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Kinetics of Nematic to Isotropic Phase Transition in Liquid Crystal Doped with Magnetic Nanoparticles

K. Csach[a,*], A. Juríková[a], J. Miškuf[a], N. Tomašovičová[a], V. Gdovinová[a], V. Závišová[a], P. Kopčanský[a], N. Éber[b], K. Fodor-Csorba[b] and A. Vajda[b]

[a]Institute of Experimental Physics, SAS, Watsonova 47, 040 01 Košice, Slovakia

[b]Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, H-1525 Budapest, Hungary

A binary mixture of bent-core and rod-shaped liquid crystals was chosen as a model substance combining the properties of both types of liquid crystals. The mixture was doped with a small amount of spherical and rod-like magnetic nanoparticles. Differential scanning calorimetry experiments were performed for the pure as well as for the doped mixture at different heating rates ranging from 1 to 16 °C/min. The addition of the magnetic nanoparticles lowered the phase transition temperature. This effect is more intensive in the case of the rod-like magnetic nanoparticles. The kinetics of the nematic to isotropic phase transition was evaluated in the framework of the differential isoconversional method. The calculated apparent activation energy showed non-monotonic behaviour and a sensitivity on the shape of added magnetic nanoparticles.

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1. Introduction

Liquid crystals (LCs) are well known in basic research as well as in development for commercial use [1]. Within the past two decades, great interest has been developed in the liquid crystalline properties of bent-core or banana shaped mesogens. They have attracted scientific interest for their unique properties compared to conventional calamitic or rod-like liquid crystals. Recently, binary mixtures of banana and rod-like LCs have been studied and many interesting physical phenomena were reported [2, 3]. The temperatures of the phase transitions of LCs are very stable at unchanged other conditions and can be used as temperature standards in thermal analysis [4, 5]. Several studies were devoted to examination of the influence of addition of the nanoparticles into LCs on the phase stability of these systems [6, 7]. It has been pointed out that doping LC with magnetic particles can modify the phase transition temperatures and increase the sensitivity to external magnetic field [7–9].

Several models were applied for the description of the kinetics of phase transitions. The most convenient description of first-order phase transitions is based on the assumption that the activation energy of the selected process is constant during the transformation. The Kissinger model describes the linear dependence of the logarithm of the heating rate and the temperature of the maximal reaction rate on the inverse temperature [10]. More complex models of phase transition kinetics were developed taking into account the conversion progress [11].

In the present work we focused on the study of the thermal properties of a binary mixture of bent-core molecules with rod-like molecules. The influence of the addition of a small amount of magnetite nanoparticles on the nematic to isotropic (N–I) phase transformation kinetics in LC mixture was studied by differential scanning calorimetry (DSC).

2. Experimental and methods of analysis

In the experiment a binary 50:50 wt% mixture of the banana-shaped 4,6-dichloro-1,3-phenylene-bis [4′-(9-decen-1-yloxy)-1,1′-biphenyl] 4-carboxylate (10DClPBBC) with the rod-shaped 4-*n*-octyloxyphenyl 4-*n*-hexyloxy-benzoate (6OO8) compounds was used [12]. The mixture was doped with spherical and rod-like magnetic nanoparticles with the concentrations of $7.5-8.5 \times 10^{-4}$. The spherical magnetic particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} salts by NH_4OH. Magnetic rod-like particles were synthesized through hydrolysis of $FeCl_3$ and $FeSO_4$ solutions containing urea. DSC experiments were performed in flowing nitrogen atmosphere using TA Instruments Q2000 apparatus with the heating rate from 1 to 16 K/min.

The set of experiments at different heating rates was carried out for studying the influence of the doping of the LC mixture by magnetite nanoparticles of different shapes. The data were analysed using Kissinger's method and by the differential isoconversional method modified by Budrugeac [11]. The software AKTS™ Thermokinetic was used for the calculations.

3. Results and discussion

DSC traces of the nematic to isotropic transition for pure LC mixture and for the ones doped with spherical

*corresponding author; e-mail: csach@saske.sk

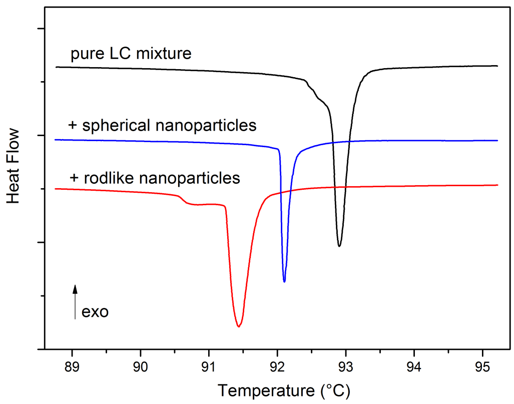

Fig. 1. DSC traces of the nematic to isotropic transition for the pure LC mixture and for the ones doped with spherical and rod-like magnetic nanoparticles.

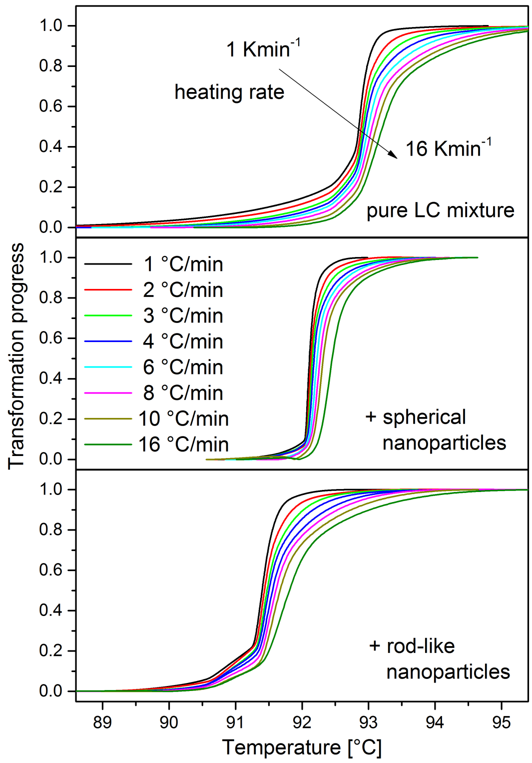

Fig. 2. Temperature dependence of the progress of the N–I transformation for the indicated LC mixtures.

and rodlike magnetic nanoparticles, taken at the heating rate of 2 K/min can be seen in Fig. 1. The addition of magnetic nanoparticles lowered the phase transition temperature. This effect is more intensive in the case of the rod-like magnetic nanoparticles. The nematic to isotropic transition temperature (determined as peak minimum) is shifted from the value of 92.8 °C for the pure mixture of LCs to the value of 92.1 °C for LC mixture doped with spherical nanoparticles and to 91.4 °C if the rod-like nanoparticles were added.

Series of DSC runs at different heating rates give a set of thermograms shifted in the temperature. Using the Kissinger method [10] the apparent activation energy of the N–I transition for the pure and the doped mixtures of LCs was calculated. For the pure LC mixture the activation energy was found to be 303 J mol^{-1}, for the mixtures doped with the spherical and the rod-like magnetite nanoparticles the values of the activation energies were determined as 278 J mol^{-1} and 215 J mol^{-1}, respectively.

In the frame of differential isoconversional method modified by Budrugeac [11] more detailed analysis of the series of DSC runs was performed. The method assumes that the activation energy for a given transformed ratio is constant. So the baseline was subtracted from the DSC traces and then the DSC peaks were integrated and normalized. The temperature dependences of the conversion degree at different heating rates for the pure LC mixture as well as for the mixtures doped with the magnetite nanoparticles of different shapes are shown in Fig. 2.

Figure 3 shows the differential isoconversional kinetic plots for all examined LC mixtures. The straight lines in Fig. 3 represent the fits of the same values of a transformed ratio at different heating rates. The slope of the fits corresponds to the activation energy at a given transformed ratio.

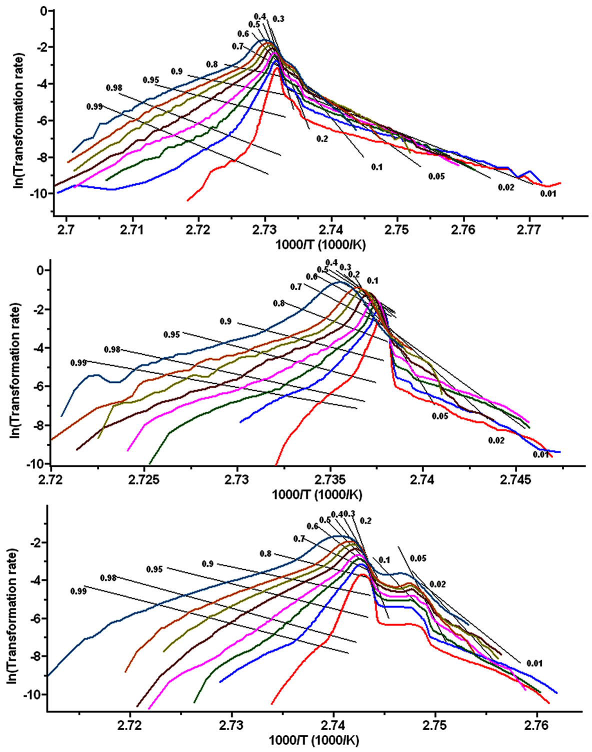

Fig. 3. Differential isoconversional kinetics of the N–I transition of the pure LC mixture (top), the mixture doped with spherical nanoparticles (middle) and with rod-like nanoparticles (bottom).

The isoconversional curves for doped LC mixtures became of bimodal form more developed in the case of doping with the rod-like nanoparticles. The shape of the doping magnetite nanoparticles plays an important role

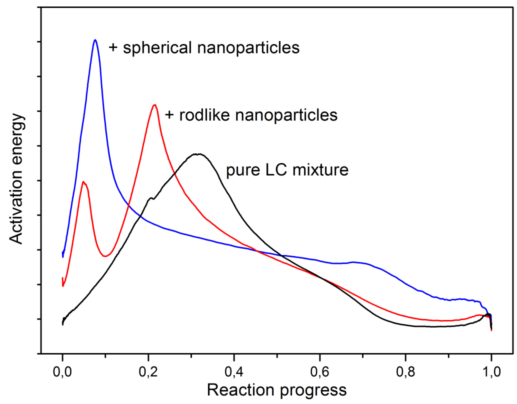

Fig. 4. Activation energy of N–I transition dependence on the reaction progress for the pure and the doped LC mixtures.

in the kinetics of the N–I phase transition in the LC mixture.

The dependences of the activation energy of N–I transition on the reaction progress is shown in Fig. 4. It can be seen that the addition of nanoparticles influences the N–I transition dominantly in the initial stages of the phase transition. This effect is more significant for doping the LC mixture with the rod-like nanoparticles where the dependence of the activation energy on the transformed ratio confirms two stages of the N–I transition.

Addition of nanoparticles into LC mixture tends to the creation of the new interfaces. Whereas in the case of the spherical magnetite nanoparticles their surface is uniform, in the case of the rod-like nanoparticles the bond conditions at interfaces are different at the ends and on the body of the rod-like nanoparticles.

4. Conclusions

Addition of magnetic nanoparticles into a mixture of liquid crystals tends to the changes in the temperatures of nematic to isotropic phase transitions.

Rod-like nanoparticles lower the phase transition temperature more than the spherical ones. Addition of magnetite nanoparticles into the LC mixture accelerates the initial stages of nematic–isotropic transition. Doping with rod-like nanoparticles makes more visible two stages of N/I transition in LC mixture. The influence of magnetite nanoparticle shape on the kinetics of N/I transition was analysed in the frame of the differential isoconversional model.

Acknowledgments

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