

A SAXS/WAXS Study of Microphase Separation in Highly Asymmetric Diblock Copolymers

I.W. Hamley,¹ B.M.D. O'Driscoll,¹ G. Lotze,¹ C.M. Moulton,¹ J. Allgaier,² H. Frielinghaus²

¹*Dept of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*

²*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH
52425 Jülich, Germany,*

The phase behaviour of diblock copolymers in the melt has attracted great interest within the last decade or two, in particular following experimental studies for model systems such as polystyrene-*b*-polyisoprene [1] and stimulated by parallel developments such as self-consistent field theory [2]. This model can account semi-quantitatively for the sequence of observed phases which include lamellar, hexagonal-packed cylindrical, bicontinuous Gyroid and cubic-packed sphere structures. The phase diagram is conventionally parameterised using χN and f , here χ is the Flory-Huggins interaction parameter, N is the degree of polymerisation and f is the composition (volume fraction) of one component. A further parameter a “conformational asymmetry” parameter, has been introduced [3,4] to allow for differences in space filling of different blocks, as a result of conformational restrictions that may result for instance from side groups on the polymer backbone. Conformational asymmetry in AB diblock copolymers may be quantified in terms of different statistical segment lengths of the two blocks, leading to a parameter $\varepsilon = \beta_A^2 / \beta_B^2$, where $\beta^2 = R_g^2 / V$, R_g being the radius of gyration and V the volume of the corresponding block [4,5]. An alternative formulation of the parameter has been used by other researchers [3].

We examined the phase behaviour of PEO-POO diblocks via SAXS/WAXS on A2 at DESY (further experiments were performed at the SRS, Daresbury and Diamond in the UK, the data presented here were obtained at DESY). POO denotes poly(octylene oxide) and this system is therefore a homologue of the PEO-PBO system investigated earlier. The side chains in the octylene oxide monomer suggest a bottle brush structure for this polymer, and hence we anticipated distinct space filling properties. Indeed the value $\varepsilon = 3.56$ determined from SANS measurements is by far the largest conformational asymmetry parameter for any diblock system examined to date. It is of great interest to investigate phase behaviour in this limit of extreme conformational asymmetry. The phase diagram includes a region of hexagonal phase stable up to $f = 0.48$. A series of POO-PEO diblocks was synthesized by anionic polymerization. Some compositions were accessed by blending appropriate pairs of diblocks.

Fig.1 presents representative SAXS measurements performed on beamline A2 at DESY. The SAXS profiles enable different structures to be identified, and this is being used to assemble a complete phase diagram for the system.

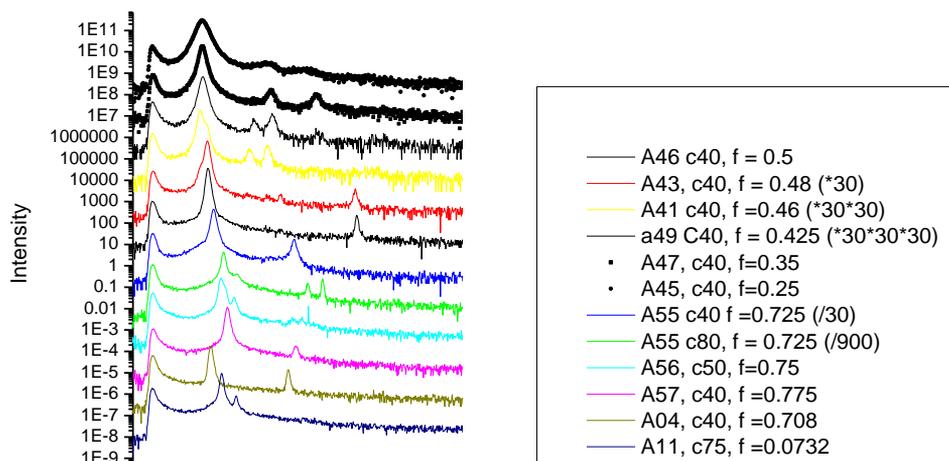


Fig.1 Representative SAXS profiles from lamellar, hexagonal, gyroid (HPL) structures at the compositions indicated

SANS is presently being performed to determine the χ parameter for this system, so that a phase diagram can be compiled. A manuscript is in preparation for submission in 2009.

References

- [1] Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* 1994, 27, 6922-6935; Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* 1995, 28, 8796-8806.
- [2] Matsen, M. W.; Bates, F. S. *Macromolecules* 1996, 29, 7641-7644.
- [3] Vavasour, J. D.; Whitmore, M. D. *Macromolecules* 1993, 26, 7070-7075.
- [4] Bates, F. S.; Fredrickson, G. H. *Macromolecules* 1994, 27, 1065-1067.
- [5] Bates, F. S.; Schulz, M. F.; Khandpur, A. K.; Forster, S.; Rosedale, J. H.; Almdal, K.; Mortensen, K. *Faraday Discussions* 1994, 98, 7-18.