

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

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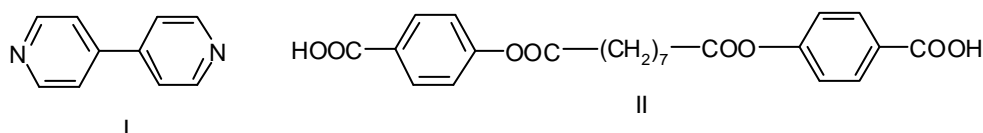
The hydrogen (H-) bonding between dissimilar molecules is known to be a mechanism for construction of both mesophase and supramolecular polymers [1]. As H-bonding is weak (compared with the covalent bonding), the molecules formed by the H-bonding rapidly break and recombine again at the melting temperature of a complex. Nowadays a question about the nature of the LC state in supramolecular polymers arises. Yet, the properties of self-assembling main chain LC polymers are difficult for observation because they can be revealed only in the melt. Particularly, neither solution light scattering nor GPC techniques cannot be used for determination of the molecular weight of supramolecular polymers. We guess, IR spectroscopy is the only method providing a direct evidence of the process of association in supramolecular complexes [2].

In a macroscopic level, association of H-bonding complexes in a supramolecular polymer leads to transformation of the isotropic liquid phase to the ordered LC phase. It allows monitoring such kind of associations using kinetic investigation of the LC phase formation. According to our recent publications [3-6], statistical analysis of the microscopic images obtained across the isotropic-ordered phase transition is a productive way for kinetic investigation. In the present study, we follow this way. Analysis of the kinetic study allowed us to draw a conclusion on molecular nature of the mesophase in the LC supramolecular polymer synthesized.

### 2.Experimental

#### 2.1.Materials

We investigated formation of a main chain supramolecular mesogen polymer from two low molecular weight compounds: 4,4'-bipyridine (component I) and bis-(4-carboxyphenyloxycarbonyl)-heptanoate (component II). Their chemical structures are given below.



Component I (Reachim, Russia, m.p. 108°C) was used as received, whereas component II (not fusible before degradation at 270°C) was synthesized as described in Ref. [7].

## 2.2. *Supramolecular polymer preparation and LC phase formation*

The equimolar mixture of the components I and II was dissolved in acetone. The solution was steamed on rotation evaporator and dried in vacuum 0.1 mm Hg at 80°C for 2 days. The mixture was then placed into a sandwich cell with a gap of 10  $\mu\text{m}$  and quickly heated to 200°C. At this temperature, the component I transits to the isotropic melt, whereas the component II slowly dissolves in this melt resulting in an isotropic liquid.

After ca. 1500 s, droplets of nematic phase (bright areas of a circular form 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)).

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## 2.3. *Optical measurements*

The phase separation and the nematic phase growth in the LC polymer synthesized were registered using a digital camera attached to the ocular of a Boetius polarizing optical microscope with a hot stage (Carl Zeiss Jena, GDR).

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

## 2.4. *IR spectroscopy measurements*

Temperature variable IR spectra were recorded using a Bruker IFS-88 instrument equipped with a home-made hot stage controlling temperature as precise as  $\pm 1^\circ\text{C}$ . The equimolar mixture of the components I and II was placed into a KBr sandwich cell from with a gap of 10  $\mu\text{m}$ , quickly heated up to 200°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 IR spectrum was recorded again. Collection of the IR spectra is given in figure 2.

## 3. Results and discussion

### 3.1. *IR spectroscopy data*

As follows from 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 recognized [2, 8] (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 intensive; it is connected with formation of the carboxylic acid dimer.

After melting and tempering the system investigated for 20 min at 200°C, its IR spectrum noticeably changes (spectrum 2). Intensity of the bands responsible for the heteromeric hydrogen-bonded complex formation at  $\sim 1915$  and  $2500\text{-}2600\text{ cm}^{-1}$  increases. Simultaneously, 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. Presence of the free hydrogen-nonbonded carbonyl groups supports appearance of the intensive band at  $3200\text{-}3500\text{ cm}^{-1}$  connected with free OH groups. The carbonyl band is separated in many bands, suggesting existence of heteromeric H-bonded complexes with different level of association.

After crystallization from the LC state and cooling to room temperature, the system did not return to its initial state. Although the free hydrogen-nonbonded carbonyl groups disappear, a part of the carboxylic acid dimers disappear too (spectrum 3). Therefore crystallization from the ordered LC state promotes conservation of the heteromeric H-bonded complexes and creates impediments for their redistribution with formation of the carboxylic acid dimers.

The results presented above 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 level of association. As the H-bonding is weak enough, the molecules formed by H-bonding rapidly break and recombine at the melting temperature.

### *3.2. Mechanism of ordered phase formation in LC polymers*

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

- (1) Interaction of components I and II generates a smooth input of heteromeric H-bonded complexes to the homogeneous isotropic solution.
- (2) This solution becomes progressively more supersaturated but remains metastable until it achieves a critical concentration at which spontaneous nucleation of LC phase begins almost discontinuously.
- (3) The initial growth of small droplets of the LC phase has a little impact on the solution, and there is period of time during which dissolved heteromeric H-bonded complexes is still being formed faster than it is 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 complex is depleted more rapidly than it can be produced by chemical reaction. 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 droplets coalescences. The process then self-repeats.
- (6) After a time as a result of volume portion growth of LC phase the process

of nucleation and new droplets formation slow down but did not stopped quite as long as exist a isotropic phase. It is fundamental difference with LC phase formation from isotropic melt of LC compounds at temperature quench.

We should emphasize that five first 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) [9]. We investigated number of the ordered phase droplets as a function of time (figure 3). The droplets number is seen to oscillate during the ordered phase formation with intensity decreasing with time. These oscillations are caused by repetitive release of supersaturation by homogeneous nucleation.

### 3.3. Kinetic investigation

Kinetics of the nematic droplets growth across the isotropic-ordered phase transition at 200°C was studied for clarification of the nature of mesophase in the linear supramolecular LC polymer. The result of digital statistical analysis of the optical images (their fragments are presented in figure 1) is representatively given in the histograms depicted in figure 4.

In the histograms presented, two overlapping statistical ensembles of nematic germs can be recognized. The germs of smaller size are attributed to the low molecular weight components, whereas the germs of larger size are related to the supramolecular polymer.

For analytical description of the histograms obtained, we used the model of reversible aggregation.

#### 3.3.1. Model

The model of reversible aggregation [10, 11] allows a generalized characterization of micro-structure in liquid systems. According to this model, stationary micro-structures are created and develop by linking energy-equivalent units in metastable clusters called the aggregates. Under thermal fluctuations the aggregates are permanently formed and decomposed; this is a condition of their reversibility. The stationary properties of the system are rapidly optimized via self-organization and any structural transformations are to run through sequences of nearly optimized stationary non-equilibrium states.

Following the model, the stationary statistical distribution  $h(s)$  of the planar size  $s$  of the micro-structural entities reads as follows [10, 11]

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

where  $a$  is 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 [6, 11a], aggregates form not a single, but rather multiple statistical ensembles. This may be caused by either consolidation of primary clusters into new superstructures (e.g., coarsening) or by the presence of different kinds of the components in a multi-component system. Besides, a

minimum (embryonic) aggregate size  $s_0$  often to be taken into account; it may be treated as a size of the smallest primary unit in an aggregate. Therefore the parameter  $s$  in Eq. (1) has to be substituted by  $(s-s_0)$ .

By taking these comments into account, Eq. (3), being applied to the LC droplets 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 could now be estimated as a normalised mathematical expectation:

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

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 regulation:

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

### 3.3.2. Kinetic of the phase transition

Fig. 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 optimized statistical ensembles all across the phase transition in the linear supramolecular LC polymer studied. We interpret 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 resulted plot is shown in figure 5.

In figure 5, two regimes of the ordered phase germs evolution can be recognized. The first regime ( $0 < t < 2500$  s) is characterized by intensive nucleation and rapid droplets growth. Because of low resolution of the optical images, we could not analyze the size of nematic germs in both statistical ensembles at the beginning of the ordered phase growth; 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 deceases; the number of droplets decreases too. The ultimate coarsening

regime is reached at about  $10^3$  s when only one cluster remains in equilibrium with the isotropic phase (see figure 1 (c)).

For analytical description of the nucleus growth, we used the universal law of the cluster growth in the form of scaling function [12]

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

This equation was basically derived for the phase ordering kinetics in the systems subjected to a temperature quench. Yet, we guess, it also could be suitable for the ordered phase evolution in a supramolecular mesogen polymer at isothermal regime. In this case, the driving force should be a chemical reaction resulted to reversibility of the H-bonding complexes and, therefore, formation and destruction of mesogenic units. This force is, of course, much lower and more complex in kinetic sense than the temperature gradient. That is why duration of the system transformation to the ordered state (above  $10^3$  s) is too large as compared with that under 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 conclusion that within the coarsening regime,  $n_1 = 0.34$  and  $n_2 = 0.37$ . According to the theoretical predictions [13],  $n = 1/3$  is a characteristic value for a phase separation of two partly immiscible liquids. Hence the system under investigation can rather be treated as a dynamic mixture of the H-bonded both low molecular weight and polymer-like complexes; due to rapid breaking and recombination of polymer chains its behaviour is similar to that for a binary mixture of two partly immiscible liquids.

#### 4. Conclusions

In this work, we synthesized a linear supramolecular LC polymer based on the hydrogen-bonded pyridyl and carboxylic acid. 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. This peculiarity also becomes apparent when 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 recognized. 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 existence of two statistical ensembles and leads to what we now consider to be a satisfactory qualitative explanation of the phase formation kinetic in 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 and 1/3 respectively. The last is known to be a typical value for phase separation of two partly immiscible liquids.

#### References

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#### Figures

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

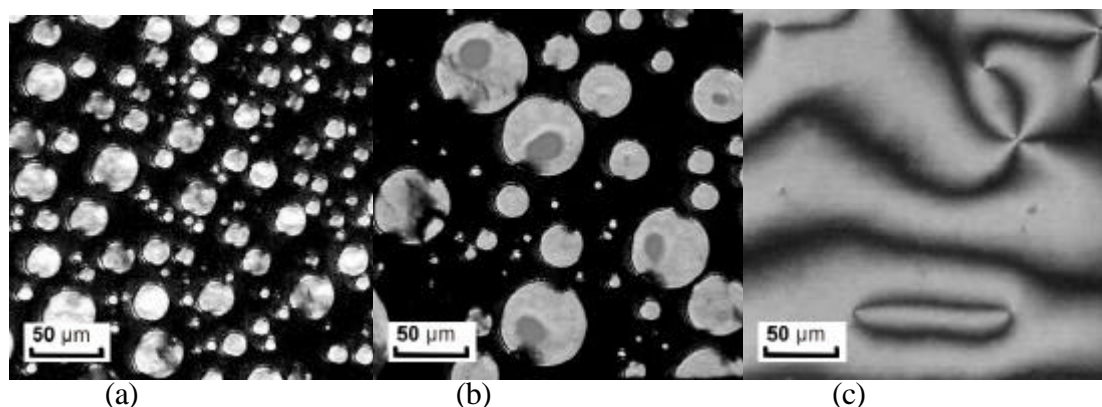


Fig. 2 IR spectra of supramolecular system under investigation for initial mixture of components (1); during heating at 200°C after 20 min (2), and 2 h (3); after cooling to room temperature (4).

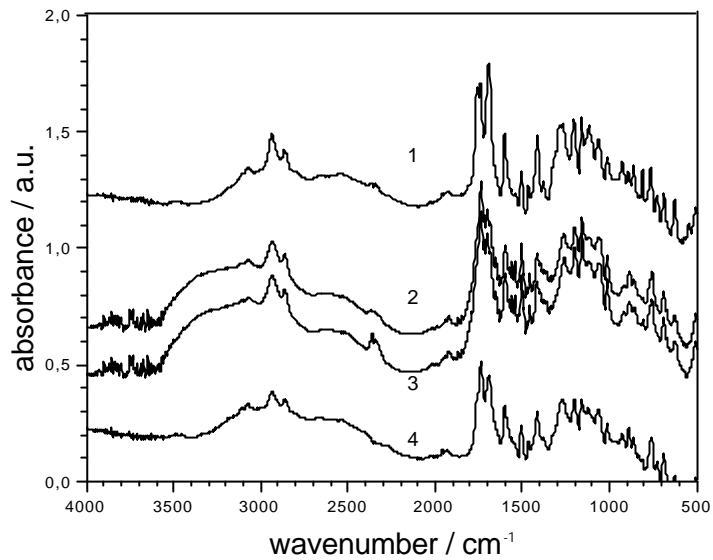


Fig. 3 Time dependence of the droplet number across the isotropic-nematic phase transition in the supramolecular polymer.

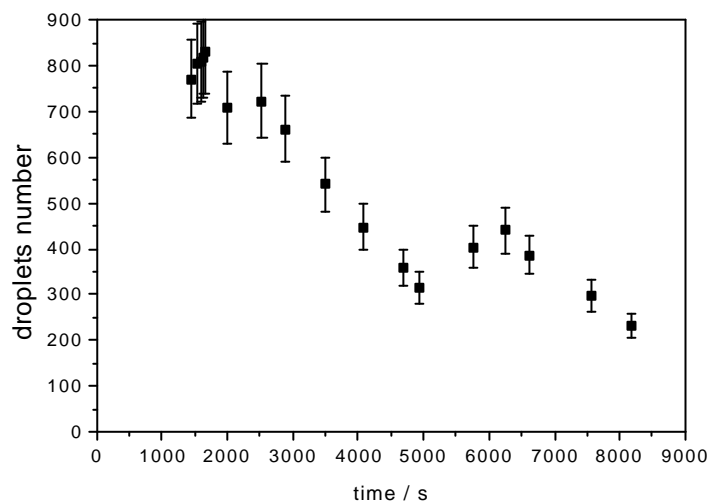
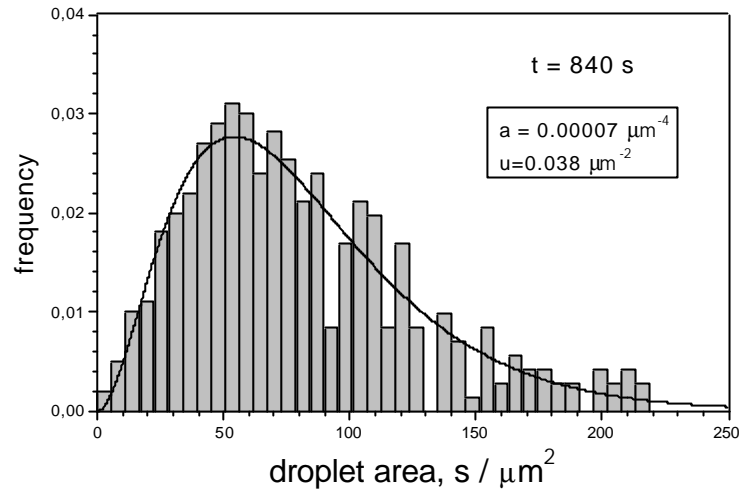
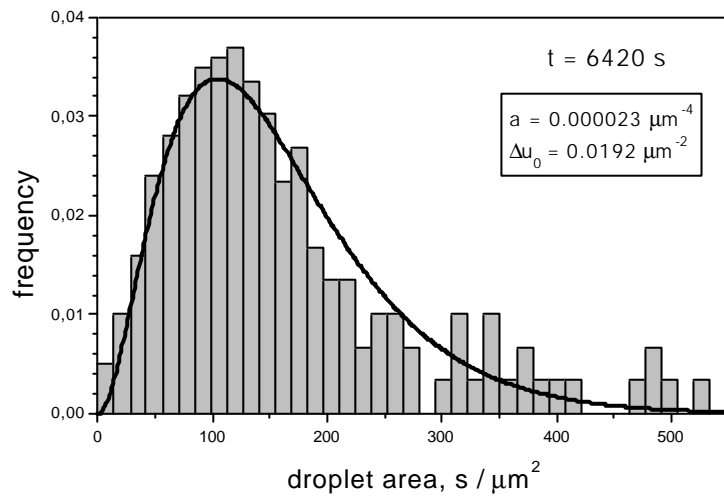




Fig. 4 Frequency distribution of the nematic droplet area for the images depicted in Fig. 1, a and b, and their description using Eq. (2) with the fitting parameters given within the boxes.



(a)



(b)

Fig. 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 Fig. 4).

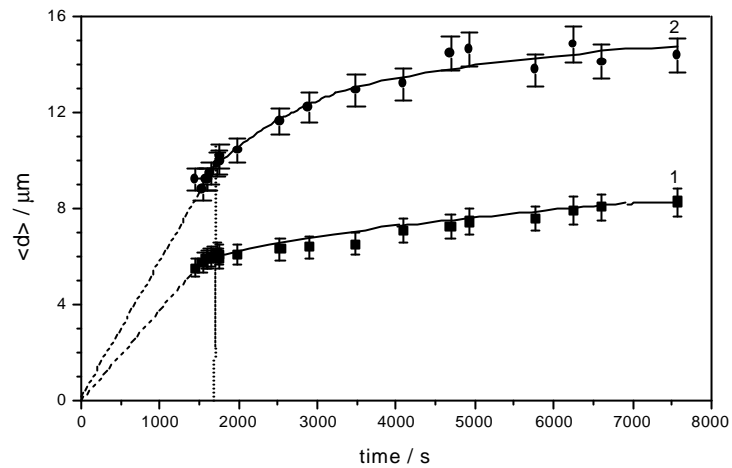


Fig. 6 Log-log representation of the data given in Fig. 5.

