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Kinetics of the ordered phase growth across the phase separation of a multi-component liquid crystalline mixture

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Summary

Kinetics of the ordered phase growth in a melted multi-component liquid crystalline mixture subjected to a deep cooling was studied using polarizing optical microscopy. The droplets of the ordered phase revealed in the optical images across the phase transition were segmented and treated statistically. In the resulting histograms, two overlapping statistical ensembles related to two main components of the mixture were recognized. These ensembles were successfully described using principles of irreversible thermodynamics and the mean droplet diameters within both ensembles were determined. Analysis of the mean droplet diameter as a function of time allowed recognition of two regimes involved in the ordered phase evolution: i) nucleation and rapid nucleus growth and ii) nucleus coarsening, i.e. Ostwald ripening. Both regimes were quantitatively described with the universal law for the cluster growth. The mechanisms responsible for the ordered phase growth were also recognized.

keywords: liquid crystalline mixture, phase separation, statistical size distribution, irreversible thermodynamics, mean droplet diameter, kinetics, ordered phase

Introduction

Both scientific and applied disciplines require quantitative description of the material properties and their variation during processing and in use. The morphology of materials seems now to be a key for understanding the material properties [1]. The main method of the morphology investigation is microscopy. Though techniques of the microscopic investigations are good elaborated, quantitative interpretation of microscopic images is still not a trivial procedure.

Morphology identification and consequent statistical analysis of the morphology entities with application of thermodynamics was shown to be a reliable tool for investigation of both chemical and physical processes in soft materials [2-8]. Following this way, thermally induced chemical transformations in polyamic acids [2-4] and the precursor curing to the rigid polymer [5] have successfully been studied. Such approach has also been applied to investigation of the phase transition and phase separation in liquid crystals [6-8].

Liquid crystals are the objects of significant interests, both theoretical and practical. Nowadays they are widely used in different technical devices as indicators,

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sensors, light modulators, etc. Technical application of *thermotropic* liquid crystals is based on their isotropic-ordered phase transitions; this is a reason why the ordered phase growth in liquid crystals across the isotropic-ordered phase transitions is an actual research task. In order to optimize technical characteristics of liquid crystals, their mixtures are often used.

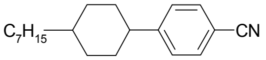
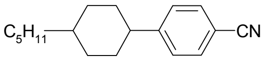
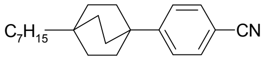
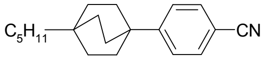
In this paper, we present the results of the kinetic investigation of the ordered phase growth in the melted mixture composed of liquid crystalline (LC) components subjected to a deep cooling.

Experimental

Sample

For our investigations, we chose an actual mixture composed of the LC components at the NIOPIK Scientific Production Association (Russia). This mixture is known to be suitable for technical exploitation within a temperature range from 0°C to 50°C. The chemical structures of the mixture components and their weights are given in Table 1.

Table 1: Chemical structures of the LC mixture components and their weigh factors.

Chemical structure	Weight factor
	30
	20
	30
	20

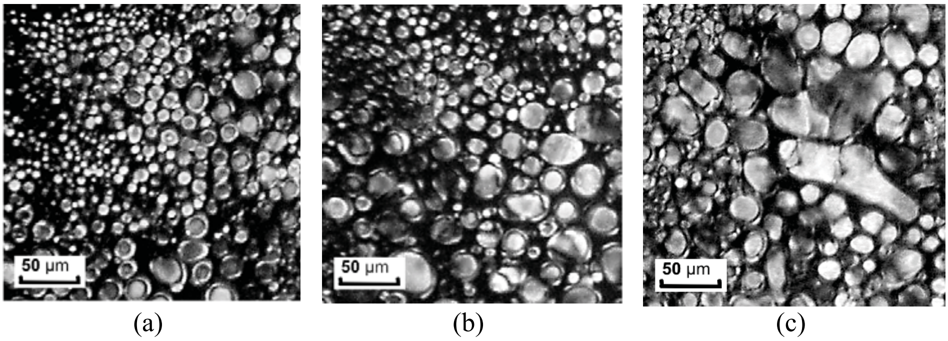
Method

As a method for investigation, we chose polarizing optical microscopy. We used a Boetius optical microscope (Germany) equipped with a THMS 600/HSF9I hot stage and a Hyper HAD SSC-DC38P digital camera (Japan) attached to the ocular. We placed the LC mixture onto a sandwich cell with a gap of 10 μm, heated at a rate of 10°C/min to the isotropic (melted) state (50°C), kept for 10 min, and then cooled at a rate of 1.3°C/min. Figure 1 shows representatively the optical images obtained across the phase separation of the LC mixture under study.

Microscopic Image Analysis

Recognition of Liquid Crystalline Nuclei

In the microscopic images, bright areas of a nearly circular form present the



(a) (b) (c)

Figure 1: Fragmentary microscopic images of the LC mixture across its phase transition from the isotropic state at (a) 2.7, (b) 3.3, and (c) 6 s after beginning of the phase separation.

ordered LC phase, whereas black background related to the isotropic phase. These images cannot be subjected immediately for image analysis; first, they should be segmented to elucidate objects of interests, i.e. LC nuclei.

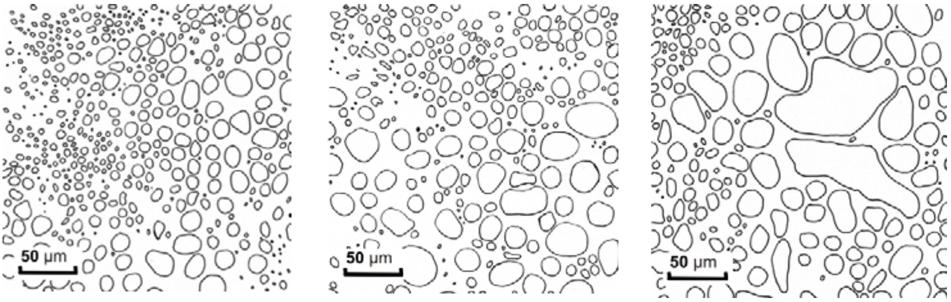
Image segmentation is one of the oldest and most difficult problems in the field of image processing and analysis, which includes sub-dividing an image into its non-overlapping objects of interests and their consequent extracting. A great variety of segmentation algorithms has been proposed in the last few decades; some of them are listed, e.g., in Refs. [1, 9, 10]. However, a unique general approach for segmentation now seems to be not available.

In the present work, the following procedures were used for segmentation: i) clustering to extract the objects of interests, ii) planar refinement to clarify the boundaries of the objects of interests, and iii) object separation to disaggregate both touching and clustered objects [10]. The result of segmentation is presented in Fig. 2.

After segmentation, the microscopic images were then subjected to digital image analysis with the ImageTool 3.0 software (Health Science Center, the University of Texas, San Antonio, USA) to elucidate the statistical size distribution of LC droplets. As a parameter for analysis, we used the droplet area. The result of statistical analysis of the LC droplet area is presented in Fig. 3.

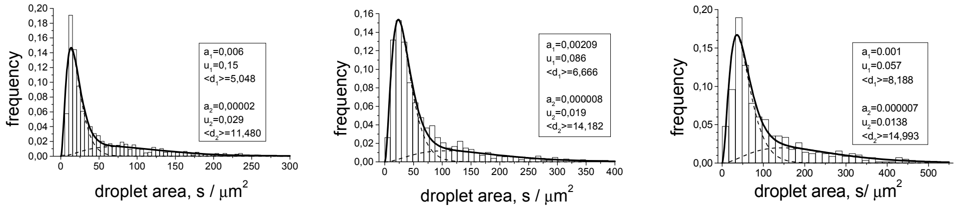
Statistical Size Distribution of Liquid Crystalline Nuclei

For analytical description of the statistical size distributions presented in Fig, 3, we used the model of reversible aggregation [4, 11]. Based on principles of irreversible thermodynamics, the model gives a generalized characterization of microstructure in liquids. In a 2D version of the model, the statistical distribution



(a) (b) (c)

Figure 2: Segmented microscopic images of the LC mixture across its phase transition from the isotropic state at (a) 2.7, (b) 3.3, and (c) 6 s after beginning of the phase separation.



(a) (b) (c)

Figure 3: Statistical size distributions of the LC mixture across its phase transition from the isotropic state at (a) 2.7, (b) 3.3, and (c) 6 s after beginning of the phase separation. Dashed lines show distributions of individual ensembles described with Eq. (1), whereas the solid lines relate to the overlapping distributions described with Eq. (2).

function $h(s)$ reads as follows

$$h(s) = as^2 \exp\left(-\frac{s\Delta u_0}{kT}\right), \tag{1}$$

where s is the characteristic aggregate size (we chose s as the droplet area), a is a normalizing parameter, Δu_0 is the aggregate energy, k is the Boltzmann constant, and T is the absolute temperature. Equation (1) can be treated as a canonical Gibbs distribution, known also as a Γ-function [12]. It has successfully been used for description of the statistical size distributions of the morphological entities in different systems [2-8, 11].

However, our attempt to describe histograms shown in Fig. 3 with Eq. (1) failed. That is why we used Eq. (1) in its poly-modal version

$$h(s) = \sum_{i=1}^{i=N} a_i s_i^2 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right), \tag{2}$$

where *i* accounts the number of statistical ensembles and *N* is their total number.

As we succeeded when used Eq. (2) with $i = 2$ and with the distribution parameters listed within the boxes, we can conclude that LC droplets form two overlapping statistical ensembles.

Equation (2) allows determination the mean droplet area $<s_i>$ related to the *i*-th statistical ensemble as a normalized mathematical expectation

$$< s_i >= \frac{\int\limits_0^\infty s_i h(s_i) ds_i}{\int\limits_0^\infty h(s_i) ds_i} = \frac{3kT}{\Delta u_{0i}} \tag{3}$$

The relation between linear and planar mean size (diameter and area, respectively) of droplets in the *i*-th ensemble is given by a simple geometrical regulation

$$< d_i >= 2\sqrt{\frac{< s_i >}{\pi}}. \tag{4}$$

Kinetics of the Liquid Crystalline Phase Growth

Using Eqs. (3) and (4), we computed the mean droplet diameter $<d>$ and plotted it as a function of time t for both statistical ensembles. The result of computation is presented in Fig. 4 where two regimes of LC droplets evolution can be recognized.

Within the first regime, $<d>$ increases rapidly and the number of droplets increases, whereas within the second regime, $<d>$ grows more slowly and the number of droplets decreases. Such behavior is typical for many LC systems [6-8]. The first regime is referred as a nucleation and nucleus growth, whereas the second regime is interpreted as a nucleus coarsening, i.e. Ostwald ripening [13].

For analytical description of the kinetic dependences presented in Fig. 4, we used the universal law for the cluster growth [13]

$$< d >= ct^n. \tag{5}$$

In order to find a value of the growth exponent n for both regimes, we plotted the data given in Fig. 5 in log-log coordinates and interpolated them linearly. These linear representations are shown in Fig. 5.

The n values obtained are shown within Fig. 5. They are in agreement with experimental results published previously [4-8]. According to the theoretical predictions, $n = 1$ within the first regime is explained by a difference in free energy of the ordered and isotropic state [13], whereas $n = 1/3$ within the second regime characterizes the diffusion mechanism of coarsening [14].

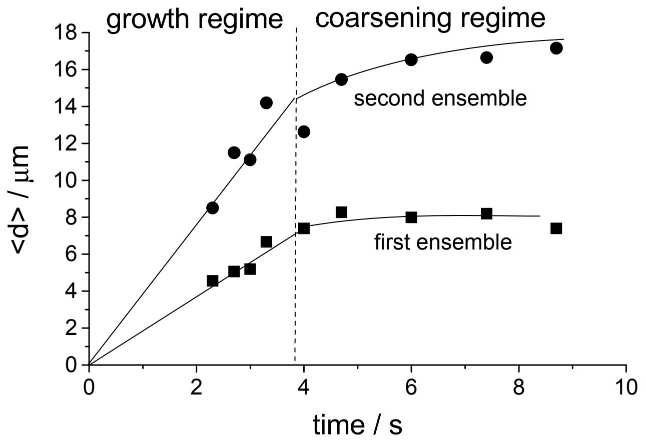


Figure 4: Time dependence of the mean droplet diameter of two statistical ensembles in the LC mixture across the isotropic-ordered phase transition.

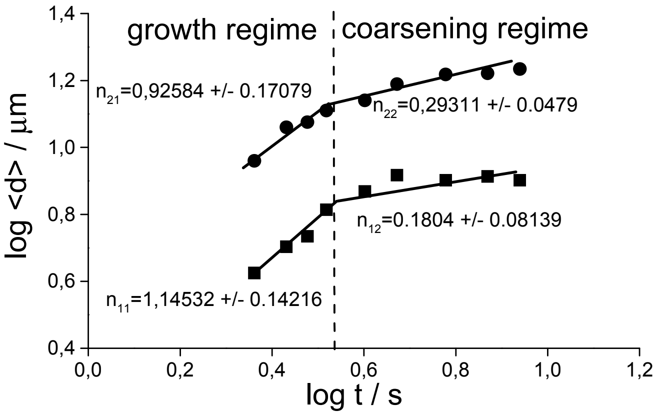


Figure 5: Log-log representation of the time dependence of the mean droplet diameter of two statistical ensembles in the LC mixture across the isotropic-ordered phase transition.

Conclusions

Kinetic investigations of the ordered phase growth in the multi-component LC mixture allowed us to conclude:

LC droplets that appear, grow, and ripen across the isotropic-ordered phase transition form two overlapping statistical ensembles related to two main components of the LC mixture. They were successfully described with principles of irreversible thermodynamics.

Two time regimes of the LC phase growth across the isotropic-ordered phase transition are recognized: first, generation and rapid nucleus growth and second, nucleus coarsening, i.e. Ostwald ripening. Both regimes are described with the universal law for the cluster growth.

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