



Experiment title:
Influence of pressure on phase transitions
in diblock copolymers

**Experiment
number:**
SC 161

Beamline: ID2 - BL4
Date of Experiment: from: 9. Febr. to: 11. Febr. 1996
Date of Report: 29. Febr 1996

Shifts: 8
Local contact(s): H. Stanley, P. Boesecke, M. Lorenzen, O. Diat
Received at ESRF : 11 MAR 1996

Names and affiliations of applicants (*indicates experimentalists):

M. Stamm Max Planck-Institut für Polymerforschung, Mainz
W. DeOdorico* Uni Frankfurt/M. and MPI-P
H. Ladynski" ILL, Grenoble
T. Albrech:* MPI-P, Mainz
R. Schnell MPI-P, Mainz

Report:

It was the purpose of the investigations to establish pressure as another thermodynamic variable for the microphase separation of diblock copolymers in the melt. It is well known from previous experiments that for instance by the influence of temperature a diblock copolymer system can transform from a lamellar ordered phase into a disordered phase at higher temperatures.

Three diblock copolymers of polystyrene and polybutadiene, P(S-b-B), of different molecular weights in the range 24.000 to 30.000 g/mol and approximately symmetric composition have been investigated by small angle x-ray scattering in a pressure cell at different temperatures. The pressure was homogeneously applied via silicon oil, and the sample was enclosed in a thin aluminum foil to avoid contact with the oil. The pressure and temperature range was 1 to 7 kbar and 70 to 140°C, respectively. A pressure scan is shown in figure 1, where the region of the morphology peak of P(S-b-B) is plotted at three different pressures (1 bar, 1.2 kbar, and 7 kbar). The peak at approximately 0.4 nm^{-1} corresponds to the lamellar periodicity in the ordered phase (lower curves) and to the intramolecular Leibler-peak in the disordered regime (upper curve). The two states of order can be best distinguished from the width of the peak, which is 0.056 rim^{-1} in the disordered and 0.033 nm^{-1} in the ordered state, respectively. Taking for instance the lowest curve at a temperature of 13 0°C and 7 kbar, one can clearly conclude that this sample is in the ordered regime at this pressure. The sample is on the other hand under normal conditions in the disordered state at this temperature, and shows a microphase separation from the ordered to the disordered regime at 100°C. Thus under the effect of pressure the microphase separation from the disordered to the ordered state has taken place. From a pressure scan at fixed temperature one can conclude that the transition occurs below 1 kbar. Due to experimental limitations with respect to

the pressure cell, however, the pressure range below 1 kbar could not be reinvestigated, and thus the microphage separation transition could not be studied in detail.

A temperature scan at approximately fixed pressure is shown in figure 2. The sample is in the ordered state and the peak position clearly shifts with temperature. This is similarly observed under atmospheric conditions, while the shift is not so pronounced. The application of pressure allows the investigation of a much wider range of χN (χ Flory-Huggins interaction parameter, N degree of polymerisation), which is very helpful for a comparison with theory and which is otherwise not accessible due to limitations in the available temperature range.

As a general result of those first investigations it is clearly demonstrated that a pressure induced microphage separation in P(S-b-B) takes place. The transition temperature seems to shift to significantly higher temperatures upon the application of pressure. Further more detailed investigations also in a lower pressure range are still to be conducted.

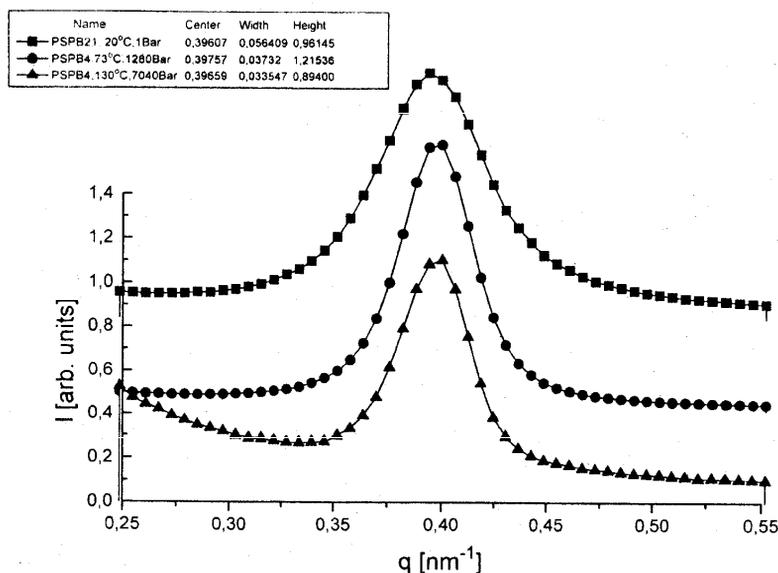


Fig.1 Effect of pressure on the small angle x-ray scattering of P(S-b-B). The sample of the upper curve is in the disordered, the ones of the lower curves in the ordered state. Curves are shifted vertically for a better reproduction.

Fig 2 Temperature scan of SAXS intensity (log scale) of P(S-b-B). Curves are shifted vertically for a better reproduction.

