


**Experiment title:**

Lamellar thickness control of tailored polyethylene oxide copolymers with specific 'spacer' segments.

**Experiment**
**number:**

**26-02-380**

**Beamline:**

26-02

**Date(s) of experiment:**

From: 21-06-2007

To: 25-06-2007

**Date of report:**

25-07-2007

**Shifts:**

12

**Local contact(s):** Kristina Kvashnina

**Names and affiliations of applicants (\* indicates experimentalists):**

Dr. Ir. Han GOOSSENS, TU/e, Eindhoven, Nederland

Dr. Giuseppe PORTALE, DUBBLE @ ESRF, Grenoble, France

Ir. Mark VAN DER MEE, TU/e, Eindhoven, Nederland

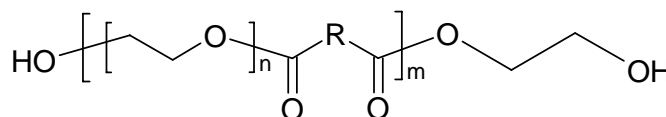
\* Dr. Guido HEUNEN, UCL, Louvain-la-Neuve, Belgium

\* Ir. Dimitri ROUSSEAU, UCL, Louvain-la-Neuve, Belgium

\* Pierre GUILLET, UCL, Louvain-la-Neuve, Belgium

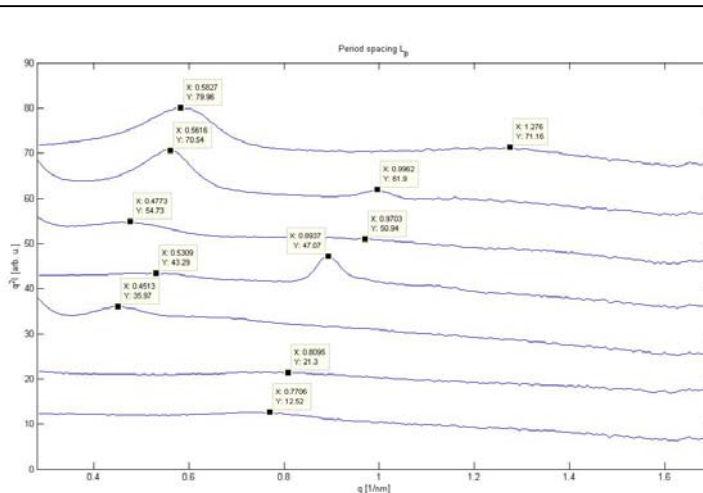
**Report:**

Here we demonstrate that the lamellar thickness in polyester copolymers based on OH-telechelic PEO ( $M_w \sim 1000$  g/mol) and dicarboxylic spacers, figure 1, with specific size, steric hindrance and/or flexibility (malonyl dichloride (MC), glutaryl dichloride (GC), phthaloyl dichloride (PC), isophthaloyl dichloride (IPC) and terephthaloyl dichloride (TPC)), is controlled by the molecular structure.



**Figure 1: Polyester molecular structure**

Figure 2 shows an overview of the long period  $L_p$  for various flexible and rigid polyester samples, and pure PEO samples. Here we can observe two distinct features. Samples of pure PEO and flexible polyesters show more than one reflection. Although, harmonics can be suggested, it does not account for all of the samples. The nature of these reflections is still under investigation. Within the same class of polyesters (i.e.



**Figure 2: Long period spacing  $L_p$**

flexible or rigid), the position of the first order reflection are similar. The rigid polyesters have much lower lamellar spacings than the flexible ones.

The temperature of fusion ( $T_m$ ), see table 1, obtained by differential scanning calorimetry (DSC), for flexible polyesters is close to the  $T_m$  of the starting PEO<sub>1000</sub>. However,  $T_m$  for the rigid polyesters is significantly lower. This suggests a strong decrease of the crystal melting enthalphy for the rigid polyesters through a lamellar thickness (Gibbs-Thomson) effect. Hence it appears possible to control the lamellar thickness by controlling the rigidity of the spacers. This is confirmed by the SAXS results.

	$M_w$ [kg/mol]	PD	$T_m$ [°C]
PEO 1000	1	1.02	38.6
PEO 10500	10	1.05	64.4
PEO 53500	53	<1.1	64.5
PEG-MC	15	1.7	41.0
PEG-GC	21	1.7	38.8
PEG-PC	9	1.6	32.7
PEG-IPC	20	1.8	29.7
PEG-TPC	17	1.9	25.6

**Table 1: DSC data, where PD = poly dispersity, heat/cool rate of 10°C/min**

Currently we are preparing a paper on the results obtained from the experiments under non-flow conditions. Furthermore we will propose a follow-up of experiments concerning PEO-polyesters under flow conditions in order to obtain details on the flow-induced self-organisation of tailored polyethylene oxide copolymers with specific 'spacer' segments.