Shear-Induced Single Crystalline Mesophases in Physical Networks of Gel-Forming Triblock Copolymer Solutions

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Polymer gels and *block copolymer* systems constitute two distinct classes of materials which both have attracted great technological and scientific interest in recent years. However, these two classes had up to the present only limited overlap in terms of materials and physical characteristics. *Polymer gels* are viscoelastic materials, combining wetting properties of liquids with the cohesive strength of solids.[1] This behavior results from the presence of a three-dimensional network of interconnected, flexible chains with the individual macromolecules linked either via permanent (chemical) or transient (physical) cross-links. *Block copolymers* formed by two or more incompatible polymer blocks self-assemble into well-defined mesoscopic aggregates both in the melt and for the polymer dissolved in selective solvents. This provides the basis for mesophases with crystalline-type long-range order.[2,3] Recently, these two classes of materials were combined into physical gels, based on triblock copolymers dissolved in a solvent selective for the midblocks and in which the gelation originates in a microphase separation process.[4−6] In the present communication we report on experimental studies on such triblock copolymer gels in which not only does self-association provide the cross-links but also where the long range ordered crystalline-type morphology characteristic of block copolymers is present, providing a novel class of gel systems in which cross-links are arranged on a regular, crystalline-type of lattice. Upon shear, this ordered gel aligns into a twinned cubic crystal.

It has been known for over 2 decades that a variety of AB- or ABA-block copolymers aggregate into microdomains when mixed with a solvent, that dissolves their A-blocks but is incompatible with their B-blocks. These microdomains consist of a dense core of B-blocks from which a corona of flexible A-block chains emerges and reveal either spherical, rod, thread, or disk-like shape.[7] If the volume fraction of microphase-separated microdomains (micelles) in the solution increases, intermicellar correlations become more pronounced and may be so strong that micelles order in a crystalline structure on the mesoscopic length scale. These structures may be cubic structures of spherical micelles, hexagonal structures of rodlike micelles or lamellar structures of extended discs.[7,8] A rather different behavior is expected in solutions of BAB-type copolymers in solvents which are good for the A-block only. The polymer midblocks, emanating from the micellar core, form either loops or intermicellar bridges, depending on whether polymer end blocks are located in the same or in different microdomains. Thus, one might expect that intermicellar bridging results in clusters of highly interconnected micelles, which for a certain copolymer concentration extend over the whole sample volume, providing a macroscopically isotropic physical gel. Depending on the lifetime of the polymer blocks associated with a given core, rheological experiments on such materials may show, even at low shear frequencies ω, a finite elastic response where the storage modulus $G'(\omega,\mathrm{T})$ becomes larger than the loss modulus $G''(\omega,\mathrm{T})$.

We have performed our studies on a series of BAB copolymer solutions, based on poly(styrene)−poly(ethylene,butylene)−poly(styrene) (SEBS) triblock copolymers with an average molecular mass, styrene content, and polydispersity of 100 000, 29%, and 1.1, respectively (KRATON G1650). The midblock selective solvent consisted of a mixture of aliphatic and alicyclic compounds with average molecular mass around 400 (FINA A360). Both components were mixed at 180 °C until a clear solution was obtained. After being quenched to room temperature, these mixtures form transparent, highly elastic gels. We used either small-angle X-ray (SAXS) or small-angle neutron scattering (SANS) with q-values ranging from 0.003 to 0.3 Å^{-1} ($q = (4\pi/\lambda)\sin\theta$; with 2θ scattering angle and λ the wavelength: SAXS, 1.5 Å; SANS, 6 Å) to study their morphologies since both techniques are able to probe the microstructure of the gels on a molecular length scale. Evidence for the existence of an extended three-dimensional network structure in our gel systems emerged from deformation experiments, indicating that the response in the microstructure is directly related to the elastic response on a macroscopic scale.[9] The microdomains, formed by associated copolymer endblocks, act as physical cross-linking points that are connected via polymer midblock chains. Since a large amount of the copolymer endblocks remains in different microdomains this accounts for the elastic response of these sytems, which resemble those of classical elastomers (rubbers) where permanent cross-links are introduced by vulcanization. The presence of microdomains can be detected in the small-angle scattering pattern.[4] The broad maximum in the scattered intensity at higher q values around 0.07 Å^{-1} is due to form factor oscillations and reveals the presence of microphase separated, spherical PS microdomains with typical radii r_0 ($r_0 = 5.76/q_{\max}$) around 80 Å, depending on the copolymer content φ in the gels. In addition, the presence of a well-pronounced maximum at low q values (around 0.018 Å^{-1}) reveals strong interdomain correlations. This maximum can be well accounted for on the basis of interactions between effective "hard spheres" around PS microdomains with radius R_{hs} ($R_{\mathrm{hs}} > r_0$) and a volume density ϕ_{hs} using the Percus−Yevick hard sphere approximation.[10] A more detailed discussion of the applicability of this model to our gel systems is presented elsewhere.[11] Since the individual microdomains are part of an extended three-dimensional network, displacement of a single microdomain would require one to extract the endblock chains, located in surrounding microdomains. This is a fact which severely restricts the mobility of individual microdomains in this type of three-dimensional networks, and one might speculate that this counteracts structural rearrangements. The time-resolved synchrotron experiments during heating clearly point toward a different behavior. With increasing temperature, the structure factor maximum becomes more pronounced and its intensity increases in a well-defined high tem-

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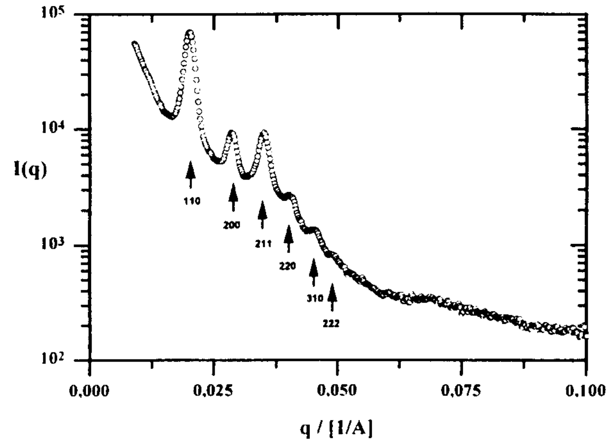

Figure 1. Small-angle X-ray pattern revealing body-centered cubic morphology, obtained from a gel sample containing 20 wt % copolymer after annealing for 18 h at 90 °C.

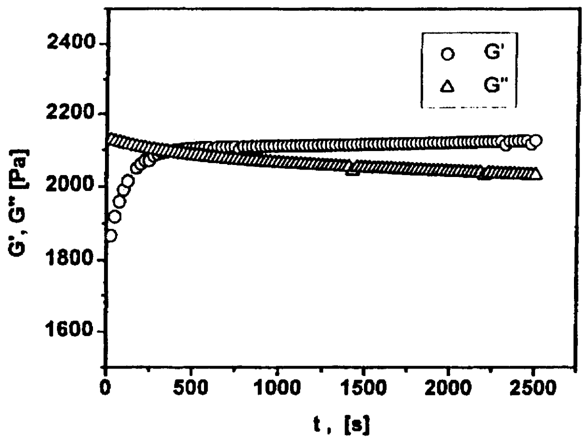

Figure 2. Evolution of the complex shear modulus (*G*′(*t*); storage modulus; *G*″(*t*), loss modulus) of a gel sample containing 20 wt % copolymer, at 90 °C measured with small amplitude oscillatory shear (1% strain, $\omega = 1$ rad/s), measured directly after subjecting the gel to large amplitude oscillatory shear (99%, 1 rad/s) for a time period of 15 min.

perature window between 50 °C and an upper temperature limit which strongly depends on polymer content, variing from 110 to 170 °C for gels containing between 20 and 40 wt % copolymer, respectively. Application of the hard sphere model to the scattering data obtained in this region indicates that the volume fraction of hard spheres increases in this range ($\phi_{\mathrm{hs}} \sim 0.4$) as compared to the situation at low temperatures ($\phi_{\mathrm{hs}} \sim 0.3$). The gel systems are in fact very close to a situation where these "hard spheres" are able to form highly ordered, crystalline-type morphologies[6,7,12] for which the limiting value corresponds to $\phi_{\mathrm{cr}} \sim 0.47$. In contrast to low molecular mass micellar systems, however, ordering processes in the present case are dominated by the polymeric nature of the constituents and microstructural rearrangements take place rather slowly.[12] They result in the formation of a highly ordered mesophase, which was detected by means of time-resolved synchrotron experiments after quenching from above to different temperatures below the solid–liquid transitions of the samples which vary between 110 and 170 °C for samples containing between 20 and 40 wt % copolymer. The time necessary for the formation of the cubic morphology at a temperature of 90 °C is about 1 h. It strongly depends on the chosen annealing temperature and increases when annealing is performed at either lower or higher temperatures. In fact, in most of the gel systems there is a temperature where this time is minimal, which at a first glance appears to be analogous to a nucleation and growth process; however, this point will be discussed in more detail in a forthcoming paper. A second factor affecting the time scale of reordering is the polymer concentration. Gels with polymer content lower than 20 wt % require a much longer time for reordering, which seems to be the result of a lower number density of micelles in the systems. SAXS patterns of samples, annealed for a sufficiently long time, correspond to a body-centered cubic-type microlattice, as indicated by the presence of well-pronounced structure factor maxima with positions corresponding to ratios of $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{5}{:}\sqrt{6}$. The scattering pattern after annealing for 18 h at 90 °C is shown in Figure 1. Apparently, ordering of the microdomains takes place in a well-defined temperature window, whereas the cubic-type microlattice disorders upon heating. The body centered cubic morphology is stable within the temperature window; however, it appears to be metastable when cooling to room temperature since long-range order slowly deteriorates over a time period of several days.[11] The disappearance of long-range order reflects some frustration, potentially from competing morphologies. The presence or absence of a three-dimensional network of interconnected microdomains which extends over the whole sample volume has a direct counterpart in the viscoelastic properties of these gels: Disordering of the cubic microstructure upon heating is accompanied by a solid–liquid transition as observed from rheology. However, even at high temperatures, where the systems behave as viscoelastic liquids, the scattering patterns display a well-pronounced structure factor maximum that can be described using the hard sphere approximation, indicating the presence of clusters of interconnected microdomains. Gel samples that were subjected to controlled thermal treatment under well-defined thermal conditions, however, reveal a polycrystalline morphology. It has been reported in several cases for diblock copolymer melts and solutions that shearing may result in the formation of arrays of long-range ordered microdomains that extend over the whole sample volume, thus forming a single crystal-type morphology. In the present case, there exists a three-dimensional network of microdomains extending over the whole sample volume. Thus, one could expect that shear might influence the microstructure of these gel systems. However, the effect of shear treatment might be 2-fold: Shearing could result in orientation of the lattice planes of individual grains with a cubic substructure, but large shear amplitudes might disrupt the network structure. In order to study this point in more detail, we used a modified Rheometrics RSA-2 instrument to apply oscillatory shear to our samples, providing in situ SANS measurements on microstructure and rheological properties.

Evidence for a disruption of the network structure comes from a time-dependent rheological experiment, performed on a preannealed sample with a cubic microstructure. Figure 2 illustrates the evolution of the complex shear modulus directly after the sample was subjected to large amplitude oscillatory shear (99% shear amplitude, 1 rad/s) for about 15 min. The experiment has been performed in parallel plate geometry[12] applying small strain amplitudes (1%, 1 rad/s) within the linear viscoelastic regime of the gel sample at 90 °C. Starting from a viscoelastic liquid, where $G'(\omega,T,t) < G''(\omega,T,t)$, clusters of interconnected micro-

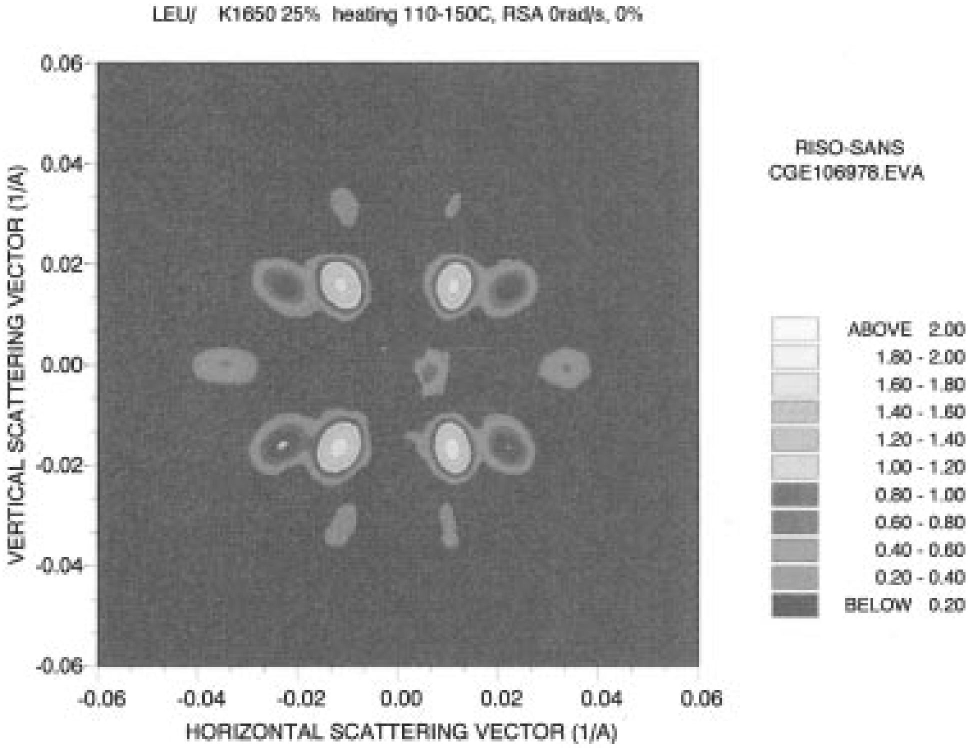

Figure 3. Small-angle neutron scattering pattern, obtained from a gel containing 20 wt % copolymer, revealing a twinned, body-centered cubic morphology. The diffraction pattern was acquired while subjecting the gel sample to small amplitude oscillatory shear, directly after subjecting the gel to large amplitude oscillatory shear.

domains start to grow until the three-dimensional domain network is built up, which is indicated by the crossover to a regime where $G'(\omega,\mathrm{T},\mathrm{t}) > G''(\omega,\mathrm{T},\mathrm{t})$ and the sample behaves as a viscoelastic solid. SANS revealed that the sample has been transformed into a highly ordered single-crystal-like morphology as indicated by the appearance of resolution-limited diffraction spots in the scattering pattern; see Figure 3. In this case, the microdomain arrangement resembles a twinned body centered cubic morphology.[2] The lattice constants vary between 360 and 450 Å, depending on the polymer content in the gel systems. Upon heating, this morphology disorders above the solid−liquid transitions of the gels but appears to be more stable upon cooling to ambient temperatures, although some additional broadening of the diffraction spots has been detected. This indicates that the application of shear results in a cubic morphology with a broader stability range.

In summary we demonstrated by using in situ rheological and structural studies, that a network of interconnected microdomains in gel-forming triblock copolymer solutions reveals reordering under well-defined thermal conditions. Reordering takes place, despite restrictions upon the rearrangement of individual microdomains due to interdomain bridging. Moreover, bridging between microdomains promotes the formation of highly ordered morphologies in these type of gels upon shear deformations. Rheological experiments revealed that large amplitude shearing disrupts the microdomain network on the grain size level, as indicated by the transformation from viscoelastic solid to a viscoelastic liquid, where reordering of randomly oriented grains takes place. During subsequent low amplitude shear experiments, the macroscopic network is built up again, and the sample transforms into a viscoelastic solid with a single crystallike microstructure.

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