy of 54.6 kJ/mol, smaller than in case of the 6BBA molecules, which is in accordance with our structural data [1]: the 5BBA molecule has more room in the unit cell than the 6BBA one. A dielectric absorption observed for 5BBA is of order of magnitude larger than in case of 6BBA. That may

be caused by a contribution of larger electric polarization (see Fig. 5 and Table). Appearance of SmE phase in 5BBA may be induced by larger component of the dipolar moment perpendicular to the long axes in case of 5BBA than in case of 6BBA molecule.

For 5BBA, below the SmB–SmE transition one can see the process observed in the smectic B phase and in addition a second one, shifted four decades towards smaller values of the relaxation time. They are presented by $\varepsilon''(\log \nu)$ for several temperatures in Fig. 7. The estimated parameters $\alpha \approx 0.3$ and $\gamma \approx 0.7$ mean large deviation of this process from the Debye one. Temperature dependence of relaxation time estimated for 5BBA using Eq. (1) and the ΔH values can be found in Fig. 6. The enthalpy values of both processes found are similar and slightly higher than the value evaluated for flip-flop motions in SmB phase.

Dynamics detected below crystallization has been observed at the same frequency range as the faster process in smectic E phase. However, motions are hindered by much smaller enthalpies, i.e., of 12.1 kJ/mol at the temperature range, where mixture of Cr(I) and Cr(II) phases were identified, and of 20 kJ/mol in the temperature region, where motions in Cr(I) occur in presence of
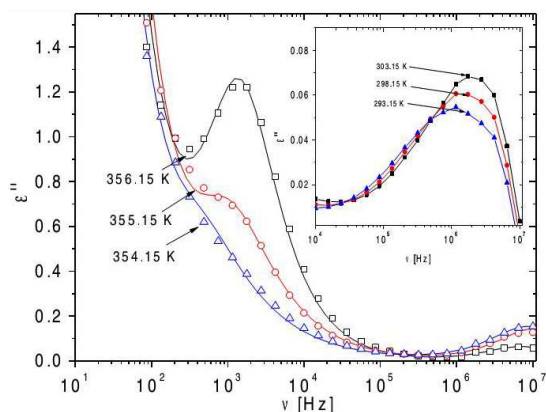
Fig. 7. Dielectric loss spectra of 5BBA in the SmE phase (temperature range of 356–354 K) and in the Cr(I) and Cr(II) phases in temperature range of 293–303 K (inset).

glass of Cr(II) in some part of the sample. The values of the calculated activation enthalpies are characteristic for the conformationally disordered crystal (CONDIS) [8–11]. In Fig. 6 one can see the change of the slopes of the $\log \tau (1/T)$ lines at the temperature region of about 293 K — the cracks appeared in the texture of crystal II at the same temperatures. These observations suggest the crystal II — glass of crystal II transformation, accompanied by a slowing down of the relaxation process [12]. However, as one can see in the inset of Fig. 7, the amplitudes of the absorption peaks observed at that temperature region are not reduced dramatically by vitrification, which means that there are still conformational motions in the crystal I. Presumably, due to the presence of areas with frozen Cr(II) phase, large strain exists. Thus, motions are more restricted, which is reflected in the growth of the hindering potential barriers and relaxation times. The mechanism of the process observed in the smectic E phase (the faster one) and in both crystalline phases seems to be related with the alkyloxy chain flexible parts rotations around the C–C and C–O bonds as the alkyloxy tail enables conformational disorder [13]. This observation confirms that the crystal I and crystal II are the CONDIS crystals. A large number of defects in the structure is characteristic for CONDIS crystal [14–16] and they are often glass-forming phases.

4. Conclusion

Dielectric spectroscopy was applied to study of dynamics of 5BBA and 6BBA members of the 4-bromobenzylidene-4′-alkyloxyaniline homologous series with molecular alkyloxy tails varying of CH_2 segment. The studies confirmed various polymorphism of the substances, indicated by polarizing microscopy. The kHz-dielectric relaxation related to molecular reorientations around short axis was found in the smectic B phase, observed in both substances, and in smectic A of 6BBA and in smectic E phase of 5BBA. For 5BBA, much faster dynamics was identified in the smectic E and in two crystal phases in the range of MHz-frequencies. It was ascribed to conformational changes of molecular chains. Vitrification of one of the conformationally disordered crystals was observed by the polarizing microscopy.

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