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Kinetics of the nematic ordered phase growth during a temperature quench of an isotropic siloxane-azomethine polymer

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Kinetics of the nucleus growth during a deep temperature quench across the isotropic to nematic phase transition was experimentally investigated for a siloxane-azomethine polyether at cooling rates of 10 and 20°C min^{-1}. Nematic droplets revealed in the optical images during the phase separation were treated statistically and the resulting statistical size distributions were described using the model of reversible aggregation. Analysis of the time-dependent distribution parameters allowed two processes involved in liquid crystal phase ordering to be identified: nucleus growth and nucleus coarsening. Both regimes are quantitatively described using the universal growth law.

1. Introduction

Phase ordering in liquid crystal polymers is a process of significant interest, both theoretical and practical, especially in comparison with solids, fluids and other types of liquid crystal systems [1, 2]. When an isotropic liquid crystal system is quenched across a phase transition, its homogeneous phase converts to the ordered low temperature phase. In this metastable state, nuclei of the thermodynamically favoured phase appear spontaneously and subsequently grow. The phase ordering is known to be described by the universal growth law: $L(t) \sim t^n$ where L is the characteristic size of an ordered phase element, t is the time and n is a power index [2]. According to the theory [3], for systems with a non-conserved order parameter, including liquid crystals, $n=0.5$ is expected at a small quench depth, whereas for a deep quench depth n has been shown to tend towards 1 ($n \rightarrow 1$) [4, 5]. These features have been verified and confirmed experimentally for different liquid crystal systems by Dierking [6–8], although for liquid crystal polymers such verification is still not established except in one case only [9].

To fill this gap, we present here the results of an experimental study of the growth of nematic droplets during a deep temperature quench of a melted siloxane-azomethine liquid crystal polymer, i.e. during its transition from isotropic to ordered (nematic) state.

The conjugated aromatic poly(azomethines) are known to be thermally stable film- and fibre-forming materials exhibiting good mechanical properties, high chemical resistance and either thermotropic or lyotropic liquid crystalline behaviour [10–13]. They have been investigated for their potential application in electronics, opto-electronics and nonlinear optics [14, 15].

Since aromatic polyazomethines are generally insoluble or infusible, they are difficult both to characterize and process. A way to improve their processibility is the introduction of siloxane spacers. Such siloxane-azomethine polymers as well as their metal complexes have been synthesized and characterized [16–20]. The thermotropic liquid crystalline behaviour of siloxane-azomethine dimers, polyesters and polyethers has already been investigated [21–23]. In this study we concentrate attention on the nematic phase evolution with time during a deep temperature quench of the isotropic melted siloxane-azomethine polyether.

Despite the successful description of the liquid crystalline nucleus evolution by the universal growth law, little attention still has been given to the actual size distribution of liquid crystalline nuclei. In the present work we analyse statistically the size of nematic nuclei in the optical images and describe the resulting statistical size distributions using the model of reversible aggregation.

2. Experimental

The chemical structure of the siloxane-azomethine polyether under investigation is presented in figure 1. This polymer was obtained by polycondensation of

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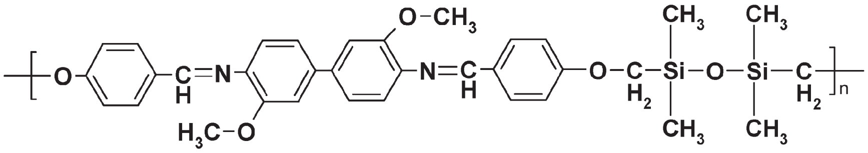
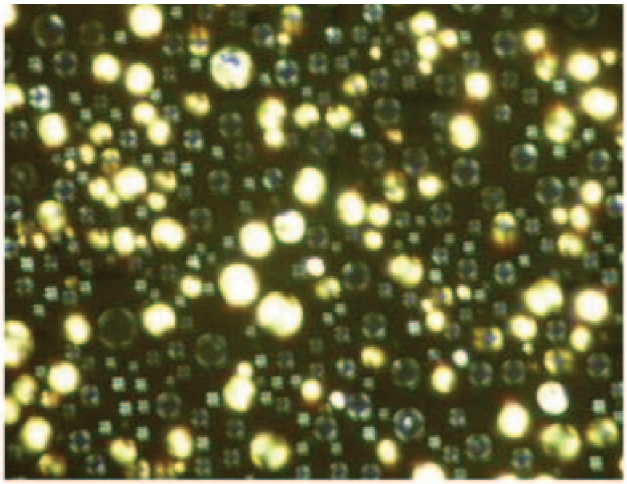


Figure 1. Chemical structure of the siloxane-azomethine polyether.

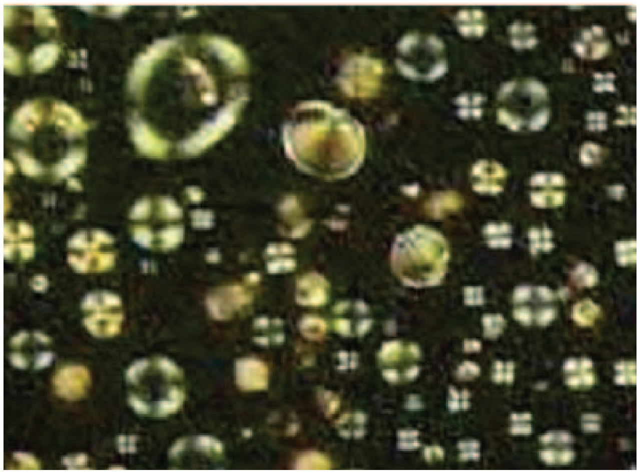
bis(chloromethyl)disiloxane and an OH-terminated azomethine macromer derived from *p*-hydroxybenzaldehyde and *o*-dianisidine [20]. Its thermotropic liquid crystalline behaviour has already been described and discussed in comparison with other siloxane-azomethine compounds. The following phase transition temperatures have been determined: Cr.–Sm 141°C; Sm–N 165°C; N–I starting point at about 200°C [23].

The mesophase texture was observed using an Olympus BH-2 polarizing light microscope fitted with a THMS 600/HSF9I hot stage and a digital camera attached to the ocular. In the present study, the samples were placed in a sandwich cell with a gap of 10 µm, heated at a rate of 20°C min^{-1} to the isotropic state (206°C), held for 10 min and then cooled at a rate of either 10 or 20°C min^{-1}.

Typical texture images observed during the phase ordering of the liquid crystal polyether studied are presented in figure 2. The optical images were subsequently segmented and subjected to digital image analysis with the ImageTool 3 software (Health Science Center, the University of Texas, San Antonio, TX, USA) to elucidate the statistical size distribution of nematic droplets. The number of nuclei amounted to approximately 250 entities, ensuring good statistical representation.



(*a*)



(*b*)

Figure 2. Fragmentary polarizing microscopy images of the siloxan-azomethine polyether during its phase ordering from the isotropic state: (*a*) at 116 s after beginning of the phase separation at a cooling rate of 10°C min^{-1}, and (*b*) at 60 s after beginning of the phase separation at a cooling rate of 20°C min^{-1}. The individual image size is $360 \times 270\,\mu m^2$.

3. Model

The statistical size distribution of the ordered phase observed in the optical images during the phase transition was analysed using the model of reversible aggregation [24–26]. Inspired by the application of irreversible thermodynamics, it gives a general characterization of micro-structures in different systems. According to the model, stationary non-equilibrium structures are created by linking the energy-equivalent dynamic units in metastable clusters called aggregates. In the liquid state they are densely packed and characterized by a definite lifetime, i.e. they are continually formed and decomposed; this is a condition of reversibility. The configuration of aggregate ensembles continuously fluctuates under thermal fluctuations and a momentary image demonstrates one of many possible, thermodynamically equivalent, configurations in the liquid state.

In the model, the statistical distribution function $h(y)$ was derived in the form [24–26]

$$h(y) = ay^p \exp\left(-\frac{\Delta u}{kT}\right) \tag{1}$$

where y is the aggregate size, a is a normalizing parameter, p relates to the dimension D of space where aggregation occurs, $\Delta u = y\Delta u_0$ is the aggregate energy defined as the standard aggregate energy per unit, Δu_0, multiplied by the aggregate size y; k is the Boltzmann constant and T is the absolute temperature. Equation (1) can be interpreted as a kind of Gibbs distribution [27]; it is also known as a γ-distribution [27].

Because of its general thermodynamic character, equation (1) has already been applied to different systems [24–26]. A first attempt to describe statistical size distribution of the ordered phase entities in liquid crystal systems using the model of reversible aggregation had previously been made [28]. Later the model was successfully applied in analysis of the nucleus growth in the liquid crystalline mixture during its phase transition [29, 30].

We analyse here the liquid crystal polymer under planar boundary condition. For this reason, equation (1) should be employed in its 2D form, i.e. p should be equal to 2 ($p=2$) and the aggregate size y should be replaced by the droplet area s. Under such conditions, equation (1) reads as follows:

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

A statistical distribution is characterized by the normalized mathematical expectation $\mathbf{M}s$, which is, in fact, the mean droplet area $<s>$

$$\mathbf{M}s = \langle s\rangle = \frac{\int_0^\infty sh(s)\mathrm{d}s}{\int_0^\infty h(s)\mathrm{d}s} = \frac{3kT}{\Delta u_0}. \tag{3}$$

A relation between linear and planar mean size (diameter $<L>$ and area $<s>$, respectively) of droplets is given by the geometrical relationship:

$$\langle L\rangle = 2\left(\frac{\langle s\rangle}{\pi}\right)^{\frac{1}{2}}. \tag{4}$$

4. Results and discussion

Figure 3 shows selectively the results of the statistical treatment of the optical micrographs (see figure 2) related to both cooling rates (10 and 20°C min^{-1}) in the form of histograms. As seen from figure 3, the histograms are successfully described by equation (2) with the fitting parameters, a and $\Delta u_0/kT$, listed inside the boxes in figure 3. This evidently indicates that the liquid crystalline droplets form thermodynamically optimized ensembles during the phase ordering.

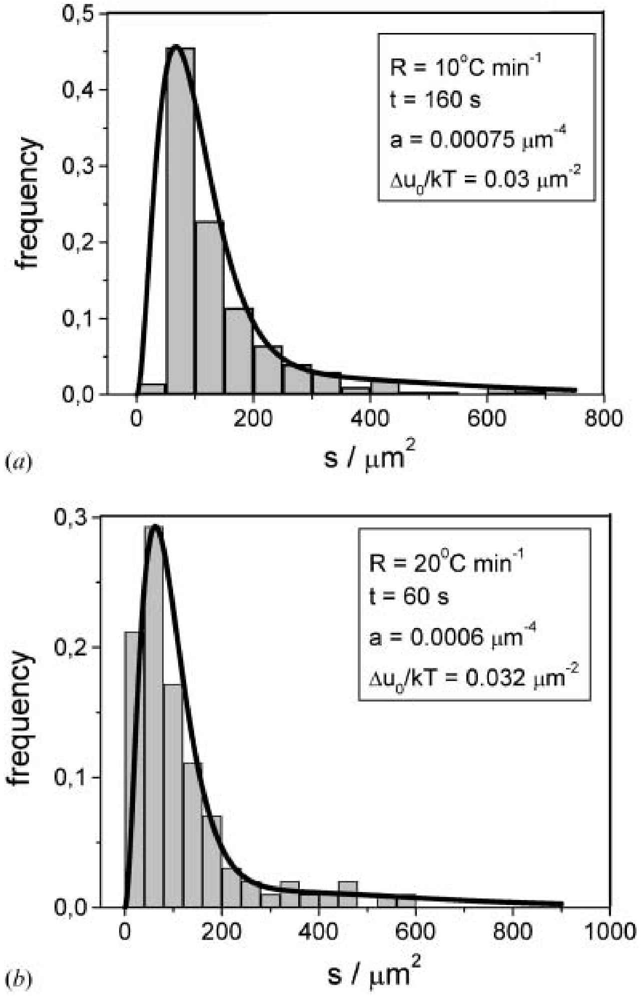


Figure 3. Statistical distributions of the liquid crystalline droplet area for the patterns depicted in figure 2 and their subsequent description using equation (2) with the fitting parameters given in the boxes.

Figure 4 demonstrates time dependence of the fundamental distribution parameter, the reduced aggregation energy, $\Delta u_0/kT$, for both cooling rates. The aggregation energy can be interpreted as a potential barrier to be overcome to create a thermodynamic ensemble of nematic droplets. Its high value at the very beginning of the phase separation reflects low probability for the statistical ensemble generation, while its subsequent abrupt decrease at larger time facilitates the statistical ensemble creation.

Taking into account equations (2) and (3), we can now compute the time dependence of the mean droplet diameter $<L>$. This is presented in figure 5 where two regimes separated by the critical time t^* depending on the cooling rate R can be recognized. Within the first regime, the mean droplet diameter increases, presumably in a linear manner. This regime is referred to as the

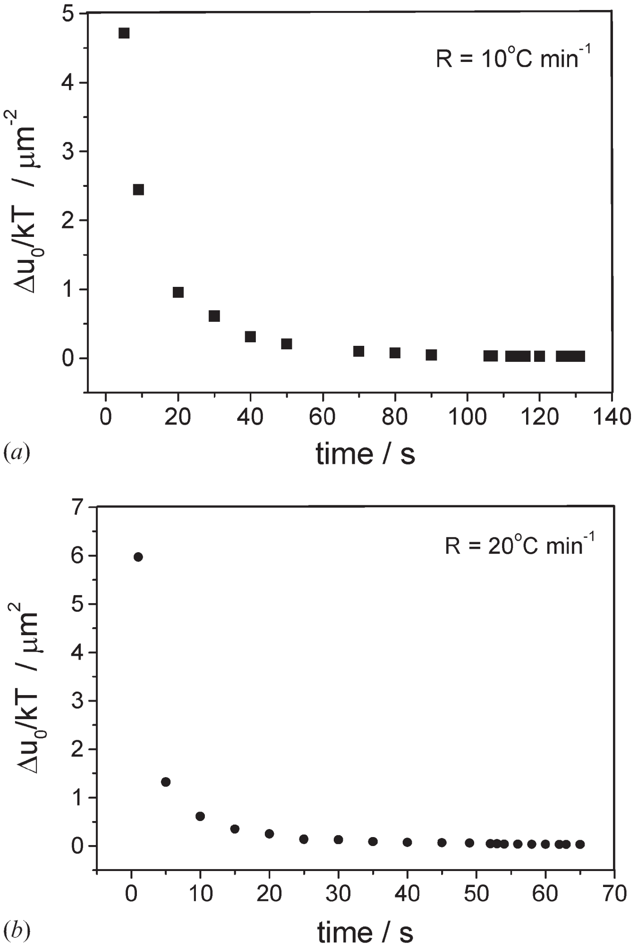


Figure 4. Time dependence of the reduced aggregation energy, $\Delta u_0/kT$, during the phase ordering at cooling rates of (*a*) 10°C min^{-1} and (*b*) 20°C min^{-1}.

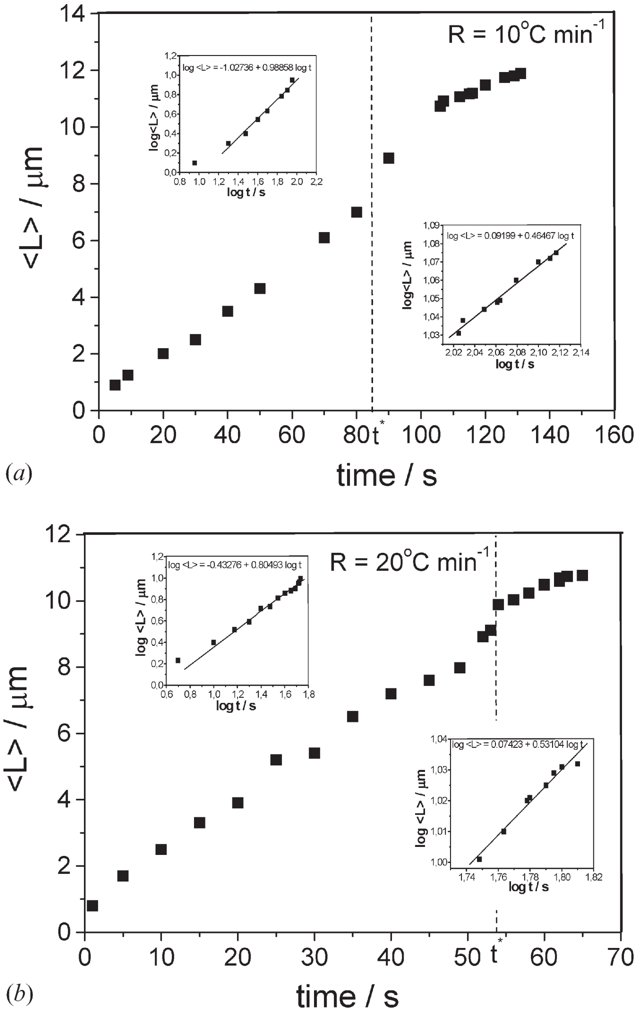


Figure 5. Time dependence of the mean droplet diameter during the phase ordering at cooling rates of (*a*) 10°C min^{-1} and (*b*) 20°C min^{-1}; t^* separates two regimes: nucleus growth and nucleus coarsening. The inserts present the time dependence of both regimes in log–log coordinates allowing determination of both n and C parameters in equation (5).

nucleus growth process [1, 5–8, 29, 30]. At $t=t^*$ it stops and a new process starts. Within the second time regime, $<L>$ grows more slowly; this regime is attributed to nucleus coarsening [1, 5–8, 29, 30]. For analytical description of the nucleus size evolution presented in figure 5, we used the universal growth law [2] in the form

$$\langle L\rangle = Ct^n. \tag{5}$$

In order to determine a value of the power index n for both time regimes, we plotted the experimental data shown in figure 5 in logarithmic coordinates (see the inserts in figure 5). The results of the linear representations are presented within the inserts and the calculated values of the C and n parameters are collected in table 1.

It follows from the table that, the nucleus growth regime can be represented by a linear function ($n\approx 1$) whereas the coarsening regime can rather be represented by a square root dependence ($n\approx 0.5$). These power law indices correlate to the results published elsewhere related to a deep temperature quench in liquid crystal systems [3–8, 29, 30].

In the nucleus growth regime, the C parameter increases with increasing cooling rate ($C=0.0876\,\mu\mathrm{m}\,s$ at $R=10°\mathrm{C\,min}^{-1}$, whereas $C=0.1762\,\mu\mathrm{m\,s}$ at $R=20°\mathrm{C\,min}^{-1}$). This means that droplets of the larger diameter may be grown at the higher cooling rate. Besides, the starting point of the nucleus coarsening regime, t^*, also depends on the cooling rate ($t^*\approx 82$ s at $R=10°\mathrm{C\,min}^{-1}$, whereas $t^*\approx 53$ s at $R=20°\mathrm{C\,min}^{-1}$). Quantitative correlations regulating the findings described should probably exist, but we need additional experimental data for their adjustment and verification.

Table 1. Parameters of the universal growth law, equation (5), for the liquid crystal polymer investigated.

	Cooling rate, R/°C min^{-1}			
	10		20	
Parameter	Growth $t^* < 82$ s	Coarsening $t^* > 82$ s	Growth $t^* < 53$ s	Coarsening $t^* > 53$ s
C/μm s^n	0.0876	1.227	0.3692	1.186
n	0.989 ± 0.058	0.465 ± 0.022	0.805 ± 0.063	0.531 ± 0.074

5. Conclusions

Analysis of the phase ordering in the melted isotropic liquid crystal polyether during a deep temperature quench allows us to conclude:

(i) Nematic droplets that appear and grow during the phase separation form quasi-stationary statistical ensembles described by the application of irreversible thermodynamics.

(ii) In accordance with general expectations, two time regimes of the nucleus size evolution are recognized on analysis of when the time dependence of the mean droplet diameter: first, generation and rapid nucleus growth, and secondly, nucleus coarsening.

(iii) Both regimes of the nematic droplets evolution are described quantitatively by application of the universal growth law. The nucleus growth regime is represented by a linear function whereas the coarsening regime is represented by square root dependence.

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