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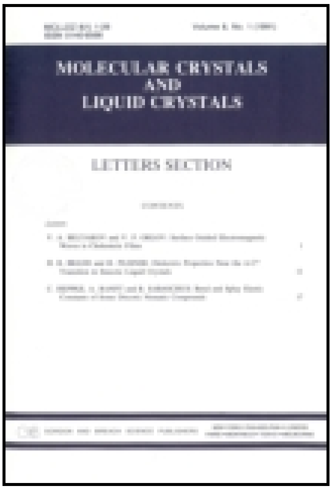

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DSC Study of Bent-Core and Rod-Shaped Liquid Crystal Mixtures

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DSC Study of Bent-Core and Rod-Shaped Liquid Crystal Mixtures

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Phase transitions of different binary mixtures of a bent-core (10DClPBBC) and a rod-shaped (6OO8) liquid crystal were studied using differential scanning calorimetry. For the binary mixture with 50:50 weight ratio of bent-core and rod-shaped molecules, the nematic to smectic transition occurred below the temperature of 40° C and crystallization was shifted to sub-ambient temperature. It was found that crystallization was the phase transition with the lowest apparent activation energy.

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Introduction

Bent-core (or banana-shaped) mesogens represent a novel class of thermotropic liquid crystals (LCs) which have become targets of extensive studies in the last two decades [1–5]. Study of the liquid-crystalline properties of bent-core molecules, such as the observation of ferroelectricity and spontaneous chiral symmetry breaking in smectic phases composed of achiral molecules has broad implications for the general field of soft condensed matter and opens new possibilities for applications [6–8]. Different substances have different phase transition temperatures and in the case of their mixtures, the transformation temperatures are changed. Creating mixtures of the bent-core and rod-shaped molecules allows to form the liquid crystalline phase at the room temperature which can be useful in possible practical applications [9–11].

Differential scanning calorimetry (DSC) is a useful tool that complements optical methods in the study of liquid crystal phase transformations [12,13]. In the present work, the phase transitions of binary mixtures of a bent-core (10DClPBBC) and a rod-shaped (6OO8) liquid crystal were studied using the DSC method. We focused on the crystallization kinetics of the pure compounds and of their binary mixtures.

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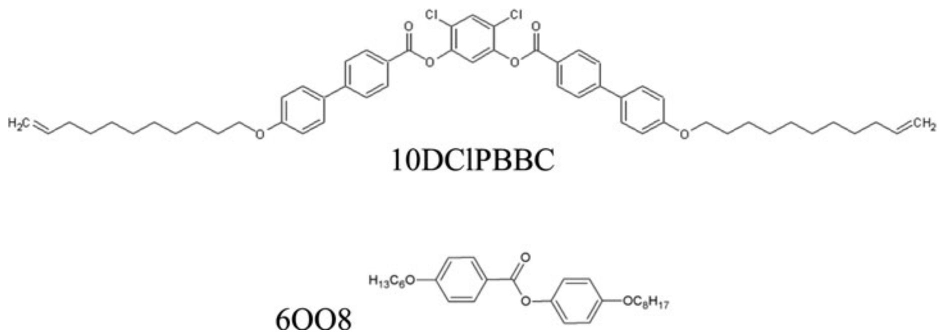

Figure 1. Structural formulas of the bent-core 10DClPBBC and the rod-shaped 6OO8 molecules used in the experiment.

Experimental

In the experiment the banana-shaped (B) 4,6-dichloro-1,3-phenylene-bis [4′-(9-decen-1-yloxy)-1,1′-biphenyl] 4-carboxylate (10DClPBBC) and the rod-shaped (R) 4-n-octyloxyphenyl 4-n-hexyloxybenzoate (6OO8) liquid crystals and their binary mixtures of different compositions were used. Three mixtures with weight ratios B:R of 15:85, 50:50 and 85:15 of the banana-shaped and the rod-shaped liquid crystals were prepared. Structural formulas of the banana and rod-shaped molecules can be seen in Fig. 1.

DSC experiments (heating and subsequent cooling cycles) were performed in flowing nitrogen atmosphere using a Perkin Elmer DSC 8000 apparatus.

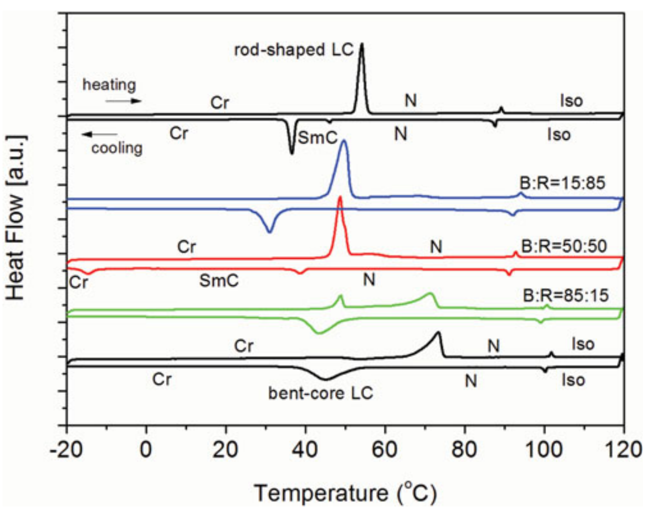

Figure 2. DSC thermograms obtained for the bent-core (B) and the rod-shaped (R) LCs and for their mixtures with different weight ratios B:R during the first heating and cooling cycle at the rate of 10°C/min.

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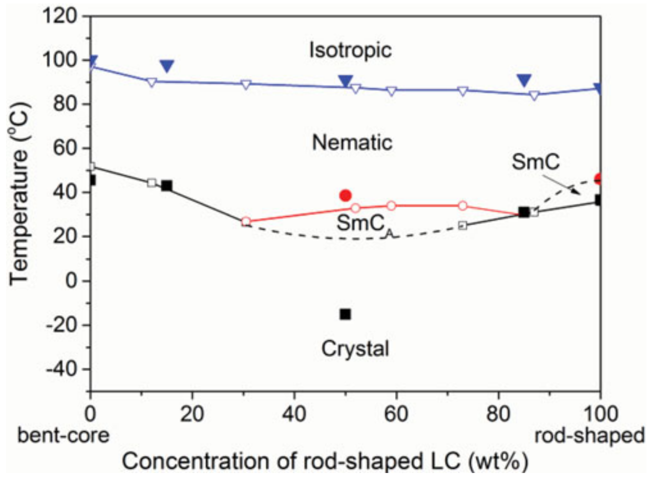

Figure 3. The phase diagram of the binary mixtures of the bent-core and rod-shaped compounds (solid symbols correspond to our DSC measurements at cooling, open symbols indicate the results of the polarizing microscope measurements in [10]).

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Results and Discussion

Typical DSC traces, indicating the occurrence of phase transitions, obtained upon a heating/cooling cycle at the rate of 10 K/min for the pure banana-shaped (B) and the pure rod-shaped (R) liquid crystals, as well as for the three binary mixtures are shown in Fig. 2. The individual phases were assigned according to the optical observations in [10]. The width of the DSC peaks depends on the type of the phase transition as well as on the shape of the LC molecules. The nematic-isotropic transition peaks are narrow, but the peaks corresponding to crystallization are wider. This latter becomes more pronounced with increasing banana content of the LC.

At heating, crystal (Cr) to nematic (N) and nematic to isotropic (Iso) transitions were observed for all examined samples. The crystal to nematic transition temperature decreased in the mixtures of bent-core and rod-shaped molecules, in comparison to that of the pure rod-shaped compound. In addition, in the case of the mixture with weight ratio of 85:15, two melting peaks were observed. The two subsequent transitions at lower and higher temperatures may correspond to the crystal to nematic transition of a mixture of the banana-shaped and rod-shaped LC and the pure banana-shaped LC, respectively; thus indicating a partial phase separation in the crystalline phase. The N-Iso transition in the mixtures occurs at higher temperatures than in the pure rod-shaped LC, but still below that of the pure bent-core compound. At subsequent cooling, the corresponding peaks do not coincide with the peaks observed at heating. They differ only slightly for the Iso-N transition, whereas the crystallization temperatures are substantially different from the melting temperatures. Whereas at cooling the pure banana-shaped compound no other phase transition was present, in the pure rod-shaped LC an additional nematic to monotropic smectic C (SmC) phase transition appeared at about 45°C. This smectic C phase disappeared in the mixture with B:R = 15:85 which had only a nematic mesophase. The binary mixture with 50:50 weight ratio, however, exhibited a monotropic nematic to smectic transition below 40°C. Upon further increase of the banana content, in the mixture with B:R = 85:15, the induced smectic phase was not present any more.

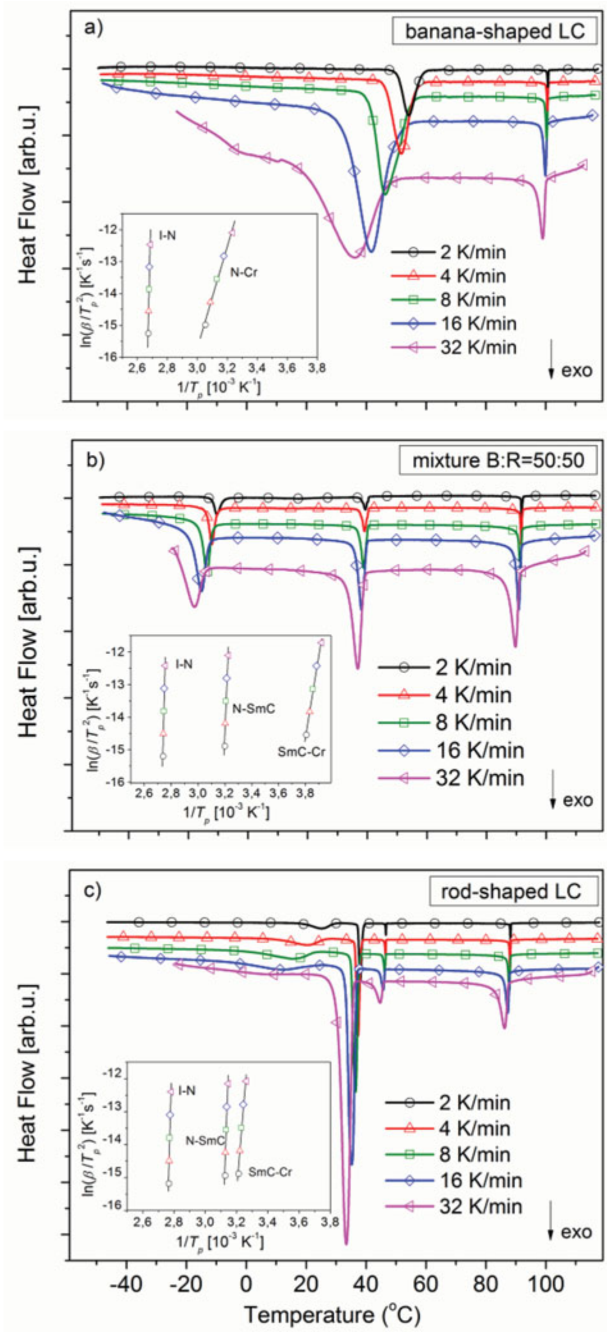

Figure 4. DSC traces obtained during cooling for the samples of a) the pure banana-shaped LC, b) the mixture of banana and rod-shaped LCs with 50:50 weight ratio and c) the pure rod-shaped LC. Insets show the corresponding Kissinger plots for the individual phase transition peaks.

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The studied 10DClPBBC – 6O08 binary system has recently been investigated by Nair et al. [10] by polarizing optical microscopy. In order to compare the results, Fig. 3 depicts the phase diagram of this binary system of bent-core and rod-shaped compounds. The solid symbols correspond to our DSC measurements, while the open symbols connected with lines and the phase identifications correspond to the polarizing microscopic measurements from [10]. One can deduce from Fig. 3that the results obtained by the two independent techniques are in a good agreement; DSC measurements confirmed the phase transition sequences observed by Nair et al. [10].

This good match approves using the results of the optical observations for assigning the individual phases of the DSC curves in Fig. 2. In particular, the induced smectic phase in the mixture of 50:50 weight ratio was identified in [10] as an anticlinic smectic phase (SmC_A) which remains stable at ambient temperatures. Indeed, the DSC results confirmed the strong supercoolability of this SmC_A phase, as crystallization occurred only at as low temperature as –15°C.

The kinetics of the phase transitions in the pure bent-core and the pure rod-shaped LCs and in their mixture of 50:50 weight ratio was also studied by DSC analysis. Figure 4 shows the traces obtained during subsequent cooling runs at five different cooling rates β (ranging from 2 to 32 K/min) starting from the temperature of 120°C. Insets show Kissinger plots for the phase transition temperatures T_p belonging to the individual DSC peaks [12]. Activation energies were evaluated from linear fits of the Kissinger plots for all phase transitions.

It was revealed that the apparent activation energy for the Iso-N and N-SmC (if it is present) transitions is relatively high for all LC samples. The apparent activation energy for the Iso-N transition decreases from about 1700 kJ/mol to 1390 kJ/mol when changing the content of the rod-shaped compound in the mixtures from 0% to 100%. The estimated apparent activation energy for the crystallization transitions is significantly much lower for all LC samples, and it increases from 130 to 470 kJ/mol at increasing the content of the rod-shaped compound in the mixtures from 0% to 100%. The apparent activation energy for the N-SmC transition is lower (830 kJ/mol) for the mixture of 50:50 weight ratio than for the pure rod-like compound (1100 kJ/mol). These values are between those belonging to the Iso-N and the crystallization transitions. Thus crystallization is the thermally most activated process in all examined samples.

Conclusion

DSC study of the phase transitions in binary mixtures of a bent-core (10DClPBBC) and a rod-shaped (6O08) liquid crystal confirmed the binary phase diagram obtained by Nair et al. by polarizing microscopy [10]. We showed that the stability region of the induced smectic phase at intermediate concentrations extends further toward lower temperatures than it had been expected. The kinetics of the phase transitions in the studied binary system of 10DClPBBC and 6O08 liquid crystals revealed that the crystallization transition has the lowest apparent activation energy in all studied liquid crystal samples.

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