Density Discontinuity at the Microphase Separation Transition of a Symmetric Diblock Copolymer

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1. Introduction. The microphase separation transition (MST) in symmetric diblock copolymers is known to be a phase transition of weakly first order.[1] Its experimental observation in polystyrene–polyisoprene diblock copolymers is possible by measurement of the dynamic shear modulus or by means of small-angle X-ray scattering (SAXS).[2] The latter method is particularly well suited as it provides direct access to the spectrum of concentration fluctuations in the sample.

In the present paper we report measurements of the temperature dependence of the density near T_{MST} using two different methods. The classical but tedious approach is dilatometry. We show that the same result may be obtained with even better precision by reflection ellipsometry. The ellipsometer operates with a variable angle of incidence and is extremely sensitive to small density variations of the bulk.

The sample under study exhibits a sudden decrease of the density on cooling below T_{MST}, i.e., on going from the disordered to the ordered state of the system. The effect is reversible with temperature without any observable hysteresis.

2. Experimental Details. The sample was synthesized by anionic polymerization in our laboratory. The molecular weight is M_N = 17 000 and the molecular dispersion M_W/M_N = 1.04. The volume fraction of polystyrene is $f = 0.44$. The transition temperature is determined by SAXS as demonstrated in Figure 1. Details of this method may be found in ref 2. The intensity at the wavevector q^* is plotted versus temperature. q^* is the wavevector of the dominant component in the spectrum of concentration fluctuations. The SAXS structure factor of the disordered state exhibits a maximum at q^*. In addition to the continuous increase of the intensity on approaching the microphase separation temperature, it displays a clear discontinuity at T_{MST}. The discontinuity marks the formation of long-range order in the sample and is accompanied by the appearance of a second-order maximum in the scattering profile. This measurement results in a transition temperature T_{MST} = 108 °C.

For the dilatometric measurements a conventional instrument consisting of a mercury-filled glass capillary in contact with the sample volume is used, allowing for the measurement of relative volume changes.[3] The system is contained in an oil-filled thermostat, and temperature is controlled with fluctuations less than ±0.5 K.

The ellipsometric measurements were performed using a reflection-nulling ellipsometer that was constructed in our laboratory. It employs a He–Ne laser at a wavelength of λ = 6328 Å, and the angle of incidence is a variable parameter. A total reflection setup is used, where the sample is in contact with the basal plane of a glass hemisphere (Schott SF57; index of refraction $n_{632.8\text{ nm}} = 1.83957$). For each temperature the ellipsometric ratio $r_p/r_s(\theta_i)$ was determined for a set of angles θ_i around the angle of total reflection θ_C, where r_p and r_s are the complex reflection coefficients for light polarised parallel and perpendicular to the plane of incidence, respectively. This provides an extremely sensitive measure of the glass–polymer interfacial structure as well as of the dielectric tensor $\tilde{\epsilon}_b$ at optical frequencies of the bulk polymer.[4]. For an optically homogeneous medium, $\tilde{\epsilon}_b$ can be replaced by the scalar quantity ϵ_b which is related to the bulk density by the Lorentz–Lorenz equation $(\epsilon_b - 1)/(\epsilon_b + 2) = r\varrho$, where r is the specific refractivity and ϱ is the density of the polymer. Since the diblock copolymer is anisotropic on a microscopic scale in the microphase-separated state, this would result in a macroscopic optical anisotropy if the lamellae were uniformly oriented over spatial regions comparable to the wavelength of the light used in the experiment. For our sample this is not the case, however, since both SAXS[2] and transmission electron microscopy investigations show that uniformly oriented stacks of lamellae exist only on a scale of <100 nm. Therefore, in our experiment ϵ_b represents the spatially averaged dielectric constant of the homogeneous ($T > T_{MST}$) and the microphase-separated ($T < T_{MST}$) sample.

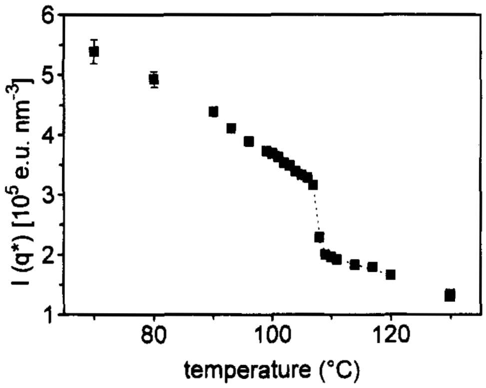

Figure 1. Determination of the transition temperature T_{MST} by SAXS at a scattering vector $q^* = 0.44$ nm^{-1}.

For the differential scanning calorimetry (DSC) measurements a Perkin-Elmer DSC7 was used at a heating rate of 20 K/min. Prior to the measurement the sample was annealed at room temperature for 4 days in order to attain the ordered state.

3. Results and Discussion. Figure 2 shows the results of the dilatometric measurements. A discontinuity of the volume approximately at $T = T_{MST}$ is clearly observable: $\Delta V/V \approx -0.3 \pm 0.1\%$. The sign of ΔV refers to a positive change of temperature, ΔT. The inset in Figure 2 shows the variation of the volume with temperature after subtraction of the linear expansion as determined in the temperature range 20–80 °C. The transition is seen to occur around 100 °C, i.e., below the temperature determined in the SAXS experiment.

Correcting the data for the volume of mercury, we derive an expansion coefficient of $\alpha = 5.8 \times 10^{-4}$ K^{-1} and a value of the density $\varrho = 0.925$ g/cm^3 at $T = 100$ °C. As is seen in the figure, the microphase-separated state possesses a lower average density than the disordered state.

This result is confirmed by ellipsometry. As can be seen from Figure 3, ellipsometry allows for the detection of minute changes of ϵ_b and therefore also of the bulk density. From the figure, an abrupt volume decrease

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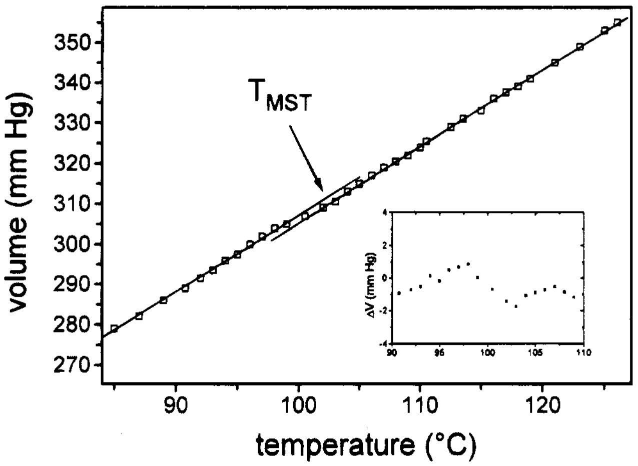

Figure 2. Results of the dilatometric measurements. The sample volume is measured in terms of the height of the mercury column in the capillary.

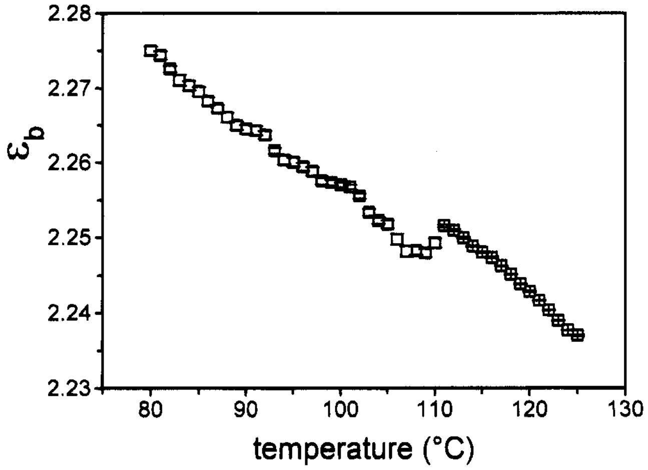

Figure 3. Bulk dielectric constant of the diblock copolymer as measured by ellipsometry.

of $\Delta V/V = -0.30 \pm 0.04\%$ is found at $T = 110$ °C on cooling. The deviation of this temperature from $T_{MST} = 108$ °C is due to a calibration offset of the ellipsometer which is caused by the fact that the temperature sensor is not in immediate contact with the sample but with the heating block. Within experimental error the value of $\Delta V/V$ agrees well with the dilatometric measurement. The structural difference between both states is the existence of lamellar order in the ordered state, which appears to be accompanied by a lower packing of the chain segments as indicated by our measurement. The shift of T_{MST} as a result of the application of pressure has also been observed in small-angle neutron scattering experiments on a partially deuterated diblock copolymer.[5]

The preceding results confirm the existence of a first-order phase transition at T_{MST}. We are therefore led to investigate the specific heat of the material in order to analyze the latent heat that should be connected to the phase transition.

In Figure 4 the DSC results of a heating run are presented. Besides a peak caused by enthalpy relaxation at the glass transition of the polystyrene block at lower temperatures, a clear endothermal peak is observed at T_{MST}. Both phenomena, the glass transition and the microphase separation transition, occur at well-separated temperatures as opposed to the situation encountered in earlier experiments.[6] The associated latent heat is $\Delta H^{DSC} \approx 0.11$ J/g. Our data now allow an estimate of the pressure dependence of the MST using the Clausius–Clapeyron equation for the slope of the coexistence curve

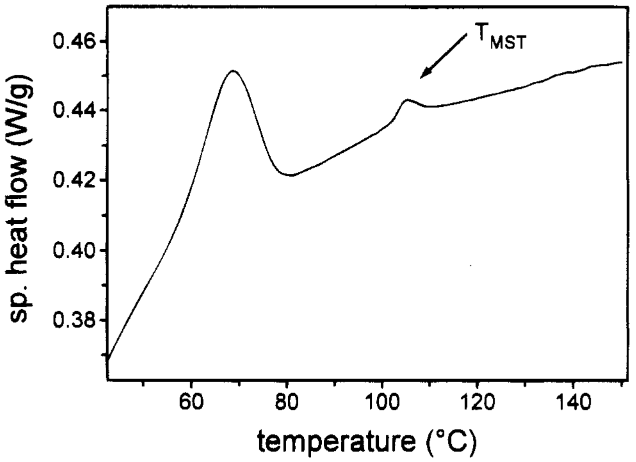

Figure 4. DSC measurement of the diblock copolymer. The heating rate is 20 K/min.

$$\frac{dp}{dT} = \frac{\Delta H}{T_{MST}\frac{\Delta V}{V\varrho}}$$

Using ΔH^{DSC}, one obtains $dp/dT \approx 1.2 \times 10^5$ Pa/K. However, ΔH^{DSC} only represents a lower bound for the latent heat of the transition. The kinetics of this process is known to be slow,[7] and the DSC signal may therefore be smeared out over a large temperature range. An independent estimate is derived from the SAXS data,[6] using the Flory–Huggins parameter χ as obtained from a fit of the scattering profiles in the disordered state. This results in a temperature dependence $\chi = \chi_H/T + \chi_s$ with $\chi_H = 13$ K and $\chi_s = 0.03$. The estimate for ΔH then is $\Delta H^{X\text{-ray}} \approx (R/\bar{M}) f(1 - f)\chi_H = 0.32$ J/g. $\bar{M}$ is the average molecular weight of a monomer. This would result in a shift of T_{MST} by 30 K to lower temperatures at a pressure of 100 bar. Scattering experiments that directly measure this shift are currently in progress.

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References and Notes

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