Time-Resolved SAXS Study of the Crystallization and Melting of Poly(ethylene oxide) Molecular Complexes

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As revealed by small angle X-ray scattering (SAXS) and differential scanning calorimetry studies, ultralong paraffins[1] and poly(ethylene oxide) (PEO) oligomers[2−6] crystallize with integral-folded (IFC) or non-integral-folded chains (NIFC), depending on their growth conditions. The occurence of NIFC crystals in the first stages of the crystallization process of oligomers of ethylene oxide was first reported by Cheng et al.[7,8] These NIFC crystals are metastable and transform into IFC crystals by a thinning or a thickening process. Raman longitudinal acoustic mode studies have shown that the chain axes in these NIFC crystals are inclined with respect to the lamellar surface.[5,6] During the conversion of NIFC crystals into IFC crystals, the chain axes become perpendicular to the basal planes of the lamellae. Large end groups such as *tert*-butoxy or phenoxy groups stabilize NIFC PEO crystals for hours to days during isothermal crystallization from the melt.[9]

The crystal structures of several molecular complexes between PEO and disubstituted aromatic compounds such as *p*-dihalobenzenes (PDX)[10,11] resorcinol (RES),[12] *p*-nitrophenol (PNP),[13] hydroquinone,[14] and 2-methylresorcinol[14] have been previously studied. Recently, we have shown that PEO−RES and PEO−PNP molecular complexes, with PEO molecular weights ranging between 2000 (2 K) and 10 000 (10 K), crystallize from the melt as IFC and NIFC crystals, respectively.[15] The SAXS study has clearly shown that the PEO6K−RES molecular complex crystallizes as extended chains (EC) lamellar crystals at temperatures higher than 60 °C. Samples crystallized at temperatures lower than 60 °C are mixtures of EC and 1IFC crystals. It is worth noting that these results have been obtained from the SAXS intensity curves recorded on samples crystallized for more than 10 h. It has been previously shown[16] that the NIFC lamellar crystals of the PEO−RES complex transform after a very long time at the crystallization temperature into integral-folded chains (IFC) and extended chains (EC) crystals. As such very long crystallization times are not very convenient for time-resolved SAXS measurements on synchrotron beam lines, we have preferred, after short crystallization times, to heat samples of PEO molecular complexes through their melting temperature or to anneal at temperature higher than the crystallization temperature.

This communication is a report of preliminary results obtained from a time-resolved SAXS study of the crystallization and melting of PEO6K−RES and PEO6K−PNP molecular complexes. The PEO6K oligomer used in this work was characterized by gel permeation chromatography. The number-average molecular weight $\langle M_n \rangle$ and the degree of polydispersity (p) are equal to 5425 and 1.09, respectively. The self-seeding technique has been used to ensure the reproducibility of the crystallization experiments.[2] The preparation of the PEO molecular complexes has already been described elsewhere.[14] The time-resolved

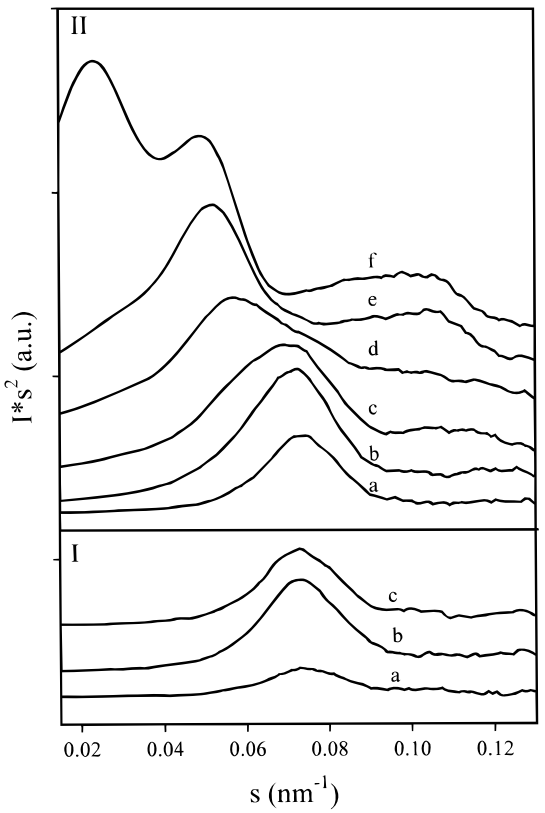

Figure 1. (I) Corrected SAXS intensity curves recorded during the crystallization of PEO6K−RES at 40 °C after crystallization times equal to 90 s (a), 210 s (b), and 1230 s (c). (II) Corrected SAXS intensity curves of PEO6K−RES crystallized at 40 °C in 1230 s recorded during the heating at 40 °C (a), 70 °C (b), 73.3 °C (c), 76.7 °C (d), 80 °C (e) and 90 °C (f). The recording time was 20 s for each SAXS curve in the crystallization and heating experiments.

SAXS measurements have been realized on the D24 SAXS beam line at L.U.R.E. (Centre Universitaire de Paris-Sud, Orsay, France). The SAXS intensities were measured with a linear position detector. The distance between the sample and the detector was 3 m. The SAXS curve of collagen fibers was used to calibrate the range of diffraction angles. The acquisition time is always equal to 20 s. The samples, wrapped between thin aluminium foils, were heated with a FP84HT hot stage (Mettler-Toledo) placed in the synchrotron X-ray beam line.

The crystallization of the PEO6K−RES molecular complex at $T_c = 40$ °C from the melt is first examined. Three Lorentz-corrected SAXS intensity curves, recorded at crystallization times (t_c) equal to 90, 210, and 1230 s display only one scattering peak, always characterized by the same long spacing equal to 13.7 nm (Figure 1, part I). As the thickness of the EC crystals of PEO6K−RES is equal to 38.2 nm,[15] the diffraction peak observed at 13.7 nm does not result from 1IFC or 2IFC crystals, but rather to NIFC crystals. The large width of the SAXS peak supports also the occurrence of NIFC crystals in the first stages of crystallization. After a crystallization time $t_c = 1230$ s at $T_c = 40$ °C, the sample was heated at 10 °C/min until it melted. Six selected SAXS intensity curves recording during the heating are presented in part II of Figure 1. The SAXS peak position continuously shifts to lower Bragg angles with increasing temperatures which is unambiguously an additional proof of the occurence of NIFC crystals in the PEO6K−RES sample initially crystallized at 40

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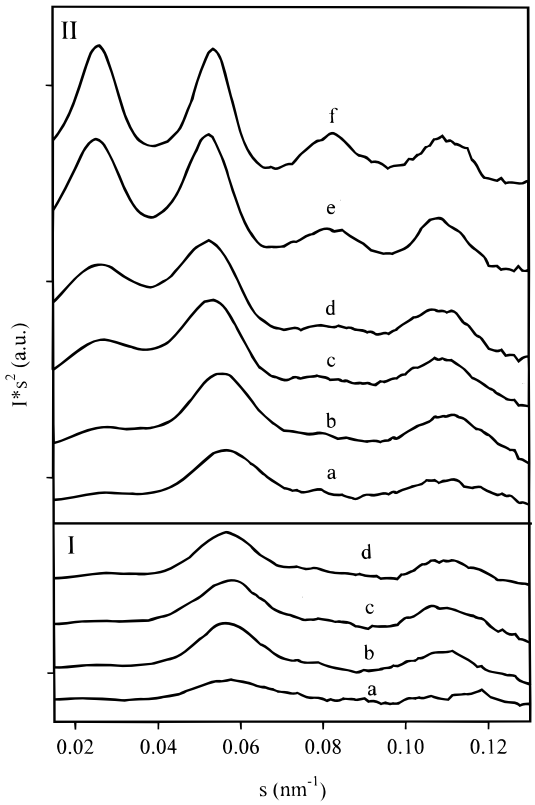

Figure 2. (I) Corrected SAXS intensity curves recorded during the crystallization of PEO6K−RES at 55 °C after crystallization times equal to 240 s (a), 280 s (b), 320 s (c), and 600 s (d). (II) Corrected SAXS intensity curves recorded during the annealing at 80 °C of PEO6K−RES previously crystallized at 55 °C in 600 s. Curves a to g refer to annealing times of 0, 54, 114, 154, 214, 814, and 1214 s, respectively.

°C. While the sample is heating, a second SAXS peak appears at 76.7 °C as a shoulder on the low diffraction angle edge of the main SAXS peak. The value of the long spacing of this shoulder is found to be equal to 18.7 nm and is attributed to the first order of 1IFC lamellar crystals. In the same time, the NIFC peak vanishes, i.e., well before the melting of the sample. Afterward, at 80 °C and at higher temperatures, a scattering peak at $s = 0.26$ nm^{-1}, corresponding to EC crystals, appears. The intensity of the scattering peak of EC crystals increases with respect to time and becomes, at 90 °C, more important than the SAXS peak of 1IFC crystals. In conclusion, up to 73 °C, only NIFC crystal thickening is observed by an annealing process. Above 73 °C, two processes are occuring simultaneously: (1) the thickening of NIFC crystals and their transformation into 1IFC crystals; (2) the transformation of 1IFC crystals into EC crystals above 85 °C. The linear degree of crystallinity in the lamellar stacks, estimated from the SAXS correlation function, is roughly constant ($v_c^{lin} = 0.82 \pm 0.02$) during the crystallization and the heating processes, indicating that the crystallinity does not depend on the morphology of the lamellar crystals (1IFC or EC).

Four typical Lorentz-corrected SAXS intensity curves recorded at increasing times of t_c during the crystallization of PEO6K−RES at 55 °C are shown in Figure 2 (part I). After a crystallization time of $t_c = 240$ s, a broad SAXS diffraction peak with a long spacing of 17.5 nm is observed. This long spacing value is close to the lamellar thickness of 1IFC crystals (18.2 nm).[15] However, taking into account the width of the SAXS peak (from 0.04 to 0.08 nm^{-1}), this attribution could be questioned and the hypothesis of NIFC lamellar crystals

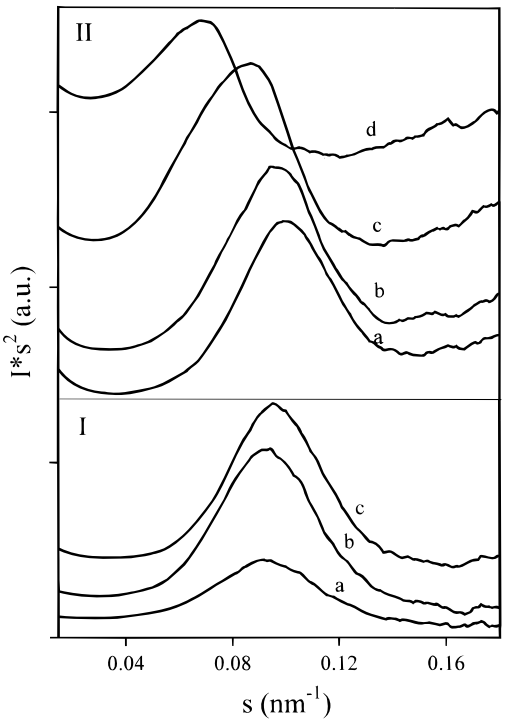

Figure 3. (I) Corrected SAXS intensity curves recorded during the crystallization of PEO6K−PNP at 60 °C after crystallization times $t_c = 120$ s (a), 220 s (b), 400 s (c), and 640 s (d). (II) Corrected SAXS intensity curves recorded during the heating of the PEO6K−PNP sample (previously crystallized at 60 °C in 640 s) at 73.7 °C (a), 80.3 °C (b), and 90.3 °C (c).

cannot be fully disregarded, as shown later. A second SAXS peak, with a long spacing of 9.1 nm, which is the second order of the first long spacing, is developing.

After a crystallization time of $t_c = 600$ s at 55 °C, the sample has been annealed at 80 °C. Some selected SAXS intensity curves recorded during this annealing are displayed in Figure 2 (part II). In the first stages of annealing, a small continuous shift of the long spacing to a lower scattering angle and a decrease of the width of the SAXS peak occur. These observations support that metastable NIFC crystals are present in the sample crystallized at 55 °C. After an annealing time of 114 s, a SAXS peak corresponding to the EC crystals ($s = 0.26$ nm^{-1}, $L = 38.4$ nm,) appears and becomes finally the most intense with increasing annealing time. The transformation of NIFC into 1IFC crystals and the thickening of 1IFC into EC crystals take place simultaneously. As for the crystallization at $T_c = 40$ °C, the linear degree of crystallinity estimated from the SAXS correlation function remains nearly constant ($v_c^{lin} = 0.87 \pm 0.02$), during the crystallization and the annealing. The degree of crystallinity of the PEO6K−RES molecular complex slightly increases with the crystallization temperature as for pure polymer samples.

Finally, a PEO−PNP sample has been crystallized from the melt at 60 °C during a given time (640 s) and afterward was heated until it melted at 2 °C/min. Four selected SAXS intensity curves recorded at $t_c = 120$, 220, 400, and 640 s are shown in Figure 3. During the crystallization, only one broad diffraction peak is observed in the SAXS curve. Its maximum slightly shifts from 11 to 10 nm with increasing crystallization time. This small decrease of the long spacing with crystallization time results from a segregation of molecular

weights, the crystallization of the longest chains being first observed. The progressive increase of the long spacing observed during heating confirms that the PEO−PNP complex crystallizes as metastable NIFC crystals. As previously reported,[15] neither IFC nor EC crystals are observed for the PEO−PNP molecular complex. The linear degree of crystallinity, estimated from the SAXS correlation function, continuously increases from 0.70 to 0.75 during the crystallization and remains constant during the heating of the sample. This v_c^{lin} value is lower than the value obtained for the PEO6K−RES samples (0.82 for $T_c = 40$ °C and 0.87 for $T_c = 55$ °C).

In conclusion, the PEO6K−RES molecular complex crystallizes as NIFC crystals in the first stages of crystallization. As for NIFC crystals observed in pure PEO oligomers with hydroxy end groups, the NIFC crystals of PEO6K−RES progressively transform into IFC and/or EC crystals. Depending upon the crystallization conditions such as temperature and time, NIFC, IFC, and EC lamellar crystals can coexist in the same sample of the PEO−RES molecular complex. The PEO−PNP molecular complex crystallizes from the melt as NIFC crystals. While the sample is heating subsequent to the crystallization, the lamellar thickness of the NIFC lamellar crystals continuously increases with temperature. Contrary to the lamellar crystals of PEO−RES, the NIFC crystals of PEO−PNP never transform into IFC crystals. Further experiments to gain insight into these modifications of the lamellar morphology of PEO molecular complexes are in progress.

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