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Self-Assembled Structures from an Amphiphilic Multiblock Copolymer Containing Rigid Semiconductor Segments

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ABSTRACT: An amphiphilic multiblock copolymer comprising nearly monodisperse poly(ethylene oxide) segments ($M_w/M_n = 1.03$) and polydisperse poly(methylphenylsilane) (PMPS) segments ($M_w/M_n = 2.0$) forms a variety of well-defined morphologies such as vesicles, micellar rods, and helices upon aggregation in water-based solvent systems, despite this polydisperse character. Since polysilanes show σ-conjugation in the main chain, the optical and electronic properties of the described block copolymer depend on its confomational behavior. It is demonstrated by microscopic and spectroscopic techniques that the conformations of the PMPS backbone can be controlled through manipulation of the aggregation behavior, i.e., by the choice of the solvent composition.

Introduction

The control over block copolymer morphologies is of great importance for the fine-tuning of the performance of structural and functional polymers and the preparation of nanoscale devices. Aggregation and microphase separation of block copolymer systems has yielded a variety of morphologies in bulk,[1] thin films,[2] and solution.[3−7] Amphiphilic block copolymers mostly form spherical or rodlike micellar structures when dispersed in water;[3] however, more recently further morphologies such as lamellar, vesicular, and even helical aggregates have been observed.[5−7] Nevertheless, the formation of such highly ordered structures by polymer systems remains rare and is confined strictly to diblock copolymers with monodisperse component blocks.

Polysilanes are linear polymers of silicon, and the σ-electrons of the polymer backbone are delocalized. This σ-conjugation gives rise to electronic properties that allow for possible applications as electroluminescent, nonlinear optical, lithographic, and semiconductor materials.[8,9] Here we describe an amphiphilic polysilane-based multiblock copolymer (PMPS$_m$PEO$_n$) consisting of well-defined hydrophilic poly(ethylene oxide) (PEO) blocks and *polydisperse* hydrophobic poly(methylphenylsilane) (PMPS) segments (Figure 1), which forms highly ordered aggregates in water-based solvent mixtures.[5] It is demonstrated that the composition of the solvent system influences the packing of the conjugated polymer blocks, as well as the molecular conformation of the silicon backbone in such a way that micellar, vesicular, and even *helical* superstructures are generated, despite the disperse molecular structure of the polymer.

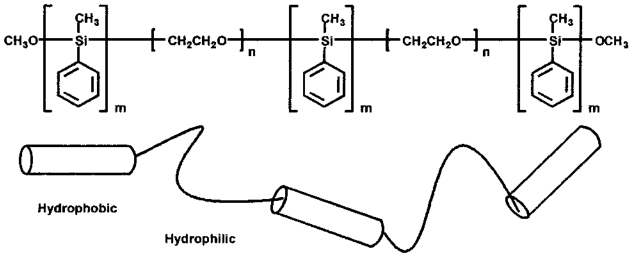

Figure 1. (a) Average molecular structure and (a) schematic representation of PMPS$_n$PEO$_m$.

Experimental Section

Synthesis. The PMPS−PEO copolymer was synthesized utilizing Schlenk techniques under a dry argon atmosphere and under exclusion of UV light.[5a] A solution of 4.78 g of poly(ethylene oxide) ($M_n = 7000$, 6.8×10^{-4} mol, $M_w/M_n = 1.03$) in toluene (10 mL) was added to a solution of α,ω-dihalopoly(methylphenylsilane)[10] ($M_n = 4400$, 6.8×10^{-4}mol, $M_w/M_n = 2.00$) in THF (15 mL) and toluene (20 mL). Subsequently, pyridine (3 mL, 3.7×10^{-2} mol) was added and the reaction solution stirred for 30 min. The solution was then added dropwise to methanol (300 mL) after which pentane (400 mL) was slowly added to the mixture. The copolymer was obtained as a yellowish white powder in 60% yield after filtration and vacuum-drying for 72 h.

The copolymer structure was confirmed using NMR spectroscopy (JEOL GX-270). ^{1}H NMR (ppm, CDCl$_3$): δ 7.5−6.0 (br m, H_{phenyl}), 3.8−2.7 (br m, CH_2), 1.1−0.5 (br m, CH_3). ^{13}C NMR (ppm, CDCl$_3$): δ 136.1 (br s, $C(2)_{phenyl}$) 134.6, ($C(4)_{phenyl}$), 133.0 ($C(1)_{phenyl}$), 126.9 (C(2)phenyl), 72.3 (OCH$_2$CH$_2$), 61.4 (CH$_2$OSi), −6.3 (CH$_3$Si).

Molecular weight characteristics were determined by size exclusion chromatography (SEC) and amounted to $M_n = 27\,000$; $M_w = 43\,200$; $M_w/M_n = 1.6$. The molecular weights quoted are based upon SEC measurements of THF solutions relative to polystyrene standards on a mixed bed 5 mm PL-gel column (Polymer Laboratories Ltd.) and using both a refractive index (RI) and a UV detector. The simultaneous use of both detectors confirmed that the product was a block copolymer.[11]

Langmuir Monolayer Experiments. Surface pressure−surface area isotherms were recorded at 20.0 ± 0.1 °C using a double barrier R&K trough of dimensions 6 × 25 cm with a

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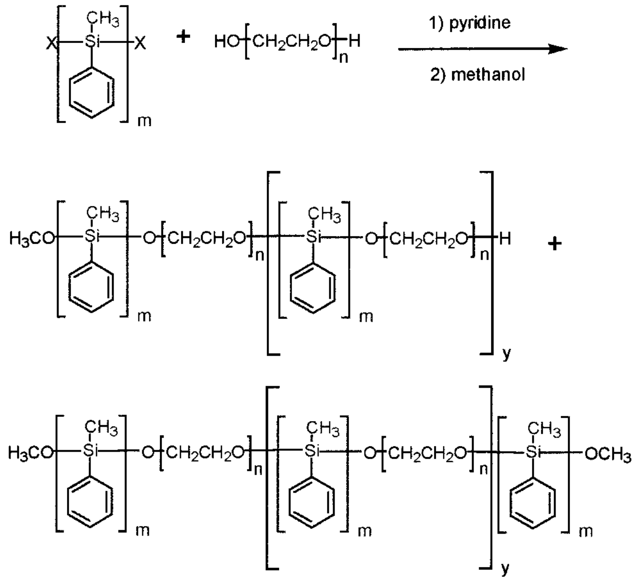
Scheme 1



compression speed of 7.0 cm^2 min^{-1}. PMPS$_m$PEO$_n$ was spread from a chloroform solution containing 0.5 mg of the copolymer per milliliter. The surface pressure was measured using Wilhelmy plates calibrated with octadecanol. The surface of compressed monolayers was studied with a Brewster angle microscope (NFT BAM-1) mounted on a home-built trough of dimensions 14 × 21 cm.

Aggregation Experiments. All aggregation experiments were carried out under the exclusion of light. Samples used for DLS, UV, and fluorescence experiments were prepared by adding water to a THF solution containing the appropriate amount of block copolymer. UV spectra were recorded using a Perkin-Elmer Lambda 5 spectrometer; fluorescence spectra were acquired using a Perkin-Elmer LS50B luminescence spectrometer.

Vesicle Preparation. The copolymer was dissolved in THF (100 mg/10 mL THF), and water (3.5 mL) was added dropwise to the stirred solution.[7e] The copolymer dispersion in water−THF was placed in a dialysis bag (exclusion limit = 20 000 Da) and dialyzed against pure water (500 mL) for 72 h.

Electron Microscopy. For TEM samples were prepared by bringing a drop of the dispersion onto a carbon-coated microscope grid. After 1 min the excess of the dispersion was blotted off with filter paper, and the sample was shadowed under an angle of 45° by evaporation of Pt or stained with a 2% (w/w) aqueous uranyl acetate solution. Freeze-fractured samples were prepared by using a Balzers freeze etching system BAF 400 D. After fracturing, the samples were etched for 1 min (ΔT = 20 °C), shaded with Pt (angle 45°; layer thickness 2 nm), and covered with carbon (layer thickness 20 nm). All samples were studied using a Philips TEM 201 microscope (60 kV). For SEM a drop of the dispersion was applied directly on a sample holder stub and after 1 min the excess solution was blotted off using a filter paper. The samples were examined under a JEOL JSM T300 operating at 3 kV.

Results and Discussion

The PMPS−PEO copolymer was synthesized by reacting poly(ethylene oxide) (M_n = 7000, M_w/M_n = 1.03) with α,ω-dihalopoly(methylphenylsilane)[10] (M_n = 4400, M_w/M_n = 2.00) in a mixture of THF and toluene using pyridine as the base (Scheme 1). The polymer was precipitated in pentane after which PMPS$_n$PEO$_m$ was obtained as a yellowish white powder in 60% yield (M_n = 27 000, M_w/M_n = 1.6). The block structure of the copolymer was confirmed by NMR spectroscopy and also by analysis of the molecular weight determinations of the copolymer and its precursors.[11] The M_n value of 27 000 for the copolymer corresponds closely to the structure shown in Figure 1, [PMPS−PEO]$_2$−PMPS, with a degree of polymerization (DP) of 2.5.[12] This is merely the most abundant structure and comprises up to 30% of the overall distribution which ranges from PMPS−PEO to (PMPS−PEO)$_{16}$.

Monolayer Formation. The ability of this *polydisperse* material to assemble into ordered structures was investigated by recording surface pressure−surface area (π−A) isotherms during the compression of Langmuir monolayers. The π−A isotherms obtained from PMPS$_m$-PEO$_n$ revealed a plateau from 20 to 10 nm^2 macromolecule^{-1} (Figure 2a), indicating a transition in which the PMPS rods that initially lie flat on the water surface adopt a more upright orientation. An increase in surface pressure was observed upon further compression and attributed to the packing of the polysilane rods under exclusion of the PEO segments, thereby creating a microphase-separated structure as indicated in Figure 2a. Brewster angle microscopy demonstrated that the

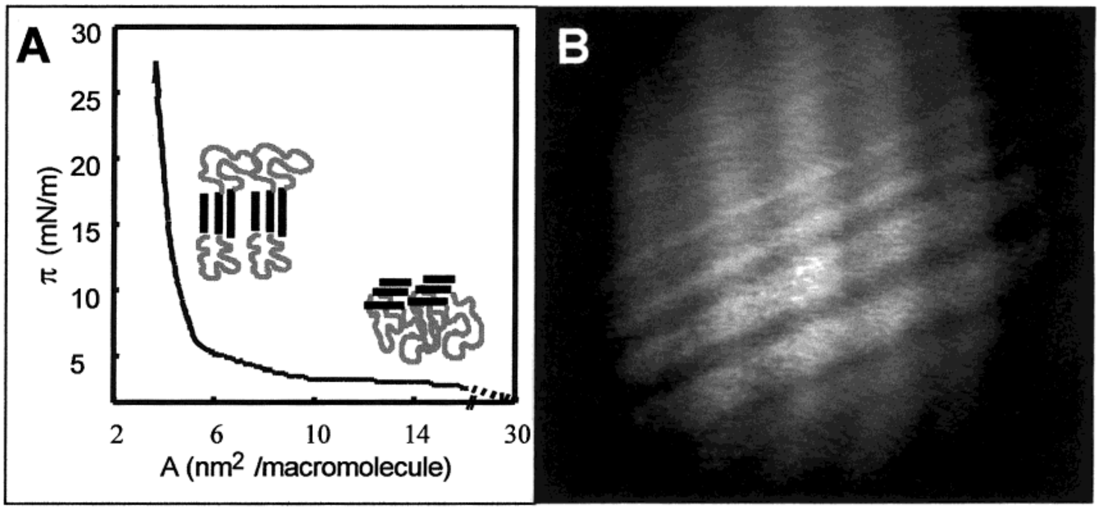


Figure 2. (a) Surface area−surface pressure isotherm of a Langmuir monolayer of PMPS$_n$PEO$_m$. Insets: schematic representations of the proposed macromolecular organization of the polymer at different states of compression. (b) Brewster angle micrograph of a compressed monolayer of PMPS$_n$PEO$_m$ taken at A = 6 nm^2 macromolecule^{-1} (spot diameter 600 μm; the vertical striping pattern is due to interference fringes of the laser beam).

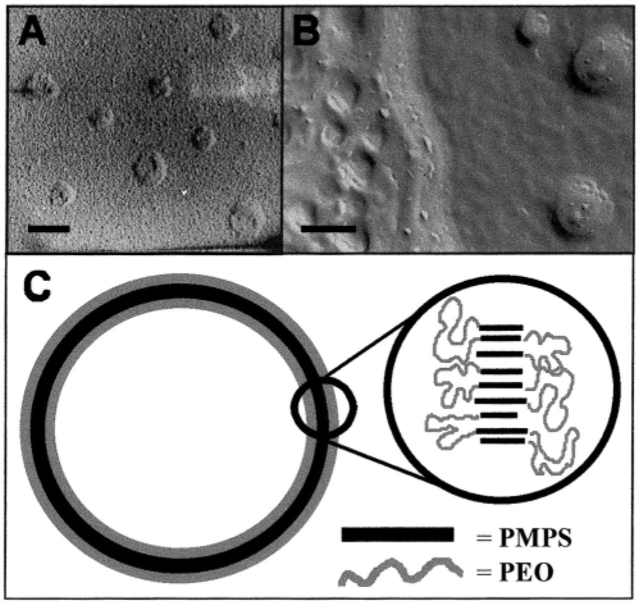


Figure 3. (a, b) TEM images of vesicle dispersions of PMPS$_n$-PEO$_m$ showing (a) a replica of intact (freeze fracturing) and (b) collapsed vesicles (platinum shadowing); bars represent 200 nm. (c) Schematic representation of the proposed structure of the vesicles showing the hydrophobic PMPS interior (black) shielded from the aqueous phase by the hydrophilic PEO layers (gray).

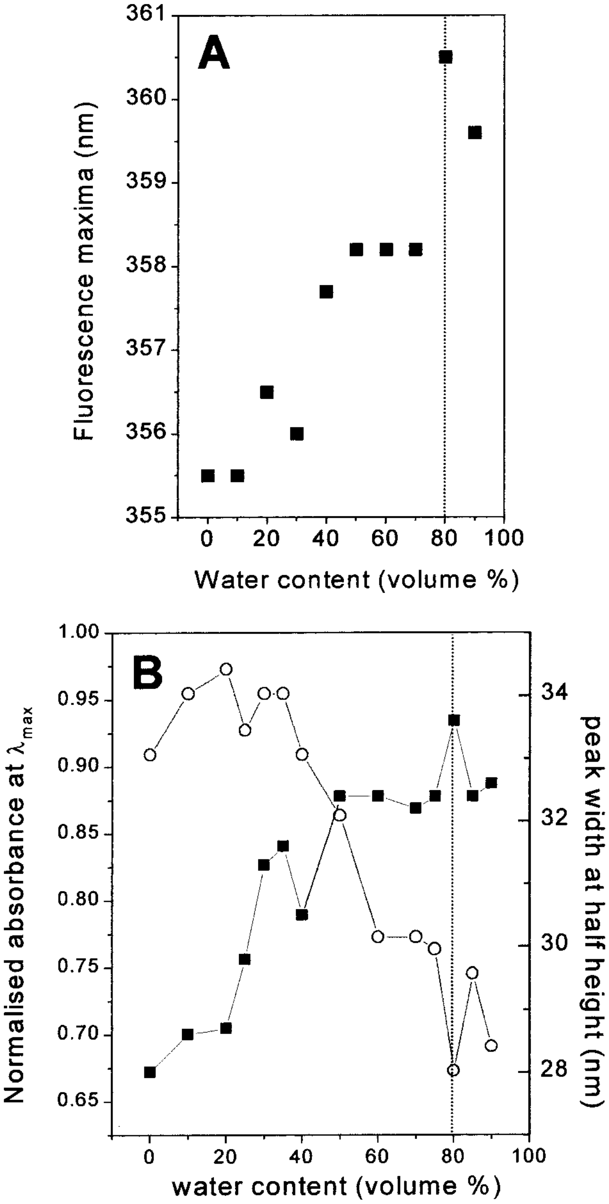


Figure 4. Changes of the fluorescence and UV spectra of PMPS$_n$PEO$_m$ in various THF/water mixtures. (a) The position of fluorescence maxima and (b) the intensity (○) and peak width (■) of the σ–σ* transition band as a function of the water concentration.

assembly of polysilane rods in such a close-packed, parallel arrangement gives rise to the formation of 2D ribbonlike domains with lengths in the order of millimeters (Figure 2b). Continued compression leads to a transition into a condensed state, characterized by a steep increase in surface pressure (onset = 5.0 nm^2 macromolecule^{-1}) and a collapse of the film at 3.7 nm^2 (π = 27 mN m^{-1}). The latter number is in good agreement with the limiting macromolecular area of 3.6 nm^2, which was estimated from space-filling models of three parallel PMPS segments having a transoid extended conformation and an orientation perpendicular to the air–water interface (Figure 2a).

Vesicle Formation. From the fact that PMPS$_n$PEO$_m$ is capable of forming large, ordered structures at the air–water interface, we anticipated that the organized 3D assembly of these PMPS segments could be achieved by dispersing the copolymer in aqueous media. Aqueous dispersions of PMPS$_m$PEO$_n$ were obtained by adding water to a tetrahydrofuran (THF) solution of the block copolymer and dialyzing the resulting THF/H$_2$O mixture (1/3; v/v) against pure water for 72 h.[7e] Transmission electron microscopy (TEM) experiments were performed using negative staining, platinum shadowing as well as freeze fracturing and revealed the formation of vesicles with diameters of 100–180 nm (Figure 3a,b). To substantiate that the observed structures were vesicles, an encapsulation experiment was performed utilizing the water-soluble fluorescent dye 5-carboxyfluorescein in the dialysis procedure.[13] After 72 h the dispersion was eluted (in water) through a Sephadex column (G150, mesh size 40–120 μm). The elution volume of the encapsulated dye (30–110 mL, emission at 519.5 nm) coincided with that of the copolymer (emission 355 nm), indicating that closed vesicles are formed. The elution volume of the free dye was substantially larger (160–190 mL).

The UV spectra of these dispersions show a Si$_\sigma$–Si$_{\sigma^*}$ transition with a maximum absorption wavelength (λ_{max}) of 342 nm, indicating that in the aggregates the polysilane chains adopt a more transoid extended conformation (compared to molecularly dissolved PMPS; λ_{max} = 337–340 nm).[14] We therefore propose that the interior of the vesicle membranes is formed by a parallel arrangement of the rigid hydrophobic PMPS blocks, separated from the water by the more hydrophilic PEO segments (Figure 3c).

Aggregation in THF/Water Mixtures. To obtain insight into the evolution of such well-defined morphological structures from a polydisperse multiblock copolymer system, we investigated the aggregation behavior of PMPS$_m$PEO$_n$ in a range of mixtures of THF and water. Fluorescence spectroscopy showed that upon increasing the water content of these mixtures from 0 to 90 vol % a small red shift was observed (from ~355 to ~360 nm; Figure 4a). This shift was attributed to a more effective (both inter- and intramolecular) energy transfer from short to longer conjugated PMPS seg-

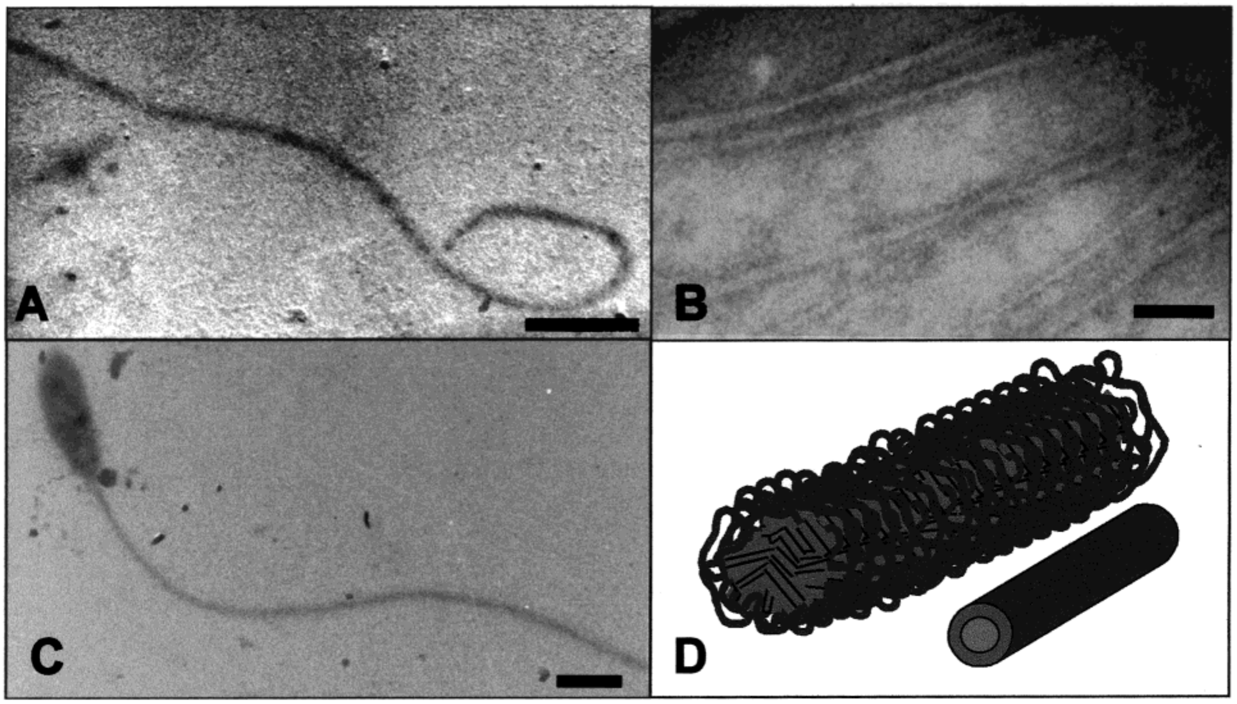


Figure 5. Micellar fibers of PMPS$_n$PEO$_m$ in mixtures of THF and water (25/75 by volume). TEM images (a) visualizing the polysilane core of micellar fibers (unstained, bar represents 250 nm); (b) revealing the PEO shell using uranyl acetate staining, (c) showing an example of the bulges found for many of these fibers. (d) Schematic representation of the structure of the micellar fibers showing the PMPS core and the PEO shell.

ments (of which the latter have a lower band gap), indicating that higher water contents induce the formation of more highly ordered assemblies of PMPS segments. UV spectroscopy showed a broadening (from 28 to 33 nm at half-height; Figure 4b) and a concomitant decrease of the Si$_\sigma$−Si$_{\sigma^*}$ absorption band intensity upon increasing the water content from 0 to 90 vol %. This indicates a larger distribution of effective conjugation lengths in the polymer backbone and hence suggests that the packing of polysilane chains during aggregation is accompanied by an increase in the number of sharp turns in the polymer chain resulting from gauche placements.[15]

Micellar Rods. Below water concentrations of 40%, TEM and dynamic light scattering did not show evidence for the formation of aggregates with diameters >5 nm, suggesting that the polymer is molecularly dissolved at these solvent compositions. However, between water contents of 40 and 80%, TEM revealed the formation of micellar fibers with diameters of approximately 20 nm and lengths of several micrometers (Figure 5a). These fibers are built up from a core of packed PMPS blocks surrounded by poly(ethylene oxide) segments (Figure 5d). Because of the electron density of the polysilane, the hydrophobic cores of the aggregates could be observed without staining (Figure 5a); the polar PEO shells were visualized using uranyl acetate staining (Figure 5b). A significant number of these fibers exhibited a bulge (Figure 5c) on one of their ends; however, at present no information is available about the origin or composition of these convexities.

Helical Aggregates. At water concentrations above 80% *helical* aggregates were observed. Left- and right-handed forms were observed by transmission (Figure 6a) and scanning electron microscopy (Figure 6b).[16] As observed for the micellar rods, the cores of these aggregates could be visualized without staining, confirming that they are primarily composed of PMPS. These superstructures had lengths of 1−2 μm, widths of 0.2 μm, and a pitch of approximately 0.15 μm. To date, there has been only one account of an amphiphilic polymer system that forms helical aggregates.[6] In that

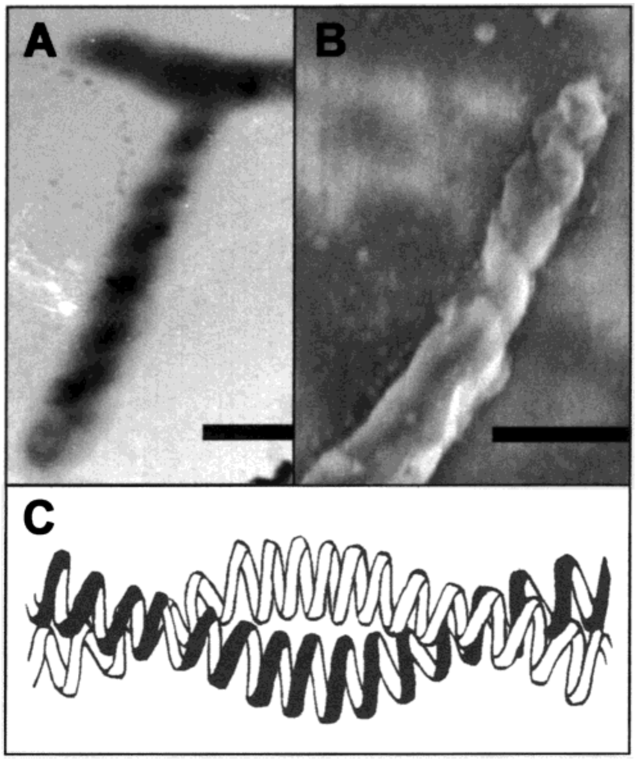


Figure 6. Helical aggregates of PMPS$_n$PEO$_m$ found in a water/THF mixture of 90/10 (v/v). (a) TEM image (unstained, bar represents 250 nm) of a right-handed helix and (b) SEM image (uncoated, bar represents 250 nm) of a left-handed helix. (c) Schematic representation of the formation of a superhelix from the coiling of two helical stands.

case superhelices were generated from *well-defined chiral diblock copolymers* of polystyrene and peptide-based poly(isocyanide)s and attributed to the close-packing of the rigid helical poly(isocyanide) segments in the aggregates. Helical conformations have been reported for polysilanes with chiral[17] as well as achiral side groups.[18] Recently, it has been shown that PMPS also adopts a helical backbone conformation (with an equal distribution of left- and right-handed helical confirmations).[19] It has been demonstrated that, depending on the screw pitch, such a helical conformation can affect the σ-conjugation in the polymer backbone of polysilanes.[20] In the present case both a broadening and an intensity decrease of the $\sigma-\sigma^*$ transition were observed at the onset of the concentration region where the helical aggregates are formed (at $\sim$80 vol % water; Figure 4b), suggesting that higher water contents affect the screw pitch of the polysilane backbone.[18c] The concomitant red shift in the fluorescence spectrum (Figure 4a) indicates an increased efficiency in the intermolecular *and* intramolecular transfer of the excited state between polymer segments and is most probably a result of the close packing of these helical polymer chains in the aggregates (Figure 6c).

Solvent-dependent helicity is common for biopolymers (e.g., the denaturation of proteins[21] and RNA[22]), but in synthetic systems it has only been reported for oligomeric phenylene ethynylenes.[23] Well-defined supercoils are formed from many biological polymers with helical conformations; for synthetic polymers such structures have been found in the solid state[24,25] but are rare in solution.[6,26] Given that PMPS−PEO is a multiblock copolymer with a random and equal distribution of screw senses, it is unlikely that these helical structures arise from the preferential aggregation of PMPS segments with identical screw senses (i.e., the formation of aggregates from only right-handed or only left-handed conformations). We therefore believe that in the present case the helical superstructures are generated through a cooperative process in which *the screw sense of the initial PMPS segment(s) determines the screw sense of the subsequent PMPS segments assembling in the aggregate*, irrespective of the general distribution of left- and right-handed screw senses of the PMPS within and between the copolymer chains.[27] Through such an assembly process both left- and right-handed superhelices can be assembled. By necessity, it implies that both screw senses of the PMPS backbone are in a dynamic equilibrium and are readily interconvertible. Another notable feature of this block copolymer system is that such well-defined aggregate morphologies can be obtained from a system that is polydisperse in its molecular structure. It is obvious that the self-assembly processes of this type of block copolymers deserve further study.

Conclusion

The generation of micellar fibers and helical aggregates comprising a core of σ-conjugated polymer surrounded by a shell of nonconducting PEO is of interest for the preparation of nanoscale electrooptical devices. To date, the aggregation of rod−coil block copolymer systems with *monodisperse* rigid conjugated blocks has yielded a variety of aggregate morphologies both in bulk and in solution and can be utilized to manipulate their physicochemical properties.[2a,4] Polysilanes display high charge carrier mobilities, and it has been demonstrated that hole transport in polysilanes can be dramatically improved through organization of the polymer molecules.[28] It is our contention that the incorporation of polysilane segments into an amphiphilic block copolymer system opens the way for the tuning of both morphologies and the semiconductor properties of these materials by controlling their aggregation behavior.

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