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## Liquid Crystals

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### Self-assembling in a living supramolecular linear nematic polymer-like system

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## Self-assembling in a living supramolecular linear nematic polymer-like system

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Self-assembling in a linear supramolecular liquid crystalline (LC) polymer based on 4,4'-bipyridine and bis-(4-carboxyphenyloxycarbonyl)-heptanoate was studied by IR spectroscopy and optical microscopy. Although just a simple single hydrogen bond is required for the formation of a polymer chain, the reversibility of the hydrogen bonding forces the supramolecular macromolecule to behave under specific conditions similar to a mixture composed of two partly immiscible low molecular weight materials rather than as a polymer. An analytical description indicates that nematic droplets form two overlapping thermodynamically optimised statistical ensembles all across the phase transition in the linear supramolecular LC polymer studied. The kinetics of the nematic nucleus growth in the melted polymer was also studied. The number of generated nematic droplets oscillates with time. Two regimes of the growth kinetics were recognised: (i) nucleation and nucleus growth and (ii) nucleus coarsening, i.e. Ostwald ripening.

**Keywords:** self-assembling; liquid crystalline polymer; hydrogen bonding; nematic nucleus growth; growth kinetics

### 1. Introduction

Hydrogen (H-) bonding between dissimilar molecules is known to be a mechanism for the construction of both mesophases and supramolecular polymers (1). Thus, H-bonding between pyridine bases and carboxylic acids has been used for the formation of low molecular weight liquid crystals (2), side-chain liquid crystalline (LC) polymers (3–9) and main-chain LC polymers (10). Since H-bonding is weak compared with covalent bonding, the supramolecules formed by H-bonding rapidly break and recombine again at the melting temperature of a complex. This gives rise to questions about the nature of the LC state in supramolecular polymers. However, the self-assembling properties of main-chain LC polymers are difficult to observe because they are only apparent in the melt. In particular, solution light scattering and GPC techniques cannot be used to determine the molecular weight of supramolecular polymers. IR spectroscopy is the only method providing direct evidence of the process of association in supramolecular complexes (11).

At a macroscopic level, association of H-bonding complexes in a supramolecular polymer leads to the transformation of the isotropic liquid phase to the ordered LC phase. This allows the monitoring of such associations via a kinetic investigation of the LC phase formation. The kinetics of the isotropic-ordered phase growth has been carefully investigated for low molecular weight compounds (12–14), dimers

(15) and polymers (16, 17) although for supramolecular complexes such investigations have yet not to be reported. As recently reported (15–18), the statistical analysis of microscopic images obtained across the isotropic-ordered phase transition is a useful method to investigate kinetics. In this paper, we report such an investigation for a supramolecular mesogenic polymer.

### 2. Experimental

#### Materials

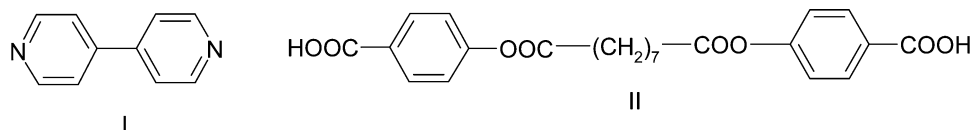
We investigated the formation of a main-chain supramolecular mesogenic polymer from two low molecular weight compounds, i.e. 4,4'-bipyridine (component I) and bis-(4-carboxyphenyloxycarbonyl)-heptanoate (component II), the structures of which are shown in Scheme 1.

Component I (Reachim, Russia, m.p. 108°C) was used as received, whereas component II (which does not melt before the onset of decomposition at 270°C) was synthesised as described elsewhere (19).

#### Supramolecular polymer preparation and LC phase formation

The equimolar mixture of the components I and II was dissolved in acetone. The solvent was removed on a rotary evaporator and the resulting solid dried in vacuo (0.1 mm Hg at 80°C) for two days. The mixture

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Scheme 1. Chemical structures of components I and II.

was then placed into a sandwich cell with a gap of  $10\ \mu\text{m}$  and quickly heated to  $200^\circ\text{C}$ . At this temperature under isothermal conditions, component I forms an isotropic melt, whereas component II slowly dissolves in this melt resulting in an isotropic mixture.

After ca. 1500 s, droplets of nematic phase (bright areas of a circular form, as shown in Figure 1(a)) appear; their number and size grow with time (Figure 1(b)). Finally, the thermodynamically favoured nematic phase is formed throughout (Figure 1(c)).

### Optical measurements

The phase separation and the nematic phase growth in the LC polymer synthesised were recorded using a digital camera attached to the ocular of a PHMK 05 polarising optical microscope equipped with a Boetius hot stage (Carl Zeiss Jena, GDR). The accuracy of the hot-stage temperature control was  $\pm 0.2^\circ\text{C}$ .

The optical images obtained were subjected to digital analysis using the ImageTool 3.0 software, from the Health Science Center, the University of Texas, San Antonio, USA, to elucidate statistical size distribution of nematic droplets.

### IR spectroscopy measurements

Temperature variable IR spectra were recorded using a Bruker IFS-88 instrument equipped with a home-made hot stage allowing temperature control to  $\pm 1^\circ\text{C}$ . The equimolar mixture of components I and II was placed into a KBr sandwich cell with a gap of  $10\ \mu\text{m}$ , quickly heated to  $200^\circ\text{C}$  and kept for 2 h. At this temperature, IR spectra were recorded every 20 min. Then the sample was cooled to room temperature and the IR spectrum was again recorded. A collection of the IR spectra obtained is shown in Figure 2.

## 3. Results and discussion

### IR spectroscopy data

As can be seen in Figure 2, at room temperature, when the system is in the crystalline state, weak absorption bands at  $\sim 1915\ \text{cm}^{-1}$  and those in the region  $2500\text{--}2600\ \text{cm}^{-1}$  corresponding to the heteromeric hydrogen-bonded OH groups are apparent (11, 20) (Figure 2, spectrum 1). This evidences low

complexation of the polymer at room temperature. The carbonyl groups have three absorption bands at  $1690$ ,  $1736$  and  $1758\ \text{cm}^{-1}$ . The first one is the most intense; it is connected with the formation of the carboxylic acid dimer.

After melting and annealing the system for 20 min at  $200^\circ\text{C}$ , the IR spectrum changes noticeably (Figure 2, spectrum 2). The intensities of the bands associated with the heteromeric hydrogen-bonded complex formation at  $\sim 1915$  and  $2500\text{--}2600\ \text{cm}^{-1}$  increase. Simultaneously, the intensity of the band at  $1690\ \text{cm}^{-1}$  decreases and redistributes to the band at  $1740\ \text{cm}^{-1}$  attributable for the free carbonyl groups. The presence of the free carbonyl groups supports the appearance of the intense band at  $3200\text{--}3500\ \text{cm}^{-1}$  connected with free OH groups. The carbonyl band is separated in to many bands, suggesting the existence of heteromeric H-bonded complexes with different levels of association.

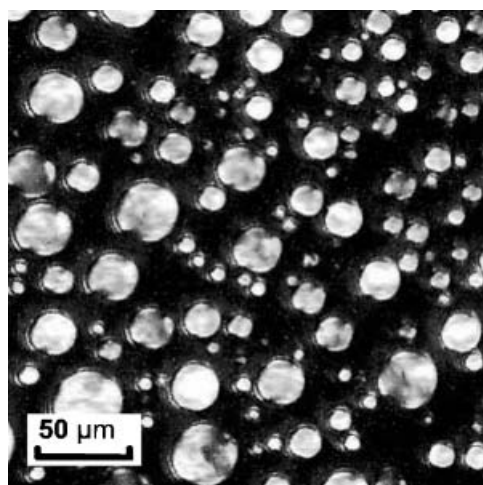
After crystallisation from the LC state and cooling to room temperature, the system did not return to its initial state. Although the free carbonyl groups disappear, a part of the carboxylic acid dimers also disappears (Figure 2, spectrum 3). Therefore crystallisation from the ordered LC state promotes conservation of the heteromeric H-bonded complexes and creates barriers to their redistribution with the resulting formation of carboxylic acid dimers.

The results presented show that even after complete transformation of the system under investigation to the mesophase, it can be treated as a mixture of the free pyridine bases, free carboxylic acids and heteromeric H-bonded complexes with different levels of association. As the H-bonding is rather weak, the molecules formed by H-bonding rapidly break and recombine at the melting temperature.

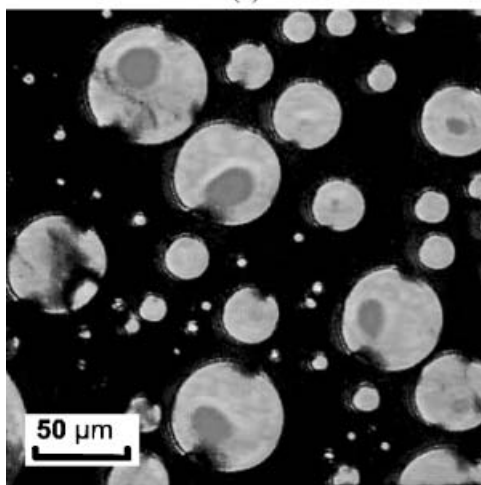
### Mechanism of ordered phase formation in LC polymers

Formation of the LC state in the system under investigation can be explained by the following qualitative mechanism for the ordered phase growth. Six specific stages are involved in the proposed mechanism:

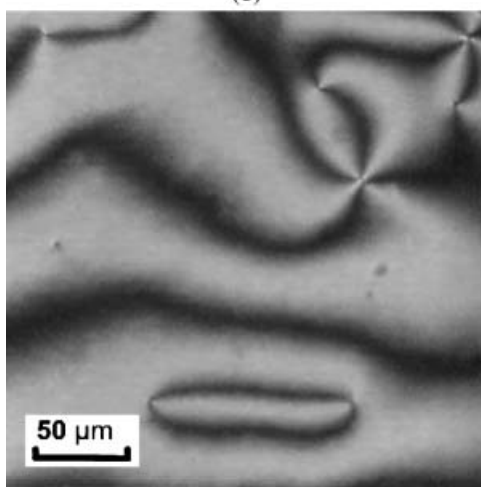
- (1) Interaction of components I and II generates a homogeneous distribution of heteromeric H-bonded complexes in the isotropic solution.



(a)



(b)



(c)

Figure 1. Fragmentary microscopic images of the supramolecular polymer across its phase transition from the isotropic state under isothermal condition at 200°C: (a) at 1760 s, (b) at 4690 s, and (c) 9680 s after beginning of cooling.

- (2) This solution becomes progressively more supersaturated with heteromeric H-bonded complexes but remains metastable until it

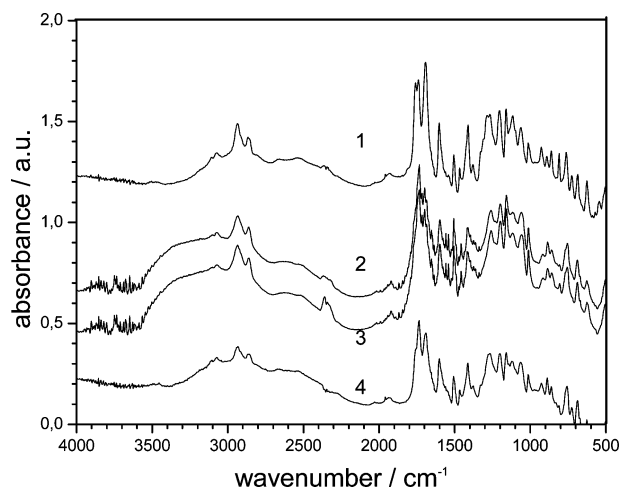


Figure 2. IR spectra of supramolecular system under investigation for initial mixture of components (1); during heating at 200°C after 20 min (2) and 2 h (3); after cooling to room temperature (4).

achieves a critical concentration of complexes and polymers with varying of degree of polymerisation at which point spontaneous nucleation of LC phase starts abruptly.

- (3) The initial growth of small droplets of the LC phase has little impact on the solution, and there is period of time during which dissolved heteromeric H-bonded complexes are still being formed faster than they are being removed by the growing droplets. During this period, a large reservoir of LC phase nuclei is formed.
- (4) Once coalescence of droplets begins, dissolved heteromeric H-bonded complexes are depleted more rapidly than they can be produced. Nucleation is no longer possible, and the smaller droplets redissolve.
- (5) When the droplets growth has almost stopped, the number of droplets decreases because of the coalescence of the droplets. The degree of polymerisation of the LC H-bonded polymer (in nematic droplets) increases because the internal LC order of droplets favours polymerisation. The process then self-repeats.
- (6) After a time, due to the large volume of LC phase, the process of nucleation and new droplet formation slows down but does not stop as long as isotropic phase is still present.

We should emphasise that the first five stages of the mechanism discussed are similar to the oscillatory gas evolution produced in a chemical reaction (see, for example, Morgan reaction, i.e. formic acid dehydration) (21). The number of the ordered phase

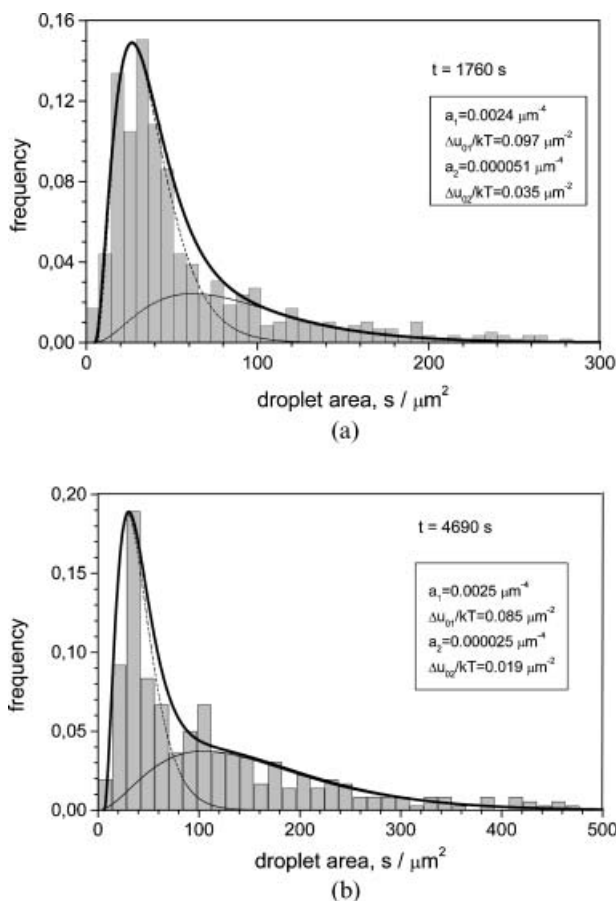


Figure 3. Frequency distribution of the nematic droplet area for the images depicted in Figures 1(a) and 1(b), and their description using Equation (2) with the fitting parameters given within the boxes.

droplets was investigated as a function of time (Figure 3). The number of droplets is seen to oscillate during the ordered phase formation while as a general trend we find a steady decrease in the number.

### Kinetic investigation

The kinetics of nematic droplet growth across the isotropic-ordered phase transition at 200°C was studied for clarification of the nature of the mesophase in the linear supramolecular LC polymer. Representative histograms from the digital statistical analysis of the optical images (some examples are shown in Figure 1) are shown in Figure 4.

In these histograms, two overlapping statistical ensembles of nematic droplet sizes can be recognised. We attribute the smaller droplets to low molecular weight components, whereas we believe the larger ones are related to the supramolecular polymer. For an analytical description of the histograms obtained, we used the model of reversible aggregation.

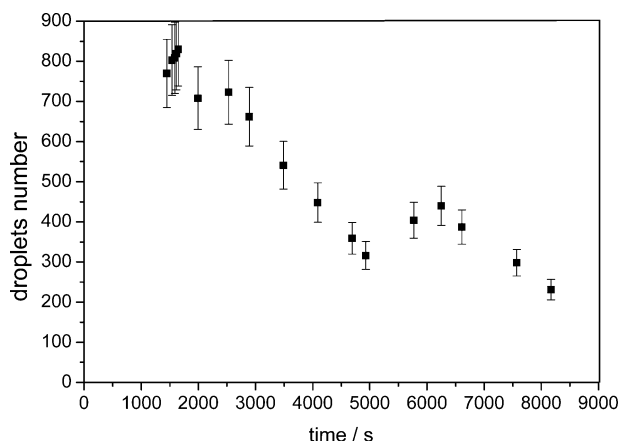


Figure 4. Time dependence of the droplet number across the isotropic-nematic phase transition in the supramolecular polymer.

### Model

The model of reversible aggregation (22, 23) allows a generalised characterisation of microstructure in liquid systems. According to this model, stationary microstructures are created and develop by linking smaller units together to form metastable clusters, the aggregates. Under thermal fluctuations the aggregates are dynamically formed and decomposed; this is a condition of their reversibility.

Following the model, the stationary statistical distribution  $h(s)$  of the planar size  $s$  of the microstructural entities is (22, 23)

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

where  $a$  is a normalising factor,  $\Delta u_0$  is the aggregate energy,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $kT$  is the energy of thermal fluctuation.

In some cases (18, 24), aggregates form not single but rather multiple statistical ensembles. This may be caused either by consolidation of primary clusters into new superstructures (e.g. coarsening) or by the presence of different components in a multi-component system. For this reason, a minimum (embryonic) aggregate size  $s_0$  should be introduced; it may be treated as the size of the smallest primary unit in an aggregate. Therefore, the parameter  $s$  in Equation (1) has to be substituted by  $(s-s_0)$ .

Taking this into account, Equation (1), which is to be applied to the LC droplet growth, becomes

$$h(s-s_0) = \sum_{i=1}^N a_i (s_i - s_{0i})^2 \exp\left(-\frac{(s_i - s_{0i})\Delta u_{0i}}{kT}\right), \quad (2)$$

where  $N$  accounts for the number of statistical ensembles of droplets and  $s_{0i}$  is the area of the  $i$ th

embryonic droplet. The mean droplet area  $\langle s_i \rangle$  in the  $i$ th statistical ensemble can now be estimated as a normalised expectation value:

$$\begin{aligned} \langle s_i \rangle &= s_{0i} + \frac{\int_{s_i=s_{0i}}^{\infty} (s_i - s_{0i})^3 \exp\left(-\frac{(s_i - s_{0i})\Delta u_{0i}}{kT}\right) ds_i}{\int_{s_i=s_{0i}}^{\infty} (s_i - s_{0i})^2 \exp\left(-\frac{(s_i - s_{0i})\Delta u_{0i}}{kT}\right) ds_i} \\ &= s_{0i} + \frac{3kT}{\Delta u_{0i}} \end{aligned} \quad (3)$$

The relation between linear (diameter  $\langle d_i \rangle$ ) and planar (area  $\langle s_i \rangle$ ) mean size of droplets in the  $i$ th ensemble is then given by a simple geometrical relation:

$$\langle d_i \rangle = 2 \left( \frac{\langle s_i \rangle + s_{0i}}{\pi} \right)^{\frac{1}{2}}. \quad (4)$$

#### Kinetics of the phase transition

Figure 4 shows the results of the histogram description using Equation (2) with the fitting parameters listed inside the boxes. Successful analytical description indicates that nematic droplets form two overlapping thermodynamically optimised statistical ensembles all across the phase transition in the linear supramolecular LC polymer samples studied. We interpret the existence of two statistical ensembles as a result of progressive generation of LC H-bonded complexes with saturation–nucleation cycles and independent evolution of nematic droplets.

Using Equations (3) and (4), the mean diameter of the nematic droplets in both statistical ensembles can be computed as a function of time. The resulting plot is shown in Figure 5.

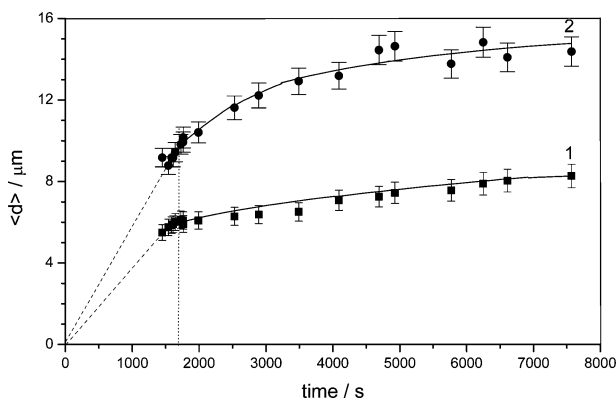


Figure 5. Time dependence of the mean droplet diameter across the isotropic–nematic phase transition in the supramolecular polymer. 1 denotes the first statistical ensembles, whereas 2 denotes the second one (see Figure 3).

In Figure 5, two regimes of the ordered phase droplet evolution can be recognised. The first regime ( $0 < t < 2500$  s) is characterised by intensive nucleation and rapid droplet growth. We could not analyse the size of nematic droplets in both statistical ensembles at the beginning of the ordered phase growth because of the low resolution of the optical images; we could catch only a tail of the growing regime. Above 2500 s, the volume fraction of the nematic phase increases because of the nuclei coarsening; the growth rate decreases; the number of droplets also decreases. The ultimate coarsening regime is reached after about  $10^4$  s (see Figure 1(c)).

For an analytical description of the nucleus growth with  $t$ , we used the scaling function (25)

$$\langle d \rangle = ct^n, \quad (5)$$

which was derived for phase-ordering kinetics in systems subjected to a temperature quench. Yet, we postulate, it also could be suitable for the ordered phase evolution in a supramolecular mesogenic polymer under isothermal conditions. In this case, the driving force should be a chemical reaction related to the reversibility of the H-bonding process and the associated formation and destruction of mesogenic units. This driving force is, of course, much lower in a kinetic sense than the temperature gradient. That is why the duration of the system transformation to the ordered state (above  $10^3$  s) is much larger compared with results obtained from a temperature quench (usually  $1-10^2$  s).

In order to find a value of the growth exponent  $n$  in Equation (5), we plotted experimental data presented in Figure 5 in logarithmic coordinates (see Figure 6). We have a lack of experimental data within the nucleus growth regime. However, linear interpolation in log–log scales allowed the conclusion

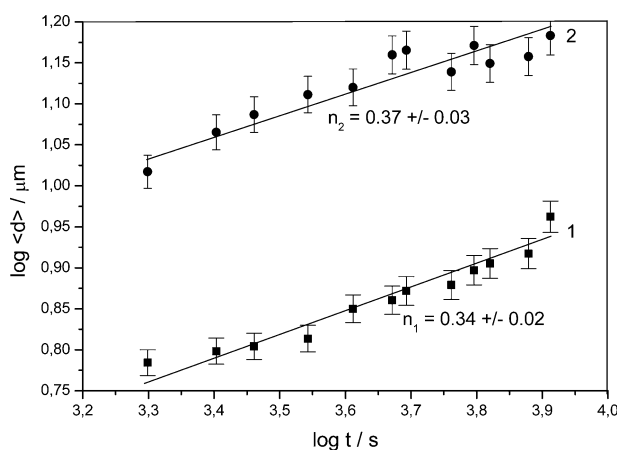


Figure 6. Log–log representation of the data given in Figure 5.

that within the coarsening regime,  $n_1 \approx 0.34$  and  $n_2 \approx 0.37$ . According to the theoretical predictions (26),  $n=1/3$  is a characteristic value for a phase separation of two partly immiscible liquids. Hence, the system under investigation should be treated as a dynamic mixture of low molecular weight and polymer-like H-bonded complexes; due to rapid breaking and recombination of polymer chains, its behaviour is similar to that of a binary mixture of two partly immiscible liquids.

#### 4. Conclusions

In this work, we synthesised a linear supramolecular LC polymer based on hydrogen-bonded pyridyl and carboxylic acid fragments. Because of reversibility of the hydrogen bonding the complex studied behaves like a mixture of two partly immiscible low molecular weight compounds rather than a polymer. We investigated kinetics of the nematic phase growth in the melted complex. Across the isotropic-ordered phase transition, two statistical ensembles of the ordered (nematic) phase could be recognised. Interpretation of our observations as progressively generation of LC H-bonded complexes with the saturation-nucleation cycles and independent evolution of the nematic droplets explains the existence of two statistical ensembles and leads to what we now consider to be a satisfactory qualitative explanation of the phase formation kinetics in a supramolecular system. The number of generated nematic droplets oscillates with time because of repetitive release of supersaturation of isotropic liquid by LC H-bonded complexes and its homogeneous nucleation in LC phase.

Two regimes of the ordered phase growth were found: nucleus growth and nucleus coarsening, i.e. Ostwald ripening. Both regimes were described using the universal law of the cluster growth with the growth exponent equal to about 1/3 for the coarsening regime; this value is known to be typical for phase separation of two partly immiscible liquids.

#### Acknowledgement

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