Simultaneous measurements of small angle x-ray scattering, wide angle x-ray scattering, and light scattering during phase transitions in polymers (invited)

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In order to obtain detailed information on structural changes in polymers during crystallization and melting, it is necessary to perform real-time measurements of the change in small angle x-ray scattering simultaneously with measurements of the change in wide angle x-ray scattering, light scattering and enthalpy (by differential scanning calorimetry). Different experimental setups to perform such experiments are described. Some examples demonstrate the variety of information that may be obtained by means of these setups. © *1995 American Institute of Physics.*

I. INTRODUCTION

Polymers consisting of long chain molecules show some characteristic features when they crystallize.[1] During the process of crystallization, so-called spherulites or other morphological units grow until they fill the material completely (Fig. 1, left side). Each spherulite consists of many thin lamellar crystals separated by sheets of amorphous regions forming lamellar stacks (Fig. 1, right side). Thus crystallization never becomes complete. The lamellar stacks are arranged in such a way that the molecular chains in the crystals are preferentially oriented perpendicular to the radius of the spherulite. The crystals and the amorphous regions are of comparatively uniform thickness l_c and l_a, respectively. The sum $(l_a + l_c)$ is called the long period L. The values of L may range from 5 nm to more than 100 nm. The crystalline fraction x_c varies between 0.2 and 0.8 depending on the polymer and the thermal pretreatment. In order to investigate such structures different experimental methods have to be used.

(1) Wide angle x-ray scattering (WAXS). Here, the scattered intensity $I(s)$ as a function of the magnitude of the scattering vector $s = (2/\lambda)\sin(\Theta/2)$, where Θ is the scattering angle, is composed of several peaks which can be identified as crystal reflections and a diffuse scattering, the "amorphous halo," caused by the amorphous regions. The area under the crystal reflections divided by the total area under the scattering curve gives the crystalline fraction x_c.[2]

(2) Small angle x-ray scattering (SAXS). This scattering arises from the difference in the density of the crystalline regions ρ_c, and of the amorphous regions ρ_a. The intensity as a function of s usually shows a monotonic decrease superimposed by a peak. By applying Braggs law, one can calculate the long period L from the angular position of this peak. A more detailed evaluation of such a curve gives the distribution of the values of l_a and l_c and even the width of the interface.[3-6] Furthermore, the total integrated SAXS intensity, the scattering power Q, is given by

$$Q = \text{const } V x_{cL}(1 - x_{cL})(\rho_c - \rho_a)^2, \tag{1}$$

where V is the volume of the lamellar stacks and x_{cL} is the degree of crystallinity within the lamellar stacks given by $l_c/(l_c + l_a)$. If the sample is totally filled by lamellar stacks $x_{cL} = x_c$, otherwise $x_{cL} > x_c$.

(3) Scattering of polarized light (LS). If the polarizer and the analyzer are arranged perpendicularly to each other (H_v), the spherulites lead to a clover-leaflike scattering pattern. From the dimensions of such a pattern, the radius of the spherulite can be determined.[7] By more sophisticated evaluations including investigations of the scattering where the polarizer and analyzer have the same orientation (V_v), information on the perfection of the orientation within the spherulites, the degree of crystallinity, the spherulitic fraction, and other parameters may be obtained.[8]

(4) Differential scanning calorimetry (DSC). By means of this method one can follow the process of chemical reactions or phase transitions such as crystallization and melting.

If one wants to study the changes in structure during crystallization, melting, deformation, or different kinds of processing of polymers, one has to perform real-time measurements of the changes in WAXS, SAXS, and LS while these processes occur. The most reliable information is obtained if all these methods are applied simultaneously. If the x rays are generated in the conventional way, the detection time for SAXS is too long in order to perform such real-time measurements. The high intensity of synchrotron radiation decreases the detection time for SAXS from hours or days in the case of conventional x-ray sources to seconds or less. Thus, completely new experiments could be performed after synchrotron radiation became available.

First measurements of SAXS during crystallization of polymers were undertaken at the beamline of the European Molecular Biology Laboratory (EMBL) outstation at DESY in Hamburg[9] using a double focusing camera and monochromatized radiation.[10] Shortly afterward, measurements on polymers were also performed at other synchrotron radiation sources.[11-14]

Due to the great variety of important measurements which became possible in polymer science with the advent of synchrotron radiation, a SAXS beamline dedicated completely to investigations of polymers was constructed at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) at

spherulites   lamellar stacks   crystals and amorphous regions
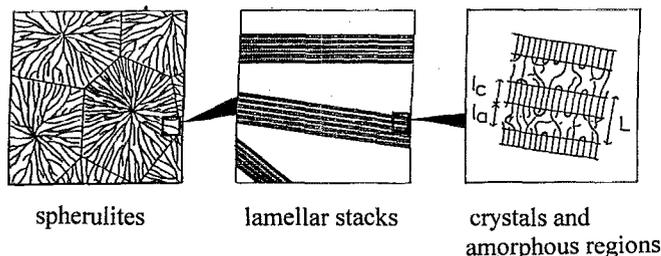
FIG. 1. Schematic representation of the spherulitical structure and the arrangement of the crystals and the amorphous regions in the lamellar stacks forming the spherulites in polymers.

FIG. 3. Change of SAXS power Q and degree of crystallinity x_c during isothermal crystallization of poly(ethylene terephthalate) at 117 °C (Ref. 2).

DESY in 1980.[15] Quite recently a beamline with ultra-high resolution in SAXS (up to 600 nm) was also built up at this source.[16] A microfocus beamline and a high brilliance beamline with ultrahigh resolution have just become available at the European Synchrotron Radiation Facility (ESRF) in Grenoble.[17]

II. DESCRIPTION OF INSTRUMENTS FOR SIMULTANEOUS MEASUREMENTS AND RESULTS

The first simultaneous measurements of SAXS and WAXS were performed in 1982 in Hamburg.[19,20] The WAXS was measured by a film with an exposure time of 1 min. The film was exchanged every minute by means of the mechanical device shown in Fig. 2. The SAXS passed through a hole in the film. It was found that during isothermal crystallization of poly(ethylene terephthalate), the SAXS power Q increased in the same way as the degree of crystallinity x_c determined by WAXS (Fig. 3). This showed that during the growth of the spherulites the scattering volume V in Eq. (1) is proportional to x_c and that the density difference between the crystals and the amorphous regions, $\rho_c - \rho_a$, does not change during the course of crystallization.

In a new device that could be operated much more easily,[21] we used a one-dimensional Gabriel detector positioned off the primary beam to detect the WAXS (Fig. 4). The SAXS passed this detector and was measured by a one- or two-dimensional detector at a larger distance. Studies of isothermal crystallization of polyethylene,[22] for example,

showed that after the sample was filled by spherulites a very slight increase in the degree of crystallinity x_c was observed by WAXS while the SAXS power Q and the long period L remained almost constant (Fig. 5). The slow increase of x_c had been observed previously. It is explained by a slow increase in the degree of crystallinity within the spherulites, a process called secondary crystallization. The constant value of Q was a new result. It indicated that secondary crystallization did not consist of the growth of new lamellar stacks within larger amorphous regions which may exist inside the spherulites. This process would increase the quantity V in Eq. (1) and would increase Q in the same way as x_c, which was not observed. The increase of x_c is rather caused by a thickening of crystals increasing l_c and decreasing l_a leaving the long period $L = l_c + l_a$ constant. Thus the process takes place within the already existing lamellar stacks which means that in Eq. (1) V is constant while x_{cL} increases. Now, an increase of x_{cL} from 0.4 to 0.5, for example, changes the product $x_{cL}(1 - x_{cL})$ from 0.24 to 0.25 which is completely within the error of the experiment. Other mechanisms of secondary crystallization were found to take place in poly(ethylene terephthalate) (PET) and in other polymers,[23,24] where crystals stacks start to grow within already existing lamellar. It should be mentioned that Schulz et al.[25] in 1979 had already shown that important information could be obtained by measuring the change of SAXS during crystallization. However, at that time without synchrotron radiation it was not possible to perform such measurements systematically.

Similar setups for performing simultaneous measurements of SAXS and WAXS have also been used at the

FIG. 2. Schematic representation of the setup for simultaneous measurements of SAXS and WAXS using films for detection of the WAXS (Ref. 2).
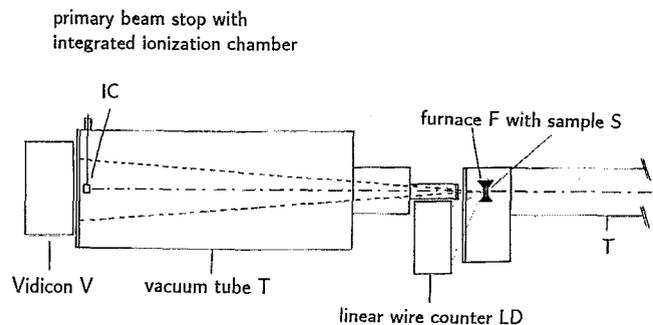
FIG. 4. Schematic representation of the setup for performing simultaneous measurements of SAXS and WAXS using a one-dimensional position-sensitive detector for WAXS (Ref. 2).
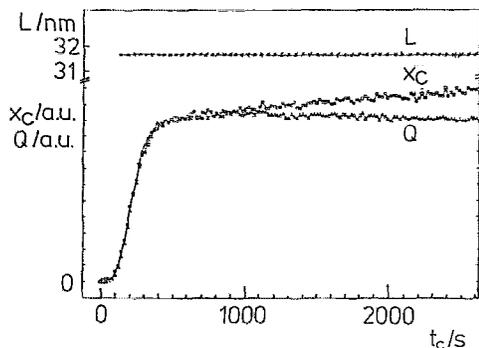
FIG. 5. Change of the SAXS power Q, the long period L, and the degree of crystallinity obtained by WAXS x_c, as a function of time during isothermal crystallization of polyethylene at 125 °C (Ref. 21).

FIG. 7. Change of WAXS and SAXS during heating at 5 °C/min of a blend of poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) and PEN-co-p-hydroxybenzoic acid oriented by drawing (Ref. 29).

sources in Daresbury[26] and Brookhaven[27] (with a circular one-dimensional detector for the WAXS). In addition, at Daresbury simultaneous measurements of SAXS and infrared absorption were performed in order to study the chemical reactions which take place during molecular order formation.[28]

In the instruments described above, because of special restrictions, it is not possible to use a two-dimensional detector for the WAXS measurements and it is also difficult to avoid a dead angle between SAXS and WAXS. To overcome these disadvantages we have constructed[29] another setup which is illustrated in Fig. 6. The WAXS pattern is transformed by a fluorescent screen into visible light which is reflected by a mirror onto a vidicon. The SAXS passes through a hole in the screen and a hole in the mirror to another two-dimensional detector positioned at a larger distance. As an example of the results, Fig. 7 shows the change of WAXS and SAXS during heating of a copolymer in which the molecules were previously oriented. At room temperature

some crystal reflections appear in the WAXS diagram whereas almost no SAXS is observed. Obviously, in the oriented polymer the amorphous regions are highly dispersed. With increasing temperature a SAXS peak appears indicating that a lamellar structure is gradually formed. At the same time the crystal reflections in the WAXS diagram become sharper which shows that the crystal sizes increase.

In order to be able to measure the light scattering in addition to SAXS and WAXS we have added[23,30,31] a laser to the instrument shown in Fig. 4. This extended set-up is depicted in Fig. 8. The laser beam passes through the sample in an opposite direction to the x-ray beam. The scattered light passes an analyzer and is finally detected by a CCD camera. From the dimensions of the light scattering pattern we calculated the average radius of the spherulites $\bar{r}$ as a function of time. Figure 9 shows Q, x_c, and $\bar{r}$ as a function of time during crystallization of poly(ethylene-2,6-naphthalene di-

S Sample
Sc Screen
M Mirror
V O Vidicon,Objective
C Counter

FIG. 6. Schematic representation of the setup for performing simultaneous measurements of SAXS and WAXS using a two-dimensional position-sensitive detector (Vidicon) for the WAXS (Ref. 29).

CCD Charge Coupled Dev.
L   Laser
PS Polarizer + Screen
S   Sample
C   Counter
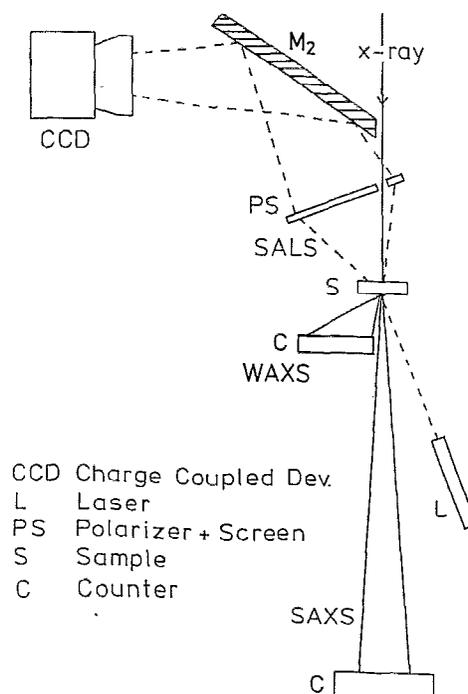
FIG. 8. Schematic representation of the setup for performing simultaneous measurements of SAXS, WAXS, and LS (Ref. 23).
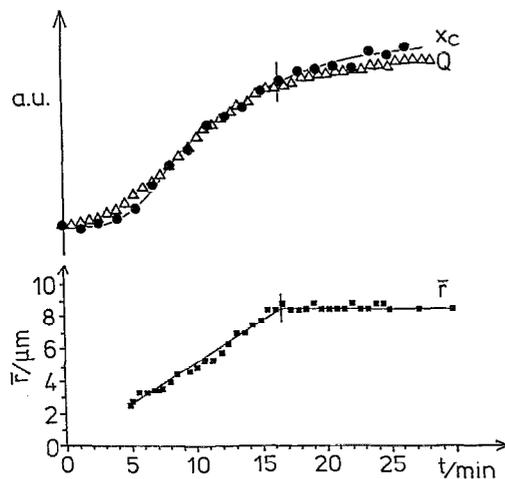
FIG. 9. Scattering power Q, degree of crystallinity x_c, and average radius of the spherulites $\bar{r}$ as a function of time during isothermal crystallization of poly(ethylene-2,6-naphthalene dicarboxylate) at 183 °C.

carboxylate) (PEN) at 183 °C. After 17 min, r becomes constant indicating that the growth of spherulites is terminated at this time. Nevertheless, x_c and, to a small amount Q, further increase indicating that secondary crystallization takes place.

A DSC cell for performing calorimetric measurements in addition to x-ray scattering was first constructed by Russel et al. at Stanford.[12] We have also included such a device into our equipment.[21] Among others, we have used this equipment to study the melting of polymers. Figure 10 shows the DSC curve, the scattering power Q and the long period L as a function of temperature during heating of poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) with a heating rate of 5 °C/min. The sample was crystallized before the measurement for 2 h at 240 °C and for 2 h at 272 °C. The DSC curve shows two melting peaks, a smaller one at 255 °C indicating some premelting and a larger one at 280 °C where final melting takes place. Which process occurs on a molecular scale during this premelting? As it can be seen in Fig. 10, the scattering power Q shows a comparatively small decrease.
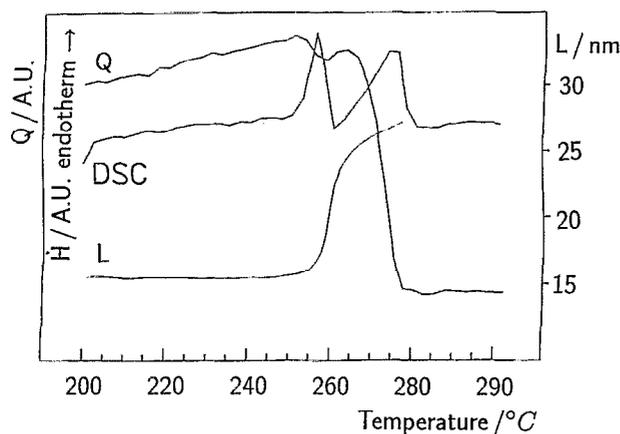
FIG. 10. DSC curve, scattering power Q and long period L as a function of temperature during heating at 5 °C/min of poly(ethylene-2,6-naphthalene dicarboxylate) previously crystallized at 240 °C and 272 °C (Ref. 29).
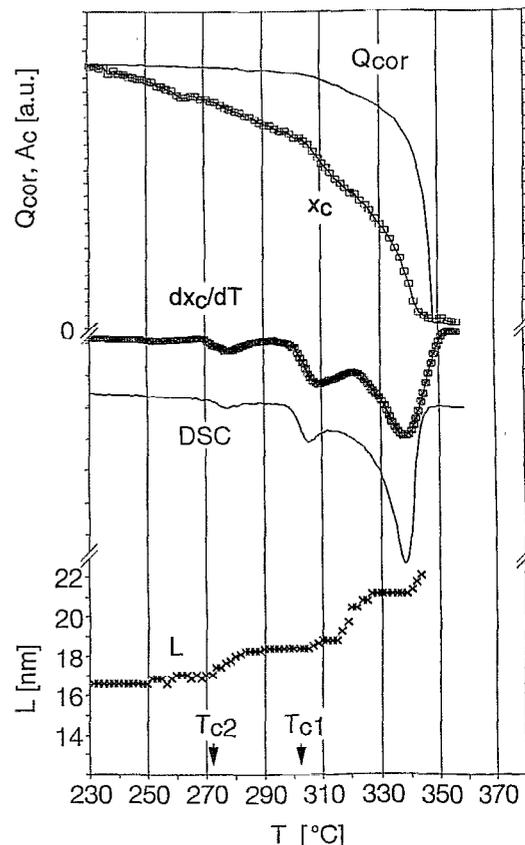
FIG. 11. DSC curve and change of corrected scattering power Q_{cor}, degree of crystallinity x_c, the first derivative of this quantity dx_c/dT and long period L during heating of poly(ether ether ketone) previously crystallized at 292 and 272 °C (Ref. 32).

From this, one has to conclude that in Eq. (1) the quantity V rather than x_{cL} is decreased during the premelting, which means that some crystals, which are thinner and therefore less stable than the others within the lamellar stacks are melting while the overall spherulite structure remains unchanged.

An even more complicated melting behavior could be observed with a sample of poly(ether ether ketone) (PEEK) which, during cooling from the melt, was first crystallized at 292 °C and then at 272 °C.[32] The results are shown in Fig. 11. Three melting peaks are obtained by DSC. In agreement with these peaks the degree of crystallinity x_c, as measured by WAXS, decreases. This is seen most clearly at the curve representing the first derivative of x_c with respect to time, dx_c/dt, which is proportional to the heat exchange. In contrast, the scattering power Q_{cor}, obtained after correction of Q for the different thermal expansions of the crystals and the amorphous regions, shows only a very small decrease during the first two melting processes. This indicates that the melting takes place within the lamellar stacks. From the accompanying increase of the long period it is concluded that within the distribution of crystals of different thicknesses, the thinner crystals are melting and thus increasing the average distance of the crystals. In the temperature region from 295 to 305 °C, the long period stays constant though melting is indicated by the DSC and x_c curves. Here "surface melting" may occur by which the thickness of the crystals is decreased.[33,34] Finally, above 330 °C a strong decrease of Q

is also observed. Here complete lamellar stacks are melting, thus decreasing V in Eq. (1).

The examples presented prove that important new information on structural changes in polymers can be obtained by simultaneous measurements of SAXS, WAXS, LS, and DSC. The field of possible investigations would further increase if, in addition, other methods such as birefringence measurements, polarized microscopy, UV and IR spectroscopy could be performed simultaneously with the SAXS and WAXS measurements. This demonstrates how scientific problems lead to demands or further improvement in instrumentation.

III. CONCLUSIONS

Using synchrotron radiation it became possible to measure rapid changes of SAXS and to perform these measurements simultaneously with measurements of WAXS, LS, DSC, and IR absorption. Such simultaneous measurements are required in order to obtain important new information on microstructural changes during crystallization, melting, and orientation of polymers. The field of possible investigations would increase further if, in addition, other methods such as birefringence, polarizing microscopy and UV spectroscopy could be applied simultaneously with the SAXS and WAXS measurements. This demonstrates how scientific problems lead to demands for further developments in instrumentation.

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