

## Preparation of nano-sized particles for improved toughness

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# Preparation of Nano-Sized Particles for Improved Toughness

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## Introduction

For brittle amorphous polymers, the *maximum impact strength* and *minimum loss in stiffness* can be obtained by using easy cavitating nano-sized modifiers. The self-assembly process of diblock-copolymers in micelles can be used to prepare such systems [1]. These micellar structures should be formed in monomers, like styrene or methyl methacrylate (MMA), which after polymerisation form the continuous phase.

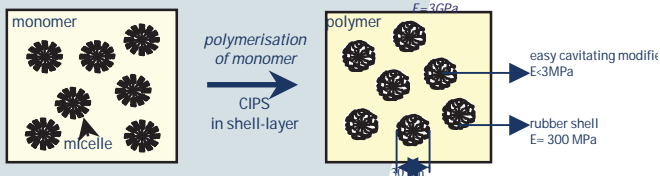


Figure 1 : Schematic representation of the proposed morphology.

## Material preparation

The diblock-copolymers were synthesized by the Atom Transfer Radical Polymerisation of methylacrylate (MA) and butylacrylate (BA) using hydrogenated poly(butadiene) (PB) ( $M_n = 3840$  g/mol) macroinitiators.

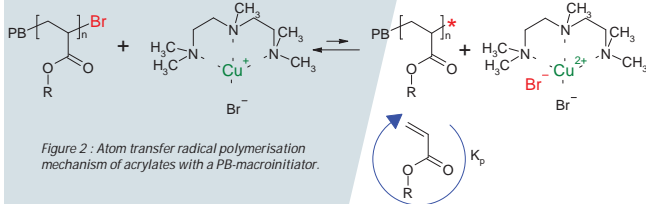


Figure 2 : Atom transfer radical polymerisation mechanism of acrylates with a PB-macroinitiator.

## Results

Diblock copolymers were synthesized with a  $M_n$  of 10000 g/mol,  $M_w/M_n \sim 1.10$  and lamellar bulk morphology.

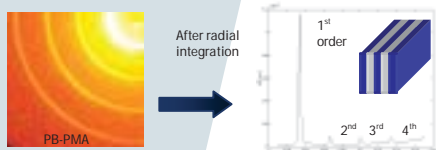


Figure 3 : SAXS pattern of PB-PMA presenting the lamellar morphology, d-spacing 179 Å.

The morphology of PS and PMMA blends was studied by:

- ❖ various microscopy techniques
- ❖ time resolved Small Angle X-ray Scattering (SAXS)

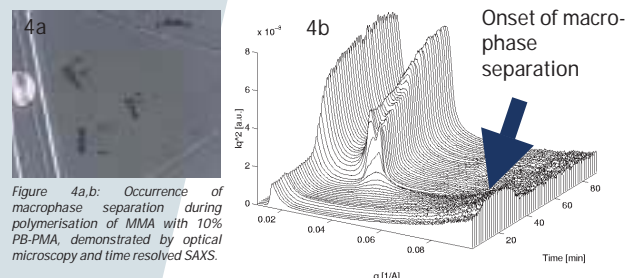


Figure 4a,b: Occurrence of macrophase separation during polymerisation of MMA with 10% PB-PMA, demonstrated by optical microscopy and time resolved SAXS.

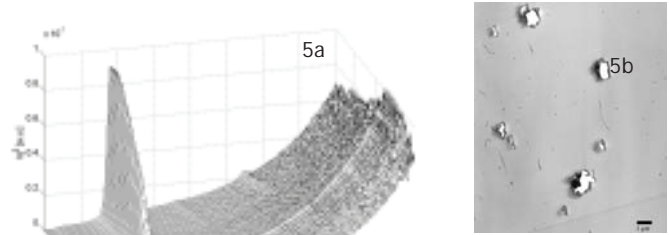


Figure 5a and b: Macrophase separation in PS blend with 10% PB-PMA, demonstrated by time resolved SAXS and TEM.

Incorporation of a strong proton-donating unit, i.e. p-(hexafluoro-2-hydroxy-isopropyl)styrene (HFS), into PS will result in *intermolecular hydrogen bonding* between PS matrix and acrylate-based copolymers and will avoid macro-phase separation [2].

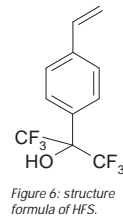


Figure 6: structure formula of HFS.

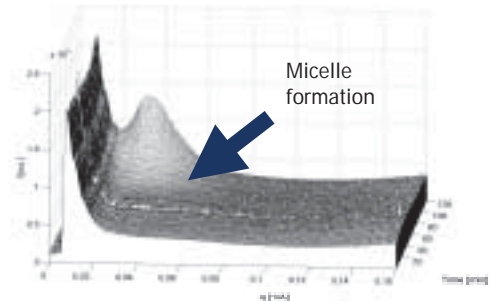


Figure 7: time resolved SAXS patterns of the polymerisation of styrene with 10% PB-PMA and 5% HFS

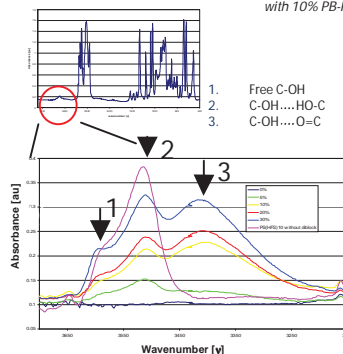


Figure 8: FT-IR plots of PS blends with 10% PB-PMA and various amounts of HFS.

Two different interactions can be detected by infrared spectroscopy:

- ❖ hydrogen bonding between the hydroxyl groups of HFS ( $3530 \text{ cm}^{-1}$ )
- ❖ hydrogen bonding between the hydroxyl groups of HFS and the carbonyl groups of the diblock ( $3390 \text{ cm}^{-1}$ )

## Conclusions

- The proposed nano-sized morphology can be made by the introduction of hydrogen bonding.
- Due to low molecular weight of the diblocks used a significant increase in mechanical properties could not be observed.
- Higher molecular weight diblocks or a crosslinked shell block should be used to increase the impact properties.

## References:

[1] Lipic, P.M., Bates, F.S., Hillmyer, M.A. *J. Am. Chem. Soc.* 120 8963 (1998)  
[2] Pearce, E.M., Kwei, T.K., Min, B.Y. *J. Macromol. Sci.-Chem.*, A21(8&9), 1181(1984)