



**DUTCH-BELGIAN BEAMLINE  
AT ESRF**

**EUROPEAN  
SYNCHROTRON  
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## **Experiment Report Form**

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
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- make sure that the text, tables and figures fit into the space available.
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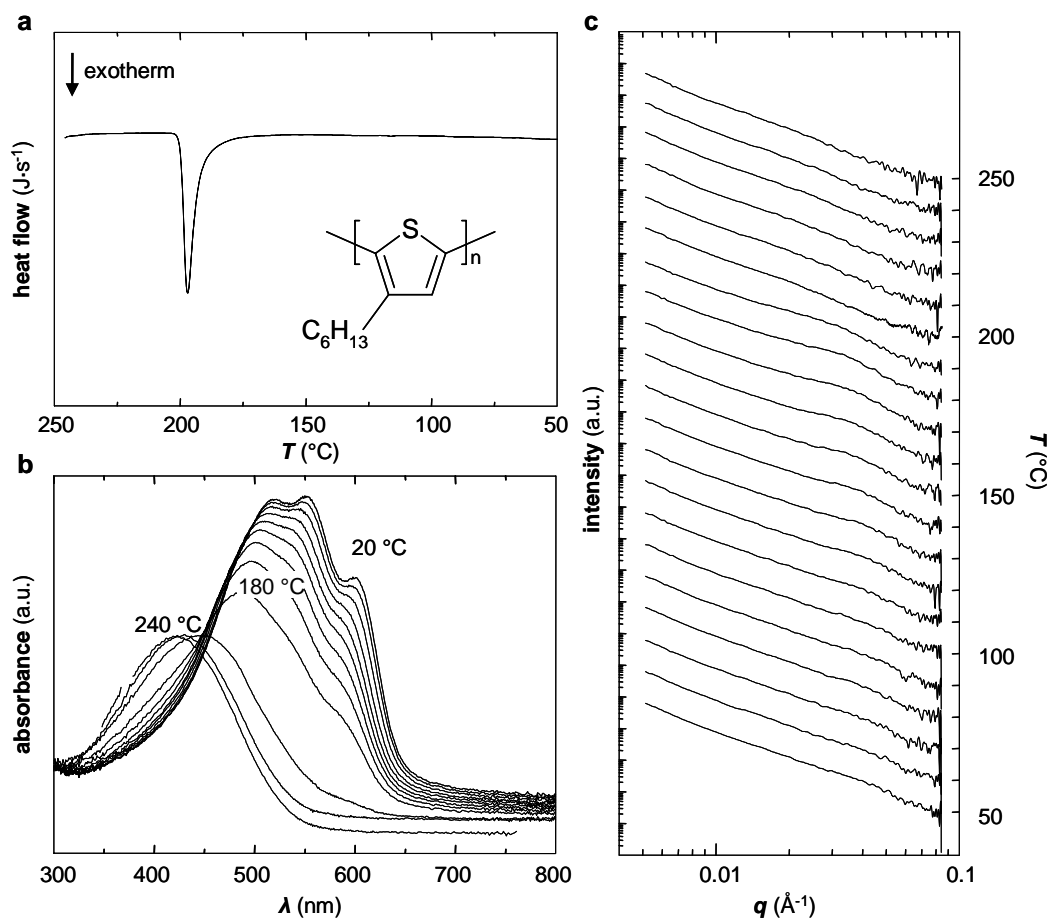
	<b>Experiment title:</b> Melt-Solidification of Poly(3-hexylthiophene)	<b>Experiment number:</b> 26-02-394
<b>Beamline:</b> BM26B	<b>Date(s) of experiment:</b> From: 21-11-2007 To: 24-11-2007	<b>Date of report:</b> 13-12-2007
<b>Shifts:</b> 9	<b>Local contact(s):</b> Giuseppe Portale	
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## Report:

Poly(3-hexylthiophene) (P3HT), a semi-crystalline, conjugated polymer, has recently received much attention as a potential material for use in various *opto*-electronic applications because it combines good processability and excellent semiconducting properties. The polymer has been found to form elongated structures when solidified from both, solution and melt, often referred to as *whiskers*.<sup>1</sup> The width of such crystalline entities has been shown to correlate well with dimensions deduced from periodicities obtained from small-angle X-ray scattering (SAXS) experiments.<sup>2</sup> Here we have attempted to characterize the development of microstructure during solidification of P3HT from the melt by means of temperature-dependent SAXS measurements.

The polymer studied here, provided by Merck Chemicals, Ltd., had an approximate weight-average molecular weight,  $M_w$ , of 22,000 g/mol, polydispersity of 1.6 and regio-regularity around 96 %. Cooling thermograms recorded with differential scanning calorimetry (DSC) revealed a sharp crystallization exotherm below  $\sim 200$  °C (cf. Figure 1a). Ultraviolet-visible light (UV-vis) spectroscopy indicated a strong shift of the absorbance maximum of P3HT from 420 to above 550 nm (cf. Figure 1b). This red-shift during solidification has previously been attributed to an increase in conjugation length along the polymer backbone because of increased order of this compound.<sup>3,4</sup>

Temperature-dependent SAXS diffractograms reveal development of a distinct periodicity around  $0.3 \text{ \AA}^{-1}$  below 200 °C –i.e. the onset of crystallization– indicating alternating amorphous and ordered domains (cf. Figure 1c). This periodicity drifts to about  $0.4 \text{ \AA}^{-1}$  or 16 nm during solidification, which is in concert with typical widths of P3HT *whiskers* reported previously. Most strikingly, and confirmed by UV-vis spectroscopy, development of the microstructure appears to continue at temperatures much below the onset of crystallization. It is also worth noting that, when approaching room temperature, SAXS reflections of P3HT significantly decrease in strength, hence, implying a highly ordered material.



**Figure 1.** **a** Differential scanning thermogram recorded during cooling from 250 °C to ambient at 10 °C/min. The polymer displays a strong solidification exotherm at ~195 °C. **b** UV-vis spectra recorded during cooling indicate a strong red-shift of P3HT below 200 °C. **c** Small-angle X-ray diffractograms collected during cooling at 10 °C/min indicate development of a distinct periodicity around 16 nm.

## References

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- (2) Zhang, r.; Li, B.; Iovu, M. C.; Jeffries-El, M.; Sauvé, G.; Cooper, J.; Jia, S.; Tristram-Nagle, S.; Smilgies, D. M.; Lambeth, D. N.; McCullough, R. D.; Kowalewski, T. *J. Am. Chem. Soc.* **2006**, *128*, 3480-3481.
- (3) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci. Polym. Phys.* **1987**, *25*, 1071-1078.
- (4) Salaneck, W. R.; Inganäs, O.; Themans, B.; Nilsson, J. O.; Sjogren, B.; Osterholm, J. E.; Bredas, J. L.; Svensson, S. *J. Chem. Phys.* **1988**, *89*, 4613-4619.