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Structural Study of Four-Armed Amphiphilic Star-Block Copolymers: Pristine and End-Linked Tetronic T1307

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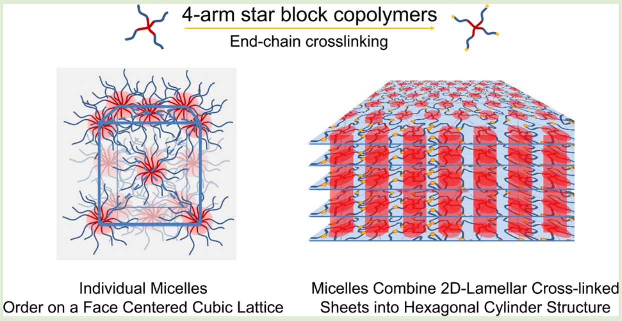
ABSTRACT: We present a comparative structural study of 30 wt % aqueous suspensions of two related systems based on 4-arm PEO−PPO type of macromolecules (Tetronic T1307, BASF) with the PPO block near the star center. One system concerns the pristine 4-arm PEO−PPO star block copolymer T1307. The second system is a 1:1 blend consisting of, respectively, tetra-amine (TAT) and tetra-*N*-hydroxysuccinimide (TNT) terminated T1307. The two systems show common characteristics which are also known from linear PEO−PPO type of copolymers (Pluronic, BASF): at low temperatures the measured structure is dominated by the characteristics of individual molecules, while at higher temperatures hydrophobic effects of the PPO domains cause self-assembly into spherical or rodlike micelles. These micelles form in both systems ordered mesophases. The pristine T1307 copolymer suspension behaves generally very similarly to linear PEO−PPO type of di- and triblock copolymers: unimers at low temperatures associating into micelles at higher temperatures, forming subsequently cubic and hexagonal phases upon further increase in temperatures. The cubic phase of the 30 wt % Tetronic T1307 has FCC symmetry. The structure of the cross-linked 30 wt % 1:1 TAT−TNT system is basically organized into two-dimensional network sheets. At low temperatures the system is rather disordered but still with a sharp correlation peak which is associated with the distance between neighboring network sheets. Upon raising temperatures, PPO self-assembly causes organization across neighboring sheets, resulting in cylinder-like assemblies perpendicular to the sheets. These cylinders form hexagonal structure.



Polymer hydrogels are polymer networks swollen in water and attract lots of attention. These gels have particular interests in context with biomedical applications toward materials such as lenses and artificial muscle, cartilage, and tendons. Such applications require advanced mechanical and/or optical properties as well as biocompatibility. Both the mechanical and the optical properties of hydrogels are significantly affected by the network structure and possible inhomogeneity of network links. The mechanical properties are among the most severe factors that limit more extended applications. One major reason for both insufficient mechanical strength and limited optical quality is cross-link inhomogeneities introduced during gel preparation. Cross-link inhomogeneities are actually present in most polymer gels. Inhomogeneous distribution of cross-links leads to stress concentration in low cross-link density regions, resulting in mechanical breakdown. There is a need for understanding how cross-link distribution affects physical properties of the polymer network and to learn how to make more ideal network structures where the network links are dictated through the design and synthesis. We have with such a goal developed a new class of hydrogels with network structures that are characterized by very regular and well-defined cross-link distributions. Other criteria, such as biocompatibility, can be accommodated through the synthesis of the end-functionalized poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) block copolymer star molecules.

PEO-types of block copolymers have been rather extensively studied the last decades and are used in wide ranges of applications. These polymers include both diblock and linear triblock copolymers. Especially the Pluronics copolymers from BASF have been studied in great detail. The specific physical properties depend on the molecular size and architecture, but generally one finds a generic type of behavior: 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 rod- or plate-like aggregates. For concentrations beyond roughly 20 wt % the micellar aggregates form liquid crystalline phases, which may be cubic BCC or FCC, hexagonal rod phase, or lamellar phase.[1,2] The physicochemical properties of these simple systems attract still lots of interest, including the effect of purity[3,4] additives[5] and a variety of applications. The gel-like properties of these materials with high mechanical moduli are a result of long-range spatial coherence in the ordered structure of the micelles.

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The reverse architecture Pluronics-R, PPO−PEO−PPO, with hydrophobic end-blocks form micellar networks with potential for more classical gels.[6] At intermediate concentrations and temperatures, these form gels with significant dispersion in the micellar density and thereby in the effective cross-link density. At higher concentrations these systems may as well crystallize into ordered structure, which may be cubic or lamellar phases. Even though the micellar cores (the cross-links) thus have formed a very ordered structure, the intermicellar chain density is likely still rather inhomogeneous. There is potential to design materials with preassigned properties by specific choice of the polymer covalently bonded to PEO. PEO−PPO types of block copolymers, which is the present example, form micellar gels upon raising temperatures. PEO−CH_n copolymers behave quite similar to PEO−PPO but with reversed temperature dependence: the ordering appears upon lowering temperatures.[7] Polystyrene-based copolymers, PS−PEO, are rather temperature independent, being fixed by the glassy state of the PS−micellar core.[8]

A highly related system with somewhat more complex molecular architecture is the Tetronic polymers from BASF. Tetronics constitute 4-armed star-block copolymers of PEO and PPO. There are still only relatively few publications concerned with these Tetronics, even though they have been available for decades.[9] Most reports seem to be related to the T904 system, which is a 6.7 kD molar mass star with PEO:PPO monomer ratio of 15:17.[10] Cho, Lee, and Webb studied Tetronic-based hydrogels with the aim to make tissue sealants.[11] They studied the gelation behavior of solutions of the Tetronic mixture of T904 and T1107 (Mw = 15 kD). Hydrogels were formed by thermal gelation and covalent cross-linking acrylated polymers. Ganguly et al.[12] studied the influence of sodium hydroxide (NaOH) on the aggregation characteristics of Tetronic T904 using dynamic light scattering (DLS) and small-angle neutron scattering (SANS). Ganguly et al. found pH-sensitive aggregation characteristics, which they associated with the presence of the central amine group attached to the PPO block. SANS and DLS studies showed a sphere-to-cylinder transition of the star-copolymer micelles as the cloud points of the copolymer solutions were approached. Kadam et al. studied the effect of copolymer concentration, temperature, pH, and salt on the micellization behavior and aqueous solution of Tetronic T904.[13] They used various methods, including DLS and SANS. Kadam et al. found that T904 forms spherical micelles at ambient temperatures with a core radius (R_c) of about 2.5 nm and a hard sphere interaction radius (R_{hs}) of 5.2 nm. An increase in micellar size and aggregation was observed upon increase in temperature and salt concentration, attributed to dehydration of the hydrated PEO shell like usual Pluronics.[1] Added salts (NaCl, Na_2SO_4, and Na_3PO_4) induce micellization and favor the micellar transition at lower temperatures, which was attributed to a "salting-out effect" following the Hofmeister sequence.

There has recently been significant interest from both fundamental and applied points of view to make ideal network systems.[14−24] Sakai, Shibayama, and co-workers presented recently a tetra-PEG gel system based on molecular four-armed star-architectures.[15−20] These basic PEG-star networks are somewhat related to the cross-linked system presented in this paper, but obviously without the property of self-assembly. The polymers were made up of a 1:1 blend of tetra-amine-terminated (TAPEG) and tetra-NHS-glutamine-terminated (TNPEG) four-arm PEG macromers. On the basis of small-angle neutron scattering studies, Shibayama et al. concluded that these TAPEG/TNPEG star molecules form a near-ideal network structure with very high degree of uniformity. The SANS data showed no indications for distinct distances within the network pattern.

Patrickios and co-workers made a study of another polymer system related to the present study, namely, a conetwork based on end-linked "core-first" star-block copolymers of poly(methyl methacrylate) (MMA) and poly(dimethylamino-ethyl methacrylate) (DMAEMA) blocks.[22] Patrickios et al. found based on SANS and AFM methods long-range ordered lamellar structure. They argue that the observed lamellar structure reflects alternating MMA and water-swollen DMAEMA layers. The fundamental star architecture forms, according to their schematic drawings, two-dimensional sheets perpendicular to the lamellar structure.

In the present study we present comparative small-angle X-ray-based structural studies of two PPO−PEO four-arm star-block copolymer systems: (i) a study with pristine star polymers and (ii) a study with the stars cross-linked into a network structure. Both studies are based on 30 wt % aqueous suspensions of Tetronic T1307 macromers. The sample-forming network structure consists of a 1:1 blend of two modified T1307 systems: one system is tetra-amine-terminated Tetronic T1307 (abbreviated TAT); the other is tetra-*N*-hydroxysuccinimide-terminated T1307 (abbreviated TNT). The molecules are shown schematically in Figure 1.

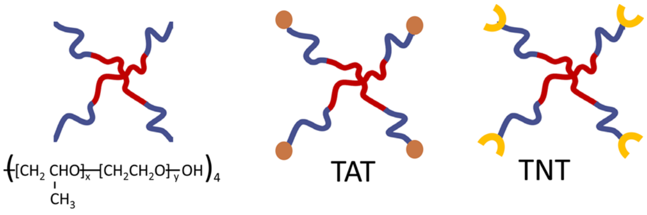

Figure 1. Schematic illustration of the molecules: Tetronic T1307, tetra-amine-terminated Tetronic (TAT), and tetra-*N*-hydroxysuccinimide-terminated Tetronic (TNT).

By mixing TAT and TNT aqueous solutions, "Tetronic networks" are formed instantaneously. Such networks can be formed not only in the laboratory but also *in vivo* with remarkable mechanical properties.[24] Such properties are required if used, for example, as materials for injectable intraocular lenses.[7] The Tetronic networks are expected to have very well-defined network structure with low degree of defects. The present study concerns structural studies with the aim to gain insight into details on the structure of both the precursor T1307 macromer suspensions and the corresponding TAT−TNT cross-linked network gel. Additional small-angle neutron scattering has been made and is in full agreement with the SAXS data. The SANS data will be published elsewhere.

The four-armed Tetronic T1307 based macromer has the chemical formula $[(OE_{72}OP_{23})_2NCH_2CH_2N(OP_{23}OE_{72})_2]$ and is shown schematically in Figure 1. Pristine Tetronic T1307 is a tetrafunctional block copolymer amphiphile terminating in primary hydroxyl groups with total (average) molecular mass equal to 18 kD.[10] The sample was obtained from BASF and used without further purification. Tetra-amine-terminated Tetronic T1307 (TAT) and tetra-*N*-hydroxysuccinimide-terminated Tetronic T1307 (TNT) were synthesized based on the same base polymer.[24]

Hydrogel networks are formed when mixing TAT and TNT molecules in aqueous solutions. Cross-link between the amine and *N*-hydroxysuccinimide terminations results in a gel that is formed instantaneously with a network structure as schematically shown in Figure 2. The mechanical properties of this gel are remarkably strong with high modulus. For a 150 mg/mL concentration gel we found a modulus of 10 MPa strength at break.[24] The mechanical values are accordingly comparable to those of native articular cartilage, which is typically characterized by 6−10 MPa at break.

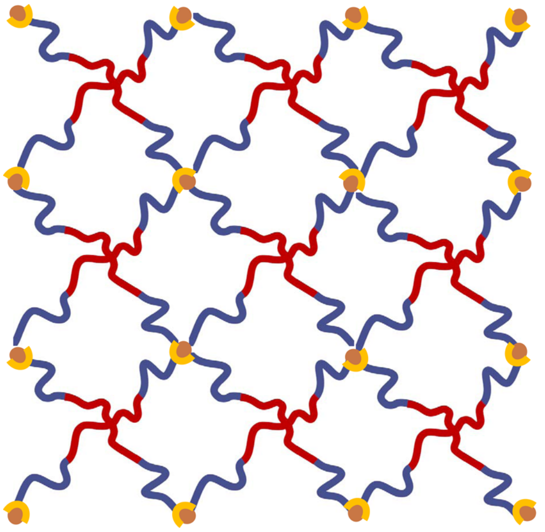

Figure 2. Schematic illustration on molecular network formed by covalently bonded TAT and TNT stars. The network forms a relative planar, two-dimensional sheet structure.

X-ray scattering was performed using the GANESHA-SAXS/WAXS instrument from SAXSLAB (Denmark) installed at the Niels Bohr Institute. The instrument is equipped with a 100XL + microfocus sealed X-ray tube (Rigaku, Japan) with Kirkpatrick−Baez focusing mirror system and a two-dimensional 300k Pilatus detector from Dectris (Switzerland). Measurements were performed with a 2 "pinhole" collimated beam using scatterless slits. The detector was positioned asymmetrically relative to the incoming beam, to obtain a large q-range within a single measurement, where the scattering vector q is defined by $q = 4\pi/\lambda \sin(\theta)$; $\lambda = 1.54$ Å is the X-ray wavelength; and θ is half of the scattering angle.

With the given SAXS/WAXS setup applied in this study, we obtained a q-range from 0.015 to 0.3 Å^{-1} within a single measurement. The SAXS/WAXS instrument is designed so the X-ray beam and sample is in vacuum. The aqueous samples were all loaded in vacuum-tight sample holders with 1 mm flight path and equipped with two 57 μm thick mica windows transparent to the X-ray. The sample holders were mounted on a temperature-controlled sample stage (Linkam Scientific Instrument, LNP95). X-ray diffraction measurements were performed within the temperature range from 5 to 65 °C. The measured X-ray scattered intensities were all corrected for cell and solvent scattering by conventional procedures. The two-dimensional isotropic scattering spectra were azimuthally averaged.

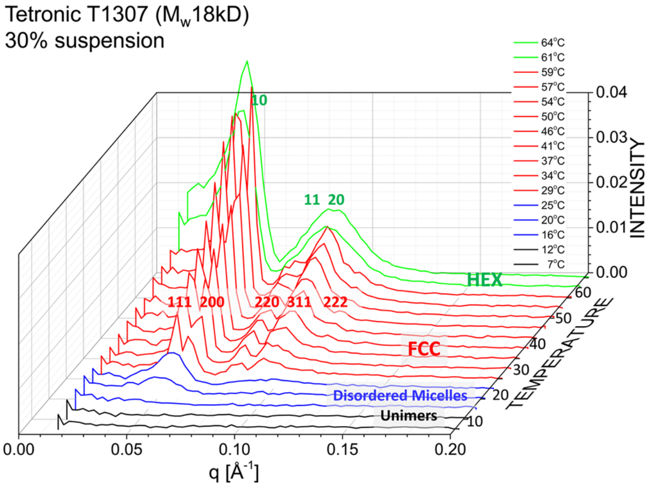

Figure 3. Structural properties of a 30 wt % Tetronic-T1307 suspension as measured versus temperature using SAXS. The numbers given in the figure specify Miller indices of the Bragg reflections of, respectively, FCC and HEX structures.

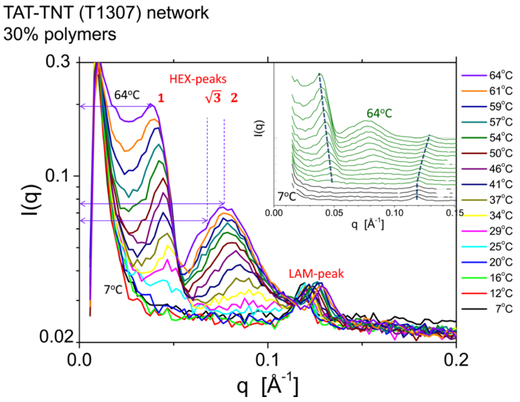

Figure 4. SAXS scattering pattern of 30% aqueous TAT−TNT T1307 gel measured as a function of temperature. The TAT−TNT polymer is based on the Tetronic T1307 star-copolymer with molar mass equal to 18 kDa. The data are shown in two presentations to make the properties more clear. The inset shows the temperature-dependent SAXS data in a waterfall representation: the lowest curve represents the 7 °C SAXS data and the highest curve the 65 °C SAXS data. The black curves represent low-temperature data where there are no PPO assemblies, and the green curves represent data with hexagonal cylinder structure of the PPO assemblies. A dotted line is a guide to the eye to show the temperature dependent-Bragg-peak positions.

The scattering patterns of the two 30 wt % aqueous suspensions of, respectively, pristine Tetronic T1307 and the TAT−TNT modified T1307 gel (Figure 3 and Figure 4) show important similarities. At low temperatures they are both characterized by low scattering intensity, indicating that properties of the individual T1307-star molecules dominate the 10−100 Å length-scale structure. Upon increasing temperature the PPO blocks get more hydrophobic, resulting in self-assembled micellar structures. The pristine T1307 molecules assemble into spherical micelles at intermediate temperatures and rod-like micelles at higher temperatures. The PPO-blocks of the TAT−TNT network self-assemble across the two-dimensional sheets into rod-like domain structures perpendicular to the dominating 2-dimensional cross-linked network. The specific findings of the 30 wt % T1307 suspension and the corresponding cross-linked TAT−TNT network will be presented in the following.

Figure 3 shows SAXS results of the pure 30 wt % Tetronics T1307 aqueous suspension. The scattering patterns reveal the characteristics known from linear triblock Pluronics: dissolved unimers at the lowest temperatures and aggregation into micelles at higher temperatures. Above approximately 18 °C, the spatial organization of the micelles gets markedly correlated as seen in the 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 $\sqrt{3}:\sqrt{4}:\sqrt{8}:\sqrt{11}:\sqrt{12}$-relationship indicating that the ordered structure is face-centered cubic (FCC). In the corresponding linear Pluronics systems, both FCC and body-centered cubic (BCC) type of ordering are observed, the given structure depending on both the specific molecular properties and on the purity of the sample.[3]

At the highest temperatures measured ($T > 60$ °C) the crystalline cubic phase transforms into a hexagonal cylinder phase, as seen from the high-temperature sequence of peak values with ratios $\sqrt{1}:\sqrt{3}:\sqrt{4}$. The two latter peaks are, however, not well resolved, thus indicating major distortion in the cylinder structure. Such disorder is further supported by the increased low-angle scattering seen in Figure 3. Transitions from cubic to hexagonal cylinder structure are also seen in the more thoroughly studied linear Pluronics.[1,2] Actually, it is striking how much the linear and the star-formed 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.

Figure 4 shows the SAXS scattering function of the corresponding Tetronic T1307 gel made up of cross-linked TAT and TNT. The observed SAXS pattern is assigned two main characteristics: a high-q peak with a q-value that increases as a function of temperature, viz., from 0.115 $Å^{-1}$ at 7 °C to 0.13 $Å^{-1}$ at 64 °C. While the q-value changes, the peak intensity remains roughly T-independent.

Another characteristic in the scattering pattern is a series of low-q peaks appearing at $T \approx 25$ °C and showing decreasing characteristic q-values as the temperature increases to 64 °C, i.e., a temperature dependence that is opposite to the high-q characteristic peak position. The low-q peaks are assigned three peaks, even though two of the peaks are only barely resolved. The three-peak assignment is in agreement with a hexagonal cylinder-like structure with the relative q-ratios $1:\sqrt{3}:2$ but where the broad peaks suggest molecular assemblies with rather low spatial correlations.

Principally we do not know whether the high-q peak reflects correlations between star centers (and/or cross-link centers) or correlations between the proposed 2D layer-like network sheets. On the basis of the results obtained at higher temperatures (see below) we find that the most probable interpretation is associated to the interlayer correlations between adjacent TAT−TNT cross-linked network sheets. The high-q peak is accordingly indexed q_L reflecting dominating lamellar-like (smectic) structure.

Upon increasing temperature three additional low-q peaks develop for T above 25 °C. These peaks are interpreted as a consequence of the PPO centers of the four-armed star molecules becoming hydrophobic and therefore self-assemble into micellar domains. This results in a cylinder-like domain structure perpendicular to the 2D network sheets, thereby effectively connecting adjacent network sheets. The PPO domains order perpendicular to the sheets into a hexagonal cylinder structure, as schematically shown in Figure 5. The hexagonal order as such is not very well developed, as seen by the second- and third-order peaks being only barely resolved. Still, the peaks are uniquely associated to a hexagonal structure with q_{10}, q_{11}, and q_{20} peaks with $1:\sqrt{3}:2$ ratio between their relative positions. The proposed structure is fundamentally rather similar to that proposed by Patrickios et al. for a different block copolymer star network.[22] In that system, however, the self-assembly leads to a lamellar structure perpendicular to the sheets rather than the cylinders we find. Patrickios et al. do not discuss the network sheets and do not observe scattering peaks corresponding to correlations between these.

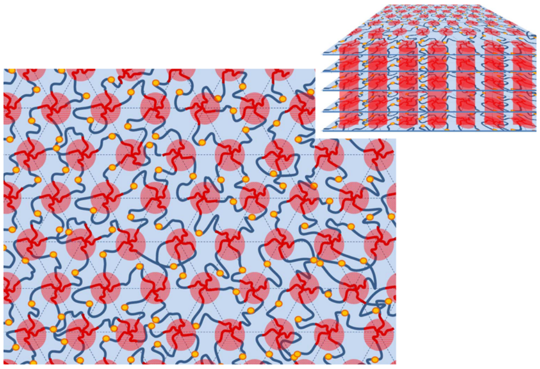

Figure 5. Schematic structure of cross-linked TAT−TNT T1307 gel network. The cross-links make up a dominating two-dimensional sheet structure. The hydrophobic PPO polymer blocks assemble adjacent lamellas in cylinder-like PPO domains, which organize themselves perpendicular to the sheets in a hexagonal pattern.

With the q-value q_L of the order of 0.12 $Å^{-1}$, we find an interlayer distance between adjacent polymer networks of the order of 5 nm. The first-order peak of the hexagonal structure has a value equal to or larger than 0.04 $Å^{-1}$, corresponding to a domain distance of maximum 15 nm. For comparison, the length of a single arm of the star-polymer system is of the order of 30 nm, assuming that the monomer size of EO and PO are both of the order of 0.3 nm. The molecular dimensions give accordingly no constrain to the observed ordering.

The position of the high-q peak (q_L) appears constant, equal to 0.12 $Å^{-1}$, until the in-plane hexagonal (low-q) structure starts to develop at $T \approx 25$ °C. Above 25 °C, q_L increases significantly corresponding to shrinking of the interlamellar distances. The in-plane hexagonal structure swells simultaneously, as seen by the decreasing values of the low-q peaks as T is increased (see Figure 4, inset). It is interesting to note that the product $q_L \times q_{10}^2$ is close to a constant, signifying a roughly T-independent unit cell volume given by the lamellar spacing and the area expressed between the star-molecular cores. The associated volume resulting from the peak positions $(2\pi/q_{10})^2 \times (2\pi/q_L)$ is of the order of 900 nm^3 within the measured $T = 25$−64 °C temperature range. Such constant overall volume is a consequence of the network structure and prevents changes in aggregation number of the PPO domains within the lamellae sheets and in agreement with the fact that we see no excess water as the temperature is changed. It is interesting to note that the measured swelling, as reported elsewhere,[24] is T-independent within this regime of ordered structures, while swelling measurements show significant T-dependence in the disordered regime. These findings are in very good agreement with the structure reported here. The T-dependent swelling at low temperatures is associated with the regime of molecular self-assembly into micellar domains.

In summary, we have shown that Tetronic T1307 star molecules self-assemble and associate into micellar organization surprisingly similar to the characteristics found in the corresponding linear Pluronics (which may be expressed as the corresponding 2-arm stars). We find self-assembly into spherical micelles at intermediate temperatures and cylinder micelles at higher temperatures. Further, the spherical micelles associate into FCC cubic order, while the cylinder micelles associate into hexagonal cylinder structure. The corresponding network of the cross-linked TAT−TNT T1307 system resembles a variety of properties from the pristine star-block copolymer: association into micellar domains that form ordered nanoscale structures. The cross-linked architecture has, however, significant influence on the developed structures: it hinders the formation of spherical domains and the associated cubic ordering seen in the pristine polymer system. At low temperatures, the TAT−TNT T1307 system forms 2-dimensional cross-linked network sheets, with relatively well-defined distances making a local lamellar-like structure. Upon raising temperatures, the hydrophobic PPO-blocks assemble into PPO-dominating domains, thereby connecting star-centers across adjacent network sheets. The structure resembles a perforated lamellar structure with PPO-dominating cylinders perpendicular to the network sheets. We propose that the high mechanical strength measured in these systems is a result of both the cross-linked network structure and the long-range coherent hexagonal order.

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Notes

The authors declare no competing financial interest.

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