



Experiment title:

Flow induced self-organisation of tailored polyethylene oxide copolymers with specific 'spacer' segments

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SC 2175

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9

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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.

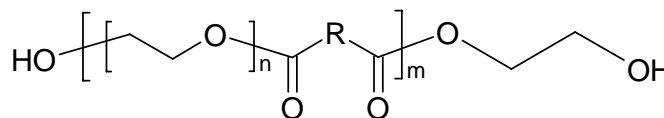


Figure 1: Polyester molecular structure

Figure 2 shows an overview of the long period L_p for various flexible and rigid polyester samples, and pure PEO samples. 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. flexible or rigid), the position of the first order reflections are similar. The rigid

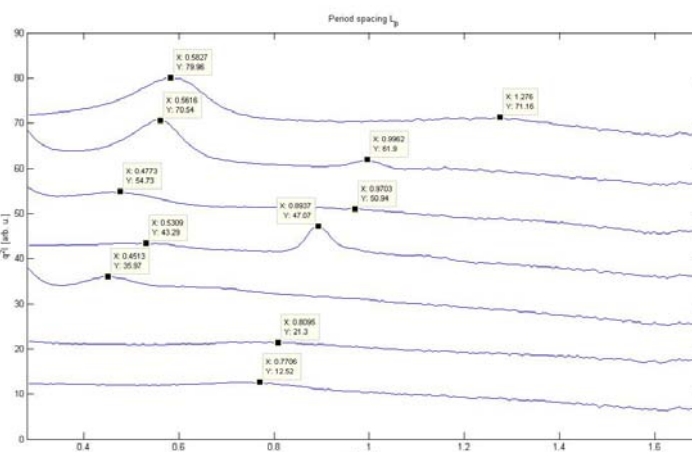


Figure 2: Long period spacing L_p

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 PEO₁₀₀₀. However, T_m for the rigid polyesters is significantly lower. This suggests a strong decrease of the crystal melting enthalpy 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°/min

Submitting polyesters to shear shows a flow induced crystallisation behaviour. The time between the applied shear and the onset of crystallisation decreases with increasing shear rates (figure 3). However, we could not yet observe details on flow-induced self-organisation.

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.

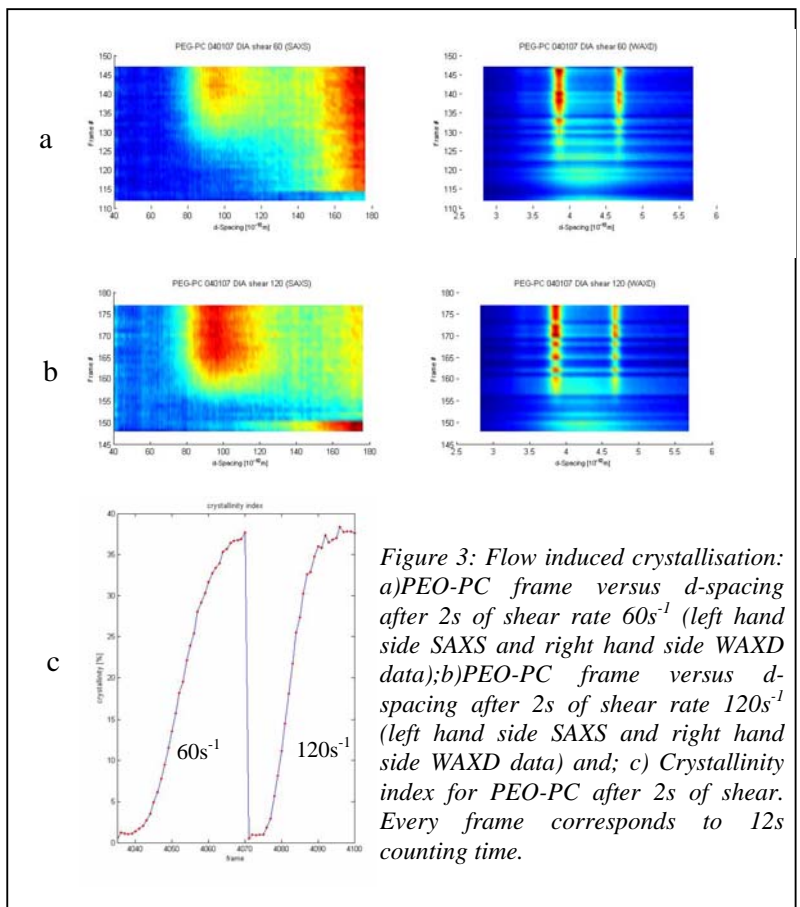


Figure 3: Flow induced crystallisation: a)PEO-PC frame versus d-spacing after 2s of shear rate 60s⁻¹ (left hand side SAXS and right hand side WAXD data);b)PEO-PC frame versus d-spacing after 2s of shear rate 120s⁻¹ (left hand side SAXS and right hand side WAXD data) and; c) Crystallinity index for PEO-PC after 2s of shear. Every frame corresponds to 12s counting time.