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Stretching-Induced Correlations in Triblock Copolymer Gels As Observed by Small-Angle Neutron Scattering

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Processing triblock copolymers of the polystyrene–rubber–polystyrene type with solvent selective for the middle block results in highly elastic gels.[1,2] It was shown by small-angle neutron and X-ray scattering (SANS and SAXS) that the insoluble polystyrene, PS, end blocks associate into spherical domains (glassy micelles), thereby providing junction points for a three-dimensional network.[3] Due to the high content of solvent (80% and higher) the conformation of the midblock, which interconnects the PS domains, can be considered as being close to a statistical coil.[4] The end-to-end distance of the midblock polymer chain can, however, differ from that of a freely dissolved chain.[4] This deviation causes an elastic force between the PS domains and results in an increased mutual short-range order.

In the present study, we have examined such micellar networks when exposed to uniaxial elongation. It is shown that various characteristic structural features develop, depending on the midblock length and flexibility and on the copolymer concentration. The observed features could include an affine (bulk body type) deformation of the network or/and an improved angular specific correlation, indicating formation of mesophases.

Triblock copolymers with polystyrene, PS, end blocks and two kinds of midblocks were studied: (I) poly(ethylene propylene), PEP, and (II) poly(ethylene buthylene), PEB. The total molar mass of the copolymers was $M_n = 200\,000$ g/mol. The PS content (mass %) was 20, 35, or 50 for PS–PEP–PS and 35 for PS–PEB–PS. The solvent was a homogeneous mixture of completely saturated aliphatic and alicyclic hydrocarbons of $M_w =$ 500 g/mol and $M_w/M_n = 1.25$. Its chemical composition is close to that of the copolymer midblock. Gels of 6, 12, 18, and 20 mass % of block copolymer were used. SANS measurements were performed at the Risoe SANS facility using $\lambda = 0.9$ nm wavelength neutrons, with wavelength resolution $\Delta\lambda/\lambda = 0.18$ and a sample-to-detector distance of 6 m. The stretching device has been described elsewhere.[5]

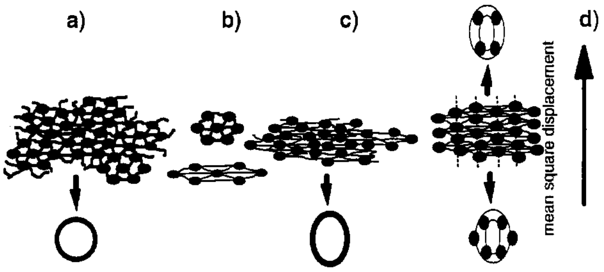

Figure 1. Two-dimensional models of the polymer network of the gel: (a) original (undeformed) network without long-range angular and spatial correlation of basic units, giving a uniform diffraction band; (b) original (upper) and deformed (lower) hexagonal basic units; (c) deformed entangled network, giving an elliptical diffraction ring with an isotropic azimuthal distribution of intensity; (d) deformed network with sufficient spatial and angular correlation of the deformed basic units (top view of the lattice) [four diffraction spots appear (upper pattern) at a relatively large (0.06) mean square displacement of the nearest neighbor domains within the basic unit and two additional equatorial spots (lower pattern) at lower (0.01) value of this displacement parameter].

The scattering function of the relaxed micellar networks has previously been analyzed in terms of both the Percus–Yevick analytical model for a hard-sphere interacting liquid and a numerical approach based on a local coordination model of slightly distorted hexagonal first-coordination symmetry,[3,4] as schematically shown in Figure 1a. No pronounced long-range distance or angular correlations have been found in the relaxed gels (unless the gel film was molded[6] at temperatures above 140 °C and a pressure about 80 MPa). Upon stretching, however, additional correlations appear in the original gel, as shown below. The scattering patterns of such a deformed polymer gel are effectively analyzed using the local coordination model.

In the absence of stretching, an azimuthally uniform broad correlation peak is observed (Figures 2a and 3a), revealing the liquid-like ordering of the micellar (glassy) PS cores. At low elongation ratios (25%) this pattern changes to a uniform elliptically shaped correlation band (Figure 2b). Such behavior appears for both the PS–PEP–PS and the PS–PEB–PS type gels, and at all the studied copolymer concentrations (4–20%).

With higher elongation ratios the structural response is no longer an azimuthally isotropic ellipse. This is seen, for example, in the 50% deformed gels of PS–PEP–PS and PS–PEB–PS, shown respectively in Figures 2c and 3b.

The most pronounced effect is the development of nonuniform azimuthal intensity distribution, effectively showing up as diffraction spots in the PS–PEP–PS type of copolymer gel with a relatively high PS content (50 wt % of the copolymer). The best resolved diffraction spots are observed for the 12% PS–PEP–PS copolymer gel (Figure 2c). Four spots are seen, arranged within the elliptical band at quadrants formed by the vertical and horizontal axes of the SANS pattern. In addition two diffuse arcs develop outside the ellipse within the equatorial direction, i.e. parallel to the stretching. The latter reflections become more pronounced with increasing deformation up to 100% (Figure 2d) and even more distinct after the sample has been kept in the 100% deformed state for 2 days (Figure 2e). It should be noticed, however, that at 100% elongation the diffraction spots within the elliptical bands firstly come together forming vertical arcs which, after 2 days, transform again into a four-spot pattern. The last observation could be a consequence either of relaxation of a first-coordination sphere symmetry or of deformation of the PS domains. Such deformation was not observed[4] at this elongation within the first few hours after stretching and should be investigated additionally.

The PS–PEB–PS type of gels with a PS content of 35% exhibits a different evolution of the scattering, as shown in Figure 3. In addition to the uniform elliptic band observed at 50% deformation (Figure 3b) this gel

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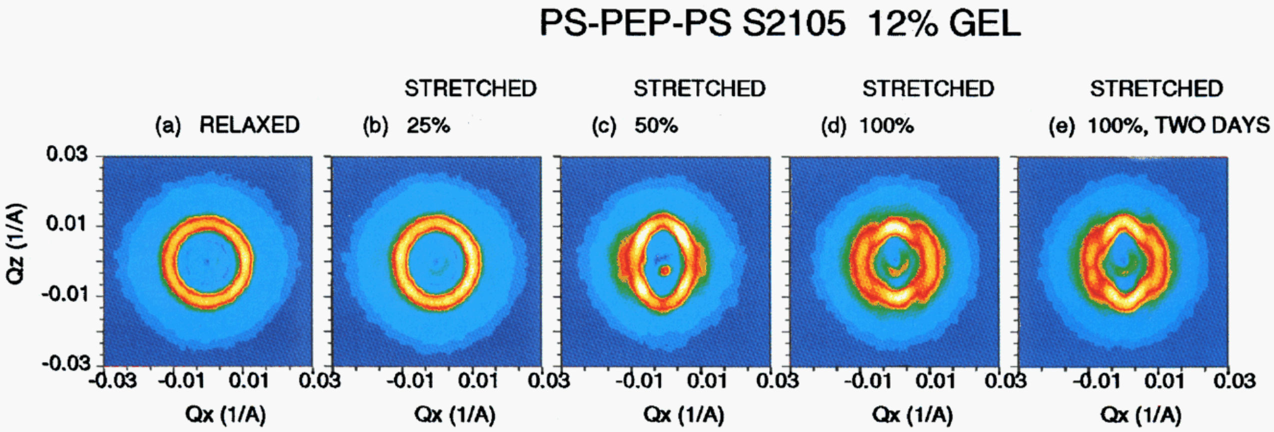

Figure 2. SANS of a 12% gel of PS−PEP−PS with 50% of PS: (a) original state; (b) 25% deformation; (c) 50% deformation; (d) 100% deformation; (e) 100% deformation for 2 days.

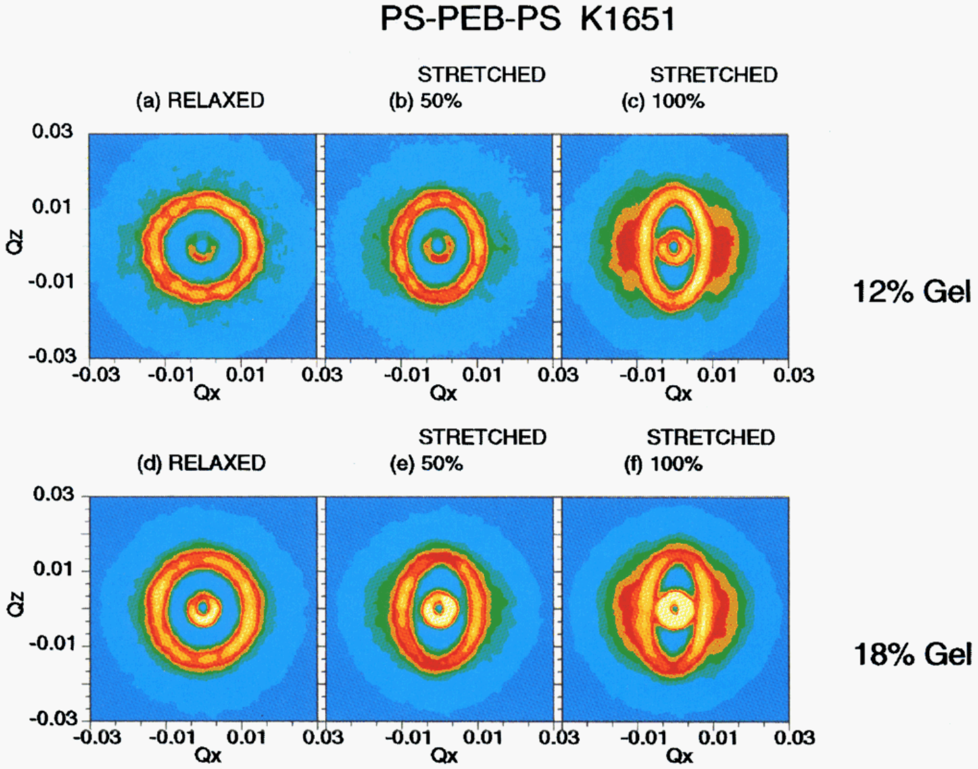

Figure 3. SANS of gels of PS−PEB−PS with 35% PS. (a−c) 12% gels: (a) relaxed state; (b) 50% deformation; (c) 100% deformation. (d−f) 18% gel: (d) relaxed state; (e) 50% deformation; (f) 100% deformation.

also scatters into two diffuse arclike reflections in the equatorial direction (100% deformation, Figure 3c,f). These arcs get weaker the higher the polymer concentration. No diffraction spots are observed, however. On the contrary, a splitting of the first-order elliptical band into two vertical arcs emerges. This is most clear in the 18% gel. For even higher deformations, the vertical correlations completely vanish, giving a butterfly-like scattering pattern.[7]

The observed scattering patterns during uniaxial deformation will now be analyzed.

The development from a circular interference ring to an elliptical band with an overall isotropic azimuthal intensity distribution points to a simple affine deformation of the micellar network, as visualized in Figure 1c. For the high-concentration gels of PS−PEB−PS, the affine deformation is further supported by the length of the axes of the ellipse: parallel to the stretching, the axis is reduced by K, K being the relative elongation; and perpendicular to the stretching, the interference peak appears at a momentum transfer of $K^{1/2}$ times that of the relaxed state. Equivalent affine deformation has been observed under specific conditions in a highly entangled chemically cross-linked amorphous polymer network (see, e.g., ref 8 and references therein).

The affine type of deformation was, however, only observed for the most concentrated gels of PS−PEB−PS (18 and 20 wt % of copolymer) at an elongation $K < 1.5$. For lower concentrations of PS−PEB−PS and for all PS−PEP−PS gels studied, the observed ratio of the larger and smaller axes of the ellipse were found to be less than that corresponding to an affine deformation. The dependence on the midblock side chain length and the concentration indicates that affine deformation is governed by entanglements of the polymer network formed by the midblocks. Such entanglements have been observed by rheological experiments for PEP elastomers extended with oil[9] and for PS−PEB−PS

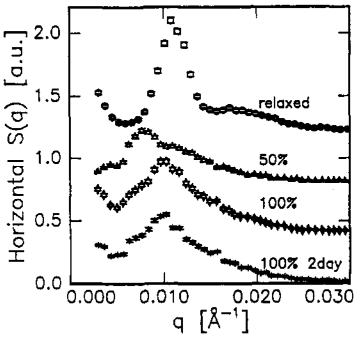

Figure 4. Horizontal cross-section of SANS pattern data shown in Figure 2 from a 12% gel of PS–PEP–PS with 50% PS: (○) relaxed; (△) 50% deformation; (◇) 100% deformation; (×) 100% deformation, kept deformed for 2 days. The relaxed, 50%, and 100% have been displaced vertically by 1.2, 0.8, and 0.4, respectively.

physical gels[10] of the same end block/midblock ratio and M_n = 100 000 g/mol.

The discussion of the additional correlations observed in the PS–PEP–PS micellar network will be based on the model schematically shown in Figure 1. This model consists of hexagons of knots (Figure 1b, upper part). The analyzed region of the network as a whole has a lack of crystalline correlations due to distortions of angles as well as translational vectors used for multiplication of the basic units into the network. No additional links between the junction points and no entanglements are at present considered. Of course, in reality the entanglements of the midblock rubber chain exist and interfere with the increased correlation, which can explain the absence of diffraction spots in the PS–PEB–PS type of gels, as discussed above.

Upon application of uniaxial stretching, both the network as a whole and the basic hexagonal units are deformed, and simultaneously a decrease of angular distortions occurs. At a certain deformation this leads to spatial correlations within specific azimuthal angles.

Consider, for instance, the hexagonal units with originally six equidistant neighbors around the central knot. They will be transformed into two connected lozenge units, as shown in Figure 1b, lower part. Now there are only four nearest equidistant neighbors around the central knot and two other more distant neighbors in the direction of elongation. Four symmetric correlation peaks therefore appear in the diffraction pattern. Simultaneously, the elongation causes formation of layers of knots (PS domains) which, perpendicular to the elongation, move toward each other, while getting more spaced along the direction of elongation. Hence, diffraction spots reflecting these layers will appear in the direction of elongation.

One can reproduce the observed diffraction pattern, shown in Figure 2, by simulation of the diffraction on the distorted lozenge lattice with a different isotropic mean square displacement $\kappa = (\delta R/R)^2$ of the PS domains as a parameter representing the extent of spatial correlation. This gives the diffraction patterns displayed in Figure 1d (below and above the model lattice). Four diffraction spots appear at relatively large values of κ (upper pattern, $\kappa = 0.06$). Two additional equatorial spots, indicating the layered organization (lower pattern), appear at a lower value of this displacement parameter ($\kappa = 0.01$). The numerical simulations were done using the CERIUS2 program[11] running on a Silicon Graphics workstation.

Simple calculation can in addition be used to check the reality of layered structure formation. For instance, at 100% deformation, the links along the deformation axis should be 2 times extended, giving a system of equally spaced domain layers of the same spacing as the original mean interdomain distance. Thus the angular position of the considered reflections should coincide with the scattering vector, q, of the original isotropic ring, as can be verified from the experimental observations (Figure 4). For 50% deformation one observes a smaller spacing, and the corresponding ratio of the scattering vectors parallel to the stretching, $q_{100\%}/q_{50\%} = 0.74$, is in excellent agreement with the expected value $K_1/K_2 = 1.5/2.0 = 0.75$. With increasing deformation from 50% to 100% the position of the four diffraction spots (Figure 2) shifts toward the meridional plane, which corresponds to a further deformation of the originally hexagonal units of the network.

In conclusion, the scattering experiments on gels based on PS–PEP–PS and PS–PEB–PS block copolymers show that poly(styrene) aggregates into PS domains, making an interconnected micellar metwork where PS domains act as knots. The scattering experiments are consistent with the PS domains being locally hexagonally arranged, but with no long-range order. Under stretching, different scattering patterns appear, depending on the molecular design of the copolymer as well as on the polymer concentration. For the 20% and 18% gels of PS–PEB–PS block copolymer with 35% PS, affine deformation is observed. In the case of 12% PS–PEP–PS, on the other hand, the stretching leads to an improved angular as well as spatial order, indicating the formation of relatively well-defined layers of regularly spaced PS domains. The diffraction patterns of all other PS–PEP–PS and PS–PEB–PS micellar gels are consistent with combinations of these two extreme cases.

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