Time-Resolved X-ray Diffraction Study of the Temperature Dependence of the Structure of Magnesium Stearate Multilayers

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A dual detector single readout system for simultaneous small- (SAXS) and wide-angle X-ray (WAXS) scattering

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Abstract

A data acquisition system is described which allows to simultaneously record X-ray scattering patterns in different angular regimes both with high spatial and temporal resolution. It consists of two linear detectors with delay-line readout connected in series. A few examples illustrate its application in the study of the polymorphism of lipid systems and their phase transitions as well as of synthetic polymers.

1. Introduction

Many amphiphilic molecules and synthetic polymers form structures with periodicities in the range from 0.2–0.6 nm due, for instance, to the lateral packing of hydrocarbon chains, and 1.5–100 nm for the supermolecular structure [1–3]. As a result, the X-ray scattering patterns of these systems display characteristic features such as sharp reflections both in the wide-angle and in the small-angle region. To cover this large angular range the diffraction patterns of the two regions are usually recorded in separate experiments. However, for investigations on radiation sensitive systems or time-resolved experiments on lipid phase transitions, where hysteresis loops can be broad and strongly rate-dependent, it is essential to measure the wide- (WAXS) and small-angle X-ray (SAXS) scattering simultaneously.

Different solutions to this problem have been described. Melting and crystallization processes in synthetic polymers were studied simultaneously in the SAXS and WAXS regions using a combination of a vidicon and a one- or two-dimensional proportional wire chamber [4,5] and of a wire chamber with a photodiode array [6]. A combination of a quadrant multiwire proportional chamber with delay line readout for the SAXS region and a curved wire chamber (INEL, Grenoble) for the WAXS capable of handling the high count rates at synchrotron sources was used for several applications [7]. A dual detector camera specifically designed for laboratory sources was also described [8].

The systems described so far for experiments on synchrotron sources consist essentially of two complete data acquisition systems for the respective angular regions. Apart from the associated costs for two complete systems and the complexity in handling and operating them, in measurements with high time-resolution this may lead to lack of synchrony, especially when very different types of detectors and readout systems are used.

Delay line detectors offer an elegant and inexpensive solution to the simultaneous recording of SAXS and WAXS. Indeed, it suffices to connect two such detectors located at the positions covering the SAXS and WAXS regions in series. In this configuration the two detectors appear as a single delay-line on a single data acquisition system, thus also simplifying the task of the operator. This approach can, of course, also be used to record different parts of a diffraction pattern in the same plane [9].

2. Experimental setup

The schematic representation of the data acquisition system in the bottom of Fig. 1 illustrates that it consists of a linear position sensitive delay-line detector with pulse shaping electronics, an optional external delay, an encoder to localize the ionizing events and computer hard- and software. These systems have been described elsewhere in detail [10–12]. The aspects relevant to the system used for the examples below are briefly summarized below.

Due to the coupling between anode and cathode a charge is build up upon arrival of a signal on the anode after an ionizing event in the surrounding gas. This pulse propagates in both directions along the delay line on the cathode and is amplified 40 times in the preamplifier built into the de-

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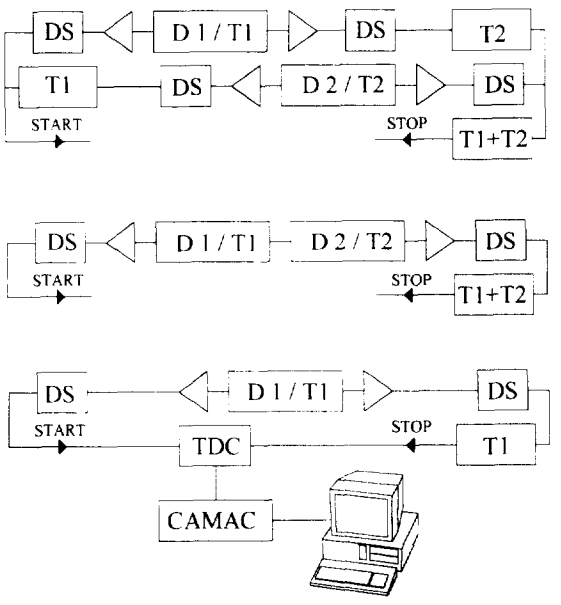

Fig. 1. Data acquisition system with a single delay-line detector with delay T1 (bottom), two delay-line detectors with delays T1 and T2 connected in series (middle) or in parallel (top) (D1: detector 1, D2: detector 2, DS: discriminator, TDC: time-to-digital converter).

tector. Further amplification with a gain around 4 and integration and differentiation times of 20 ns in the timing filter amplifier (EG&G Ortec 474) are used for pulse shaping before the signals are fed to the lower level discriminators (EG&G Ortec 473) to suppress the noise. On more recent versions of such systems, the output of the preamplifier is fed directly into the discriminators (Phillips Scientific 715, Mahwah NJ). The external delay (EG&G Ortec 416A), slightly longer than the length of the delay line, guarantees that the STOP pulse always arrives after the START pulse. The temporal information is digitized by a time-to-digital converter (LeCroy 4201, Geneva) with an interface [11] containing the rejection logic for double, false or incomplete events, which transfers the address to be incremented to a histogramming memory.

This single detector can be replaced by two (or more) detectors connected in series leaving the remaining part of the data acquisition system unchanged as shown in the middle part of Fig. 1, except that the value of the external delay must be adjusted to the sum of the delay lines of the detectors. Note that the delay lines are directly connected (i.e., one of the preamplifiers in each of the detectors has been bypassed). The additional detector may be a linear, circular or quadrant detector since the latter also only have one delay line. In principle it is also possible to apply this method to combinations of linear and area detectors or two area detectors but it is more difficult, however. In the experiments on lipids described below, the SAXS detector was 200 mm long with a 200 ns delay line, whereas the WAXS detector was 80 mm long with a 175 ns delay line. The external delay was set to 375 ns giving a processing time of 750 ns per event. Since at DORIS the revolution time for one bunch is about 1 μs, addition of a second delay line does not affect the efficiency at single bunch operation provided only one photon per bunch is scattered into either detector. During multi-bunch operation, however, the efficiency of the system may be limited by the length of the delay line. It is well-known from the properties of the Poisson distribution that, as a rule of thumb, the efficiency of a detector drops by a factor of 10 when the signals change from periodic to random (see e.g. Ref. [13]). If necessary, the external delay can be removed. The electronic count-rate limit around 1 MHz can, however, usually not be reached in practice since especially with strong scatterers like lipids the local count-rate and the ensuing space charge effects are the limiting factors. Therefore, although higher count-rates could have been obtained in the experiments described below, the intensity of the primary beam was reduced to give overall rates below 200 kHz.

The alternative arrangement in the top of Fig. 1 where the two detectors are connected in parallel with appropriate delays gives a cleaner separation of the signals but at the expense of more electronics. This is preferable when the two detectors have very different signal characteristics as in the case where a linear detector is combined with quadrant or circular detectors which are intrinsically noisier due to their larger areas.

The data acquisition system with two linear detectors connected in series is now routinely used for simultaneous SAXS and WAXS measurements on thermally induced phase transitions in phospholipids [14,15]. Transitions are induced either under near equilibrium conditions at heating or cooling rates down to 0.1 K/min or under non equilibrium conditions using an infrared laser to heat the samples rapidly and homogeneously by up to 15°C at rates of 5 K/ms. The experimental setup is schematically illustrated in Fig. 2 where the WAXS is recorded with detector 1 and the SAXS with detector 2. The details of the sample environment depend, of course, on the specific case but for most experiments on lipids a thin-walled quartz capillary filled with the sample is placed in a temperature controlled brass block. The laser beam for rapid temperature jumps is directed onto the sample and reflected by an X-ray transparent Kapton foil coated with aluminium to increase the homogeneity of the temperature profile after the jump. The primary flux is measured with an ionization chamber in front of the sample. A fast shutter is used to protect the sample from irradiation during the periods where no data is taken. The timing of the shutter and the laser is controlled by the data acquisition system. Except for a few centimetres around the sample the entire X-ray path is in vacuum. The distance between the sample and the SAXS detector can be varied between 0.5 and 4.5 m by inserting appropriate sections of vacuum pipes. The mechanical construction to extract the WAXS patterns is optimized for experiments on lipids and covers the range

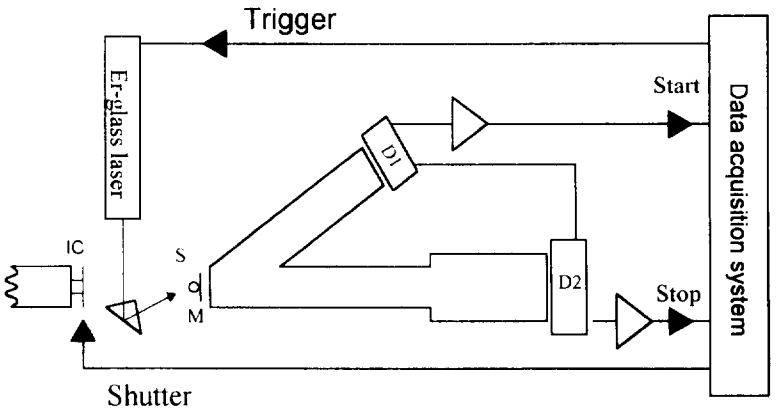

Fig. 2. Experimental setup for the study of laser induced phase transitions on phospholipids. (IC: ionization chamber, S: sample holder, M: aluminized Kapton foil, D1: detector 1 for WAXS, D2: detector 2 for SAXS).

from $(0.36\ \text{nm})^{-1}$ to $(0.63\ \text{nm})^{-1}$. Using a slightly different construction and a 200 mm long detector it is possible to record a larger angular region with a similar resolution.

To convert the channels on the detectors into values of the scattering vector dry rat tail tendon collagen is routinely used as reference for the SAXS and high purity tripalmitin for the WAXS region. It should be noted that apart from giving an undistorted angular scale provided the centre of curvature of the detector is exactly at the position of sample, the use of a curved detector does not present any main advantage. It certainly does not affect the diffraction geometry (Ewald sphere) as sometimes erroneously implied [7].

The superimposed patterns of collagen for the SAXS and tripalmitin for the WAXS obtained using two linear detectors in series are shown in Fig. 3. Both samples were exposed for 10 s. The distance from the sample to the SAXS detector was 2.7 m, the focus of the beam was close to detector 2 (Fig. 2). In this setup the SAXS region covers orders 2 to 22 of the collagen repeat of 65 nm [16] whereas the WAXS region covers a range of spacings (d) from $0.63 > d > 0.36$ nm using the spacings of tripalmitin as reference [17,18]. To a first approximation the angular resolution $\Delta(2\Theta)$ is given by [19]:

$$\Delta(2\Theta) = \lambda\Delta s - s\Delta\lambda\,.$$

For the small angle reflections $\Delta s = 0.0053\ \text{nm}^{-1}$. With $\lambda = 0.15$ nm and $\Delta\lambda/\lambda = 10^{-3}$ the angular resolution is $\Delta(2\Theta) = 0.046$, whereas for the wide-angle reflections $\Delta s = 0.021\ \text{nm}^{-1}$ and $\Delta(2\Theta) = 0.2$. These values should be compared with those given for a similar system [6]. The effective spatial resolution is 0.57 mm/channel on the SAXS and 0.28 mm/channel on the WAXS detector, both measured by homogeneous irradiation with a ^{55}Fe source through a mask with 0.8 mm diameter holes with 2.54 mm centre to centre distance. These figures are comparable to the electronic resolution, i.e., if the number of channels is divided by the active length of the detector, which results in 0.58 mm/channel for the SAXS and 0.26 mm/channels for the WAXS detector, respectively.

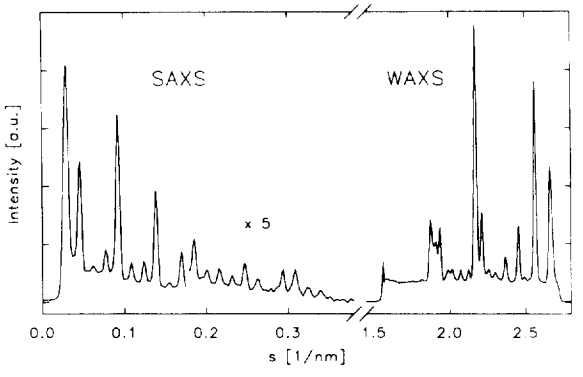

Fig. 3. Merged diffraction patterns (10 s exposures) of collagen in the small-angle (SAXS) and tripalmitin in the wide-angle (WAXS) region taken with the same setup. Raw data without background subtraction are shown.

3. Study of phase transitions in phospholipids

Phospholipids display a rich polymorphism depending on their molecular structures and on thermodynamic variables and provide valuable model systems for biological membranes. Apart from the well known lamellar structures, non-lamellar cubic and hexagonal phases have been detected [20–22] which may play a role as transient or local intermediates in a number of biological processes [23,24]. Two examples illustrating the performance of the system for experiments on lipid phase transitions are given below. In the first one the sequence of phases during moderate heating rates of 1°C/min is established, and in the second the kinetics of a transition under non-equilibrium T-jump conditions with 200 μs time-resolution is investigated. The latter experiments would be difficult if not impossible to perform

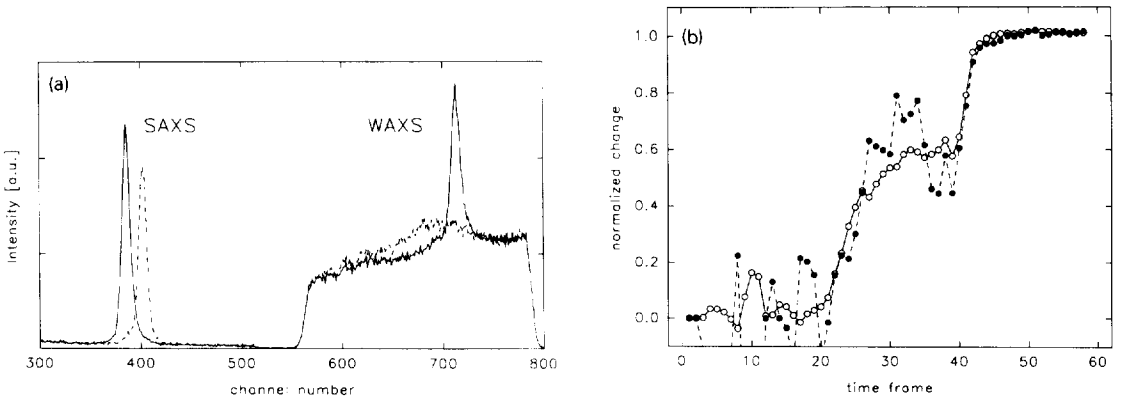

Fig. 5. (a) Superimposed SAXS and WAXS patterns of fully hydrated dimyristoylphosphatidylethanolamine (DMPE) in the gel (L_β, solid line) and liquid crystalline (L_α, dashed line) phases with 2 s exposure times. The raw data are shown. (b) Changes of the SAXS (○) and WAXS (●) reflections normalized to primary beam intensity versus time frame number. (frame 1: 500 ms, 2:100 ms, 3–40: 200 μs, 41–58: 100 ms, laser trigger at frame 11).

or to synchronize with most other simultaneous SAXS and WAXS systems, especially those using integrating detectors (vidicon, photodiode arrays).

A 1:2 (mol/mol) mixture of dilauroylphosphatidylcholine (DLPC) with lauric acid (LA) dispersed in 70% water (w/w) forms different structures depending on temperature. A sequence of SAXS and WAXS patterns of 3 s exposure time taken every 30 s during a heating scan from 7 to 70°C is shown in Fig. 4. Below 21°C strong and numerous wide-angle reflections are seen which are characteristic of a rigid crystalline structure. The small-angle patterns suggest a phase-separated lamellar mixture of DLPC/LA and LA with a lamellar spacing of 5.1 nm. At 25°C a gel phase appears, some of the wide-angle reflections disappear and two small-angle reflections shift to positions corresponding to a lamellar repeat of 6 nm. At temperatures above 38°C the sharp wide-angle reflections disappear and

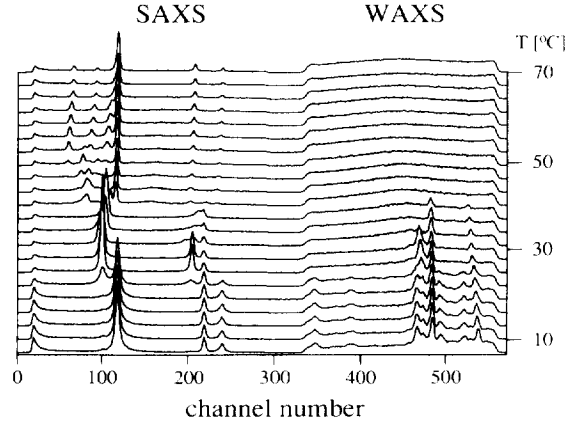

Fig. 4. Diffraction patterns of a mixture of DLPC/LA in a temperature scan at 1°C/min during which 3 s exposures were taken every 30 s. The raw data are shown.

new reflections, which index on cubic lattices, appear at small angles. It is beyond the scope of the present article to discuss these transitions in more detail, but the example clearly illustrates the potential of the system for rapid and precise determination of phase diagrams and combined X-ray and thermal measurements.

The limit for the time resolution of the present system is around 1 μs. The second example illustrates the study of the kinetics of the transition from the gel to the liquid crystalline state of dimyristoylphosphatidylethanolamine (DMPE) dispersed in excess water. Diffraction patterns below and above the main transition are presented in Fig. 5a, showing the first order reflections of the lamellar lattice and the reflections from the aliphatic chains in the gel (L_β) and liquid crystalline (L_α) phase. In the experiment 20 cycles of laser heating and passive cooling were accumulated in the histogramming memory before the data were stored on disk. The sample was heated from 41°C to about 52°C within 2 ms. One cycle consists of 64 frames with different exposure times as described in the legend of Fig. 5b. To estimate the kinetics of the transformation the degree of transition is plotted against frame number. At frame 11 the laser flash lamp is fired, lasing starts with a delay of 1.2 ms. An additional delay until the onset of the transition arises from the energy necessary to heat the sample from 41°C to the transition temperature at 48°C. The time course of the structural changes of the lamellar lattice almost coincides with that of the chain packing except for the middle of the transition where a slight lead of the structural changes in the wide angle region is observed. No disordered or intermediate structures were observed on this time scale, suggesting that the main transition from the gel to the liquid crystalline phase occurs via a two-state martensitic mechanism. The latter involves concerted disclinations about lattice connecting transition planes as suggested previously for the transition on fully hydrated stearoyl-oleoyl-phosphatidylethanolamine (SOPE) [25].

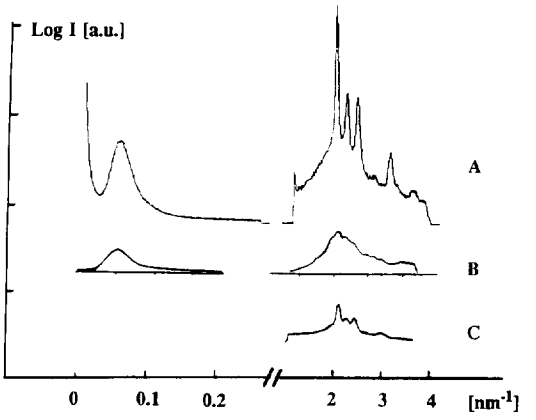

Fig. 6. (a) SAXS and WAXS patterns of PEEK obtained with two delay line detectors in series. (b) PEEKK (from Ref. [26]) obtained with a delay line detector for the SAXS and a fluorescent screen and vidicon for the WAXS. (c) WAXS pattern of an identical sample of PEEKK obtained separately with a delay-line detector.

4. Study of synthetic polymers

The approach also presents definite advantages over other systems in the study of synthetic polymers, although these experiments are in general less demanding in terms of time-resolution than those on biological systems. This is illustrated by the comparison of the patterns of PEEK (poly(ether ether ketone)) and PEEKK (poly(ether ether ketone ketone)) in Fig. 6. The pattern of PEEK was obtained with two delay-line detectors in series and that of PEEKK which is very similar with a linear delay line detector for SAXS and a vidicon for the WAXS [26]. The poor resolution of the WAXS pattern in the latter case is clearly due to the fluorescent screen and vidicon system as shown by comparison with the same pattern obtained with a delay line detector in Fig. 6c. Using two delay-line detectors in series both the SAXS and WAXS patterns are well resolved. The time-resolution used for the study of crystallization phenomena is usually of the order of seconds so that the readout time of vidicon systems and synchrony problems between detectors can be neglected. In the case of faster phenomena (e.g. spinning) this is no longer the case and the use of delay line detectors in series is also more advantageous.

5. Conclusion

The modifications required to use delay line detectors for simultaneous detection of SAXS and WAXS reflections are extremely simple and provide a system with a good spatial resolution that is well suited for time-resolved experiments down to the sub-millisecond range as illustrated by the examples taken from studies on phase transitions in lipids. Such a system allows to investigate a wide range of fundamental and technological questions.

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