

Lyotropic Liquid Crystalline Structures Formed by Amphiphilic Heteroarm Star Copolymers

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ABSTRACT: Polystyrene/poly(ethylene oxide) heteroarm star copolymers (i.e., star-shaped polymers consisting of a central poly(divinylbenzene) core bearing an equal number of short polystyrene and long poly(ethylene oxide) arms, PS₁₀PEO₁₀) were synthesized by anionic polymerization, and their phase behavior was investigated in aqueous solutions as well as in water–oil solvent mixtures. Because of their amphiphilic character and despite their star architecture, these polymeric species self-assemble under equilibrium conditions into lyotropic liquid crystalline structures.

Introduction

Block copolymers have received considerable attention due to their ability to self-assemble into a variety of ordered microstructures. In selective solvents diblock AB and triblock ABA copolymers associate, forming micelles of various morphologies such as spheres, cylinders, vesicles, etc.¹ In the bulk (absence of solvent) microphase separation occurs under appropriate conditions, leading to the formation of various microstructures like spheres, hexagonally packed cylinders, lamellae, and bicontinuous phases.^{2–6} In all cases the interactions between the unlike segments (e.g., either between A and B segments and/or between A or B and the solvent) and the molecular characteristics of the copolymer (degree of polymerization, composition, architecture) dictate the obtained structures.^{7–11}

The intermediate state of concentrated solutions of amphiphilic block copolymers has been investigated recently. Poly(ethylene oxide)/poly(propylene oxide) block copolymers have been shown to self-assemble in water as well as in oil–water mixtures, forming a wide variety of lyotropic liquid crystalline structures^{12–16} similar to those afforded by common surfactants.¹⁷ A remarkably rich structural polymorphism (i.e., nine different phases) was observed in a ternary isothermal system consisting of a PEO–PPO–PEO triblock copolymer water and oil (where water and oil are selective solvents for the PEO and PPO blocks, respectively).¹⁸

In recent years, nonlinear block copolymers have been put under investigation in an attempt to study the influence of the macromolecular architecture on the structure–property relationships. A number of well-defined new macromolecular architectures have been synthesized by “living” polymerization methods such as single graft, super H, star block, and heteroarm star, and their phase behaviors have been explored in the bulk.^{19–29}

Amphiphilic heteroarm star copolymers are a novel type of nonlinear block copolymers constituted of a

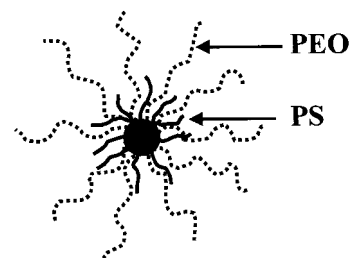


Figure 1. Schematic representation of the PS₁₀PEO₁₀ heteroarm star copolymer.

central core bearing two kinds of pure arms of different nature (i.e., one being hydrophilic and the other hydrophobic).^{30–33} Their syntheses rely on sequential “living” copolymerization techniques and comprise a three-step procedure.³⁴ In the first step, the first generation of arms is formed. These “living” linear polymers are used in a subsequent step to initiate the polymerization of a small amount of a suitable bis-unsaturated monomer. A “living” star-shaped polymer is thus formed, bearing within its core an equal number of active sites with its arms. In the final step a second generation of arms is growing from the core upon the addition of another suitable monomer. The final product is a star-shaped copolymer of the type A_nB_n where *n* is the number of the A and/or B arms. These species can also be viewed as *n* identical AB diblock copolymers joined together at their A/B junction points. The polymer under investigation is an amphiphilic heteroarm star copolymer consisting of 10 short polystyrene arms and 10 long poly(ethylene oxide) arms emanated from a central very tight poly(divinylbenzene) nodule, PS₁₀PEO₁₀ (Figure 1).

The A_nB_n star-shaped block copolymers, although they exhibit rather complex architecture, they do have the ability to self-assemble under appropriate thermodynamic conditions. In dilute solutions and in a solvent selective for the one type of arms the heteroarm star copolymers are associated into polymolecular micelles, adopting a core–shell structure of spherical shape.^{31,35–38} As has been shown recently for the polystyrene/poly(2-vinylpyridine) (PS_nP2VP_n)–toluene system, the effect of architecture on micellization phenomena is signifi-

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cant. The A_nB_n star copolymers exhibit cmc's 3 orders of magnitude higher and much lower aggregation numbers with respect to the corresponding linear AB diblock copolymer.³⁶

In the bulk state the thermodynamic driving force for microphase separation is the incompatibility between the different arms expressed in the $\chi_{AB}N_0$ product, where χ_{AB} is the Flory–Huggins interaction parameter between the unlike monomers and $N_0 = N_A + N_B$ (N_A and N_B being the number of the repeat units of the A and B arms, respectively).³⁹ In the case of the A_nB_n stars, theory predicts that the order–disorder transition occurs at the critical value $\chi_{AB}N_0 = 10.5$, which is the same for the corresponding diblock irrespective of the number of arms.³⁹ A number of ordered mesophases such as lamellae cylinders and bicontinuous structures have been observed recently.^{26,40}

The aim of the present study is to explore the ability of the amphiphilic heteroarm star copolymers to self-assemble in concentrated aqueous solutions, an intermediate situation between the bulk (solvent-free) and the dilute solution state. For the first time we have observed the formation of lyotropic liquid crystalline structures in the presence of a small amount of organic solvent.

Materials and Methods

Synthesis of the Polymer. The PS₁₀PEO₁₀ heteroarm star copolymer was synthesized by anionic polymerization under argon atmosphere. A three-step sequential “living” copolymerization procedure was used.³¹ In the first step the polystyrene arms were prepared using cumyl potassium as the initiator at $-40\text{ }^\circ\text{C}$ in THF. After the consumption of the styrene monomer a small amount of divinylbenzene was added to the reaction medium. Star-shaped polystyrene (PS_n) was thus formed, part of which was deactivated and sampled out for the purpose of characterization. The rest “living” star polymer was used to initiate the polymerization of a chosen amount of oxirane that was added to the reaction medium at $-30\text{ }^\circ\text{C}$. The temperature was then left to increase at $35\text{ }^\circ\text{C}$ and maintained at this level for 24 h to ensure complete polymerization of oxirane. The reaction mixture was then deactivated with degassed methanol, and the final product was recovered by precipitation in cold ether, dried, redissolved in benzene, and freeze-dried.

Polymer Characterization. Size exclusion chromatography (SEC), static light scattering (sLS), ^1H NMR, and differential scanning calorimetry (DSC) were employed for the characterization of the sample.

Size Exclusion Chromatography. SEC was carried out using an apparatus equipped with a differential refractometer (model 401, Water Associates). A set of three μ -Styragel columns (10^3 , 10^4 , and $10^5\text{ }\text{\AA}$) was used, and the calibration curve was obtained by PS standards. The mobile phase was tetrahydrofuran (analytical grade), and the flow rate was $1\text{ cm}^3\text{ min}^{-1}$.

NMR Spectroscopy. The copolymers were characterized by ^1H NMR spectroscopy using a Bruker Avance DPX 400 MHz spectrometer and CDCl_3 as solvent.

Static Light Scattering. The light scattering experiments were carried out using a thermally regulated ($\pm 0.1\text{ }^\circ\text{C}$) spectrogoniometer model SEM RD (Sematech, France) equipped with a He–Ne laser (633 nm). The refractive index increments dn/dc required for the light scattering measurements were obtained by means of a Chromatic KMX-16 differential refractometer operating at 633 nm .

Differential Scanning Calorimeter. DSC measurements were performed using a TA instrument model 2920 calorimeter. The heating rate was $10\text{ }^\circ\text{C min}^{-1}$.

The M_w of the PS arms was obtained by SEC using PS standards. The M_w of the PS_n was determined by sLS and was used for the determination of the weight-average functionality

Table 1. Molecular Characteristics of PS₁₀PEO₁₀

$M_w(\text{PS}_{\text{arm}})$	by GPC	3100
$M_w(\text{PS}_n)$	by sLS	34 500
n	calcd eq 1	10
W_{PEO}	by NMR	87.9%
$M_w(\text{PS}_n\text{PEO}_n)$	calcd eq 2	285 000
$M_w(\text{PEO}_{\text{arm}})$	calcd eq 3	25 000
$T_g(\text{PS}_n)$	by DSC	370 K
$T_m(\text{PS}_n\text{PEO}_n)$	by DSC	334 K
χ_c	calcd eq 4	44.4%

of the star, n . Taking into account the weight of the core, n can be calculated by the equation

$$n = M_w(\text{PS}_n) / \{M_w(\text{PS}_{\text{arm}}) + m_0[\text{DVB}]/[\text{LE}]\} \quad (1)$$

where $[\text{DVB}]/[\text{LE}]$ is the divinylbenzene per living ends mole ratio and m_0 is the molecular weight of divinylbenzene. The molecular weight of the PS₁₀PEO₁₀ was calculated from the $M_w(\text{PS}_n)$ and the weight content of PEO determined by NMR.

$$M_w(\text{PS}_n\text{PEO}_n) = M_w(\text{PS}_n) / (1 - W_{\text{PEO}}) \quad (2)$$

Provided that the PS and PEO arms are equal, the length of the PEO arms can be calculated by the formula

$$M_w(\text{PEO}_{\text{arm}}) = M_w(\text{PS}_n) W_{\text{PEO}} / n(1 - W_{\text{PEO}}) \quad (3)$$

Thermal characterization of the sample was also performed by DSC. The glass transition temperature of the PS_n star was obtained at half of the C_p change. Crystallinity of the PS₁₀PEO₁₀ was detected by DSC and calculated from the melting endotherm by using the equation

$$\chi_c = \Delta H_f / \Delta H_f^0 \quad (4)$$

where ΔH_f is the enthalpy of fusion per unit mass of the PEO in the copolymer and ΔH_f^0 is the enthalpy of fusion of 100% crystalline PEO ($\Delta H_f^0 = 205\text{ J g}^{-1}$). All the characterization data are collected in Table 1. Details of the synthesis and the characterization are reported elsewhere.³¹

Sample Preparation. Samples were prepared individually by weighting appropriate amounts of copolymer, water, and oil into 8 mm (i.d.) glass tubes which were immediately flame-sealed. The samples were centrifuged repeatedly in alternating directions over the course of several days to facilitate mixing (when viscous) and then in one direction to speed up phase separation (if not single phase); the samples were kept at $25 \pm 0.5\text{ }^\circ\text{C}$.

Small-Angle X-ray Scattering (SAXS). The measurements were performed on a Kratky compact small-angle system equipped with a position-sensitive detector (OED 50M from M Braun, Graz, Austria) containing 1024 channels with a $53.0\text{ }\mu\text{m}$ width. Cu K α radiation of wavelength $1.542\text{ }\text{\AA}$ was provided by a Seifert ID300 X-ray generator at 50 kV and 40 mA. A $10\text{ }\mu\text{m}$ thick nickel filter was used to remove the K β radiation, and a 1.5 mm tungsten filter was used to protect the detector from the primary beam. The sample-to-detector distance was 277 mm . The volume between the sample and the detector was kept under vacuum during data collection in order to minimize the background scattering. The temperature was kept constant at $25\text{ }^\circ\text{C}$ ($\pm 0.1\text{ }^\circ\text{C}$) with a Peltier element. All samples X-rayed were one-phase and well-equilibrated. We have not subtracted the background of the capillary, as its scattering intensity is orders of magnitude lower than that of the sample. At the relatively low q range where we observed the main scattering peak, smearing has a noticeable effect on the q position of the peak; thus, characteristic length scales have been obtained by desmeared data.

Results and Discussion

A number of PS₁₀PEO₁₀/water solutions were first prepared at concentrations from 5 to 38% (w/w). Upon

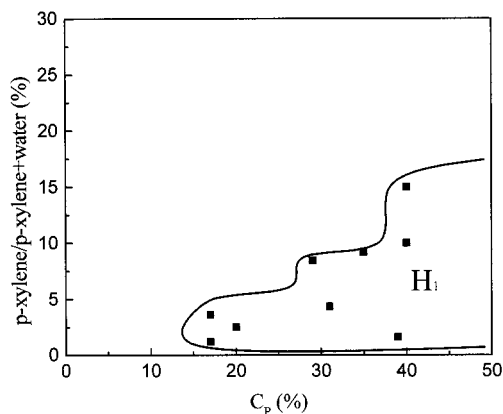


Figure 2. Section of phase diagram of the PS₁₀PEO₁₀/water/*p*-xylene ternary system at 25 °C in which the *p*-xylene content of the binary water/*p*-xylene mixture has been plotted against the polymer concentration. H₁ denotes the normal hexagonal liquid crystalline phase.

rigorous stirring and equilibration at 25 °C the following observations were made. The 5 and 10% polymer solutions exhibit a two-phase system constituted of clear domains and gel-like domains which are weakly birefringent (anisotropic). The solutions of 15 and 25% are turbid, highly viscous, and birefringent while that of 38% is a stiff gel.

The solutions were then heated at 75 °C for several hours. At that temperature all the samples became homogeneous, revealing a one-phase system. Subsequently, they have been left progressively to be cooled at 25 °C. After several days equilibration (and even months) the following characteristics were observed. The 5% solution is a bluish, faint turbid and of low viscosity solution showing the presence of large aggregates (probably spherical micelles).^{36,41–44} The 10 and 15% are clear, highly viscous solutions while those of 25 and 38% are birefringent gels. It is obvious that at the higher concentrations the heteroarm star copolymers have been self-assembled in supramolecular structures. However, nonequilibrium non-well-defined structures have been attained by the thermal treatment as revealed by SAXS investigations.

To aid the system to attain equilibrium, an amount of nonpolar, water-immiscible, organic solvent (*p*-xylene, a selective solvent for the PS chains) was added to the aqueous solutions. A number of ternary solutions were prepared (polymer/water/xylene) at room temperature and were left to equilibrate several days or weeks after rigorous stirring and without any thermal treatment.

Every sample was then macroscopically checked for phase separation and birefringence under polarized light prior to the characterization by SAXS. The above inspections lead to the construction of an isothermal phase diagram obtained at 25 °C in which the *p*-xylene content of the binary water/*p*-xylene mixture is plotted against the polymer concentration (Figure 2). An extended one-phase region can be observed in Figure 2. The solutions in that region are clear, very viscous (stiff gel), and anisotropic as they are strongly birefringent. SAXS characterization (see below for details) of the birefringent gels reveals that the heteroarm star copolymers self-assemble into a well-defined lyotropic hexagonal liquid crystalline structure (H₁). The obtained structures are stable since their characteristics remain unaltered even after months, implying that thermodynamic equilibrium should be attained.

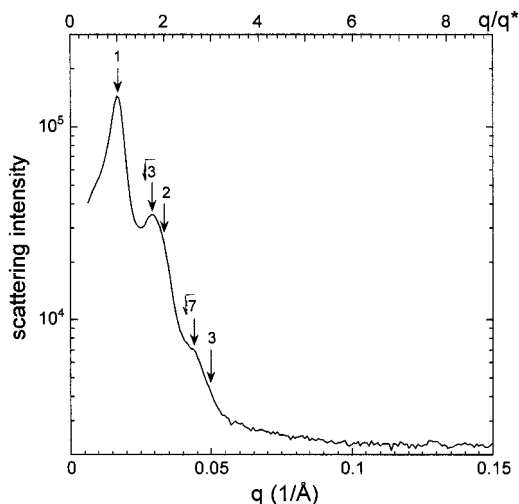


Figure 3. Slit-smeared SAXS diffraction pattern obtained from the normal hexagonal liquid crystalline phase of the PS₁₀PEO₁₀/water/*p*-xylene (composition: 40/51/9) sample.

As we have mentioned, amphiphilic block copolymers bearing highly hydrophobic blocks like polystyrene cannot be dissolved directly in water and require the use of an organic cosolvent and/or heating the solutions at elevated temperatures for long periods.^{41–44} Chain exchange between the obtained micelles is extremely low or not observable at all. This situation leads to the so-called kinetically “frozen” states.^{45–48} Recently, Rager et al. have shown that the micelle formation proceeds by fragmentation of the polymer powder into smaller and smaller pieces but not by association of singly dissolved block copolymer chains.⁴⁹ More recently, the same group, investigating the behavior of poly(acrylic acid)-*b*-poly(methyl methacrylate) block copolymers in mixtures of water with organic solvents, observed that the addition of an organic, water-immiscible, solvent to the aqueous polymer solutions does not lead in general to an accelerated chain exchange, except in the copolymer with the lowest number of methyl methacrylate monomer units ($N = 20$). The above findings lead them to assume that the rate of the micelle unimer exchange equilibrium is not kinetically hindered (i.e., determined by the T_g of the core material of the micelle) but controlled by a strong thermodynamic preference for the aggregated state.⁵⁰

Coming to our system, it seems that the presence of *p*-xylene causes swelling of the PS hydrophobic domains increasing therefore the PS chain mobility (*p*-xylene act as plasticizer lowering T_g), aiding fragmentation and presumably increasing the chain exchange (N_{PS} is low), leading eventually to the formation of stable liquid crystalline structures.

The normal hexagonal liquid crystalline phase (H₁) is stable in 15–40 wt % copolymer range and can swell with 1.5 up to 15 wt % *p*-xylene for the most concentrated polymer solution examined. A characteristic SAXS diffraction pattern obtained for the sample with polymer/water/xylene, composition 40/51/9 wt %, is presented in Figure 3. The relative positions of the SAXS diffraction peaks obey the relationship 1: $\sqrt{3}$:2: $\sqrt{7}$:3 (:2:3 peaks appear as shoulders) characteristic for the hexagonal structure, i.e., cylindrical assemblies organized in a two-dimensional hexagonal lattice as depicted schematically in Figure 4.

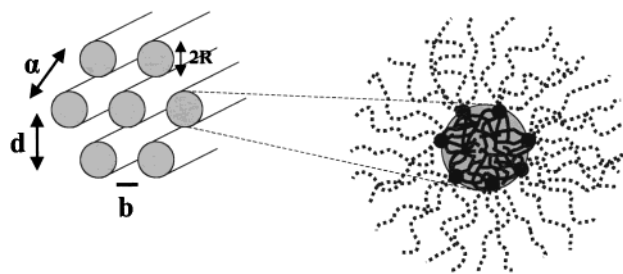


Figure 4. Schematic representation of the self-organization of the amphiphilic PS₁₀PEO₁₀ heteroarm star copolymers into the normal hexagonal liquid crystalline structure. Magnification of the cross section of a cylinder is included in the graph to illustrate the expected organization of the heteroarm star copolymers.

The heteroarm star copolymers form the cylindrical arrays where the DVB cores of the stars are located on the polar/unpolar interface (i.e., on the surface of the cylinders) and the PS arms are segregated on the interior of the cylinders, while the PEO arms are located in the polar aqueous domains. As we have shown previously, the segregation of the heteroarm star copolymers leads to thicker interfaces than those expected for diblock copolymers due to their specific architecture constraints.⁴⁰

Characteristic length scales of the hexagonal liquid crystalline structure can be estimated by the first diffraction peak of the desmeared SAXS spectra and the volume fraction, f , of the unpolar (PS + xylene) components of the ternary system. Assuming that all the xylene molecules are located in the interior of the hydrophobic domains, as it is almost insoluble in water (bad solvent of PEO and good solvent of PS), the apolar volume fraction can be estimated by the expression

$$f = \Phi_{\text{PS}} + \Phi_{\text{xyl}} \quad (5)$$

where Φ_{PS} is the volume fraction of polystyrene and Φ_{xyl} is the volume fraction of xylene in the ternary system. Thus, the characteristic parameters of the hexagonal structure can be calculated using eqs 6–9

$$q^* = \frac{2\pi}{d} \quad (6)$$

$$\alpha = 2d\sqrt{3} \quad (7)$$

$$R = \alpha \left(\frac{\sqrt{3}}{2\pi} f \right)^{1/2} \quad (8)$$

$$b = \alpha - 2R \quad (9)$$

where d is the distance between adjacent row of cylinders, α is the distance between the centers of adjacent cylinders, R is the apolar cylinder radius, f is the volume fraction of the apolar components at a given copolymer–oil–water composition, and b is the shortest distance between nearest-neighbor polar/apolar interfaces and corresponds to the smallest thickness of two overlapping and interacting PEO layers. The structured parameters obtained from eqs 6–9 for the 40/51/9 sample are presented in Table 2.

It is interesting to compare the distance between the centers of adjacent cylinders, α , with the hydrodynamic radius, R_h , of the PS₁₀PEO₁₀ micelles formed in aqueous dilute solutions. Stable micelles have been prepared by

Table 2. Structural Parameters of the PS₁₀PEO₁₀/Water/*p*-Xylene (40/51/9) Ternary System

lattice spacing	d	384 Å
apolar volume fraction	f	0.152
distance between the centers of adjacent cylinders	α	443 Å
apolar cylinder radius	R	91 Å
nearest-neighbor distance between polar/apolar interface	b	261 Å

step dialysis with the aid of an organic solvent which exhibit a spherical morphology with R_h equal to 240 Å.⁵¹ This value is quite comparable with $\alpha/2$ (222 Å) and provided that the PS cylindrical domains are swollen from the presence of xylene, a narrow interpenetration of the PEO layers occurs, leading to a slightly more compact structure.

In conclusion, we have observed for the first time that amphiphilic heteroarm star copolymers of the type A_nB_n self-assemble in water–oil mixtures to form a hexagonal lyotropic liquid crystalline structure. Further work is in progress, aiming to explore other compositions in the ternary phase diagram as well as to investigate the influence of architecture (comparison with a diblock copolymer AB having the same block size with the arms) and the role of the oil nature on the self-assembly of the amphiphilic heteroarm star copolymers in water–oil mixtures.

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