



Experiment title: Influence of pressure on phase transitions in diblock copolymers	Experiment number: SC 214	
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Report:

Diblock copolymers consist of two distinct, usually immiscible homopolymer blocks, covalently bond together at one end. Driven by the entropy on one side and by the enthalpy of unfavourable interactions between the segments of the blocks on the other, they undergo a transition on cooling from a state in which the segments are homogeneously mixed to one in which they are segregated locally. This so-called microphase separation transition (MST) is known to be controlled by the degree of polymerisation N , the composition f , i.e. the volume fraction of one component and by the strength of monomer interaction between components, described by the Flory-Huggins segment interaction parameter χ [1, 2].

Here we report the microphase separation transition of a diblock copolymer melt on application of pressure.

After having established pressure as a thermodynamic variable for the MST (exp. nr. SC 161) we now used a pressure cell with a lower pressure range in order to investigate the MST of symmetric poly(styrene-*b*-butadiene) in detail. As before the samples were enclosed in a thin aluminium foil to avoid contact with the pressure transmitting silicon oil and several isotherm pressure scans at temperatures above the microphase separation transition temperature (T_{MST}) were made (for an example see fig. 1). Starting from a homogeneous phase at e.g. 120° C and atmospheric pressure we changed pressure in steps of 100 bar up to 2000 bar and back.

So we were able to establish and investigate a pressure driven MST by analysing the maximum intensity, the width and the position of the morphology peak. This peak, in the disordered phase due to intramolecular density fluctuations and in the ordered phase to the lamellar periodicity [3], undergoes during MST a distinct shift to lower Q values (Q is the scattering vector: $Q = (4\pi/\lambda) \sin \theta/2$). The peak intensity increases and the width (Δ_{FWHM}) decreases.

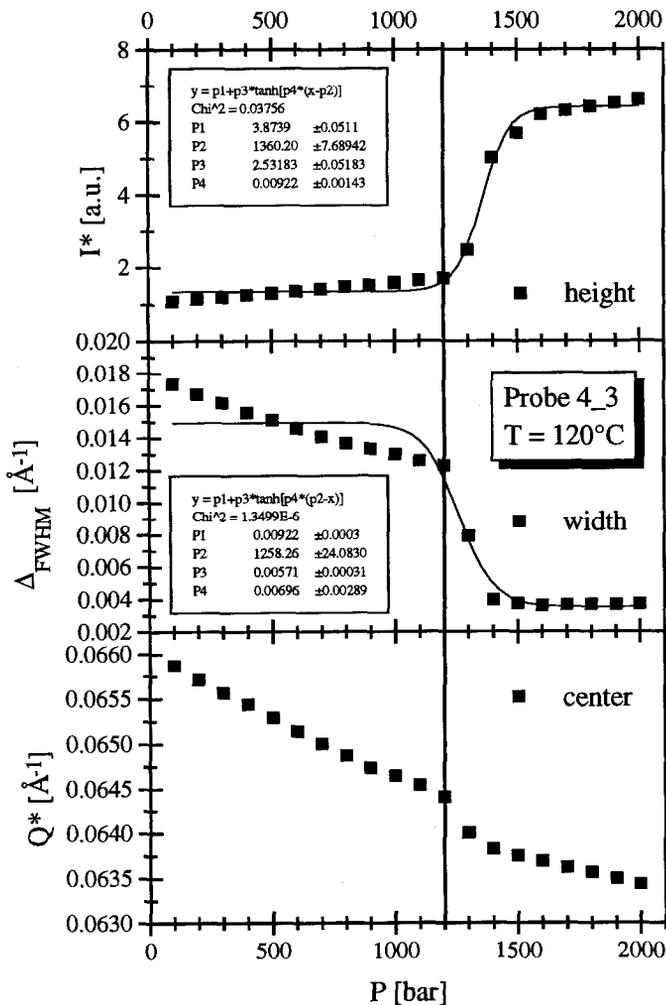


fig. 1: Pressure driven microphase separation transition (MST) of a symmetric diblock copolymer of polystyrene and polybutadiene. Morphology peak -maximum (I^*) -width (Δ_{FWHM}) and -position (Q^*) change during MST as expected from the preceding temperature dependant experiments. The transition is situated at approximately 1200 bar which indicates a shift of T_{MST} (the microphase separation transition temperature which is under atmospheric conditions 100°C) of approximately $1^\circ\text{C} / 60$ bar.

Each data point has been obtained by "lorenz fitting" the Q dependent intensity, which before has been corrected for sample thickness, empty sample holder scattering, electronic background and transmission. (Q is the scattering vector: $Q = (4\pi/\lambda) \sin \theta/2$) The two lines are tanh. fits.

References

- [1] BATES F.S. and FREDRICKSON G.H., Ann. Rev. Chem., 41 (1990) 525
- [2] BATES F.S., Science, 251 (1991) 898
- [3] LEIBLER L., Macromolecules 13 (1980) 1602