A High-Temperature Cubic Morphology in Triblock Copolymer Gels

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ABA-type triblock copolymers form soft rubbers when blended with a solvent that is selective for their B-midblocks. Over a broad temperature range, these mixtures appear as highly elastic solids with properties resembling those of thermoplastic elastomers at low temperatures. At temperatures above the solid−liquid transition their low melt viscosities make them easy to process. The elastic properties are thermoreversible and the temperature range where rubberlike behavior is observed can conveniently be adjusted by changing the amount of selective solvent. Small angle X-ray scattering experiments are a well-suited tool to study the microscopic processes controlling these properties. They reveal the existence of spherical microdomains, embedded in a matrix formed by the amorphous solvent/midblock phase.[1−4] At ambient conditions the domains have only short range order.[2] Stretching resulted in affine and nonaffine deformations of the microstructure[5] demonstrating that the physical network of interconnected microdomains is crucial for the elastic properties. The existence of the microdomains, which act as physical crosslinks in the three-dimensional network, is due to repulsive interactions between the polystyrene endblocks of the block copolymer and the matrix of midblock chains and selective solvent. These interactions are affected by variations in temperature or composition. Changes in these parameters directly influence the stability of the domain network and thus the rubberlike behavior. One might draw a comparison with the morphological development as in the order−disorder transition of bulk blockcopolymers, separating a regime where stable long-range concentration modulations appear due to microphase separation, from a temperature regime where only unstable concentration fluctuations take place. The question then arises as to the kind of structural rearrangement that should take place in these systems during a solid−liquid transition, since the as-prepared system reveals only short-range interdomain order at ambient conditions. In this communication, we present a study of thermally driven morphological changes in gel-forming triblock copolymer solutions. The solutions are based on polystyrene−poly(ethylene,butylene)−polystyrene triblock copolymers (SEBS) with an average molecular mass, styrene content, and polydispersity of 100 000, 29% and 1.1, respectivly (KRATON G1650). The solvent, selective for the polymer midblocks, consisted of a mixture of aliphatic and alicyclic compounds with an average molecular mass of 400 (FINA A360). The components were mixed at temperatures around 180 °C until a clear solution was obtained. After being quenched to room temperature, the mixtures formed transparent, highly elastic materials. Further details of the preparation are described elsewhere.[6] Morphological studies of these systems were carried out at the X33 small-angle X-ray scattering camera of the EMBL in HASYLAB at the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY) at Hamburg.[7,8] Scattering measurements covered a range 0.03 $\text{nm}^{-1} \le q \le 3\ \text{nm}^{-1}$ (with $q = 4\pi(\sin\theta)/\lambda$, where 2θ is the scattering angle and λ is the wavelength, 0.15 nm). Individual frames were collected within 60 s, upon slow heating of the sample with a rate of 2°/min in a Mettler FP-80 hot stage. The 2 mm thick samples were sealed into brass containers with very thin aluminium windows in order to avoid any degradation during extended annealing periods. Static SAXS experiments during long-term annealing were performed with a RIGAKU small-angle X-ray camera and a rotating anode source operated at 7 kW. A homemade furnace with a temperature accuracy of about ±2° was used during these experiments.

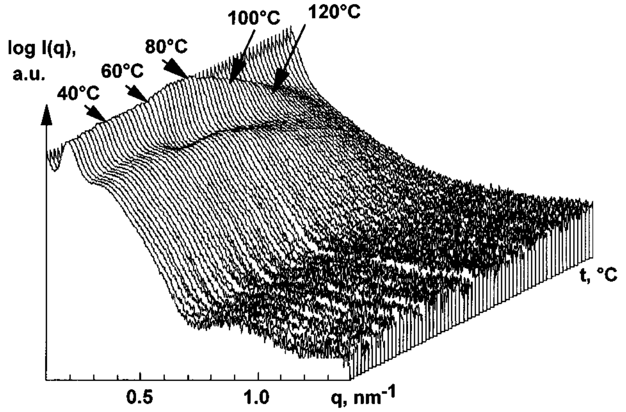

Figure 1. Small-angle X-ray patterns, collected during heating of a quenched 12% SEBS gel in the temperature range from 20 to 150 °C (rate 2°/min; 60 s data aquisition time per profile).

Figure 1 shows the results from dynamic SAXS experiments during heating a SEBS gel system, containing 12 wt % triblock copolymer. The characteristic features of the scattering pattern are one or two well-pronounced structure factor maxima at low q values near 0.18 nm^{-1} and a broad form factor maximum at higher q values near 1 nm^{-1}. Such a scattering behavior originates from a microstructure where spherical PS-domains are embedded in a midblock/solvent matrix.[1−3] Higher molecular weights of the triblock copolymer with a similar composition result in increasing domain sizes and interdomain spacings due to increased mid- and endblock dimensions.[2,4] An increase in the selective solvent content of the gel results in larger interdomain distances (dilution effect) but in smaller domain sizes[1−4]—see Table 1—which may be ascribed to the delicate balance of the interactions of the different components (PS−PEB, PS−solvent, PEB−solvent).

Similar scattering patterns were obtained at all sample temperatures, although a closer examination points to morphological changes during temperature variation as demonstrated with selected scattering patterns in Figure 2. Structural changes are shown by

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Table 1. Results from Percus-Yevick Fits to Typical Scattering Profiles of Triblock Copolymer Gels in the “Low-” and “Intermediate-” Temperature Range

	SEBS content		
	7%	12%	20%
	Low Temperature Regime		
r_0/nm	5.9 (25 °C)	6.2 (25 °C)	6.2 (25 °C)
R_{hs}/nm	18	16.5	14
ϕ_{hs}	0.26	0.32	0.35
T_{low}/°C	55	55	55
	Intermediate Temperature Regime		
r_0/nm	5.8 (70 °C)	6.2 (80 °C)	6.1 (90 °C)
R_{hs}/nm	17.5	17	14
ϕ_{hs}	0.29	0.4	0.43
T_{high}/°C	95	105	115

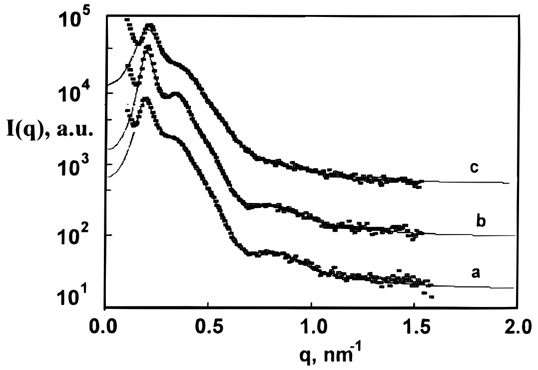

Figure 2. Small-angle X-ray patterns of a quenched 12% SEBS gel in the “low-” “intermediate-” and “high-temperature” range at 30 °C (a), 70 °C (b), and 120 °C (c), respectively. Curves were fitted by the Percus–Yevick hard sphere model.

a shift in the position of the structure factor maximum and by variations of its peak width. On the basis of these criteria, three different regimes can be distinguished.

1. *A low temperature regime* is observed first, up to a temperature $T_{low} \sim 60$ °C, where the structure factor maximum and thus the interdomain order remains unaffected. The upper limit of this regime appears to be independent of the polymer content.

2. *An intermediate temperature regime*, is second, where the shape of the structure factor peak in all systems evolves continuously. Here an increase in intensity of the structure factor maximum and a decrease in peak width both reflect greater ordering within the interdomain arrangement. This regime starts at $T_{low} \sim 60$ °C and extends up to a limit T_{high} which depends on the polymer content, closely resembling the behavior around an “order–disorder” transition as observed in case of bulk block copolymer systems. For the present systems T_{high} lies between 90 and 115 °C.

3. *A high temperature regime*, above T_{high}, is third where the structure factor maximum continously decreases in intensity and increases in width, thus pointing towards a disordering of the physical network.

The Percus-Yevick hard sphere approximation[9] gives a quantitative description of the scattering behavior of these systems. This model represents a good approximation for scattering from bulk di- and triblock copolymers with highly asymmetric compositions and their solutions in selective or nonselective solvents.[10–12] The model assumes “hard spheres” (volume fraction ϕ_{hs}) with an interaction radius (R_{hs}) much larger than the actual radius of the microdomains r_0 as determined from the position of the form factor maximum ($r_0 = 5.76/q_{max}$). This “hard sphere radius” may be interpreted in terms of an extended shell around the polystyrene microdomain cores formed by the dissolved polymer midblocks. On the basis of this approach, the scattered intensity is described by

$$I(q) = \Delta\rho^2 N F(q) S(q)$$

arising from scattering contributions of individual spherical PS microdomains $F(q)$ which result in oscillations at high q values

$$F(q) = \{3/(qr_0)^3(\sin(qr_0)(qr_0)\cos(qr_0))\}^2$$

and a structure factor contribution $S(q)$ at low q values taking into account the hard sphere interactions described by

$$S(q) = [1 + 24\phi_{hs} G(qR_{hs})/(qR_{hs})]^{-1}$$

where $G(qR_{hs})$ is a trigonometric function, depending on the hard sphere radius R_{hs} and volume fraction ϕ_{hs}.[9] As can be seen from the scattering profiles shown in Figure 2, this model describes the detected scattering behavior very well. However, a more detailed discussion of results, obtained by fitting this model to the scattering profiles is presented elsewhere.[13] In the following we focus on the results (summarized in Table 1) derived by fitting of typical scattering patterns in the low- and intermediate-temperature region. Fitting revealed typical radii of the polystyrene domains of about 6 nm and hard sphere interaction radii of the order of 17 nm. In all gels, the hard sphere volume fraction in the low temperature regime is rather low, typically $\phi_{hs} = 0.3$, as compared to the volume fractions where formation of highly ordered structures can be expected.[10,11] This reflects a relatively low degree of order in the as-prepared systems at ambient conditions. In the intermediate temperature regime above $T_{low} \sim 60$ °C, the materials have a tendency to form more ordered structures, as indicated by an increase in the hard sphere volume fraction ϕ_{hs} from 0.3 to values close to 0.4. The hard sphere and polystyrene domain radii remain unchanged. Since $\phi_{hs} = 0.47$ represents the lower boundary for the existence of an ordered cubic arrangement of spherical microdomains,[10,11] this suggests that a transformation towards a more ordered morphology might take place in the present systems. Indeed, samples annealed for extended periods in this temperature range clearly reveal a further structural development, with the resulting morphologies shown by the scattering profiles in Figure 3. While the first structure factor peak remains nearly unaffected, the second maximum splits into two separate peaks with maxima at either side of the original q values, indicating a transformation to a highly ordered microdomain network. Such a rearrangement only takes place upon heating or cooling into the intermediate temperature regime above $T_{low} \sim 60$ °C. The time necessary for the rearrangement varies between one and several hours, depending on the annealing temperature in the intermediate regime and the triblock copolymer content of the gels. However, a gel sample containing 20% triblock copolymer requires 1 day of annealing at 90 °C in order to achieve a stable, equilibrium-like micromorphology in the intermediate temperature regime. After this time period no degradation or loss of selective solvent could be detected. The scattering patterns, collected after annealing at 90 °C, are shown in parts a and b of Figure 3 and reveal diffraction peaks with their maxima in the

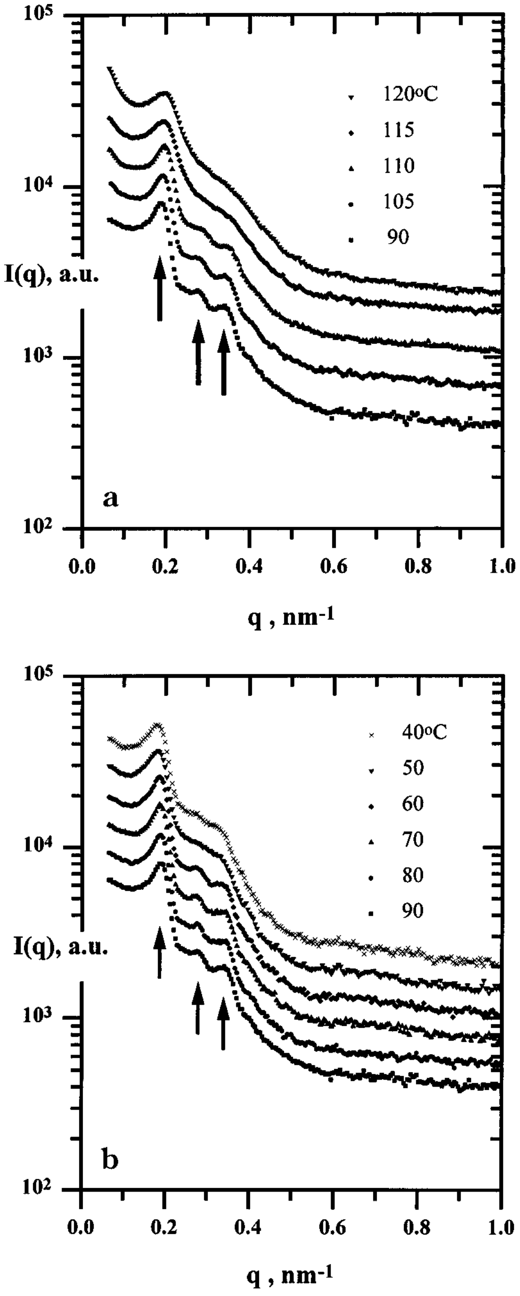

Figure 3. Small-angle X-ray patterns, collected from a 20% SEBS gel, after preannealing at 90 °C for 1 day: recorded during heating (a) and cooling cycle (b), showing structural disordering at high temperatures T_{high} and low temperatures T_{low}.

sequence $1:\sqrt{2}:\sqrt{3}$, indicating the presence of an ordered, cubic microstructure. These scattering patterns are observed at all temperatures within the intermediate regime. On the basis of the scattering profiles shown in Figure 3, one cannot unambiguously chose between a simple or body-centered cubic arrangement (face-centered cubic can be ruled out by the sequence of diffraction peaks), although our recent results strongly support a bcc-type morphology. For this purpose additional synchrotron experiments, also involving shear-aligned samples, are currently in progress. From the scattering patterns collected after heating and further equilibration for one hour, see Figure 3a, it is appearent that the cubic-type morphology is stable up to a temperature of $T_{\mathrm{high}} \sim 115$ °C. Above this temperature, higher order interference maxima disappear and the main interference peak broadens significantly. This phase transition closely resembles a first order "order–disorder" transition process as detected in bulk copolymer systems.[14] However, as shown in figure 2c, even in the high-temperature regime the structure factor maximum can be fitted using the Percus–Yevick hard sphere approximation. This might indicate that even at temperatures above the order–disorder transition there are microscopic regions where aggregated polystyrene endgroups form spherical domains. We believe that the Percus–Yevick type scattering behavior at temperatures above the order–disorder transition reflects the persistence of swollen PS-domains, with some residual coordination. The broadening and decrease in intensity of the main interference peak however reflects a continuous dissolution of the network of PS-domains with increasing temperature.

The morphology, finally detected at ambient conditions, appears to be rather complex and strongly depends on the thermal history of the sample during cooling. A structural disordering of the gels could be detected during cooling, as shown by the scattering profiles in Figure 3b. The highly ordered cubic-type morphology exists as long as the temperature remains above $T_{\mathrm{low}} \sim 60$ °C. Further slow lowering of the temperature at 1°/min and equilibration for 1 h prior to the scattering experiments results in weakening or even disappearance of the additional structure factor maxima. With fast quenching to the low-temperature regime, the cubic-type morphology still persists; however, the structure factor maxima reveal an increase in their widths, indicating that the cubic-type morphology becomes more distorted below 60 °C. Further broadening of the structure factor maxima as a function of time indicates that long-range order slowly deteriorates after several days and only one structure factor maximum is finally present in the scattering pattern. A tentative explanation of this behavior is based on the idea that stresses are introduced into the network upon cooling, since "solidification" of the network takes place as it would be due to a glass transition within the polystyrene-rich microdomains. This is supported by the fact that the lower disordering temperature T_{low} appears to be independent of the polymer concentration in the gel. A lower value of the glass transition temperature than is the case for bulk polystyrene appears to be reasonable, particularly since the selective solvent might not be completly excluded from the polystyrene microdomains of diameters around 12 nm. This has been confirmed by TEM studies on rather similar triblock copolymer gel systems.[4] Solvent penetration into the microdomains should also decrease scattering contrast of the domains with respect to the matrix, a feature which is evident from the form factor maxima that appear to be less pronounced with increasing temperatures; see Figure 1. However, with respect to recent structural studies and rheological work on gels based on higher molecular weight (240 000) SEBS triblock copolymers, this explanation seems to be less plausible since in that case the "low-temperature" disordering takes place around 150 °C, much higher than the glass transition of pure polystyrene.

In summary, structural rearrangements have been observed in triblock copolymer solutions, which form physical gels emerging from the presence of a microscopic three-dimensional network of highly interconnected endblock domains. The most striking feature is the formation of a high-temperature cubic-type morphology observed after preannealing at high temperatures. We studied the stability of the cubic-type morphology in triblock copolymer gel systems and detected a disordering when the sample is heated above a well-defined temperature limit, a behavior resembling the order−disorder process in bulk block copolymers. Moreover, the morphology appears to be metastable at ambient conditions, since scattering experiments revealed a structural disordering. The high-temperature disordering process strongly depends on the polymer concentration, most likely as a consequence of a change in segregation tendency with changing solvent content. In contrast, the low-temperature disordering is independent of the polymer content. All the structural rearrangements appear to be thermoreversible. However, this point and further studies on the low-temperature transition process are under investigation, using time-resolved scattering experiments, and will be discussed in detail together with the structure formation kinetics in a forthcoming paper.

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