



Experiment title: Polymer-diblock polymer systems prepared via in-situ polymerisation of monomer: morphology control for ultimate mechanical properties	Experiment number: SC-611	
Beamline: BM 26	Date of experiment: from: 24-9-1999 to: 28-9-1999	Date of report: 17-02-2000
Shifts: 12	Local contact(s): Dr. Wim Bras	<i>Received at ESRF:</i>
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Report:

The brittleness of amorphous polymers is the result of strain localization in the form of crazes. Considering the network density, the intrinsic toughness of PS is expected to be higher than PC known as a ductile polymer, which deforms via shear yielding. The occurrence of crazing or shear yielding can be found in the relative extent of intrinsic strain softening and strain hardening. A high network density causes a more pronounced strain hardening enhancing delocalization of defects. PS suffers from strong strain softening in combination with limited strain hardening, giving rise to an extreme localization during deformation by crazing. Delocalization can be used to toughen PS, since this will transfer the high intrinsic ductility to the macroscopic level. Maximum toughness is expected for an easily cavitating modifier, which subsequently supports the strain hardening process at higher strain. These requirements can be obtained using a self-assembly process of block-copolymers in solution (micelles). These micellar structures should be formed in a monomer, which after polymerization forms the brittle amorphous matrix. The monomer should be a selective solvent for the block copolymer, i.e. a good solvent for one block and bad for the other block. The shell block can be a rubber or other easily deforming soft polymer. The inner block should possess a low resistance against cavitation. The final particle size is dependent on the competition between phase separation and polymerization and the relative time scales involved. A restricted mobility may result into fixation of non-equilibrium morphologies.

For this study, diblock-copolymers were synthesized by the ATRP of ethylacrylate and butylacrylate using hydrogenated polybutadiene and PEO macro-initiators. The PMMA blends were prepared by isothermal bulk-polymerization of the homogeneous diblock-copolymer/monomer solutions. For thermal initiation of the polymerization, DBPO and AIBN were used as initiator. In order to determine the influence of the reaction conditions on the morphology, the polymerizations were performed at different temperatures and initiator.

To study the morphology development upon in-situ polymerization of MMA, time resolved SAXS experiments were performed. Solutions were transferred into Lindemann capillaries and sealed subsequently. The capillaries were placed in a capillary holder fixed on a Linkam THMS 600 hotstage. The SAXS patterns were collected every 2 minutes on a 2D detector positioned 8.5 meters from the sample. The SAXS patterns for the polymerization of MMA at 100°C with 5-wt% PB-PBA are depicted in Figure 1. The increased intensity after approx. 30 minutes at small angles indicates that macrophase separation occurs, resulting in PMMA-rich and block-copolymer-rich phase. Simultaneously, a diffraction peak comes up (d-spacing = 228Å), which originates from the block-copolymer-rich phase and corresponds to the first order of the cylindrical phase. This leads to an internal structure in the copolymer-rich phase similar to the characteristic

micro-phase structure of the block-copolymer itself (Figure 1b). Comparable results were found for all polymerizations with PBA-based diblock copolymers.

The SAXS patterns for the polymerization of MMA at 100°C with 10-wt% PB-PEA are depicted in Figure 2a. From these results, it is also evident that macrophase separation occurs during the polymerisation for these systems. But after the onset of phase separation after approx. 40 minutes, two reflections are observed which merge into one after 60 minutes. At the same time, a second order reflection appears. This may be indicative for the presence of two types of structures within the block-copolymer rich domains. One which is still swollen by the monomer and one which is dried. On continued polymerisation, the monomer concentration is reduced and the structure of the block-copolymer rich domains resembles more and more the structure of the pure block-copolymer, resulting in the appearance of the second order. In figure 1c the pattern for the pure PB-PEA diblock is depicted.

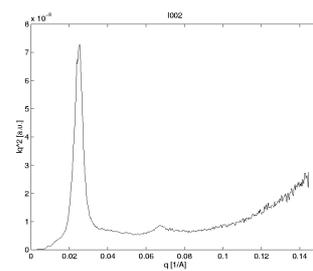
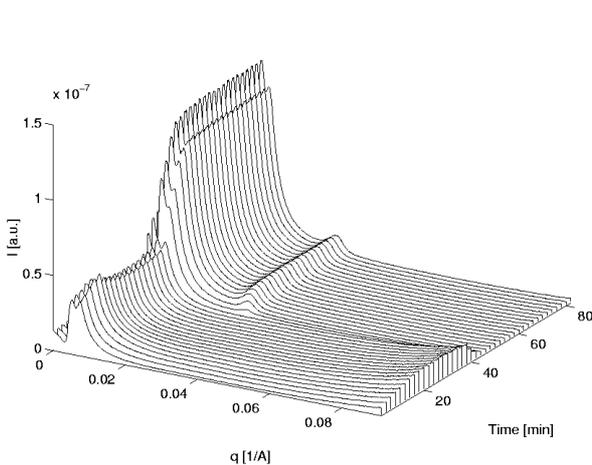


Figure 1b: Pure PB-PBA

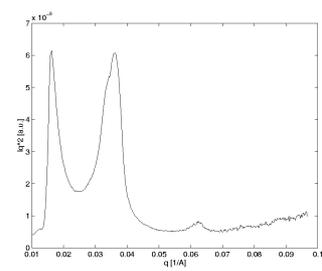


Figure 1c: Pure PB-PEA

Figure 1a: Time resolved SAXS spectra for the polymerization of MMA with 5-wt% PB-PBA, T =100°C.

10%PB-PEA

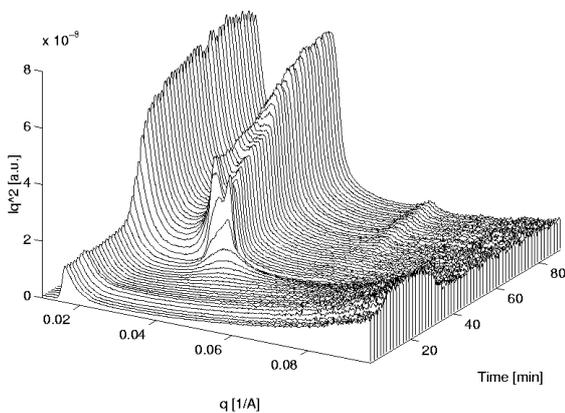


Figure 2a: Time resolved SAXS spectra for the polymerization of MMA with 10-wt% PB-PEA, T =100°C.

The SAXS patterns for PEO blends didn't show any macrophase separation and transparent blends were obtained.

Conclusions

The experimental results from the SAXS measurements gave more insight in the influence of temperature and composition on the final morphology. The macrophase separation between monomer/polymer phase and diblock-copolymer during polymerization averts a nano-sized morphology and should be avoided.