

Impact of morphology on T-NIL with semi-crystalline P3HT

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Regarding the low cost and simple fabrication of organic electronics (OPVCs, OTFTs and OLEDs), semi-conducting polymers are highly interesting. P3HT (poly 3-hexylthiophene) is an interesting material in this group, due to its easy fabrication, stability and high mobility. Mobilities as high as about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are reported for ordered crystallites with a π - π stacking, similar to the one of the backbone of the molecule¹. In contrast, the mobility in the disordered amorphous region is lower than $10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Therefore, the number, the size and the orientation of the crystallites (morphology) play a significant role in improving the electrical properties of P3HT for industrial demands. Thermal nanoimprint is a good candidate for controlling the morphology of P3HT².

To control the morphology³ of semi-crystalline P3HT we investigated material with different regularities (50% and 92%). By DSC (differential scanning calorimetry⁴) the glass transition temperature T_g was found to be about $5 \text{ }^\circ\text{C}$ and $-10 \text{ }^\circ\text{C}$ for the regio-random and regio-regular material, respectively (Fig.1). In addition, the measurement indicates a melting of the crystallite at about $235 \text{ }^\circ\text{C}$ and a re-crystallization at about $200 \text{ }^\circ\text{C}$ with regular P3HT, only. The low T_g is responsible for some reflow obtained at room temperature with the random material (Fig. 2a). Under similar conditions no reflow is observed with regular P3HT (Fig. 2b) due to the crystallites that have only small amorphous regions between.

With regular P3HT, the morphology is influenced by crystallinity, which is e.g. determined by imprint temperature and cooling rate. Fig. 3 shows the imprint result for regular P3HT obtained at different temperatures. At $200 \text{ }^\circ\text{C}$ the rough surface indicates that crystallites are still present at $T_{\text{imp}} < T_m$. In contrast, at $250 \text{ }^\circ\text{C}$ the surface is flat as the crystallites have been melted at $T_{\text{imp}} > T_m$. During cool-down the cooling rate determines the final size of the re-formed crystallites.

We will demonstrate that the degree of crystallization can be increased by a controlled slow-down of the cooling process, where the interaction with substrate and mold surface also directs the crystal orientation. The crystalline orientation will be probed by transmission measurements with s- and p- polarized light.

¹ H. Sirringhaus et al., Nature 401, 658 (1999)

² M. Aryal, K. Trivedi and W. Hu, ACS Nano 3, 3085 (2009)

³ R. J. Kline et al., Macromolecules 38, 3312 (2005)

⁴ Y. Zhao, G. Yuan, P. Roche and M. Leclerc, Polymer 36, 2211 (1995)

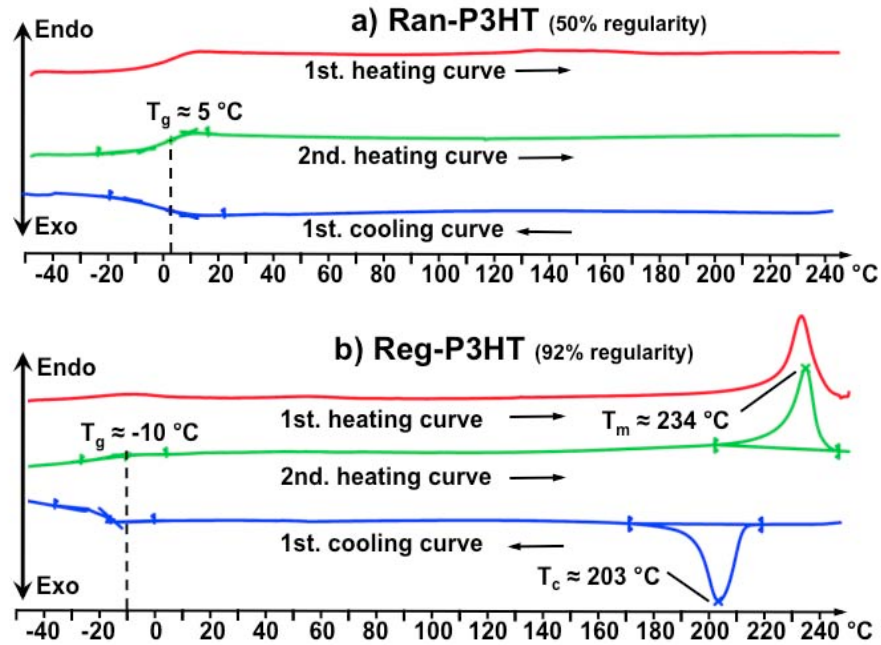


Figure 1: DSC measurement under Ar flow (30 ml/min) with cooling and heating rate 10 °C/min, a) random-P3HT, b) regular-P3HT. Only regular P3HT features melting (T_m) and re-crystallization (T_c).

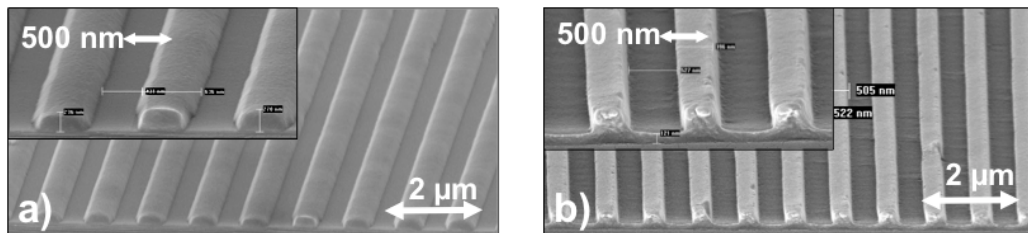


Figure 2: Imprint results with 5 min, 100 bar (line/space 500 nm/500 nm and height 350 nm), a) Ran-P3HT (initial layer 100 nm) imprint at 200 °C, b) Reg-P3HT (initial layer 300 nm) imprint at 250 °C. The rounding of the profile with Ran-P3HT (a) is due to reflow at room temperature ($T_g \approx 5$ °C).

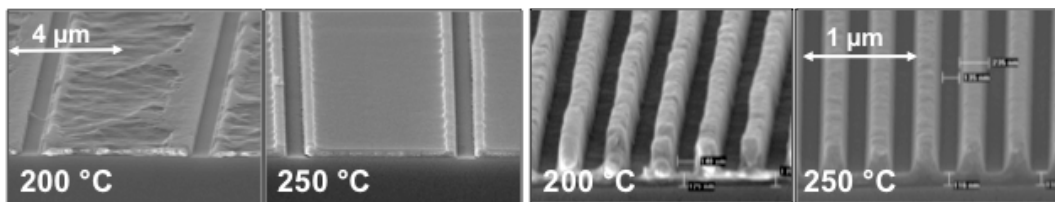


Figure 3: Morphology of the reg-P3HT at different imprint temperatures (line/space 500 nm/5 μm and 190 nm/190 nm). With an imprint below T_m the structures are rough as the crystallites have not yet melted.