

Use of time-resolved X-ray scattering methods for investigation of structural formation in polymer liquid crystals

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The paper gives general information about the advantages of using synchrotron radiation in investigation of polymer liquid crystals. Examples are given with thermotropic polymer liquid crystal Poly(heptane-1,7-diyl-4,4'-biphenyldicarboxylate). The melt formation of smectic liquid crystal phase and consequent crystallization at decreasing temperature is depicted. Detailed description of different structural parameters, derivable from appropriate analysis of the experimental results, is given. With the aim of all those parameters an overall hierarchical structuring during phase transitions could be revealed.

Since some basic terms about liquid crystals and polymer liquid crystals are given, the paper would serve as an introductory reading in the field.

Key words: Polymer liquid crystals, Time-resolved experiments, X-ray scattering, Structure formation, Phase transitions.

INTRODUCTION

Curiously till the early sixties, synchrotron radiation has been considered only as an unwanted but inescapable by-product of elementary particle acceleration. Today, it is irreplaceable tool for investigation of structure and properties of vast classes of materials. Synchrotron facilities enlarge much further the possibilities of scientific investigation, helping to reveal much more details on the structure, and providing deeper inside about the mechanism of many processes (dynamics and kinetics), information which is inaccessible with the ordinary laboratory equipment.

The present paper aims to introduce to the reader the advantages of synchrotron radiation sources by giving an example with structural transformation of thermotropic liquid crystals. We also hope that this manuscript would serve as an introductory reading in the field of polymer liquid crystals and their structural investigation at diverse conditions.

BASIC KNOWLEDGE

1. *Synchrotron radiation.* Synchrotron radiation has been firstly observed in synchrotrons (storage

riings). It is an intensive electromagnetic radiation generated when high energy particles, accelerated to nearly the speed of light, are deflected in a strong magnetic field [1]. The radiation emitted by the orbital electrons covers broad range of the electromagnetic spectrum and the synchrotron radiation has continuous spectral distribution. The relativistic effects provoke a sharp forward peaking of the radiation and a large increase in the total radiated energy takes place.

The synchrotron radiation properties of interest for structural investigations could be summarized as follows [1]: continuous spectrum from infrared to hard X-rays; very high intensity of radiation and brightness of the source as compared with the conventional sources; high collimation of the beam; highly polarized radiation with an electric field vector in the orbital plane; well defined time structure which is a copy of the electron pulse structure of the beam. Owing to these synchrotron radiation features, because of the very short measurements times, one is able to investigate very fast processes (in order of nano- or even picoseconds). Because of the high brightness, together with utilization of two-dimensional detectors, one can gather very accurate and space and time discriminate experimental information. Another very important achievement is the possibility of simultaneous performance of several different experiments. For instance

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wide-angle x-ray diffraction (WAXD), small angle x-ray scattering (SAXS) and differential scanning calorimetry (DSC) can be run in the same time on only sample. Such approach leads to complete consistence of the obtained results and eliminates all doubts about the exact repetition of the experimental conditions, when each of the methods is employed separately.

2. *Liquid crystals*. Since many years, subject of great interest are structures having intermediate, between those of crystals and ordinary liquids, properties. For the sake of completeness, there are several states of matter displaying such intermediate behavior. They have common name – mesomorphic phases, divided into three main subclasses – liquid crystals, plastic crystals and condic crystals [2, 3]. In the present paper we focus our attention on liquid crystals only.

The nature of the liquid crystallinity (LC) is still not completely understood. One very important feature of liquid crystals is that the molecule (or part of it) shows rigidity. In most of the cases, one can imagine stiff rods, having lengths much greater than their diameter. Some authors [4] have proven that not only stiffness and asymmetry in shape but also electrical, steric, biphylic and flexibility molecular asymmetry play important role in LC appearance. Independently of the reason, the molecular segments giving LC are called mesogens.

Complete liquid crystals nomenclature could be found in the papers of International Union for Pure and Applied Chemistry [5, 6]. One possible division is according to the molecular weight: when the molecules are small – one deals with low-molar-mass or molecular liquid crystals (MLC), and otherwise – with polymer liquid crystals (PLC). In addition, since polymers are in fact very long molecules, there are many ways to incorporate

the mesogens along the chain. According to the molecular architecture, there are more than 20 different types of PLC [2, 5, 6].

Independently of the molar mass, liquid crystallinity can appear at different conditions. One distinguishes three main types of substances – lyotropic (when LC is caused by a solvent), thermotropic (LC caused by temperature variation) and barotropic (at varying pressure).

Now let us turn attention to one very important fact. Objects having shape other than spherical may possess three types of order, giving rise to different LC phases. If the symmetry axes of the objects are on average parallel to a well-defined spatial direction (called director, \vec{n}) then the substance shows orientational order (OO) (One can imagine spaghetti in a box). Translational order (TO) exists, when the system stays invariant under translations in space by an integer number of specific vectors (Imagine a crystal lattice and translation with respect to any of its unit cell vectors). The third possible order is called bond orientational order (BOO). It is not connected with the chemical bonds, but with the line in space which connects two adjacent molecules. If the direction of these lines is preserved over a long range, then BOO exists in the material (One can imagine here the view from above of densely packed spaghetti. The order looks like repeated hexagons).

Nematics are structures which possess only OO (Fig. 1A). Smectics are substances which display OO and TO in at least one direction (Fig. 1B). Some of the smectic phases may have also BOO. Cholesterics are special kind of materials, which possess OO, TO in one direction and also some persistent angle of inclination of the average molecular axis of one layer to its neighboring layer (Fig. 1C).

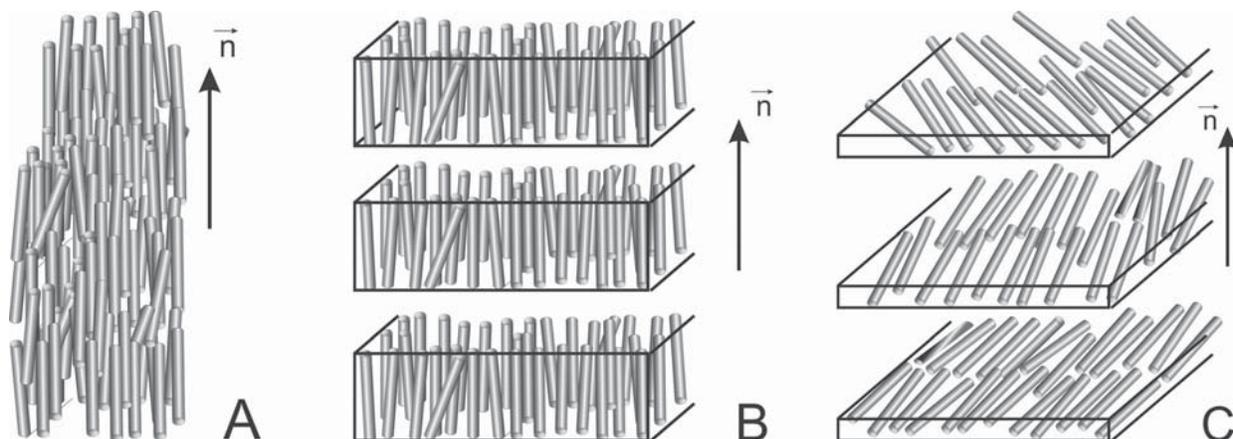


Fig. 1. A) Nematic Liquid crystal; B) Smectic liquid crystal; C) Cholesteric liquid crystal

MATERIALS AND METHODS

The investigated material is Poly(heptane-1,7-diyil-4,4'-biphenyldicarboxylate), P7MB. It belongs to the class of thermotropic main-chain liquid crystalline polyesters. Details of polymers preparation could be found elsewhere [7]. The intrinsic viscosity of P7MB was measured in chloroform at 25 °C and it was 1.03 dL/g.

Real-time variable isothermal temperature X-ray scattering and diffraction experiments were carried out at the beam line A2, HASYLAB (Hamburg, Germany). The wave-length of the X-ray beam was $\lambda = 0.150$ nm. Details about the experimental set-up could be found in our previous papers [8, 9, 10].

P7MB forms Smectic CA liquid crystalline phase [11]. This smectic structure is stable only in a limited temperature interval. At low temperatures the smectic structure partially crystallizes and at high temperatures it melts [9, 10]. The transition isotropic melt – smectic phase takes place in several minutes and it is very fast followed by partial crystallisation. Hence, with the ordinary laboratory equipment only the final semi-crystalline phase is reachable. Using synchrotron radiation we were able to follow up the kinetics of the phase transformation and to establish the mechanisms of the observed transitions.

The data treatment in the WAXD region is based on Bragg's law

$$(d = \frac{\lambda}{2 \sin \theta} = \frac{1}{s},$$

where λ is the x-ray wavelength, θ is the position of angle at the scattering peak maximum, and s is the scattering vector at the maximum) [1, 9]. Usually, polymeric materials undergo partial phase transfor-

mation and WAXD region is used to calculate degree of crystallinity

$$(X_{cr} = \frac{\sum I_{cr}}{I_{tot}},$$

where $\sum I_{cr}$ is the sum of the integrated intensities of all crystalline reflections and I_{tot} is the total integrated intensity) [1, 9]. Fig. 2A demonstrates the time evolution of WAXS patterns at isothermal temperature $T_{iso} = 135$ °C, and Fig. 2B – the method of deconvolution [1]. For deeper inside about the meaning of the results, the reader is referred to our already published results [8, 9, 10].

MAXS scattering interval is connected with mesogenic layer spacing, d_{MAXS} . The d_{MAXS} was calculated again according to Bragg's formula and its time dependence was established. Additional information about the domain dimensions in direction perpendicular to the mesogenic planes, D_{MAXS} , could be derived from Scherrer's formula:

$$D_{MAXS} = \frac{1}{\delta s}$$

(δs is the width of the peak half maximum). Important information could be extracted also from integrated intensity, I_{MAXS} , because it corresponds to the quantity of the material, which undergoes phase transformation. Fig. 2A presents MAXS peak time evolution at $T_{iso}=135$ °C and Fig. 3A demonstrated the time dependencies of all three discussed parameters. Actually, there are two d-spacings – at initial times there is a smectic d-spacing, having higher value and later on the crystallization takes

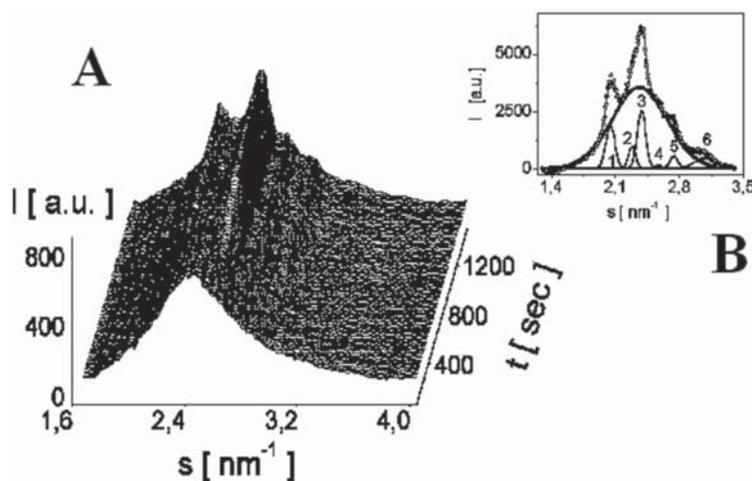


Fig. 2. A) WAXS pattern time evolution at $T_{iso}=135$ °C; B) deconvolution of the WAXD peaks

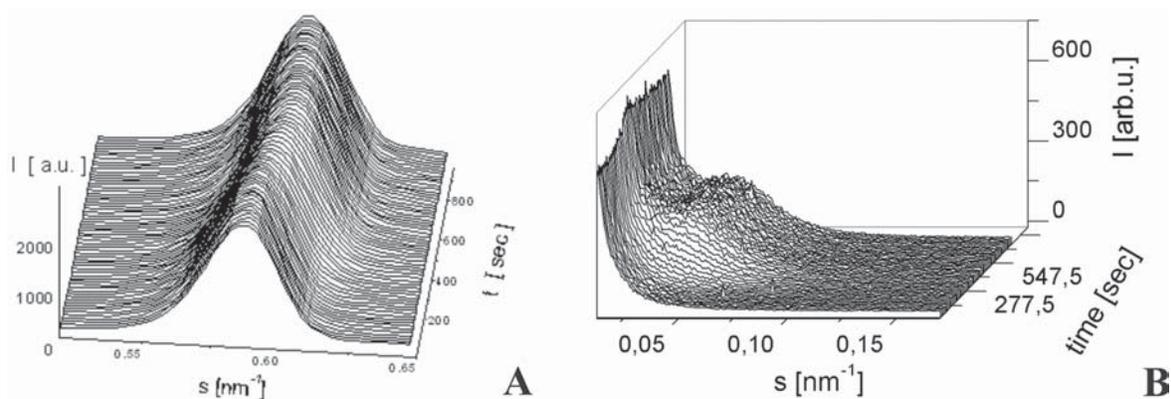


Fig. 3. MAXS (A) and SAXS (B) patterns time evolution at $T_{iso}=135\text{ }^{\circ}\text{C}$

place (lower d-spacing). The deconvolution of both peaks was only possible because the experiments were taken at synchrotron. In the results for I_{MAXS} and D_{MAXS} different symbols show the results for each d-spacing. The detailed analysis of the curves could be found elsewhere [9, 10].

SAXS scattering interval shows whether there is a hierarchical structuring in the material. In such case so called Long period appear (SAXS peak). Its values can be determined from the position of the

peak maximum in Lorentz corrected SAXS patterns, L_{Lor} , or from the maximum of the normalized one-dimensional correlation function, $\gamma_1(x)$,

$$(\gamma_1(x)) = \frac{\int_0^{\infty} s^2 I(s) \cos(2\pi x s) ds}{\int_0^{\infty} s^2 I(s) ds},$$

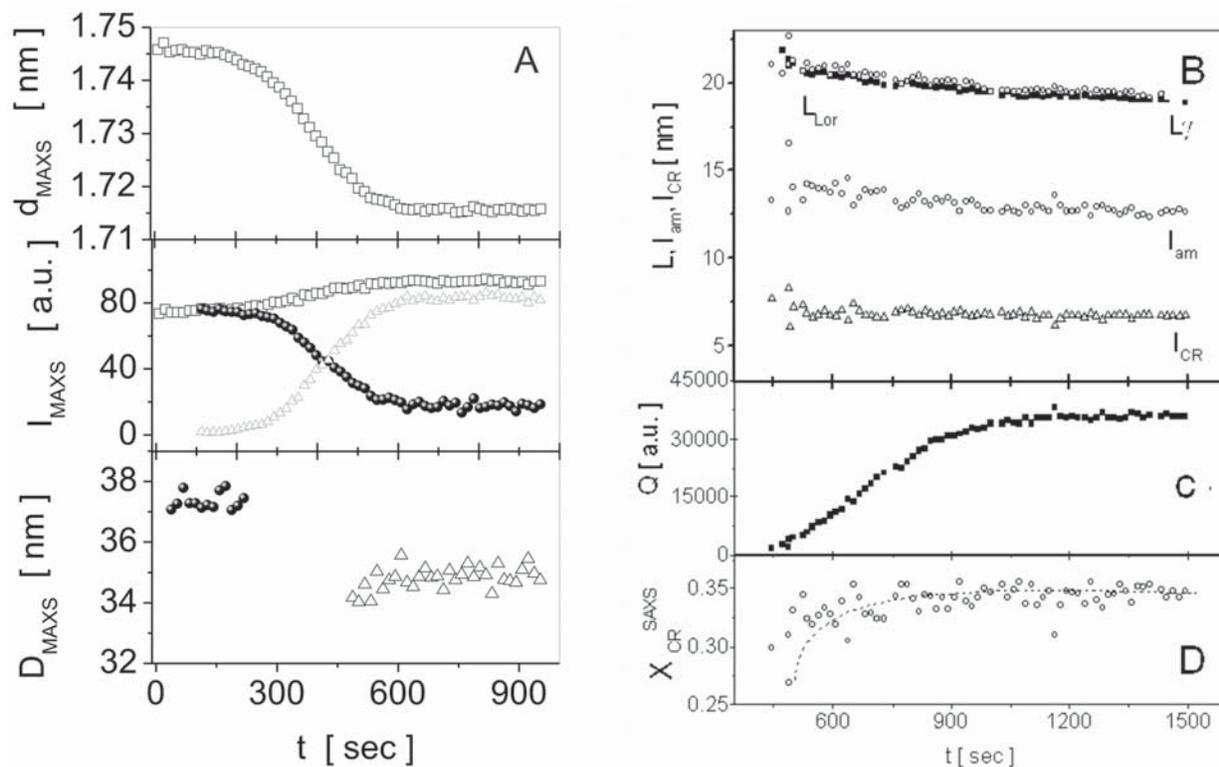


Fig. 4. d_{MAXS} , I_{MAXS} , D_{MAXS} time evolution (A); Results from one dimensional correlation function analysis of long period, crystal and amorphous layer thickness (B), Porod's invariant (C) and crystallinity with the stacks (D)

where $I(s)$ is smoothed and corrected for background SAXS intensity) [1, 10]. The analysis of $\gamma_j(x)$ gives also the degree of crystallinity within the lamellar stacks X_{cSAXS} , the lamellar thickness, l_c , the thickness of the amorphous layer, as well as the Porod's invariant, Q which is measure of the electron density difference between the present phases. For further readings see the books of Baltá-Calleja and Vonk [1] and Roe [12]. The results for P7MB are given in Fig. 4B, Fig. 4C, and Fig. 4D.

One can describe the overall picture of phase transformation only if all X-ray intervals are investigated. The exact structure determination and the mechanisms of phase transformation can be unambiguously assessed when the time (or temperature in case on non-isothermal processes) dependencies are known. In case of very fast processes, and when the changes are small (see for instance d_{MAXS}) the ordinary laboratory equipment fails to reveal the processes and only time-resolved synchrotron experiments are in help to the scientists.

CONCLUSIONS

Synchrotron radiation appears to be very useful tool for investigating thermotropic polymer liquid crystals. With its help many details about structure and the nature of the observed phase transition could be derived. SAXS, MAXS and WAXS experimental methods were performed simultaneously, which avoided the ambiguity coming from the problem with exact repetition of the experimental conditions

when each method is performed at different time and with different equipment.

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ПРИЛОЖЕНИЕ НА РЕНТГЕНОВИТЕ МЕТОДИ ЗА ИЗСЛЕДВАНЕ НА СТРУКТУРНОТО ФОРМИРАНЕ В ПОЛИМЕРНИ ТЕЧНИ КРИСТАЛИ

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(Резюме)

Настоящата статия дава обща информация относно предимствата при употреба на синхротронно лъчение за изследване на структурното формиране на полимерни течни кристали. Дадени са примери с термотропният полимерен течен кристал Poly(heptane-1,7-diyil-4,4'-biphenyldicarboxylate). Описано е формирането от стопилка на смектична течено-кристална фаза, последвано от кристализация при намаляване на температурата. Детайлно са описани различни структурни параметри, които са извлечени чрез подходящ анализ на експерименталните резултати. С помощта на разглеждане на всички тези параметри в цялост, може да се разкрие пълното йерархично структуриране по време на фазовото превръщане.

Статията може да служи и като въвеждащо четиво в областта, доколкото в нея са въведени и описани основните термини за нискомолекулните течните кристали и полимерни течни кристали.