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Networks of gel-forming triblock copolymer solutions: In situ SANS and rheological measurements

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Abstract

Triblock copolymers in a solvent, selective for their middle blocks provide the basis for the formation of novel physical networks where cross-links are formed by self-assembled domains of the end-blocks. Triblock copolymers of poly(styrene)-poly(ethylene,butylene)-poly(styrene) (SEBS) dissolved in a mixture of aliphatic and alicyclic compounds constitute such a network system. Using a Rheometrics RSA-2 instrument modified for in situ measurements of small-angle neutron scattering and rheology provides a unique possibility for detailed understanding thermodynamics of such a gel. The self-association of the PS-blocks do not only promote formation of highly inter-connected end-block domains, but within a narrow temperature range these domains furthermore constitute a network with body-centered cubic (BCC) microstructure. Upon large amplitude oscillating shear the polycrystalline soft gel can be aligned into a twinned BCC monodomain.

Keywords: Triblock copolymers; SANS; Rheological measurements

1. Introduction

Block copolymers formed of two or more incompatible polymer blocks self-assembles both in the melts and when dissolved in selective solvents into well-defined aggregates which may provide the basis for ordered mesophases.

Symmetric triblock copolymers, ABA, form micellar aggregates when mixed with a solvent selective for the the A-blocks. Such micelles have been extensively studied during the past years, including their crystalline mesoscopic structures, as recently reviewed [1].

A different behavior is expected in solutions of BAB-type copolymers in solvents selective for the middle block. The A-blocks of those polymers form either loops, starting and ending within the same core, or bridges between different micelles giving a gel as illustrated in Fig. 1.

2. Material

We have studied a series of BAB triblock copolymer solutions, based on poly(styrene)-

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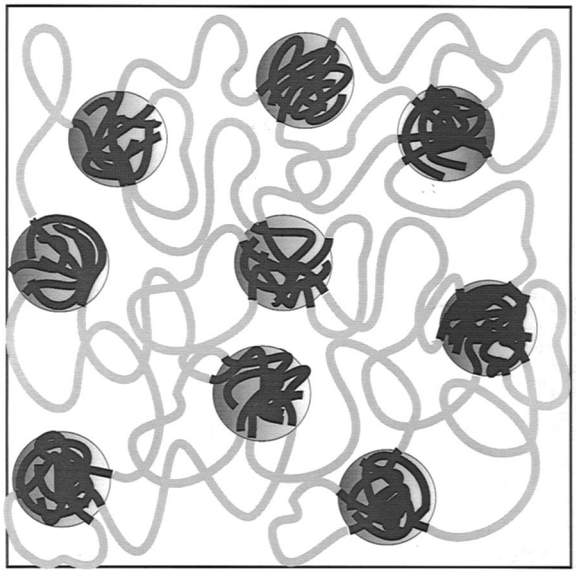

Fig. 1. Illustration of the dispersed micellar morphology in a SEBS gel.

poly(ethylene butylene)-poly(styrene) (SEBS) triblock copolymers with molar mass of 100.000, and styrene content of 29%. The midblock selective solvent consisted of a mixture of aliphatic and alicyclic compounds.

3. Small-angle scattering

Small-angle scattering was performed at the Risø-SANS facility. The SEBS-samples were studied in a variety of auxiliary facilities, including stretching devices to measure the structural response to external elongation [2,3], and a Rheometrics-II instrument modified to make in situ structural and mechanical measurements [4].

4. Structure

Evidence for the existence of an extended three-dimensional network structure in the SEBS-gel systems emerge from scattering experiments [5,6] and electron microscopy [7].

The high-q regime of the scattering function $I(q)$ is dominated by the form factor revealing spherically assembled polystyrene domains with radii between 55 and 80 Å, depending on the copolymer content in the gels. A maximum in $I(q)$ at $q \approx 0.018$ Å^{-1} reflects strong inter-micellar correlations, which can be well described by the hard-sphere Percus–Yevick approximation [8], as recently reported [6].

The polystyrene cores act as physical cross-links giving rise to elastic response. Deformation experiments show that the response in the microstructure is directly related to the macroscopic deformations [2,3].

With increasing temperature, the structure factor peak becomes clearly more pronounced revealing enhanced effective volume fraction. For polymer concentration of 20% or more, this causes ordering above $T \approx 55$°C [9]. At even higher temperatures the structure factor becomes again broader showing that the ordered structure is stable within a limited temperature window.

It is well known that the texture of block copolymer mesophases may transform into a mono-domain morphology when exposed to shear. In the three-dimensional network of SEBS-micelles, the effect of shear may be twofold: shearing might result in such alignment of lattice planes, or shear may disrupt the network. When the SEBS-sample at ambient temperature is exposed to oscillatory shear (99% shear amplitude, 1 rad/s), the observed two-dimensional scattering pattern remains unchanged.

If, however, similar shear is provided above $T = 55$°C, within the temperature range characterized by the narrow structure factor peak, the correlation ring abruptly transforms into resolution-limited Bragg peaks. The scattering pattern resembles a twinned body-centered cubic morphology with lattice constants of the order of 400 Å.

High-resolution small-angle X-ray scattering [4] confirms the body-centered cubic-type microlattice, as indicated by the presence of well-pronounced maxima with positions corresponding to ratios of 1 : 2 : 3 : 4 : 5 : 6 [9].

Upon cooling to ambient temperatures, the characteristic BCC-pattern remains, even though the peaks may broaden. This may reflect that the BCC

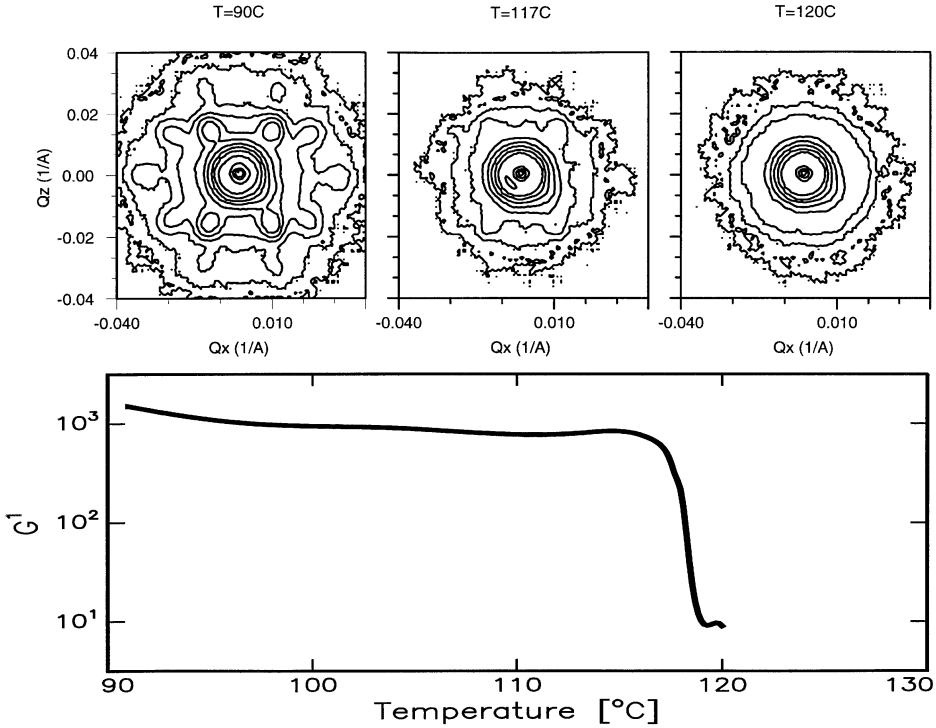

Fig. 2. Simultaneous results of scattering pattern and rheology near the order–disorder transition in SEBS-gels.

structure is thermodynamic unstable in this range, but that the twinned BCC-structure is frozen in due to the glassy poly(styrene) micellar cores. The twin pattern remains for years. One may speculate that the increase in hard-sphere volume fraction, and the associated hard-sphere crystallization on heating is a result of swollen PS-cores in the melted phase relative to that of the glass states.

Upon heating to approximately 120°C, the BCC morphology disorders, and the elastic properties reveal a solid–liquid-like transition. Simultaneous measurements of modulus and structure makes it possible to follow in detail the changes near the order–disorder transition as seen in Fig. 2 [4].

5. Summary

In summary, we have demonstrated that the use of rheological instruments in situ with SANS facilities provides the basis for detailed insight into the thermodynamics of complex block copolymer systems. It has been shown that interdomain bridging of triblock copolymer micelles promotes the formation of highly ordered morphologies upon shear deformation. The rearrangement takes place despite the restrictions that are imposed on the mobility of individual micelle.

Acknowledgements

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