CHAPTER 5

Structural Studies on PEO-b-PPO-based Amphiphilic Polymer Co-networks

KELL MORTENSEN*[a]

[a]University of Copenhagen, Niels Bohr Institute, Universitetsparken 5,
Copenhagen 2100, Denmark
*E-mail: kell@nbi.dk

5.1 Introduction

Amphiphilic polymer co-networks (APCN) are defined, according to Iván and Kennedy,[1] and Erdodi and Kennedy,[2] as two-component networks of covalently interconnected hydrophilic–hydrophobic phases of co-continuous morphology. Such networks will potentially swell both in water and in hydrocarbons, and may respond to changes in the medium by morphological transformation.

The term 'amphiphilic polymer co-networks' calls attention to the presence of two network constituents, *i.e.* hydrophilic and hydrophobic and is often distinguished from networks obtained by crosslinking amphiphilic block copolymers of hydrophilic and hydrophobic monomers. However, even such copolymer networks may qualify for the definition of 'amphiphilic polymer co-networks', though depending on their mesoscopic phase behaviour.

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By strictly applying the definition of APCNs, networks that contain dispersed, *i.e.* not co-continuous (such as systems with spherical micellar cores) hydrophilic and hydrophobic nanophases may not be considered APCNs. True APCNs, however, are only those in which both the hydrophilic and hydrophobic nanophases are continuous from edge to edge of the entire construct, thereby allowing both water and hydrocarbons to separately (and simultaneously) permeate/percolate the material. This is the case for systems ordered into cylindrical or worm-like mesophases, lamellar or gyroid structures.

5.2 APCN Hydrogels

Since APCNs swell in water, they satisfy the definition of hydrogels. However, as these networks also swell in hydrocarbons, APCNs are not considered as 'classical' hydrogels. In contrast, APCNs are quite special with unique properties that make them attractive for a number of applications. First of all, these materials have revolutionised the field of soft contact lenses. Today, most extended-wear soft contact lenses in use or under development are based on APCNs (see Chapter 12 on extended-wear soft contact lenses, but also Chapters 8 and 15). Furthermore, APCNs are materials highly relevant to many biomedical applications, such as uses as matrices for drug delivery and tissue engineering, and tissue replacement (artificial muscles, cartilages, and tendons).

Biomedical applications require advanced mechanical and, possibly, optical properties, as well as bio-compatibility. Both the mechanical and optical properties of hydrogels are significantly affected by the network structure. The mechanical properties are among the most crucial factors that limit a large variety of hydrogel applications. One major reason for these limits stems from crosslink inhomogeneities introduced during gel preparation. Crosslink inhomogeneities are actually present in most polymer gels and lead to severe problems that have led to a number of studies. Inhomogeneous distribution of crosslinks leads to opaque materials and stress concentration in high crosslink density regions, which may result in mechanical failure. Therefore, there is a continued need for studying how crosslink distribution affects the physical properties of the polymer network and to learn how to design and prepare more ideal network structures where the network links are regularly and homogeneously distributed.

5.3 Block Copolymer-based Amphiphilic Polymer Co-networks

The phase behaviour of block copolymers, as for example the poly(ethylene oxide)- (PEO-)based block copolymers, has been the subject of numerous experimental and theoretical studies, both when in the melt state and when dispersed in selective solvents. Depending on the block copolymer architecture, the mutual interaction parameter and solubility in given solvents, various nanoscale structures will appear. The most well-established phases are the spherical micellar phase, the cylinder-like micellar phase, the lamellar phases and other bi- or tri-continuous phases. These phases often form long-range ordered structures, such as the body-centred cubic (BCC) micellar structure, the hexagonal cylinder-structure, the lamellar structure, and the gyroid tri-continuous structure. Only the spherical micellar phase forms an isolated dispersed domain-structure without continuity. The cylinders, the lamellae and the gyroid-networks form continuous domain structures embedded in a continuous matrix, as illustrated in Figure 5.1.

Such block copolymers typically possess gel-like characteristics, but without necessarily being true networks. The individual polymer molecules are, even in the ordered phases, quite mobile and move from one self-assembled domain to another on a time-scale depending on solution properties, typically from minutes to hours. However, under certain conditions, these self-assembled block copolymer structures may form effective networks with 'crosslinks' that have physical rather than chemical origin. This is the situation when the self-assembled cores freeze the dynamics, which happens when the core is in either a crystalline or glassy state.

Polyethylene (PE) is an example of a polymer that may contribute a block forming a crystalline micellar core. Richter *et al.*[3] and Yin and Hillmyer[4] have, among others, shown that the PE component in dispersions of PE-based block copolymers crystallises in lamellar sheets of thickness 40–80 Å, surrounded on both sides by a soluble brush that exhibits a close to parabolic density profile, as shown in Figure 5.2. The disk-like morphology is ascribed to the crystallisation of PE, driving the formation of disk-like structures in this stepwise 'micellisation–crystallisation' process. Furthermore, as shown by Yin and Hillmyer using small-angle neutron scattering (SANS),[4] chain exchange between micelles is absent, proving that the crystallisation was confined within each 'frozen' micelle.

In analogy with the crystalline cores, glassy cores may also 'freeze' the chain dynamics, resulting in a true physical network structure. Such materials have extensive applications. Most applications concern materials based on hydrocarbon matrices with a typical example being thermoplastic

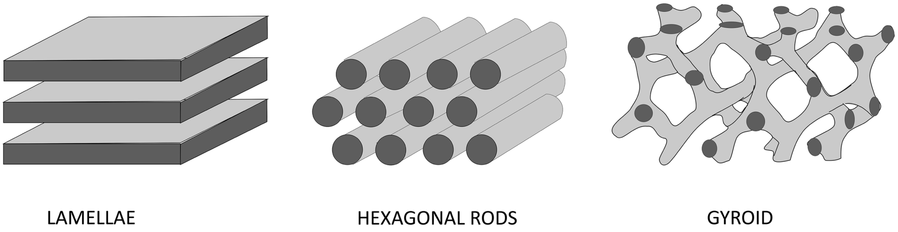
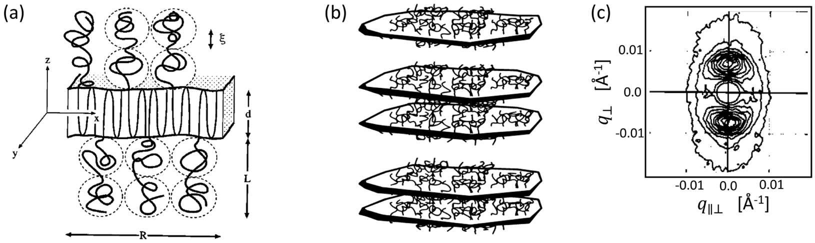


Figure 5.1 Schematic illustration of amphiphilic triblock copolymer structures, all ordered into structures where both types of blocks form phases continuous throughout the material. The phases represent the lamellar structure, the hexagonal cylinder structure and the gyroid structure.



Lamellar sheet with crystalline core Lamellar stacks of sheets SANS Pattern of Shear Aligned System

Figure 5.2 Schematic illustration of block copolymer systems with two continuous phases: a phase of a crystalline core and a phase of dissolved chains. (a) Schematic of the crystalline core. (b) Stacks of lamellar sheets as given in (a). (c) SANS data of a shear-aligned system. Reproduced from ref. 3 with permission from American Chemical Society, Copyright 1997.

elastomers. However, there also exist examples of hydrogels with glassy cores, including ABA triblock copolymers of polystyrene (PS) and PEO with PEO mid-blocks (PS-*b*-PEO-*b*-PS). Such copolymers will both in the melt and in aqueous suspension self-assemble into micellar networks where most copolymers will link (bridge) two different micellar cores. The remaining small percentage of the copolymers will start and end in the same core (loops), thereby not contributing to the network crosslinking density.

Figure 5.3 shows the structural characteristics of such ABA triblock copolymers, as exemplified by the PS–PEO–PS system. The example illustrates cylinder-shaped micelles. If the micellar cores are glassy, these cores will assume the role of physical crosslinks in the network. In the case of PS–PEO–PS, the PEO phase constitutes the water-swollen domain. The cylindrical cores of polystyrene may principally be swollen in organic solvents. This triblock copolymer system thereby forms a material with two distinct continuous phases, which can be swollen in different media, water and a non-polar solvent.

Figure 5.4 shows the structure factor for a 20 wt% aqueous solution of a PS–PEO–PS triblock copolymer,[5] as measured using SANS. The SANS pattern is dominated by a strong first order correlation peak and two weaker peaks at $\sqrt{3}$ and $\sqrt{4}$, thus indicating the hexagonal cylinder structure discussed above. The relatively intense scattering observed at the lowest angles indicates significant inhomogeneity in the network structure, suggesting a system which is far from ideal with respect to the distribution of the network chains and crosslinks.

The amphiphilic triblock copolymer co-network systems with continuous glassy or crystalline core structures form principally two independent continuous phases throughout the sample, the cores and the matrix. Still, however, such systems are generally able to swell only in the aqueous phase and not in the hydrophobic phase.

Both the crystalline and the glassy cores will generally dissolve upon swelling and the effective crosslinks given by the frozen domains will

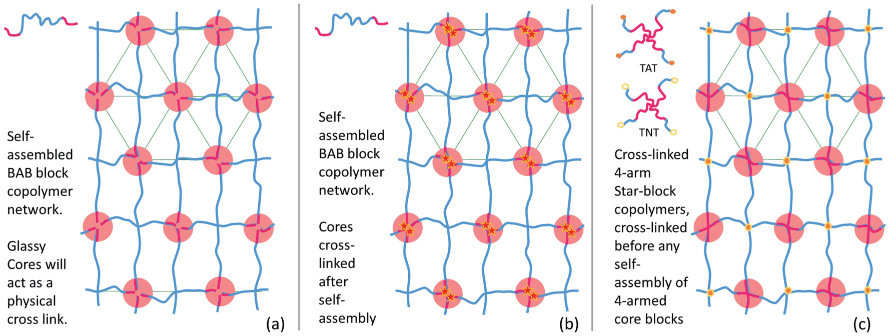


Figure 5.3 Schematic illustration of copolymer co-network structures obtained from (a) simple self-assembly, (b) self-assembly followed by cross-linking of the cores and (c) crosslinking of star block copolymers. The figure illustrates cylindrical micelles oriented perpendicularly to the plane of the figure.

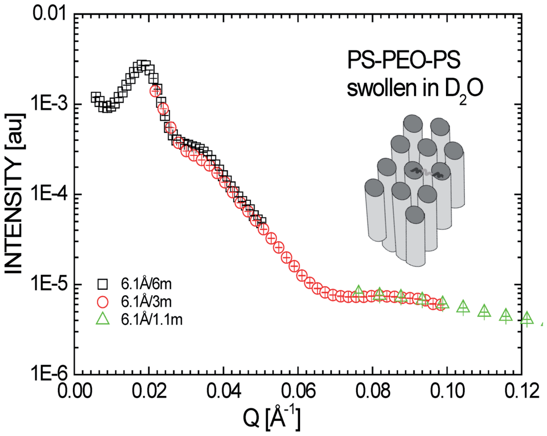


Figure 5.4 SANS profiles of a PS–PEO–PS triblock copolymer system, self-assembled into an hexagonal cylindrical structure. Reproduced from ref. 5 with permission from American Chemical Society, Copyright 2016.

thereby disappear. To keep the true network structure upon swelling the cores, these must actually be chemically crosslinked. A number of studies have been carried out on crosslinked micellar systems, but most studies were performed on dilute systems in the attempt to create crosslinks in the dispersions of nanoscale spherical micelles, rather than crosslinking the concentrated continuous structures. Examples include the crosslinking of the micellar core,[6] the micellar shell or more complex systems with an intermediate layer between the polymeric core and the polymeric corona.[7] Such systems are attractive as, for example, drug-carrier and drug delivery systems, but they do not constitute copolymer co-networks. The chemical methods used in these systems, however, could be used for introducing the crosslinks in block copolymer-based amphiphilic co-networks. Figure 5.3b shows how such block copolymer-based co-networks should be prepared.

5.4 PEO–PPO-based Block Copolymers

PEO-bearing block copolymers have generally been rather extensively studied and are used in a wide range of applications. These polymers include both linear diblock and linear ABA triblock copolymers, but also more complex, star-shaped block copolymers. Especially the Pluronics, triblock copolymers based on PEO and poly(propylene oxide) (PPO), have been studied in great detail.

Most studies have focused on ABA triblock copolymers with the less hydrophilic PPO block in the middle, but also the reversed architecture with a hydrophilic PEO block in the middle has been studied as well. The specific physical properties depend on the molecular size, composition and architecture, but generally one finds a generic type of behaviour: at the lowest temperatures and concentrations, the copolymers form dispersions of unimers (single copolymer chains); at intermediate temperatures and concentrations the copolymers self-assemble into spherical micelles, while at higher temperatures and concentrations the assemblies typically transform into cylinder-shaped or lamella-like aggregates. For concentrations beyond roughly 20 wt% the micellar aggregates form liquid crystalline phases, which may be cubic BCC or FCC, hexagonal, or lamellar, as shown by Mortensen[8] and Alexandridis *et al.*[9] The gel-like properties of these materials with high mechanical moduli are a result of long-range spatial coherence in the ordered organisation of the micelles.

The physicochemical properties of these simple systems still attract lots of interest, including the effects of purity[10,11] and additives.[12] A variety of studies concern new applications. Such polymers may also form the basis for novel amphiphilic polymer co-networks, provided the molecular architecture and possibly chemical crosslinking fulfil specific requirements for the co-network nature. For the linear triblock copolymer systems, only the reverse Pluronics with a PEO block in the middle may result in true co-network structures.

A highly related PEO–PPO system with somewhat more complex molecular architecture is the Tetronic family of star block copolymers also from BASF.[13] Tetronics comprise four-armed star block copolymers of PEO and PPO. There are still only relatively few publications concerned with Tetronics, even though they have been available for decades.[14] Most reports seem to be related to the T904 system, which is a 6.7 kDa molar mass star block copolymer with 15 EO and 17 PO monomer repeating units in each of its four arms. The hydrophobic PPO blocks in the centre of the star-shaped molecules would constitute, to a large extent, the crosslinks in the micellar cores as shown in Figure 5.3b. However, the free PEO end-blocks would also contribute to the co-network structure.

The scattering patterns from the free (non-crosslinked) T1307 PEO-PPO star block copolymer (comprising 72 EO and 23 PO monomer repeating units in each of its four arms) reveal all characteristics known from linear PEO-PPO-PEO triblock copolymers: dissolved unimers at the lowest temperatures and aggregation into micelles at higher temperatures, as shown by Mortensen and Annaka.[15] In our view, it is striking how much the linear and the star-shaped block copolymer assemblies resemble each other with respect to both micellation and the subsequent micellar nanoscale ordering and order–order transformations. One could have expected larger effects of the molecular star geometry of the Tetronics. Above approximately 18 °C, the spatial organisation of the micelles becomes markedly correlated, as verified by a pronounced correlation peak. At temperatures above a critical value, T_c, between 25 and 29 °C, the micellar correlations lead to an ordered, crystalline nanophase. The Bragg peak positions show a $\sqrt{3}:\sqrt{4}:\sqrt{8}:\sqrt{11}:\sqrt{12}$ -relationship, indicating that the ordered structure is face-centred cubic (FCC). In the corresponding linear Pluronics systems, both FCC and body-centred cubic (BCC) type of ordering are observed, the given structure depending on both the specific molecular properties and on the purity of the sample as shown by Mortensen *et al.*[10] At the highest temperatures measured ($T > 60$ °C), the crystalline cubic phase transforms into a hexagonal cylindrical phase, as verified by the high-temperature sequence of Bragg peak with ratios $\sqrt{1}:\sqrt{3}:\sqrt{4}$. The latter two peaks are, however, not well resolved, thus indicating a major distortion in the cylindrical structure. Transitions from cubic to hexagonal cylinder structure are also seen in the more thoroughly studied linear Pluronics.

In an attempt to make a true co-network structure based on the PEO–PPO star block copolymer system, Annaka and co-workers end-functionalised these star block copolymers to enable the formation of crosslinks between the termini of the PEO blocks. To this end, two types of end-functionalised PEO–PPO star block copolymers were developed, one end-functionalised with a primary amine group and the other with an *N*-hydroxysuccinimide group.[16] Therefore, by mixing at the stoichiometric (1 : 1) ratio such tetra-amine-terminated Tetronic T1307 (abbreviated as TAT) and tetra-*N*-hydroxysuccinimide terminated Tetronic T1307 (abbreviated as TNT) (see Figure 5.5), an ideal network without dangling chains should be formed, as shown in Figure 5.3c.

Based on the fact that the pristine star block copolymers behave, to a large extent, like linear PEO–PPO–PEO triblock copolymers, one would expect the formation of molecularly dispersed micellar systems at ambient temperatures. The crosslinked stars should, therefore, not form the basis for an amphiphilic polymer co-network structure. Only at elevated temperatures, or very high copolymer concentrations, would the formed continuous

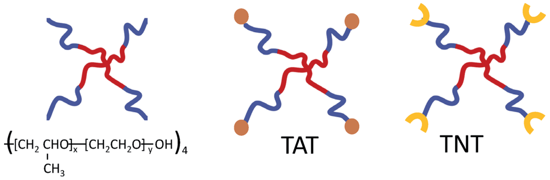


Figure 5.5 Schematic illustration of the pristine (original, hydroxyl end-functional) and end-functionalised (TAT and TNT) four-armed star block copolymers.

cylindrical or lamellar micellar cores secure the doubly continuous structure required for the co-network. However, as shown below, it appears that the crosslinked system forms cylinder-like micellar structures already at ambient conditions, securing a true co-network structure for these star block copolymer-based systems.

5.5 Networks of Star-shaped Block Copolymers

There has recently been significant interest from both fundamental and applied points-of-view to form ideal polymer network systems by crosslinking well-defined four-armed star homopolymers. Sakai, Shibayama, and co-workers have pioneered this area by carrying out several studies on PEO-based four-armed star architectures, the so-called tetra-PEG gel system.[17–23] These PEG-star networks are structurally related to the crosslinked system of the PEO–PPO molecular star block copolymers, but with the former not possessing the property of self-assembly, which is the result of the amphiphilic nature of the latter star block copolymer system. On the basis of SANS studies, Shibayama *et al.* concluded that 1 : 1 blends of tetra-amine terminated (TA-PEG) and tetra-NHS-glutamine terminated (TN-PEG) four-armed PEG star homopolymers form near-ideal network structures with a very high degree of uniformity. SANS proved that these tetra-PEG gels have a remarkably homogeneous network structure.[18] The SANS data on these tetra-PEG systems showed no indications of distinct or characteristic distances within the network pattern. This is in contrast to our finding on PEO–PPO based four-armed star co-networks, which show correlation peaks both as a consequence of the PPO-driven self-assembly, but also a correlation peak that is not part of the self-assembled structure.[15] The latter correlation peak is though not as well established, and it apparently depends on sample preparation.

Patrickios and co-workers studied another star block copolymer system highly related to the PEO–PPO system, namely a co-network based on end-linked 'core-first' star block copolymers of poly(methyl methacrylate) (MMA) and poly[2-(dimethylamino)ethyl methacrylate] (DMAEMA).[24] Using SANS and atomic force microscopy (AFM), these researcher found a long-range ordered lamellar structure. The observed lamellar structure reflects alternating PMMA and water-swollen PDMAEMA layers. The fundamental star architecture forms well-defined two-dimensional sheets perpendicular to the lamellar structure.

Tetronic- (PEO–PPO four-armed star block copolymer-) based co-networks were formed upon mixing 1 : 1 aqueous solutions of tetra-amine (TAT) and tetra-*N*-hydroxysuccinimide (TNT) end-functionalised Tetronic T1307.[16] The Tetronic T1307 building blocks (macromers), having the chemical formula $[(EO_{72}\text{-}PO_{23})_2\text{-}NCH_2\text{-}CH_2N\text{-}(PO_{23}\text{-}EO_{72})_2]$, are shown in Figure 5.5. Pristine (starting) Tetronic T1307 is a four-armed star block copolymer amphiphile with four primary alcohol end-groups, and a total (average) molar mass equal to 18 kDa.[13] Tetra-amine-terminated Tetronic T1307 (TAT) and tetra-*N*-hydroxysuccinimide-terminated Tetronic T1307 (TNT) were synthesised using the same tetrahydroxyl starting polymer. Structural studies were carried out using small-angle X-ray scattering (SAXS) and SANS. While the two techniques are quite similar, it appears that the different contrast conditions of X-ray and neutrons make the X-ray technique more sensitive for detailed structural analysis of these systems.

Hydrogel networks were formed when mixing TAT and TNT macromers in aqueous solutions. This arises from the reaction between the amine and *N*-hydroxysuccinimide end-groups, which gives crosslinks and results in a gel that is formed instantaneously with a network structure as shown in Figure 5.3c. The mechanical properties of this gel are remarkable, presenting a relatively high modulus with little frequency dependence.[16] For a 30 wt% polymer concentration in the gel, we found an elastic shear modulus of 10 kPa within the frequency range from 0.1–100 s^{-1}.[16] The Young's modulus was also of the order of 10 kPa. These values can be compared to reported values for the mechanical properties of native articular cartilage, which, however, vary according to the specific system and the applied frequency range. Reports on native articular cartilage give values ranging from kPa to MPa.

The Tetronic networks are expected to have a very well-defined network structure with only a small occurrence of defects, similar to the tetra-PEG gels. The SAXS patterns of the TAT–TNT T1307 gel (Figure 5.6) show important similarities with the characteristics of aqueous solutions of both pristine (tetrahydroxyl) T1307 and related linear PEO–PPO block copolymer systems in general. At low temperatures, the scattering is characterised by low intensity. In pristine PEO–PPO systems, this indicates individual PEO–PPO block copolymer molecules. In the TAT–TNT crosslinked system, the molecules are obviously not independent. Still, however, the scattering appears to be dominated by polymer characteristics with no intermolecular correlations within the 1–10 nm length-scale.

Upon increasing the temperature, the PPO blocks become more hydrophobic. This apparently results in the formation of self-assembled micellar structures, in analogy with the non-crosslinked PEO–PPO systems. While the pristine (non-crosslinked) four-armed star block copolymer molecules, like most other PEO–PPO block copolymer systems, self-assemble into spherical micelles at intermediate temperatures and rod-like micelles at higher temperatures, the four-armed star network structure self-assembles directly into a hexagonal cylinder structure. This is seen from the ordered structure in the SAXS pattern, showing a relationship between the Bragg peaks equal to $\sqrt{1}:\sqrt{3}:\sqrt{4}$. The PPO blocks of the TAT–TNT network apparently self-assemble across the local two-dimensional sheets. The four-armed stars thereby self-assemble into cylinder-like domain structures perpendicular to the local two-dimensional crosslinked network. This cylinder-like structure secures the amphiphilic co-network characteristics, but only at ambient and higher temperatures. Below roughly 20 °C, the PPO star cores are still not assembled, and, therefore, do not constitute a continuous phase.

The SAXS pattern shown in Figure 5.6 shows at high scattering angles, *i.e.* at high q-values, a relatively weak peak with a q-value that increases with temperature, *viz.*, from 0.115 Å^{-1} at 7 °C to 0.13 Å^{-1} at 64 °C. The q-value is the scattering vector defined as $q = (4\pi/\lambda)\sin\theta$, with λ being the radiation wavelength, and θ one-half of the scattering angle. While the q-value changes, the peak intensity remains roughly T-independent. In our original study, we attributed this high q-peak as reflecting a local sheet-like character of the polymer network.[15] The correlation peak reflects a correlated distance between the sheets. Additional studies, however, have shown that this 'lamellar' peak is not well-reproduced. Its presence apparently depends on the method of preparation of the gel. Nonetheless, even without this distinct Bragg reflection, it is clear from inter-molecular correlations that the

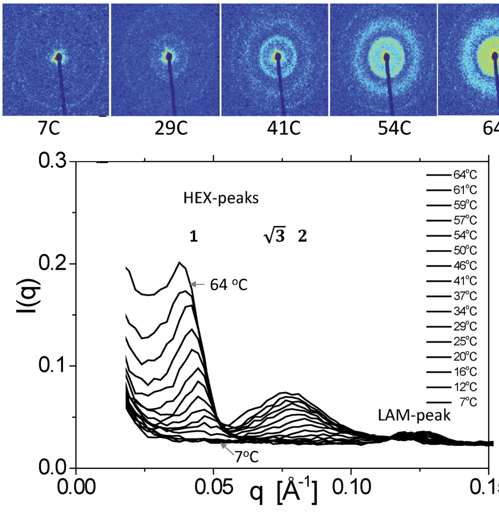


Figure 5.6 SAXS patterns of the crosslinked star block copolymer co-networks, exhibiting a hexagonal cylinder structure of the hydrophobic domains as sketched in Figure 5.3c.

unique network structure causes, at temperatures above the micellisation temperature, cylinder-like self-assembly, and not spheres as in the pristine materials.

The cylinder-like structure of the micellar PPO-cores provides the basis for true amphiphilic co-networks, as mentioned above. The overall materials properties are given by two distinct phases, both of which form continuous structures throughout the construct. Namely, the crosslinked aqueous PEO-matrix, and the micellar cylinders made up of the core of the four-armed stars. The structure must be relatively stable upon swelling both the matrix and the cores. We have, though, still only investigated the swelling of the PEO-matrix phase.

The network structure also provided the basis for a variety of materials characteristics. The unique mechanical properties of the gel, as reported by Annaka *et al.*,[16] arises from its network structure. Diffusion properties in soft matter like the TAT–TNT gels strongly depend on obstruction, interactions and structural dynamics. The network structure of the gels, and, in particular, such amphiphilic polymer co-networks, influences the solvent permeability, *i.e.* the diffusion of small and large molecules, and, thereby, indirectly, the swelling and elastic properties of gels. Also, the collective diffusion coefficient of the gel, D_c, is related to the mechanical properties of the gel and the network characteristics. The water permeability of the polymer network reflects the local viscosity of water passing though the gel network and the mesh size of the network.

Figure 5.7 shows the temperature-dependence of the swelling ratios relative to the volume at 25 °C: $W(T)/W(25\ °\mathrm{C})$, of the aqueous 30 wt% TAT–TNT T1307 gel. The volumes gradually decrease with increasing temperature. It was speculated that the combination of enthalpic and entropic changes of the whole system lead to a lower critical solution temperature (LCST) type of phase behaviour.[16] At low temperatures, the formation of ether–water hydrogen bonds results in a favourable excess free energy, consistent with the swollen state in water. Increasing the temperature leads to a reduction in the favourable ether–water interaction due to breakup of ether–water hydrogen bonding. In addition, the entropically unfavourable structure of water molecules surrounding hydrophobic moieties (waters of hydrophobic hydration) becomes less ordered bulk water with increasing temperature. As a result, polymer chains lose hydrophobic hydration and increase contacts within the chains. This may lead to a decrease in the characteristic mesh size of the gel. This swelling behaviour occurs reversibly. It is interesting to note that the swelling is highly correlated with the self-assembly process, which is also a result of the changes in hydration of mainly the PPO blocks, but to a lesser extent actually also the PEO blocks.[8] The insert of Figure 5.7 shows the inverse-intensity of the first order hexagonal Bragg peak as plotted *versus* temperature, where this Bragg intensity is a measure of the self-assembly. The two properties, swelling and reverse SAXS intensity, follow exactly the same temperature-dependence.

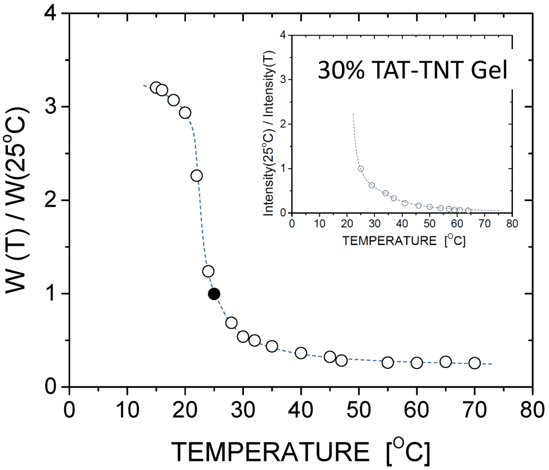


Figure 5.7 Temperature-dependence of the swelling ratios, $W(T)/W(25\ °C)$, of aqueous 30 wt% TAT–TNT gel, equilibrium swollen in water. The insert shows the inverse of the X-ray scattering intensity of the first-order hexagonal correlation peak, normalised to the value at 25 °C.

5.6 Summary

In summary, we have discussed the demands for making amphiphilic polymer co-networks based on block copolymer systems. Even the simple linear ABA-type of triblock copolymers may very well give rise to structures of two continuous phases, where the glassy or crystalline state of the one phase may secure effective physical crosslinks, thereby yielding a true network. Examples are gels based on ABA triblock copolymers of PS–PEO–PS or PE–PEO–PE. Typically, however, only one of the continuous phases will be able to swell without destroying the fundamental two-phase system; the glassy or crystalline phase would melt and dissolve upon swelling in an apolar solvent. Only with more complex molecules and/or chemical crosslinks, one is able to make true amphiphilic polymer co-networks based on block copolymers. The specific example shown in this chapter is based on commercial, four-armed star block copolymers of PEO and PPO. We have shown that these star copolymer molecules, even in the crosslinked situation, self-assemble and associate into a micellar organisation. While the structure shows surprising similarities to the characteristics found in the corresponding linear PEO–PPO block copolymers, we see that the crosslinking induces important differences, which are required for the conetwork characteristics. Even the pristine, tetrahydroxyl, four-armed star polymers form as their base self-assembled structure spherical micelles, but the crosslinked architecture has significant influence on the developed structures: it hinders the formation of spherical domains and the associated cubic ordering seen in the pristine polymer system. The crosslinked

TAT–TNT T1307 system forms locally two-dimensional network sheets. Upon raising temperature, the hydrophobic PPO blocks assemble into cylindrical PPO-based domains, thereby connecting star-centres across adjacent network sheets. We propose that the shear modulus measured in these systems is a result of both the crosslinked network structure and the long-range coherent hexagonal order.

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