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Thermal and optical characterization of liquid crystal 4′-hexyl-4-biphenylcarbonitrile/4-hexylbenzoic acid mixtures

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ABSTRACT

We present the thermal and optical properties of binary mixtures formed from hydrogen-bonded liquid crystal 4-hexylbenzoic acid (6BA) and 4-hexyl-4′-biphenylcarbonitrile (6CB) mesogens. Phase transition temperatures and enthalpy values are evaluated by differential scanning calorimetry (DSC) and phases identified by polarized optic microscopy (POM). The experimental results obviously show that the 6BA/6CB binary mixtures exhibit nematic and smectic phases. The most interesting result is that although the smectic phase is not observed in pure components 6BA and 6CB, it is observed in their some binary mixtures. The thermal properties like phase peak temperatures, enthalpy changes and thermal span of binary mixtures are affected by depending on the mixture ratio. The nematic range increase in the binary mixture compared to the individual mesogen, and also the phase transition temperature values and the nematic thermal stability factor increase as heating rate increases. Furthermore, the calculated activation energy values show that the reorientation of the molecules during the phase transitions of the mixture occurs on an orderly basis.

1. Introduction

The nematogenic homologous p-(n-alkyl)-p′-biphenylcarbonitrile (nCB, where n = number of carbon atoms in the alkyl tail) and 4,n-alkylbenzoic acid (nBA) series are two of the well-known mesogenic series of liquid crystal (LC) family. Since the early 1970s [1,2] they have been applied to both academic investigations and practical use in technological applications [3–7]. Although many studies have been carried out on these liquid crystal series in the last two decades [8–14], there is not enough study on their mixtures. This is the reason that motivated us to study binary mixtures of nBA and nCB. Liquid crystalline phases exhibited by nCB and nBA below the isotropic liquid depend on the number of carbons in the alkyl tails [15–17]. For example, while smectic A (SmA) phase occurs for $n \geq 8$ with the disappearance of the nematic (N) phase for $n \geq 10$ of nCB, nematic phase occurs for $2 \leq n \leq 7$. Similar results are also observed in nBA liquid crystal series. In the present work, we present our experimental results on thermo-optic properties for binary mixtures of 4-hexylbenzoic acid (6BA) and 4-hexyl-4′-biphenylcarbonitrile (6CB). 6BA and 6CB, as well as other members of nBA and nCB homologous series, have very important properties for the technological applications due to the possession of an excellent thermal and chemical stability. Alkyl tail length of the pure 6BA and 6CB mesogens is the same, but the molecular sizes of 6BA and 6CB are different from each other. In addition, these liquid crystals show only a nematic phase but their phase transition temperatures are different from each other because of their molecular structures. According to previous studies [12,18–20], while the pure liquid crystal 6CB mesogen exhibits a nematic phase at room temperatures, the pure liquid crystal 6BA mesogen exhibits a nematic phase at higher temperatures. Therefore, a liquid crystal mixture having a larger nematic area, which is the aim of this study, can be obtained by mixing the 6BA and 6CB liquid crystals. In this context, we examined the phase transition properties of 6BA/6CB binary mixtures using differential scanning calorimeter, and also identified the phase transition and phase structure of the binary mixtures using polarized optic microscopy.

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2. Experimental

2.1. Materials

The liquid crystal mesogens 4-hexyl-4′-biphenylcarbonitrile (6CB) and 4- hexylbenzoic acid (6BA) were supplied by Sigma Aldrich, Germany and were used without further purification: their phase transition temperatures were in good agreement with the data given in Catalogue. The chemical structure of pure nematic mesogens 6CB and 6BA used in this study is shown in Fig. 1.

2.2. Preparation of 6BA/6CB mixture samples

The binary mixtures were produced by weighing at ratios of 1:3 (25% 6BA + 75% 6CB), 1:1 (50% 6BA + 50% 6CB) and 3:1 (75% 6BA + 25% 6CB) from the pure liquid crystals, and after forming heterogeneous mixtures at room temperature they were heated on a heating table which is inside a glove box filled with an argon atmosphere. The samples were heated in a sealed tube to avoid losses by evaporation. The heated samples were mixed for 20 min at the phase transition interval by using mechanical stirring methods. In order for all the mixed samples to have a completely homogeneous structure, mixing and heating processes were repeated with 30-min interval, and then the sample tube was suddenly immersed in cold water to maintain a homogeneous mixture formation. To avoid oxidation, the interaction of the sample with air is hindered as much as possible. The thermal properties like phase transition temperatures and enthalpy values of mixed liquid crystal mesogens were investigated by DSC (Perkin-Elmer DSC-8000) using continuous heating and cooling under a pure argon atmosphere. In order to ensure reliable temperature and heat release values, the DSC was calibrated using In (99.999 wt % of pure In) standard. Masses of about 2 mg for pure mesogens and 6BA/6CB mixtures are accurately weighed by using a precision balance and the weighed samples were sealed in aluminium pans. The samples were heated up to a temperature above the estimated clearing temperature and hold at its isotropic temperature for two minutes so as to attain thermal stability. Then they were cooled at rate of 10 °C/min to ambient temperature (~25 °C).

The sandwich-type LC cells were formed by two glass lamellas with a spacer with thickness of 40 μm between them to use in POM studies. Thus, the glass lamellas were sensitively cleaned with ethanol and distilled water at 80 °C for 1 h in an ultrasonic cleaner, and immersed in the ethanol. Then, the lamellas were left to dry in a sterile oven at 100 °C. After this process, both sides of lamellas were coated with a spacer, and a sandwich structure was formed by superimposing the lamellas by leaving a short space. During LC cell formation, cells were prepared by using sterile gloves without bare-hand contact. LC mixture sample produced by mechanical stirring methods was filled in its isotropic phase to LC cell in sandwich type. When the LC cell was heated on a heating plate, liquid crystal sample was placed between the lamellas of 2 × 3 cm^2 by capillary action. To prevent the degradation of the material by melting the spacer at high temperatures, the edges and end parts of the LC cell were adhered with a heat resistant adhesive. Thus, LC cell to be used in polarized optical microscope experiments was prepared. LC cell was placed on the heating plate of a Leica 180 DM LP polarized optical microscope for optical textural studies, then a current of 0.7 A was applied to the system and the temperature increased from −10 to 110 °C. After the isotropic phase was completely observed, the LC cell was left to cool at ambient temperature. Optical textures of mesogens were captured by using the POM with a CCD camera during heating run at rate of 10 °C/min, and according to the captured textures, the morphological analyses of liquid crystal samples were performed.

3. Results and discussion

In the present study, we have investigated the liquid crystal 6CB/6BA mixtures to determine whether they show liquid crystalline properties. Thus, DSC experiments were firstly performed on the 6CB/6BA mixtures, and then the POM studies were done to make the phase identification.

3.1. DSC studies

The DSC heating and cooling scans for both pure mesogens 6CB

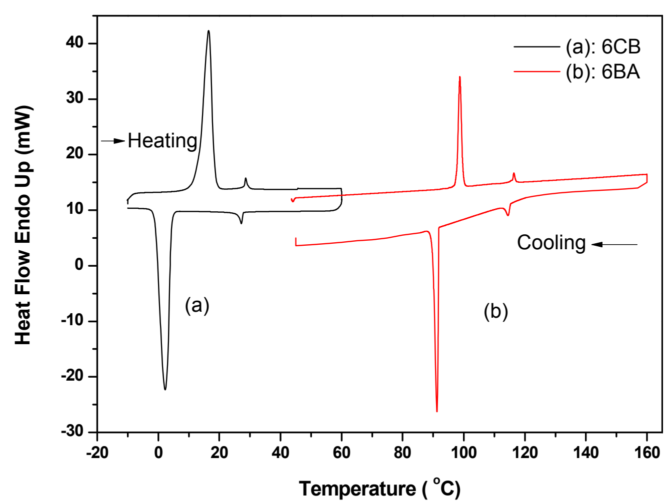


Fig. 2. Continuous DSC thermograms obtained during heating and cooling from pure 6CB and 6BA.

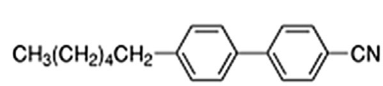
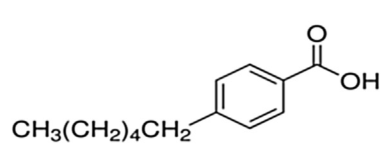
LC	Structural Formula	Chemical Structure	Molar Mass (g/mol)
6CB	$CH_3(CH_2)_5C_6H_4C_6H_4CN$		263.38
6BA	$CH_3(CH_2)_5C_6H_4CO_2H$		206.28

Fig. 1. Molecular structures of 4-hexyl-4′-biphenylcarbonitrile (6CB) and 4-hexylbenzoic acid (6BA).