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ESRF		
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Report

Pressure Dependence of the Microphage Separation Temperature in Block Copolymers

Since the first theoretical work of Leibler [1] about the microphage separation in block copolymers a lot of experiments were conducted with that class of **materials.** Recently interest arises in the pressure dependence of the microphage separation temperature T_{MST} [2,3]. In [3] the question whether T_{MST} shifts to lower or to higher values by applying pressure is discussed controversially. In both papers [2] and [3] a **styrene/isoprene** diblock copolymer with similar composition was analyzed.

Here we show preliminary results of the pressure dependence of the T_{MST} of the diblock **styrene/methyl-phenylsiloxane**, M = 29600 g/mol, N = 254, f= 0.56 (M: number average of molar mass; N: total number of **monomers; f:** volume fraction of styrene). A system with similar composition but with higher molar mass was described first in [4]. It offers the possibility to study the microphage separation well above the glass transition temperature of the two blocks. Two types of experiments were conducted at the BL4 of the ESRF:

(1) The intensity I(q) $(I(q)$ is proportional to the structure factor S(q); $q = 4\pi \sin(\Theta/2)/\lambda$; Θ: scattering angle; $\lambda = 0.099$ nm) was measured as function of temperature T with fixed pressure P. Two runs were performed with P = 250 bar and P = 500 bar, respectively.

(2) Pressure jumps (p> 1 bar to p = 1 bar) with fixed temperature were conducted. I(q) was measured as function of time t after triggering the pressure jump.

In both cases the I(q) curves were corrected (weighted by transmission) for the apparatus background scattering (diamond windows, thickness = 1.5 mm; pressure transducing oil (FINA Vestan A360 B), total layer thickness ≈ 4 mm; 12 μm Kapton foil wrapping the sample; sample thickness = 3 mm).

Values for T_{MST} are extracted from a plot of $1/S_L(q^*)$ vs $1/T$ (S_L: structure factor for block copolymer scattering proposed by Leibler [1]; q^*: value of the scattering vector corresponding to the maximum of S_L). S_L is separated from the experimental I(q) curve by fitting the following function in analogy to [4]:

$I(q) = a_1 + a_2 \exp\{-a_3 q^2\} + a_4 S_L(N, f, \chi, R_g, q)$, ($a_1$: constant inherent background scattering; a_2, a_3: parameter for sample inherent diffuse scattering, approximation with the small particle formula of Guinier;

a_4: number density and contrast factor for the Leibler scattering; χ: interaction parameter; Rg: radius of gyration of the block copolymer coil).

Some results of the fits are shown in Fig. 1, the fitting function describes the measured curves quite well. With $\chi = A + B/T$ (**A**, **B**: constants), the plot $1/S(q^*)$ vs $1/T$ reveals a straight line above T_{MST}. The changes in the slopes of the curves are correlated with the T_{MST}, see Fig. 2.

The following conclusions for the pressure coefficient can be drawn:

(i) $(\partial T_{MST}/\partial P)_{\xi,N} < 0$, this is in agreement with [2]

(ii) $(\partial T_{MST}/\partial P)_{\xi,N} \approx$ -70 mK/bar, P = 250 to 500 bar (see Fig. 2)

The value of $(\partial T_{MST}/\partial P)_{\xi,N}$ is in the order of magnitude given in [2].

The pressure jump experiments confirm the statement (i), i. e. by decreasing P the system moves towards the microphage separated region. In Fig. 3 an example is given for the development of I(q) with time t (t> 0 after triggering the pressure jump). The plotted curves are $I(q, t) - I(q, t < 0)$. After the pressure jump the scattering intensity grows which is interpreted with the moving of the system towards the microphage separated region. This is in analogy to Fig. 1 where the increasing scattering intensity (by lowering temperature) is related to a shift of the system towards microphage separation.
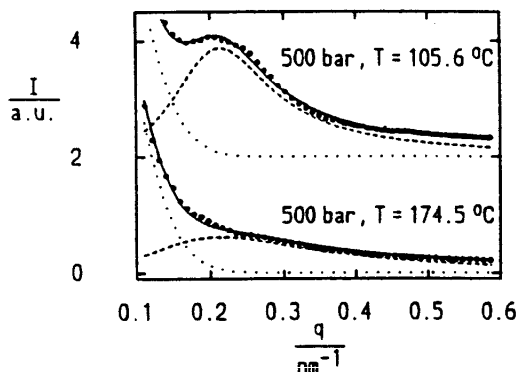

Fig. 1: Scattering intensity I vs q for two different temperatures. Bullets: experimental data; full line: fitted function; broken line: Leibler part; dots: Guinier part. The constant background a_1 is not shown. The low temperature curve is shifted by 2 units.
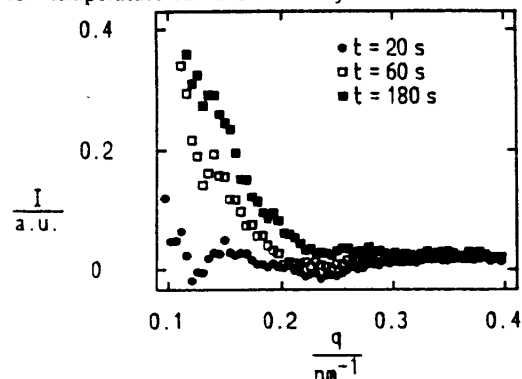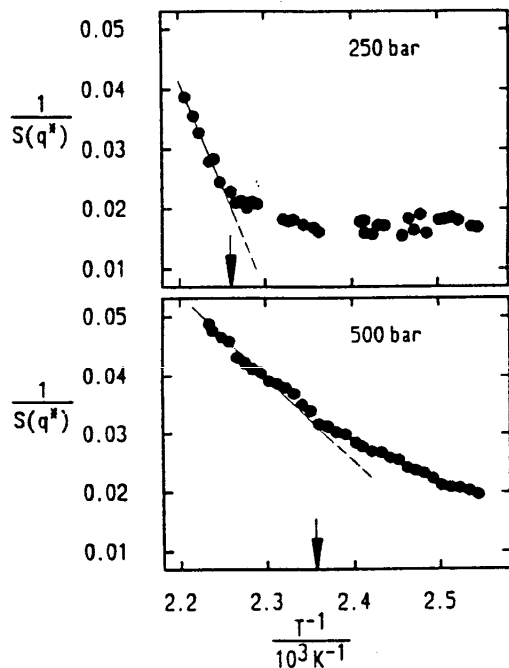

Fig. 2: Determination of T_{MST}: $1/S(q^*)$ vs $1/T$ ($S(q^*)$: maximum of the Leibler structure factor). The microphase transition is indicated by deviations from the straight line. 250 bar: T_{MST} = 169 °C; 500 bar: T_{MST} = 151 °C.

Fig. 3: Development of the scattering intensity after a pressure jump at t = 0 from P = 250 bar to P = 1 bar, T = 164.5 °C. With $I \equiv I(q, t) - I(q, t < 0)$.

Literature:
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