

## Energy-dispersive small-angle x-ray scattering for investigating polymer morphology: Static and time-resolved experiments

Giuseppe Portale

*Dipartimento di Chimica, Università degli Studi "La Sapienza" Piazzale A. Moro 5, 00185, P.O. Box 34-ROMA 62, Roma, Italy*

Alessandro Longo

*Istituto per lo Studio dei Materiali Nanostrutturati, Via Ugo La Malfa 153, 90146 Palermo, Italy*

Lucio D'Ilario<sup>a)</sup> and Andrea Martinelli

*Dipartimento di Chimica, Università degli Studi "La Sapienza" Piazzale A. Moro 5, 00185, P.O. Box 34-ROMA 62, Roma, Italy*

Ruggero Caminiti

*Dipartimento di Chimica, Università degli Studi "La Sapienza" Piazzale A. Moro 5, 00185, P.O. Box 34-ROMA 62, Roma, Italy and Istituto Nazionale di Fisica della Materia, Università degli Studi "La Sapienza" Piazzale A. Moro 5, 00185 Roma, Italy*

(Received 20 May 2004; accepted 20 September 2004)

Energy-dispersive small-angle x-ray scattering couples the information given by small-angle experiments and the advantages of energy-dispersive methods, mainly in carrying out time-resolved experiments. Preliminary small-angle measurements on some semicrystalline polymers using a laboratory-based energy-dispersive diffractometer and the bremsstrahlung continuum generated from a commercial tube as x-ray source are presented. The results are in agreement with those obtained with the classical method. The apparatus utilized could be considered a promising tool to perform both wide and small-angle scattering or diffraction. © 2004 American Institute of Physics. [DOI: 10.1063/1.1823586]

Small-angle x-ray scattering (SAXS) is a very helpful technique for probing the morphology of biological macromolecules, synthetic polymers, and other advanced materials. Semicrystalline polymers are ideal objects to be studied by SAXS, showing electron density variations whose correlation length is usually well within the range covered by this technique (typically 1–100 nm). Probably the most important result of small-angle scattering in polymer science has been the recognition that, in a first approximation, the density distribution within a semicrystalline sample corresponds to a two-phase structure in which crystalline and amorphous regions alternate. In polymers having such a regular and ordered morphology a SAXS intensity correlation peak is observed at a characteristic  $q_{\max}$  value, due to the separation of crystalline and amorphous domains within the material. The peak can be associated with the first-order Bragg's reflection from the crystalline lamellae and the average value of the period  $L$  (the so-called long-period) can be obtained from Bragg's law,

$$q_{\max} = \frac{2\pi}{L}, \quad (1)$$

where  $q$  is the modulus of the scattering vector, defined as  $(4\pi \sin \theta)/\lambda$ ,  $\theta$  being the scattering angle and  $\lambda$  the x-ray wavelength. According to the simple two-phase model, the long-spacing represents the distance between the centers of two adjacent crystalline lamellae and  $L$  is thus the sum of the crystalline and amorphous layer thickness. Usually, for systems characterized by isotropically distributed lamellar mor-

phology, the multiplication of the intensity function by the Lorentz factor  $q^2$  is applied to the SAXS intensity prior to the determination of the peak position.

In a classical SAXS experiment, the scattering profile is measured using a monochromatic x-ray beam as a function of the scattering angle. In contrast, with an energy-sensitive detector, one can collect the scattering profile as a function of the scattered x-ray energy at a fixed angle using a polychromatic x-ray source (ED-SAXS). The energy  $E$  of the scattered photons is related with the scattering parameter  $q$  by

$$q = \frac{4\pi E \sin \theta}{12.398}, \quad (2)$$

where  $\theta$  is the employed scattering angle. The higher energy of the polychromatic beam photons involves some important advantages as an x-ray absorption decrease, an expansion of the accessible  $q$  range in the reciprocal space and a reduction in the spectrum acquisition time. This, together with the immobility of the experimental apparatus during data collection, makes energy-dispersive x-ray scattering a powerful technique in the study of time-dependent phenomena, like phase-transitions. On the other hand, the main inconvenience of the energy-dispersive method is a decrease in  $q$  resolution given by

$$\frac{\Delta q}{q} = \frac{\Delta E}{E} + \frac{\Delta \theta}{\tan \theta}, \quad (3)$$

where  $\Delta \theta$  and  $\Delta E$  are the angular resolution of the experimental setup and the energy resolution of the detector, respectively. However, this is not a real drawback when the diffraction or scattering patterns present broad oscillations, like in semicrystalline polymers.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: lucio.dilario@uniroma1.it

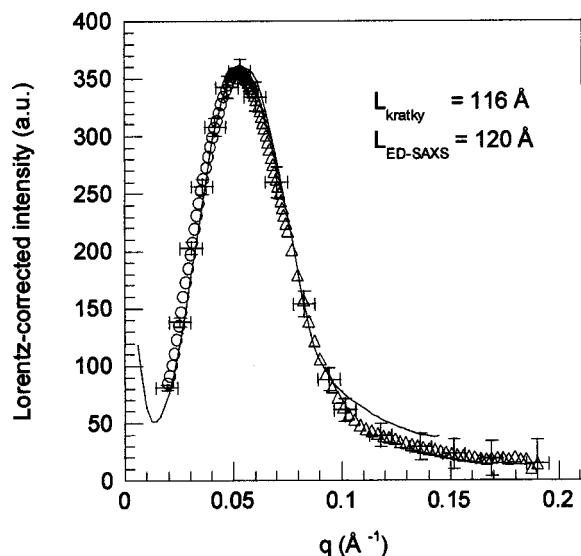


FIG. 1. Scattering profile of a standard Lupolen sample. (○) Corrected ED-SAXS profile measured at  $\theta=0.09^\circ$ . (Δ) Corrected ED-SAXS profile measured at  $\theta=0.22^\circ$ . (—) Desmeared SAXS intensity from a conventional Kratky camera.

Energy-dispersive small-angle x-ray scattering couples the information given by small-angle experiments and the advantages of energy-dispersive methods. ED-SAXS studies have already been done, especially by using the synchrotron radiation,<sup>1,2</sup> while only initial experiments were performed on polyethylene by Schultz<sup>3</sup> employing a commercial tungsten x-ray tube and the Kratky collimator system. However no further papers on this topic appeared after the Schultz publication which, in any case, did not show the entire scattering profile of the polyethylene samples analyzed, being limited to just one diffraction angle.

The energy-dispersive apparatus in use in our laboratory employs the bremsstrahlung continuum generated from a commercial tube as x-ray source and is based on a typical diffractometer design (short sample-detector distance) and a three-moving-slit collimation setup.<sup>4</sup> The capability of such instrument to perform ED-SAXS measurements was checked by investigating the morphology of two semicrystalline polymers, Lupolen and PPS, and the results obtained were compared with those obtained from a conventional angle-dispersive SAXS camera.

Lupolen is a crystalline polyethylene with well-known density and morphology at room temperature. It is commonly used as a standard to calibrate the SAXS intensity profile of a small-angle Kratky compact camera. In Fig. 1 the energy-dispersive results for a Lupolen sample are reported compared to those obtained by means of a conventional angle-dispersive Kratky camera.

Two scattering angles,  $\theta=0.09^\circ$  and  $0.22^\circ$ , were used to cover the characteristic small-angle  $q$  range. The useful x-ray energy of the incident beam ranged from 13 to 45 keV. The portion of the spectra at lower energy was not included in data processing, containing the fluorescence lines of the x-ray tube W anode. To obtain the corrected ED-SAXS profile comparable to that measured with the classical SAXS instrument, the raw energy-dispersive intensity was first corrected for the sample absorption and then normalized for the incident beam spectrum. The corrected data were then joined together and were multiplied by the factor  $q^2$  to obtain the

entire Lorentz-corrected ED-SAXS spectrum. The solid line in Fig. 1 is the Lorentz-corrected desmeared SAXS intensity of the sample, obtained by correction of the Kratky profile for the slit-length effect. The Vonk method,<sup>5</sup> specific for semicrystalline polymers, was used to perform the desmearing process. As shown in the figure, Lupolen exhibits a strong correlation peak in the small-angle region, well pointed out by both the angular and the energetic scan techniques. The  $L$  value of 120 Å, as well as the shape of the peak, revealed by the energy-dispersive data is in good agreement with that obtained by using the conventional angle-dispersive apparatus. On the contrary, a slight difference can be seen between the two profiles for  $q > 0.1 \text{ \AA}^{-1}$ , in the so-called Porod region. This difference could be generated from the desmearing process of the SAXS data, in which a careful background computation and subtraction in the tail region is necessary. The reported ED-SAXS data stop at  $q \approx 0.018 \text{ \AA}^{-1}$ , corresponding to  $\approx 350 \text{ \AA}$ . In fact, for lower  $q$  values, the x-ray scattering generated by air and by the collimation system becomes important. Measurements under vacuum, as well as reduction and subtraction of the parasitic scattering coming from the collimation system are necessary to reach lower  $q$  values.

To test the performance of our energy-dispersive x-ray spectrometer in time-resolved small-angle analysis, the evolution of the small-angle profile during the isothermal cold-crystallization of PPS was studied. Poly(*p*-phenylene sulphide) (PPS) is one of the most important and studied engineering polymers. It exhibits very good thermal stability, good mechanical properties and, when doped with  $I_2$ ,  $AsF_5$ ,  $SO_3$ , or  $TaF_5$ , it can become conductive. The crystallization kinetics of PPS from the solid amorphous state at different temperatures was already studied in our laboratories<sup>6</sup> by means of the wide-angle energy-dispersive x-ray diffraction and other techniques. Cold-crystallization experiments<sup>7</sup> on melt-quenched PPS were followed using four different diffraction angles ( $\theta=0.08^\circ$ ,  $0.15^\circ$ ,  $0.2^\circ$ , and  $0.25^\circ$ ) at the same temperature ( $T_c=104^\circ\text{C}$ ) for several hours, with an acquisition time of 300 s for each spectrum. The overall ED-SAXS profiles were then obtained by joining, after the appropriate corrections, the different x-ray spectra recorded at the different diffraction angles for equivalent acquisition times. The time-resolved ED-SAXS profiles are reported in Fig. 2 in double logarithmic scale as a function of the scattering vector  $q$ . For convenience each curve is shifted along the intensity axis.

After 900 s, a very broad hump appears and increases slightly in intensity with time. The final large peak obtained, after a crystallization time of 20 400 s, is centered at about  $q=0.06 \text{ \AA}^{-1}$ , corresponding to a long period of about 105 Å. This can be attributed to a low perfection lamellar packing that occurred at the low crystallization temperatures. The value of 101 Å, found for the long period of the same sample from an angle-dispersive scan, indicates, like in the previous Lupolen case, the good agreement between our energy-dispersive data and those obtained with the conventional Kratky camera. In order to study the crystallization kinetics, one can follow the evolution in time of the area of the overall Lorentz-corrected ED-SAXS profiles, the so-called invariant  $Q$ ,

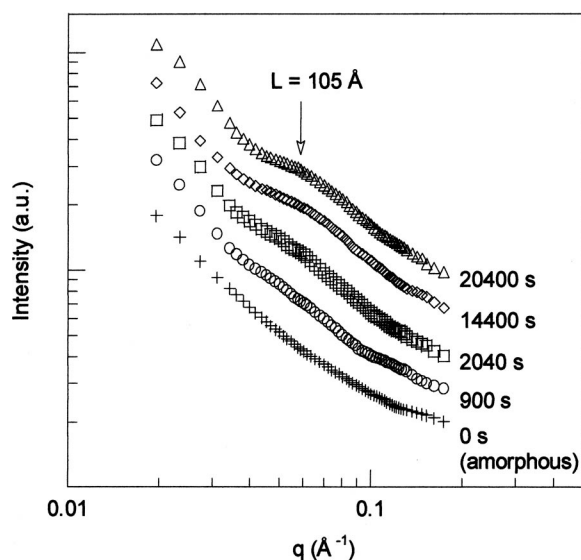


FIG. 2. Time-resolved energy-dispersive small-angle x-ray scattering profiles of PPS during the cold-crystallization process at  $T_c=104$  °C.

$$Q = \int_0^{\infty} I(q)q^2 dq. \quad (4)$$

In practice, to obtain precise values for  $Q$ , the experimental intensity must be extrapolated to the origin and to very large  $q$  values. However, integration of the Lorentz-corrected curves between the experimental limits,  $q_1$  and  $q_2$ , represents an adequate assessment of the invariant magnitude.

The evolution of the invariant during the isothermal cold-crystallization of PPS at 104 °C is shown in Fig. 3. The parameters for the overall crystallization process calculated by analyzing the evolution of  $Q$  by means of the model proposed by Ravindranath and Jog,<sup>8</sup> proved to be in accordance with those obtained for the same temperature with FTIR, wide-angle EDXD, and DSC analysis in our previous study.<sup>6</sup>

In conclusion, despite the lack of other evidence on the applicability of the ED-SAXS technique after the 30 year old Schultz paper, we have demonstrated the applicability of such a technique having found the solution to the nontrivial corrections problems to be faced when dealing with it, which will be discussed in a forthcoming wider paper. We have also shown that ED-SAXS makes it possible to deal with the structural evolution of polymer science time-dependent phenomena without requiring either the difficulties of access to

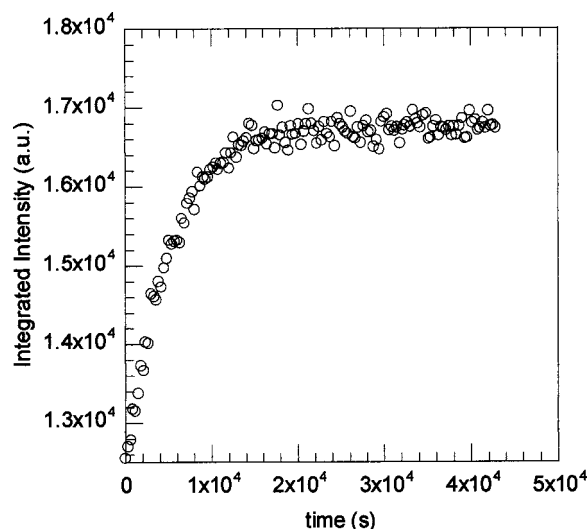


FIG. 3. Time evolution of the ED-SAXS invariant during the isothermal cold-crystallization of PPS at 104 °C.

synchrotron facilities or those concerning the use of slit-collimation small angle cameras like the Kratky one. Moreover the perspectives opened by our results of getting reliable results with the same laboratory instrument on both the wide and small angle regions let us foresee that useful modifications of the apparatus setup could be easily done and that a much larger application of this technique than today could be achieved.

Work is in progress to apply the energy-dispersive apparatus to studying other polymeric and nonpolymeric systems. The advantages and limits in performing small-angle measurements with our apparatus, as well as the description of the geometry of the collimation system, will be discussed in a detailed forthcoming paper.

<sup>1</sup>J. Bordas, *J. Appl. Crystallogr.* **11**, 434 (1978).

<sup>2</sup>K. L. Yu, C. H. Lee, C. S. Hwang, H. C. Tseng, P. K. Tseng, T. L. Lin, S. L. Chang, R. J. Sheu, and S. H. Chen, *Rev. Sci. Instrum.* **70**, 3233 (1999).

<sup>3</sup>J. M. Schultz and T. C. Long, *J. Mater. Sci.* **10**, 567 (1975).

<sup>4</sup>R. Caminiti, C. Sadun, V. Rossi Albertini, F. Cilloco, and R. Felici, *Proceedings of the 25th National Congress of Physical Chemistry, Cagliari, Italy, 17–21 June 1991; 1993, It. Pat. 01261484, 1991.*

<sup>5</sup>C. G. Vonk, *J. Appl. Crystallogr.* **4**, 340 (1971).

<sup>6</sup>R. Caminiti, L. D'Ilario, A. Martinelli, and A. Piozzi, *Macromol. Chem. Phys.* **202**, 2902 (2001).

<sup>7</sup>S. X. Lu, P. Cebe, and M. Capel, *Macromolecules* **30**, 6243 (1997).

<sup>8</sup>K. Ravindranath and J. P. Jog, *J. Appl. Polym. Sci.* **49**, 1395 (1993).

Applied Physics Letters is copyrighted by the American Institute of Physics (AIP).  
Redistribution of journal material is subject to the AIP online journal license and/or AIP  
copyright. For more information, see <http://ojps.aip.org/aplo/aplcr.jsp>