

## Change of phase behaviour of diblock copolymers upon application of pressure

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Received: 2 August 1995/Revised version: 21 August 1995/Accepted: 2 September 1995

### Summary

Poly(styrene-*b*-paramethylstyrene) block copolymer samples have been prepared in a mechanical press, cooled under pressure below the glass transition temperature and investigated by small angle neutron scattering. We observe a microphase separation transition from an order to a disorder state with ascending pressure. The observed effect is not expected solely due to pressure, but the situation in the press is more complicated: (i) Ascending pressure leads to an increase of the glass transition temperature which slows down relaxations and hinders the evolution of thermodynamic equilibrium, (ii) the uniaxial movement of the piston leads to an uniaxial shear field and samples get oriented. An adiabatic heating during the pressing procedure has been found to be of minor influence. The situation is discussed with respect to common sample preparation conditions and processing.

### Introduction

Diblock copolymers are widely used as model systems for the investigation of order disorder or microphase separation transitions (MST) [1, 2]. Thermodynamics is driven by the temperature behaviour of entropic and enthalpic contributions to the mean segment interaction described by the Flory-Huggins parameter  $\chi$ . A block copolymer melt with a lower critical solution temperature (LCST) undergoes a MST from a disordered to an ordered state when temperature is raised above a transition temperature  $T_{\text{MST}}$ . Block copolymer systems with an upper critical solution temperature (UCST) show the opposite behaviour, and it has only recently been shown that both types of thermal behaviour can exist in one system [3]. Depending on the composition  $f$ , i. e. the volume fraction of one component, different ordered phases are observed like la-

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mellar, micellar, cylindrical [1, 2] or even more complex structures [4]. The influences of temperature  $T$ , degree of polymerisation  $N$ , and composition  $f$  have been studied extensively [1, 2], while the influence of pressure has been largely neglected. To our best knowledge, there are so far only reports on pressure dependences in homopolymer blends [5, 6] or pressure induced melting of block copolymers in aqueous solutions [7]. In the latter system the mesophase transition was dominated by the interaction between solvent and one of the blocks.

In this work we describe, how the thermodynamic state of a pure block copolymer with UCST behaviour is affected by varying pressure in a press. Although the influence of pressing procedures is very complicated and not only controlled by pressure, this kind of experiment seems very interesting to us, since many samples for various types of experiments are prepared right in this way. Furthermore industrial processes (e. g. extrusion) are often quite similar to this kind of experiment, in contrast to experiments in a hydrostatic pressure cell, where the pressure is applied homogeneously.

The mean segment interaction in polymers is described by the Flory-Huggins-parameter  $\chi$  and theory [8] predicts for symmetric diblock copolymers that MST occurs at a constant value  $\chi N = 10.5$  where  $N$  is the degree of polymerisation. We have studied poly(styrene-*b*-paramethylstyrene) (P(S-*b*-pMS)) showing an UCST behaviour. Since styrene and paramethylstyrene monomers are very similar to each other  $\chi$  is small in comparison to other systems. Therefore the microphase separation temperature  $T_{\text{MST}}$  is accessible although the molecular weight  $M_w = 420$  kg/mol is quite large. P(S-*b*-pMS) has been studied in the bulk [9] and as thin films [10, 11]. Thermodynamic parameters of the system and phase behaviour with temperature are thus well known.

## Experimental

The block copolymer material used in this work was obtained from Polymer Standards Service, Mainz, Germany. It has a molecular weight of  $M_w = 420$  kg/mol and a composition  $f = V_{\text{PS}}/(V_{\text{PS}} + V_{\text{PpMS}}) = 0.57$ . This leads to degrees of polymerization of  $N_{\text{PS}} = 2300$  and  $N_{\text{PpMS}} = 1500$ . Polydispersity is  $M_w/M_N = 1.2$ . Neutron scattering contrast is achieved by deuteration of the polystyrene block. At atmospheric pressure  $T_{\text{MST}}$  is found to be located at 200 °C.

Samples of 13 mm diameter and 1 mm thickness have been prepared either in a mechanical press or in an Instron machine between two Teflon discs. Different pressures have been applied (atmospheric pressure  $< p \leq 900$  MPa or  $8 < p < 120$  MPa, respectively). In a first preparation step the sample is heated up to 160 °C. Then pressure is applied and held constant for the whole preparation procedure. Samples are allowed to relax for exactly 1 h. Subsequently the samples are cooled down to room temperature in the press. PS and PpMS have glass transition temperatures at

atmospheric pressure between 100 °C and 110 °C, and the obtained structure is frozen in at room temperature.

SANS measurements have been carried out at Risø National Laboratory, Denmark. All measurements have been done at room temperature for 1 or 3 hours. A neutron wavelength  $\lambda = 10 \text{ \AA} \pm 18 \%$  has been chosen. The scattering vector is defined as  $q = (4\pi/\lambda) \sin(\theta/2)$  with scattering angle  $\theta$ . Because of the high scattering contrast between the deuterated PS-block and the protonated PpMS-block a background subtraction is not necessary.

## Results and Discussion

SANS intensities  $I(q)$  at different pressures are compared in figures 1 and 2. A correlation hole peak [8] occurs at scattering vector  $q \approx 0.01 \text{ \AA}^{-1}$ . In figure 1 it is clearly seen, that the maximum intensity  $I^*$  changes with pressure over more than one order of magnitude. At low pressures a second order reflection is found (figure 2), which vanishes for ascending pressure. The exact dependences of (a) the maximum intensity  $I^*$ , (b) the maximum position  $q^*$ , and (c) the full width at half maximum FWHM of the peak with applied pressure are plotted in figure 3. Evidently (i) the maximum intensity  $I^*$  significantly decreases, whereas (ii) the maximum position  $q^*$  and (iii) the FWHM increase with pressure. The second series of measurements (solid symbols) are displaced to slightly smaller pressures with respect to first ones (open symbols) possibly caused by slightly different sample preparation procedures. However, in both cases the transition regime is located between  $10^7$  and  $10^8$  Pa and results are reproducible. By a comparison with previous temperature dependent measurements [9], our data strongly indicate a MST occurring between  $10^7$  and  $10^8$  Pa. Recent experiments with poly(styrene-*b*-butadiene) block copolymers (showing an UCST behaviour, too) in a press lead to similar results [12].

Although our data are plotted against pressure, we do not expect our results to be a sole consequence of the application of pressure. In contrary, we have found in recent pressure cell experiments on P(S-*b*-pMS) [13] that the spinodal temperature seems to be shifted to higher temperatures with the application of homogeneous pressure.

Therefore the situation in the press has to be more complicated. First one has to consider changes of the glass transition temperature  $T_g$ . From isobar  $pVT$ -measurements with a similar but fully protonated copolymer with  $M_w = 370 \text{ kg/mol}$  we have determined the pressure dependence of  $T_g$  as  $T_g/^\circ\text{C} = 107 + 0.23p/\text{MPa}$ . At 230 MPa  $T_g = 160 \text{ }^\circ\text{C}$  is reached. But even earlier the vicinity to  $T_g$  will strongly slow down relaxations, which are quite slow anyway because of the high molecular weight. Then the relaxation time of 1 h may not be sufficient to reach equilibrium and a nonequilibrium structure may be frozen in.

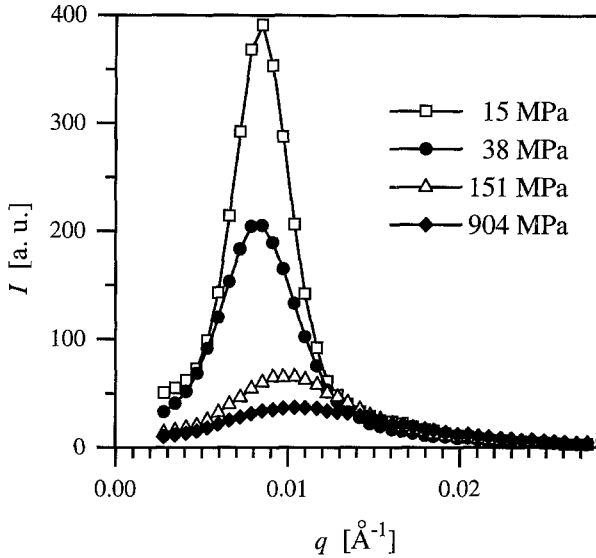


Figure 1: Scattered intensity  $I$  from measurement 1 as function of scattering vector  $q$  for different pressures. All samples have been prepared in a press at  $160\text{ }^\circ\text{C}$  for 1 h. For clarity only four curves are shown. The lines connect the data points and are guides for the eye. The change of the maximum intensity  $I^*$  is of the order of one magnitude.

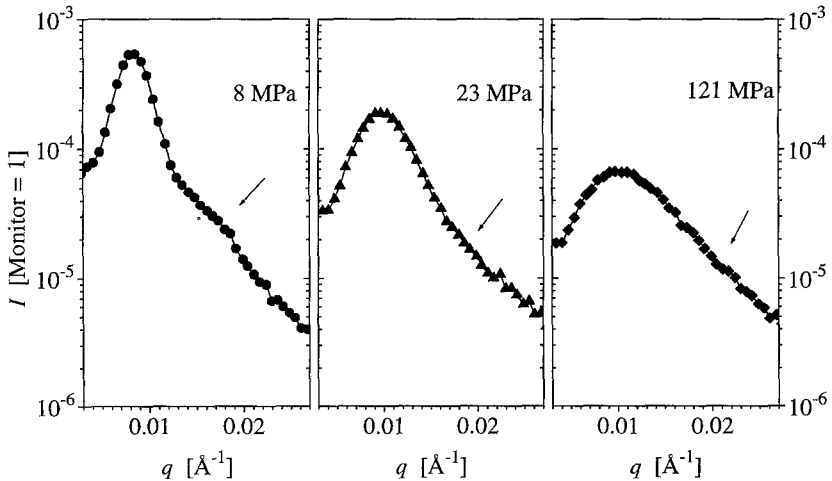


Figure 2: Scattered intensity  $I$  as function of scattering vector  $q$ . For clarity only three pressures are shown. Samples have been prepared in an Instron machine at  $160\text{ }^\circ\text{C}$  for 1 h. Thin lines connect the data points and are guides for the eye. At 8 MPa a second order reflection (see arrow) can still be identified, which vanishes for ascending pressure.

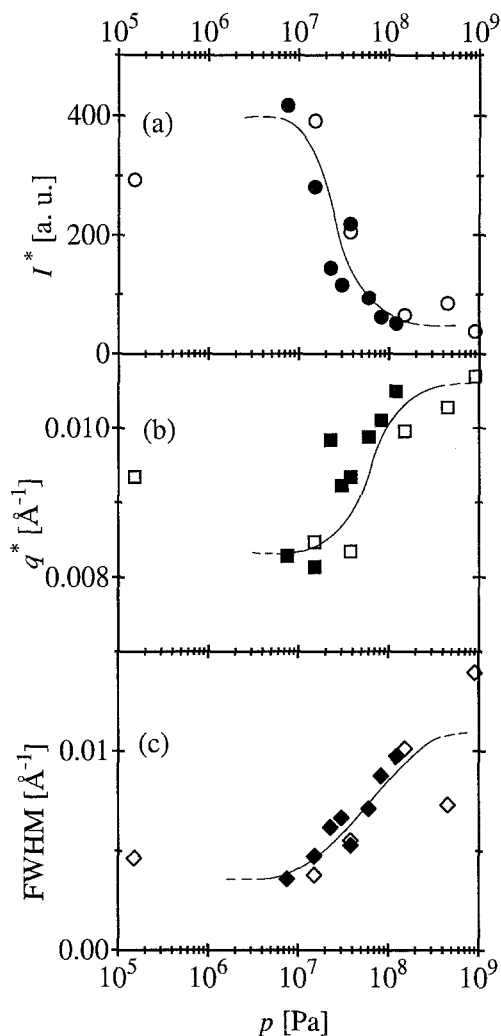


Figure 3: Dependences of (a) maximum intensity  $I^*$ , (b) maximum position  $q^*$  and (c) full width of half maximum FWHM of the scattering peak as functions of applied pressure. The open symbols correspond to the first, the solid symbols to the second measurement series where samples have been prepared in the mechanical press or Instron, respectively. Solid lines are guides for the eye. Statistical errors are not larger than the size of the symbols and scattering of the data points is probably due to small differences in sample preparation.

It is an interesting question, which effect causes the obtained MST and the structure, which is frozen in by raising  $T_g$  with pressure. There are two other influences besides pressure. First the uniaxial movement of the piston in the press leads to an uniaxial shear. This shear field might influence the phase behaviour towards a homogenous state. Secondly an adiabatic heating will occur when pressure is applied since a heat exchange is slow due to the Teflon discs and the low thermal conductivity of the stainless steel pressing tool. Finally the temperature at the sample position might be different from the temperature of the pressing tool core, where the thermocouple for temperature control of the heating device is located.

To investigate the temperature effects in situ, we firstly have used a pressing tool with a 0.25 mm hole in the bottom piston in which a thermocouple fits. For an applied pressure of 380 MPa the temperature jump is approximately 5–6 °C in pure polystyrene. This temperature difference is expected to be too small to cause the observed effects. In another experiment we have investigated the temperature difference between sample and pressure tool core. For this experiment we have used a pressure tool with a 1 mm hole in the core and a polystyrene sample of 5 mm thickness. Pressure has not been applied. The obtained sample temperature was slightly higher than the core temperature ( $\approx 5$  °C), probably due to a non perfect temperature contact between thermocouple and core. However, this small temperature difference does not influence the phase behaviour significantly.

At small applied pressures intensity is slightly increasing. This effect and perhaps some of our other observations might be due to an orientation effect, caused by the uniaxial shear. To investigate if orientation has taken place, we have measured a sample (prepared at  $p \approx 40$  MPa) in two directions: (i) in the normal direction perpendicular to the disc and (ii) in the parallel direction. Therefore we have cut the disc into stripes and tilted them to 90°. In this latter case a slight orientation is visible. It will affect especially the height of the scattering maximum  $I^*$  which amounts to a reduction of the peak intensity by approximately 30 % in the present case. This finding is consistent with results on poly(styrene-*b*-butadiene) [12]. In summary one thus might speculate that the observed changes after the pressing of our samples are a combination of the above mentioned effects.

The shift of the peak maximum, i.e. of the critical wave vector  $q^*$ , is consistent with theoretical work [14–19] and corresponding simulations [20–22]. These references explain the shift of  $q^*$  as a chain stretching before and at MST. This change in  $q^*$  is concluded already in our previous studies [9] and has been related to chain stretching just recently by a measurement of the single chain conformation [23]. In addition to the change of chain conformation at the MST, the inclusion of voids also leads to a swelling of chains and change of  $q^*$  [22].

It should be emphasized that the observed effects will have implications on sample preparation procedures, where quite often pressure is applied, as well as for the understanding of processing properties of materials. Thus one will have to be cautious using samples prepared in a press without further relaxation without pressure. Effects observed in our system p(S-*b*-pMS) may be in particular pronounced because of the vicinity to  $T_{MST}$ , the high molecular weight of the material and the vicinity of the glass transition. Thus relaxations are slow and the microphase separation occurs already at pressures, which are easily reached in a mechanical press. The situation is on the other hand not so much different with P(S-*b*-B) [12] where the transition is observed in a comparable pressure range and orientation effects are even more severe. Also in this case a non-equilibrium structure is frozen in, although the glass transition of one component is lower. Relaxation to equilibrium during heating at atmospheric pressure is, however, much faster due to the lower molecular weight. Also in polymer processing and engineering (e. g. extrusion, injection moulding etc.) quite often a combination of temperature, flow, and pressure is applied. Also there one has to be cautious about the influence of those parameters on phase behaviour and glass transition, since in particular also the application of pressure might change mechanical and processing conditions quite significantly. Details are presently far from being understood.

## Conclusion

From SANS experiments of a diblock copolymer in a press it is concluded that we have observed a microphase separation transition where the system transforms from an ordered to a disordered state with increasing applied pressure. Thus the SANS maximum intensity, maximum position and half width change significantly connected with the disappearance of the second order peak. This effect is not expected to be solely pressure dependent but a complicated combination of different effects is taking place. Further experiments will be needed for a better understanding.

Our findings will have important consequences on the preparation of samples for scattering and other types of experiments, where samples are usually prepared in a press. Especially in quenched samples an uncontrollable thermodynamic state might be frozen in. Also for applications in industrial processes, which are frequently carried out under pressure and flow, our findings may be of interest, since a simple transfer of results from purely pressure dependent measurements will be difficult.

## Acknowledgement

We acknowledge stimulating discussions with Dr. V. Abetz, Dr. T. Pakula, Dr. D. Schwahn, and Dr. T. A. Vilgis. S. Klein and J. Vennemann prepared the samples and

M. Bach helped during the in situ measurements of sample temperature in the pressing tool. This work was financially supported by the European Community within the Large Installation Programme.

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