EXPERIMENTAL REPORT

Title: GIXD study of alignment process and formation of new structures of thin layers of p-BTTT. In situ study of structural transitions under heating.

Experiment number: HC-1143

Instrument: BM02 (D2AM)

From 2014 / 01 / 30th to 2014 / 02 / 3rd

Local contacts: N. Blanc and N. Boudet.

Purpose of the proposal:

The in-plane and out-of-planes structures of highly oriented and crystallized thin layers of several semi-conducting conjugated polymers of the poly(2,5-bis(3-alkyl)thieno[3,2-b]thiophene p(BTTT) family have been studied by GIXRD. The studied polymers were provided with different alkyl side groups C_8H_{17} (C8-pBTTT), $C_{12}H_{25}$ (C12-pBTTT), $C_{14}H_{29}$ (C14-pBTTT) and $C_{18}H_{37}$ (C18-pBTTT) and also had different molecular masses.

All these samples were prepared as rubbed thin layers at different temperatures. In such a way we wanted to check the influences of the molecular mass, the side groups and the rubbing temperature.

So we studied the list of following samples:

C8pBTTT M=25k

C12pBTTT M=8k Rubbing Temperature 100°C. We have studied this sample as a function of temperature in order to follow the phase transition which was previously observed by electron microscopy.

C12pBTTT M=45k Rub Temp 100°C

C12pBTT M=27k RubTemp 240°C

C12pBTTT M=81k Rub Temp 100°C. We have studied this sample as a function of temperature in order to follow the phase transition which was previously observed by electron microscopy and also to compare with the low mass polymer.

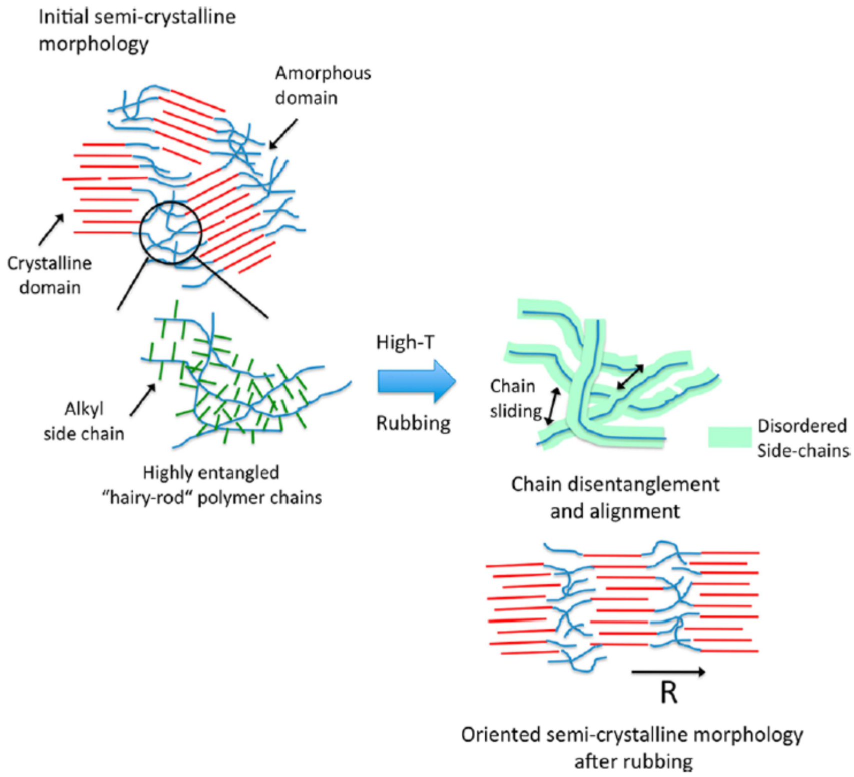
C14pBTTT M=27k RubTemp: 100°C

C18pBTTT M=45k RubTemp=170°C.

In addition to this family we also studied first one sample of poly(3-Hexyl-thiophene) –P3HT with a mass of 43 k and a rubbing temperature of 180°C and one polyfluorene film with a 56k mass and which was rubbed at 125°C.

The complete analysis of the whole data is not yet completed. In particular we are working on the results obtained for the in situ experiments in order to put in parallel these results with results obtained by in situ measurement of electron microscopy and buy UV-vis spectroscopy.

However we could establish from these first measurements done on different type of conjugated polymers that high-T rubbing is a promising and general method to align conjugated polymers without resorting to an alignment substrate. These polymers show a gradual increase of orientation with increasing temperature during rubbing. The optimum rubbing temperature depends on molecular weight and the molecular weight distribution as evidenced for P3HT and C12-pBTTT and it can be limited by a transition to a Liquid Crystal phase. Higher molecular masses require higher rubbing temperatures. This trend indicates an alignment mechanism whereby the progressive disordering of alkyl side chains allows the hairy-rod-like macromolecules to disentangle and align upon rubbing. (see scheme below).



Schematic illustration of the mechanism responsible for the alignment of "hairy-rod" semiconducting and semicrystalline polymers upon high temperature mechanical rubbing.

All these conclusions have been drawn from the comparison of some of data obtained on BM02 with results obtained by electron microscopy and UV-vis spectroscopy. We have already published these results in the following paper:

"High Temperature Rubbing: A Versatile Method to Align pi-Conjugated Polymers without Alignment Substrate", L. Biniek, S. Pouget, D. Djurado, E. Gonthier, K. Tremel, N. Kayunkid, E. Zaborova, N. Crespo-Monteiro, O. Boyron, N. Leclerc, S. Ludwigs, M. Brinkmann, **Macromolecules** (2014) dx.doi.org/10.102/ma500762x.