A Polystyrene−Oligothiophene−Polystyrene Triblock Copolymer

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Abstract: A well-defined triblock copolymer is synthesized by using a strategy in which the α-coupling of 11 thiophene rings of the middle block and the monodispersity (DP = 30 and $\bar{M}_w/\bar{M}_n$ = 1.1) of the two polystyrene outer blocks is ensured. Monofunctional polystyrene **1** is first modified with an α-terthiophene unit **2** to form **3**, and two of these units are coupled in a double Stetter reaction of **4** with a difunctional α-terthiophene **5** to yield a tetraketone **6** as the precursor of the triblock copolymer, which was formed with excess Lawesson's reagent. The polymer **7** is fully characterized with IR and NMR spectroscopy and MALDI-TOF mass spectrometry. Size exclusion chromatography, transmission electron microscopy, and scanning force microscopy show that **7** is self-assembled into spherical, micellar structures with average diameters of 12 nm, which corresponds to about 60 block copolymer molecules per aggregate. The optical properties of **7** are in full agreement with an associated unsubstituted oligothiophene. Electrochemical doping is hampered by the polystyrene shell; however, chemical doping afforded small nanoscopic charged aggregates that are soluble in organic solvents.

Introduction

Polythiophenes have received much attention in the area of conjugated polymers because of their chemical stability both in the neutral and doped states.[1−3] The electrical and optical properties of conjugated polymers depend critically on the effective conjugation length, but in the case of polythiophenes, this is not a rigorously defined quantity due to mislinkages and cross-links thought to occur in the polymerization of thiophene. Well-defined thiophene oligomers, prepared via step-by-step procedures, have allowed a correlation of the physical properties with the degree of oligomerization and the study of the concept of effective conjugation length.[4−6] The controlled chain lengths and physical properties of the oligomers have led to their targeted use in molecular electronic and optical devices.[7,8] The strongly decreasing solubility with increasing chain length of oligothiophenes has been tackled by introducing alkyl substituents at α- or β-positions of the thiophene units.[1]

Here, we describe an alternative approach to increase the solubility by linking two polymer chains to both ends of a well-defined oligothiophene segment. The concept is based on two considerations. (i) The triblock copolymer is prepared by linking two polystyrene-substituted oligothiophenes to yield an even longer thiophene block. In this way, the solubility problems that occur in the formation of yet not achievable long oligothiophene segments can be circumvented, without introducing substituents in the β-positions of the thiophene rings. (ii) Combination of an insoluble center block with well-soluble outer blocks can be expected to lead to the formation of micelles. In the solvent-free state, the molecules will assemble to micro domains with one phase being the electrically conductive polythiophene. Variation of the relative length of the constituent blocks will allow a tailoring of morphologies and formation of defined nanometer-sized electrically and optically active spherical, rodlike, and lamellar structures.

So far, attempts to control the nanoscopic organization of π-conjugated polymers and oligomers by incorporation into a block copolymer structure are rather limited. In most cases, short conjugated segments have been linked by flexible spacers to multiblock polymers.[9,10] François et al. have described the

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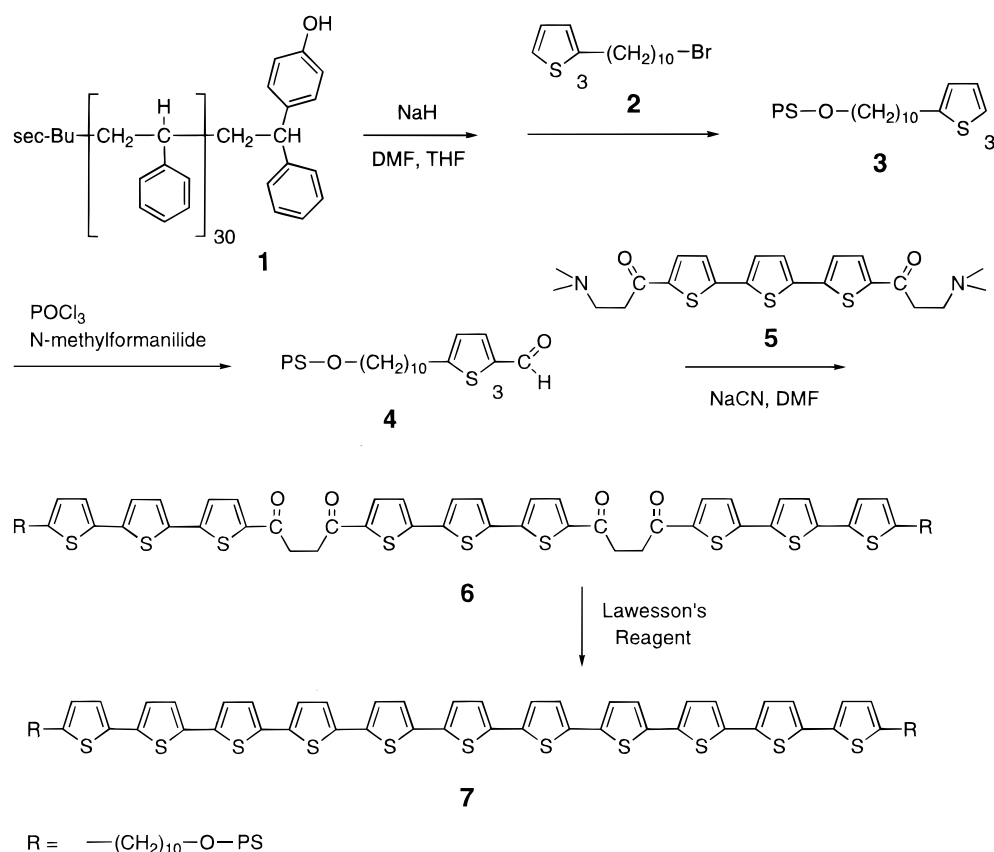(7) Geiger, F.; Stoldt, M.; Schweizer, H.; Bäuerle, P.; Umbach, E. *Adv. Mater.* **1993**, *5*, 922.
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Scheme 1

synthesis and dissipative structure formation[11] of polystyrene diblock copolymers with poly(*p*-phenylene)[12] and polythiophene.[13] Recently, polystyrene−oligothiophene diblock copolymers with controlled block lengths were reported.[14] In this paper, we present the synthesis and characterization of a triblock copolymer of monodisperse polystyrene−undecithiophene−monodisperse polystyrene. It represents a well-defined block copolymer with an unprecedented long array of 11 β-unsubstituted thiophene (11T) rings.

Results and Discussion

Synthesis of the Triblock Copolymer. The triblock copolymer was built from two polystyryl-terthiophene units that were linked to the α-positions of a central terthiophene unit using the Stetter coupling reaction, ensuring the formation of a strictly α-coupled oligothiophene block. The employed route (Scheme 1) started with the synthesis of the polystyrene blocks.

Polystyrene (PS) chains of controlled lengths (average DP = 30) and a low polydispersity were prepared anionically, end-capped with 1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-1-phenylethylene[15] and subsequently deprotected with Bu$_4$N$^+$F$^-$ in THF to 4-hydroxyphenyl-terminated polystyrene. The silylox-

yphenyl- and 4-hydroxyphenyl-functionalized PS **1** had a low polydispersity, $\bar{M}_w/\bar{M}_n$ = 1.1 (size exclusion chromatography (SEC) vs polystyrene in THF). Monolithiation of 2,2′:5′,2″-terthiophene[16] at the α-position using butyllithium, followed by reaction with an excess of 1,10-dibromodecane produced 5-(10-bromodecyl)-2,2′:5′,2″-terthiophene (**2**). Alkylation of 4-(hydroxyphenyl)-PS (**1**) with terthiophene **2** gave **3**. Formylation of 5-(10-(polystyryloxy)decyl)-2,2′:5′,2″-terthiophene (**3**) was accomplished in a Vilsmeier−Haack reaction using phosphorus oxychloride and *N*-methylformanilide.[17] In a Stetter reaction,[4,18] 2 equiv of formylated α-terthiophene **4** were coupled with the bis-Mannich base 5,5″-bis[3-(dimethylamino)propionyl]-2,2′:5′,2″-terthiophene (**5**) to yield the tetraketone **6** as the precursor to PS-11T-PS. In the final step, this precursor was reacted with an excess of Lawesson's reagent[16] to give the PS-11T-PS triblock copolymer **7**.

Molecular Characterization. The triblock copolymer was characterized using a variety of analytical and spectroscopic techniques to assess its structural identity and its physicochemical properties. Combustion analysis is consistent with MW and elemental composition. The absence of carbonyl groups, indicating uncyclized **6**, was verified using FT-IR. The molecular mass of PS-11T-PS, measured by means of MALDI-TOF mass spectrometry,[19] was found to be 7939.0. This molar mass perfectly matches the calculated mass 7939.67, if a degree of polymerization DP = 30 is taken for the polystyrene chains. Peaks with gradually decreasing intensities occur at lower and

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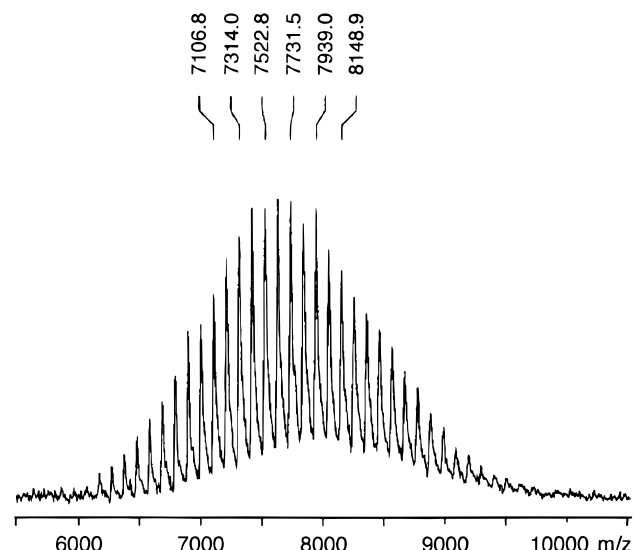(14) Li, W.; Maddux, T.; Yu, L. *Macromolecules* **1996**, *29*, 7329.

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Figure 1. MALDI-TOF spectrum of the PS-11T-PS triblock copolymer.

higher mass numbers in the spectrum and vary by the mass of one styrene unit (104.15) (Figure 1).

Size exclusion chromatography (SEC) in THF and CHCl$_3$ showed a bimodal molecular weight distribution (Figure 2). In THF, a high molecular mass peak was observed, which corresponded to a polystyrene calibrated mass of 56.000 g/mol, and a less intense, broader signal with a maximum at 12.000 g/mol, was observed. In CHCl$_3$, only a very small fraction of the low molecular mass component was observed in the SEC trace, and the major fraction eluted corresponding to a high molecular mass component. Irrespective of the mismatch of the PS calibration line, the low molecular weight peak can be assigned to individual triblock chains and low associates, while the sharp high molecular mass peak corresponds to higher associates or micelles. Variation of the fraction of high and low molecular weight components upon changing the solvent is expected for an equilibrium association and is consistent with a closed association controlled by the steric demands of the polystyrene chains. In addition to calibration by narrow molecular weight polystyrene standards, an attempt was made to determine the absolute molecular mass by means of a multiangle light scattering detector. The peak molecular weight of the high molecular mass component in THF resulted to 6.4 × 10^5 g/mol while the value in CHCl$_3$ was 8.7 × 10^5 g/mol. These numbers are somewhat uncertain because the evaluation of the light scattering had been based on an average dn/dc value which is an approximation in the case of this heterogeneous block copolymer.

More evidence that the triblock copolymer forms associated species was obtained from scanning force microscopy (SFM). A thin layer of a dilute solution of PS-11T-PS in toluene was evaporated on mica. Figure 3 shows a tapping mode scanning force micrograph of a sample where the substrate was only partly covered by PS-11T-PS. In addition to areas where the PS-11T-PS molecules formed a closed layer, small particles are depicted which can be assigned tentatively to be single micelles of PS-11T-PS. The thickness of the closed layer was determined to be 8 ± 3 nm from the height profile of the film. Figure 4 shows the enlarged structure of the closed layer.

The as-cast film (Figure 4) consisted of egglike particles with axes of about 10 and 14 nm. Molecular modeling shows that PS-11T-PS in extended conformation has a total chain length of 15 nm, which matches the observed diameter of the

aggregates. Assuming a bulk density of about 1 g/cm^3 for the polymer and an average diameter of 12 nm for the spherical aggregates, each of these aggregates corresponds to about 60 block copolymer molecules. This value is rather consistent with the roughly 80 molecules per micelle as indicated by the SEC experiments.

The formation of a monomicellar film was also indicated by transmission electron microscopy (TEM). A solution of PS-11T-PS in toluene (1 mg/mL) was stirred with HAuCl$_4$.[20] A rapid color change from red to blue evidenced the transport of the gold salt to the thiophene core, followed by electron transfer from the oligothiophene to the gold salt and the deposition of gold metal (Au^0) particles in the thiophene core. A drop of the solution was transferred to a carbon-coated grid, and the solvent was evaporated, leaving the micelles in an arrangement similar to that shown in Figure 4. The transmission electron micrograph in Figure 5 shows the gold-stained micellar cores as dark spots.

Electronic Properties. The electronic absorption spectrum of PS-11T-PS recorded in *o*-dichlorobenzene (ODCB) solution (Figure 6 (top)) exhibited an intense π−π* transition with an absorption maximum at 2.58 eV (478 nm) and a small shoulder at 2.20 eV (563 nm). Addition of methanol as a nonsolvent to a solution of PS-11T-PS in ODCB resulted in a significant solvatochromism as shown in Figure 6 (top). At a 2:1 ODCB/MeOH (v/v) ratio the absorption maximum has shifted to 2.80 eV (442 nm), while the shoulder at 2.20 eV has remained at the same position but is transformed into a distinct peak. At least two other shoulders were now distinguished between 2.20 and 2.80 eV.

The solvatochromic behavior is consistent with the formation of nanoscopic aggregates of PS-11T-PS upon addition of methanol. The observed blue shift of the absorption maximum upon addition of methanol can be explained by the molecular exciton model, assuming a parallel orientation of oligothiophene segments (H-aggregates).[21] The parallel orientation of the 11T segments as inferred from the optical absorption is consistent with X-ray diffraction studies of unsubstituted and α,ω-substituted oligothiophene crystals and thin films.[22] Various examples of similar blue shifts have been observed for shorter unsubstituted and α,ω-substituted oligothiophenes in Langmuir−Blodgett films and vacuum-deposited thin films.[23−27] The additional small shoulder or peak near the onset absorption spectrum is also a well-established spectral feature of oligothiophene aggregates and thin films and varies approximately

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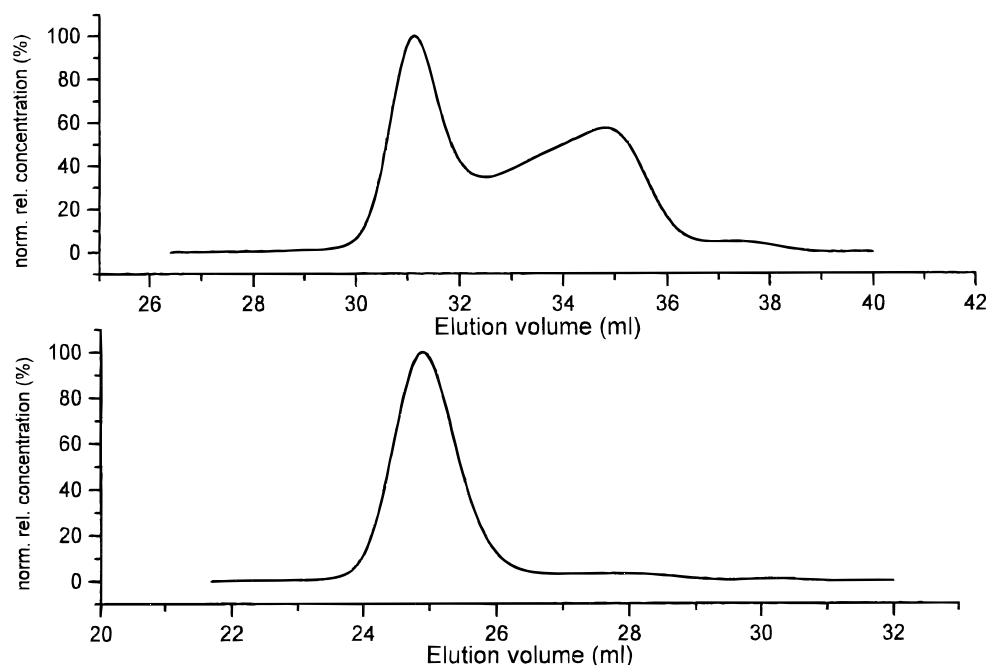
Figure 2. Size exclusion chromatograms of the PS-11T-PS triblock copolymer in THF (top) and in CHCl₃ (bottom). Small elution volumes correspond to high molecular weight molecules.
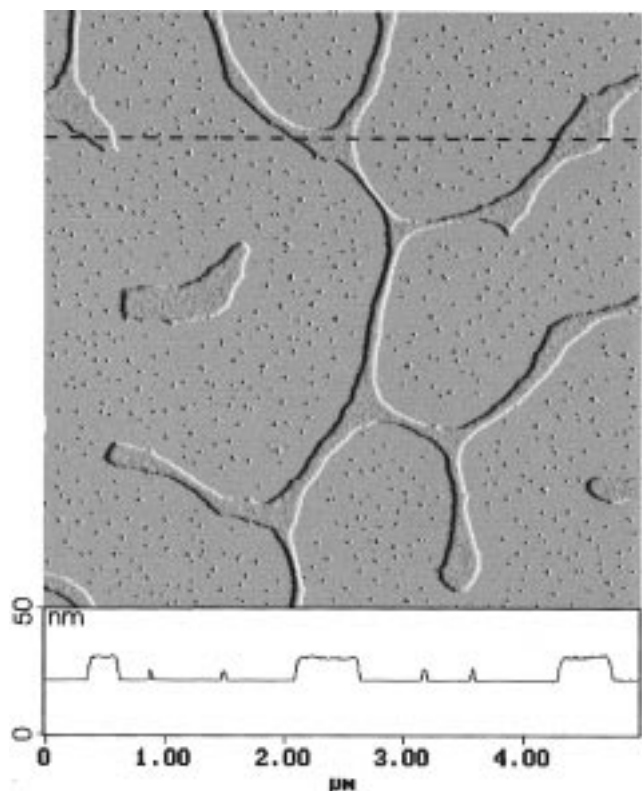
Figure 3. Phase SFM image of the PS-11T-PS triblock copolymer on a mica substrate from a solution of PS-11T-PS in toluene (1 mg/mL).

linear with a $1/n$ relation, where n is the number of thiophene units. The value of 2.20 eV for PS-11T-PS is consistent with an extrapolation of the thin film data for α,ω-MeT$_n$Me by Hotta et al.[25] and for T$_n$ published by Egelhaaf and Oelkrug.[26] The small peak is generally attributed to the 0−0 transition of the $1^1B_u \leftarrow 1^1A_g$ transition,[24,25] although recently it has been suggested that this transition is due to the formally forbidden $2^1A_g \leftarrow 1^1A_g$ vibronic excitation which has gained intensity from the neighboring B_u transition.[26]

It is important to note that the observed blue shift of the absorption maximum of PS-11T-PS aggregates as compared to free chains in solutions strongly contrasts with the significant red shift observed for aggregation of poly(3-alkylthiophenes) and poly(3,4-dialkoxythiophenes).[28,29] The red shift in the latter is explained by a decrease of inter-ring conformational disorder and a substantially lower exciton coupling as a result of the β-substituents that keep the polymer chain apart.[24]

Photoexcitation at 2.80 eV of PS-11T-PS in ODCB solution produces a strong fluorescence at 2.18 eV, with low-energy vibronics at 2.05 and 1.87 eV (Figure 6 (bottom)). Addition of MeOH reduces the fluorescence intensity by 1 order of magnitude, with a concurrent reversal of the relative intensities of the three emissions (at 2.19, 2.03, and 1.87 eV) at the highest methanol content. The decrease of fluorescence quantum efficiency as a result of aggregation of oligothiophenes in solid films or microcrystallites is well-documented.[30,31] The inset in Figure 6 shows the emission spectra of PS-11T-PS in 2:1 ODCB/MeOH (v/v) at three different excitation energies, normalized to the emission at 1.87 eV. These spectra demonstrate that the emission is a superposition of two fluorescence spectra. The low-energy emission (<1.90 eV) is identical (after normalization) for the three excitation energies, but the high-energy side contains a varying contribution of another emission. The latter is assigned to the emission of free chains, while the former is attributed to PS-11T-PS aggregates.

Attempts to determine the oxidation potentials of the triblock copolymer in dichloromethane using cyclic voltammetry were unsuccessful, since no redox waves could be observed in the range between 0 and 2 V vs SCE. This is rationalized by the presence of a polystyrene shell around oligothiophene aggregates

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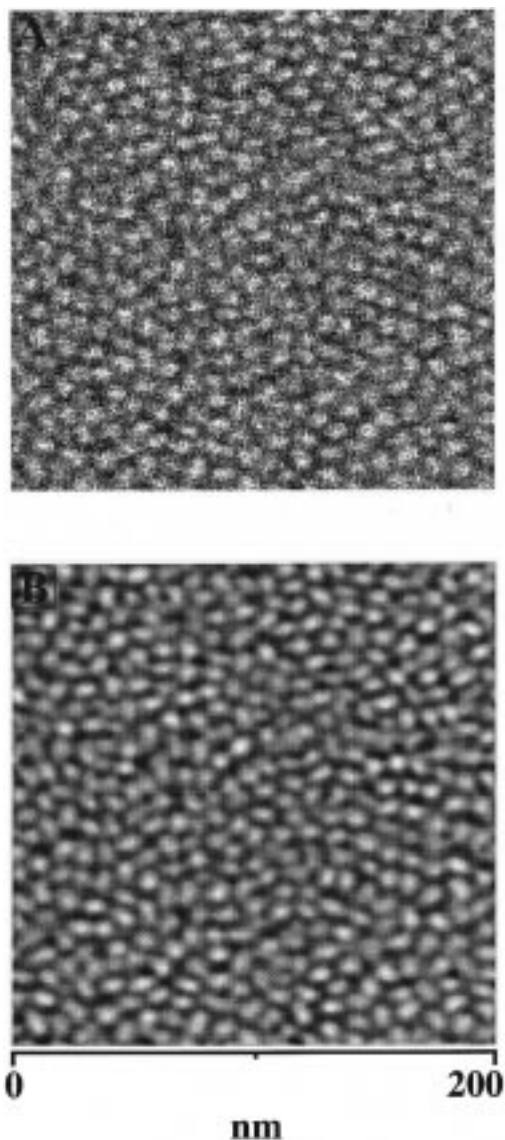
Figure 4. Phase SFM image of an area with a closed film of the PS-11T-PS triblock copolymer micelles on a mica substrate as recorded (top) and after Fourier filtering (bottom).

that prevents the oxidation reaction to occur at the platinum electrode. Chemical oxidation, however, was readily accomplished with thianthrenium perchlorate ($THI^+ClO_4^-$) as an oxidizing agent. The addition of small aliquots of THI^+ to a solution of PS-11T-PS resulted in the gradual loss of the $\pi-\pi^*$ absorption band in the UV/vis/near-IR absorption spectrum (Figure 7) with the concurrent formation of subgap absorption peaks. These changes were accompanied by the appearance of an isosbestic point at 2.35 eV. At the lowest oxidation levels, two subgap bands, M_1 and M_2, were found at 0.53 and 1.43 eV, while, at higher oxidation levels, the bands D_1 and D_2 appeared at 0.86 and 1.78 eV, respectively. The M_1 and M_2 bands are attributed to cation radicals of PS-11T-PS and correspond to transitions from the highest doubly occupied molecular orbital (MO) to the singly occupied MO and from the singly occupied MO to the lowest unoccupied MO, respectively. The position of the M_1 and M_2 bands is consistent with an oligomer length of 11 units, when compared to oxidized states of long β-substituted oligothiophenes.[32,33] The D_1 and D_2 transitions at higher energies are attributed to π-dimers or π-stacks of the PS-11T-PS cation radicals.[34] The blue shift is a consequence of the interaction between the transition dipole
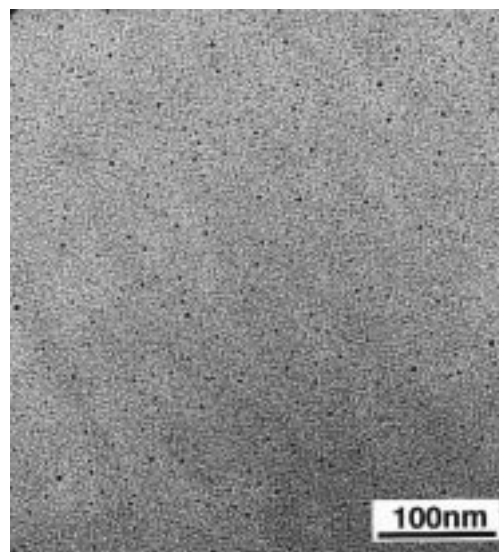
Figure 5. Elastic bright field transmission electron micrograph of the PS-11T-PS triblock copolymer cast from dilute toluene solutions on carbon film. Dark spots represent small gold particles formed inside the PS-11T-PS micelles.
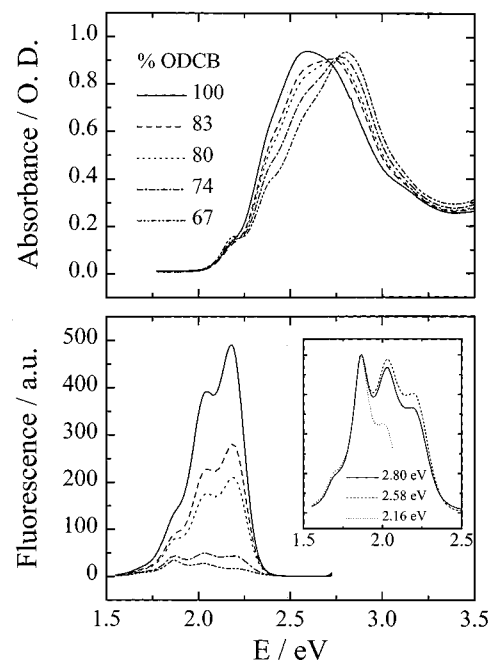
Figure 6. UV/vis absorption (top) and fluorescence (bottom) spectra of PS-11T-PS in ODCB/MeOH mixtures at room temperature. Excitation was performed at 2.80 eV. The inset shows the fluorescence of PS-11T-PS in 2:1 ODCB/MeOH (v/v) at three different excitation energies.

moments on adjacent cation radicals in the π-dimer or π-stack, and its magnitude of $\sim$0.3 eV is similar to the shifts reported for π-dimers of shorter oligothiophene cation radicals.[35] Although these optical data are in good agreement with the characteristics of π-dimers, the alternative explanation that the signals D_1 and D_2 are due to bipolarons cannot be ruled out at the moment.[36]

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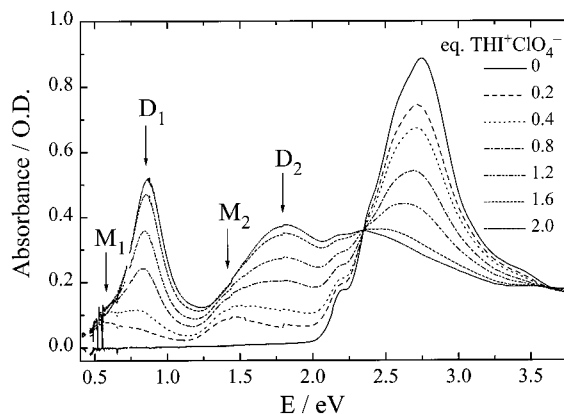
Figure 7. UV/vis/near-IR spectra of PS-11T-PS recorded during chemical oxidation with thianthrenium perchlorate in dichloromethane solution. The bands labeled M_1 and M_2 are attributed to PS-11T-PS cation radicals, while the D_1 and D_2 bands are assigned to π-dimers or π-stacks of PS-11T-PS aggregates.

At low oxidation levels, the ESR spectrum of PS-11T-PS in dichloromethane shows an inhomogeneously broadened transition of the cation radical. The increase of ESR intensity parallels the formation of the M_1 and M_2 bands in the UV/vis/near-IR, and a subsequent decrease is observed as soon as the D_1 and D_2 bands gain intensity.

Conclusion

The linking of polystyrene chains to the α-positions of undecithiophene led to a triblock copolymer which formed soluble associated species in regular organic solvents. The highly insoluble undecithiophene block had a mass fraction of around 11% in PS-11T-PS and consequently caused the copolymer to organize as micellic species in solution. Size exclusion chromatography in $CHCl_3$ evidenced the existence of micelles in solution. Changing the solvent to THF led to the formation of lower associates and individual chains. These features indicate that an equilibrium exists in solution between aggregated species and free chains. Evidence for the occurrence of individual chains was found in the fluorescence measurements and, moreover, individual chains were observed exclusively in the MALDI-TOF experiment.

The SFM images showed that the block copolymer forms stable egg-shaped micellic aggregates in the solid state.

Gold-stained micelles, obtained by chemical oxidation of the cores with $HAuCl_4$ in toluene, were evaporated to thin films. The gold-stained cores appear as dark spots in TEM images. Although the undecithiophene block could be oxidized by chemical oxidants such as thianthrenium perchlorate and $HAuCl_4$, it is shielded by the polystyrene chains too effectively to allow electrochemical oxidation. Chemical oxidation led to soluble doped micellic species. Higher volume fractions of the oligothiophene block are expected to give rodlike or lamellar organization of these blocks, producing fascinating morphologies with a continuous conducting phase. These are the subject of present investigations.

Experimental Section

Materials. *n*-Butyllithium (1.6 M in hexanes), *sec*-butyllithium (1.3 M in hexanes), 2-acetylthiophene, Lawesson's Reagent, dimethylamine hydrochloride, paraformaldehyde, 2-thiophenecarboxaldehyde, 4-hydroxybenzophenone, sodium hydride (60% dispersion), methyltriphenylphosphonium bromide, *tert*-butyldimethylsilyl chloride, tetrabuty-

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lammonium fluoride, and phosphorus oxychloride were obtained from Aldrich. Silica gel 60 (70−230 mesh), $CDCl_3$, and all solvents (pa grade) were obtained from Merck. *N,N*-Dimethylformamide (DMF) and *N*-methylformanilide were dried over molecular sieves (3 Å), and tetrahydrofuran (THF) and toluene were distilled from potassium benzophenone under argon. 2,2′:5′,2″-Terthiophene[16] and 5,5″-diacetyl-2,2′:5′,2″-terthiophene[37] were prepared according to published procedures.

Equipment. SEC measurements were carried out in THF using microstyragel columns with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å (Waters) and a dual detection system consisting of a differential refractometer (Waters model 410), a differential viscometer (Viscotek model H502), and a Wyatt Dawn DSP−F laser photometer, measuring scattered intensities at 18 angles between 15.6 and 144.5° at a wavelength of 632.8 nm. Molecular masses were calculated with an average dn/dc = 0.189 mL/g which can lead to a certain error for the heterogeneous triblock copolymer. A calibration line was made with the SEC setup, using narrow polystyrene reference standards in THF, and the molar mass of polystyrene 3000 was referenced to this line. ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz and on a Varian Unity 400WB spectrometer at 400 MHz.

The molecular mass of PS-11T-PS (**7**) was measured by means of matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF),[19] using a Bruker REFLEX mass spectrometer. A solution of PS-11T-PS in THF was mixed with a matrix material (2,5-dihydroxybenzoic acid) at a molar ratio of ca. $1:10^{-3}$ (matrix: polymer) and crystallized on the target immediately before measurement.

For the SFM images, a solution of PS-11T-PS in toluene (1 mg/ mL) was transferred to a mica substrate and evaporated, leaving the surface covered with a thin film of PS-11T-PS aggregates. Scanning force microscopy was performed with a Nanoscope III operating in the tapping mode. Height and phase images were measured simultaneously at the resonance frequency of the Si probes with 125 μm long cantilevers (280−340 kHz).

TEM sample preparation was done according to the following. A solution of PS-11T-PS in toluene (1 mg/mL) was stirred with $HAuCl_4$ for 24 h. A drop of the solution was transferred to a TEM carbon-coated grid, and the solvent was evaporated, leaving a thin micellar film. Elastic bright field TEM images were recorded using a ZEISS EM 902 microscope at 80 kV. An energy filter in the optical system was employed in order to monitor only the elastically scattered electrons for the images.

Optical spectroscopy was performed using a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer. ESR spectra were recorded using a Bruker ESP300E spectrometer.

4-Hydroxyphenyl-Terminated Polystyrene (1).[15] Polystyrene (DP = 30), prepared anionically in toluene (400 mL) from styrene (70.0 g, 0.672 mol) and *sec*-butyllithium (23.3 mmol), was end-capped with 1-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-1-phenylethylene (1.2 equiv in dry diethyl ether). The reaction was quenched with degassed MeOH, and the functionalized polystyrene was isolated by precipitation in MeOH and dried under vacuum. A solution of the silyloxy-functionalized polystyrene (65 g) and $Bu_4N^+F^-\cdot3H_2O$ (10 g, 32 mmol) in THF (300 mL) was stirred overnight at room temperature. Analysis by TLC (SiO_2/toluene, R_f = 0.3−0.5) showed a complete removal of the protecting *tert*-BuSiMe₂ group. The mixture was stirred with dilute HCl and concentrated, and the polymer was precipitated two times in MeOH and dried under vacuum. The silyloxy- and hydroxy-functionalized PS have the same low polydispersity ($\bar{M}_w/\bar{M}_n$ =1.1). Anal. Calcd for $C_{258}H_{262}O$ (3378.92): C, 91.71; H, 7.82; O, 0.47. Found: C, 91.15; H, 7.76; O, 1.09.

5-(10-Bromodecyl)-2,2′:5′,2″-terthiophene (2). *n*-Butyllithium (3.8 mL, 6.08 mmol) was added to a solution of 2,2′:5′,2″-terthiophene[16] (1.5 g, 6.04 mmol) in THF (20 mL) at −20 °C, under argon. After 30 min of stirring, hexamethylphosphorous triamide (HMPT, 3 mL) was added, followed by 1,10-dibromodecane (9.6 g, 32 mmol) in THF (10

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mL). The cooling bath was removed and stirring was continued for 2 h. In the absence of the highly toxic HMPT, the reaction can be carried out at 50 °C.[38] The solvents were evaporated and the residue was purified by chromatography on silica gel (1:4, toluene/hexane, $R_f = 0.55$): yield 0.82 g (1.75 mmol, 29%); mp 87 °C; ^{1}H NMR (CDCl$_3$) δ 1.29 (m, 12H, 3+4+5+6+7+8-CH$_2$), 1.68 (m, 2H, 2-CH$_2$), 1.85 (m, 2H, 9-CH$_2$), 2.79 (t, 2H, $J = 7.6$ Hz, 1-CH$_2$), 3.40 (t, 2H, $J = 6.9$ Hz, 10-CH$_2$), 6.68 (d, 1H, $J = 3.4$ Hz, 4-H), 6.97−7.06 (m, 4H, 4′+3′+4″+3-H), 7.15 (dd, 1H, $J = 3.6$, 1.1 Hz, 3′-H), 7.20 (dd, 1H, $J = 5.2$, 1.1 Hz, 5″-H). Anal. Calcd for C$_{22}$H$_{27}$BrS$_3$: C, 56.52; H, 5.82; S, 20.57. Found: C, 56.36; H, 5.77; S, 18.90.

5-(10-(Polystryryloxy)decyl)-2,2′:5′,2″-terthiophene (3). NaH (0.22 g, 5.5 mmol) was added to a solution of 4-hydroxyphenyl-terminated PS (**1**) (16.3 g, 4.8 mmol PhOH) in dry THF (60 mL) and DMF (15 mL), under argon. After 1 h of stirring, **2** (2.57 g, 5.5 mmol) was added, and the mixture was stirred overnight at 60 °C. The mixture was added dropwise to MeOH (500 mL) to precipitate the polymer. TLC analysis (SiO$_2$/toluene, $R_f = 1$) gave evidence of a complete conversion. SEC showed the same narrow MW distribution as the polystyrenes mentioned above. Anal. Calcd for C$_{280}$H$_{288}$OS$_3$ (3765.55): C, 89.31; H, 7.71; O, 0.42; S, 2.55. Found: C, 89.42; H, 7.79; O, 0.26; S, 2.53.

5-(10-(Polystryryloxy)decyl)-2,2′:5′,2″-terthiophene-5″-carboxaldehyde (4). A mixture of **3** (14.2 g, 3.7 mmol), POCl$_3$ (3.0 g, 19.5 mmol), and *N*-methylformanilide (2.8 g, 21 mmol)[17] in toluene (50 mL) was stirred at 60 °C for 6 h, under argon. The mixture was cooled in an ice bath, saturated aqueous sodium acetate was added, and stirring was continued for 2 h. The product was precipitated in MeOH, purified by chromatography (SiO$_2$/toluene, $R_f = 0.5$), precipitated again in MeOH, and dried under vacuum. The brightly yellow material, obtained in 90% yield, was stored under argon. Anal. Calcd for C$_{281}$H$_{288}$O$_2$S$_3$ (3793.56): C, 88.97; H, 7.65; O, 0.84; S, 2.54. Found: C, 88.91; H, 7.67; O, 0.96; S, 2.46.

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5,5″-Bis[3-(dimethylamino)propionyl]-2,2′:5′,2″-terthiophene (5). A mixture of 5,5″-diacetylterthiophene (0.5 g, 1.5 mmol), paraformaldehyde (0.16 g, 1.8 mmol), NMe$_2$·HCl (0.15 g, 1.8 mmol) in *N*-methylpyrrolidone (10 mL) was stirred at 60 °C for 16 h. The Mannich base hydrochloride was made alkaline using NH$_3$ (25% solution in H$_2$O) and extracted with CH$_2$Cl$_2$. Drying over Na$_2$SO$_4$ and evaporation of the solvent yielded the free Mannich base **5** (0.45 g, 1.0 mmol, 67%): ^{1}H NMR (CDCl$_3$) δ 2.29 (s, 12H, CH$_3$), 2.76 (t, 4H, $J = 7.3$ Hz, O=C−CH$_2$), 3.06 (t, 4H, $J = 7.3$ Hz, CH$_2$−N), 7.19 (d, 2H, $J = 4.0$ Hz, 3(3″)-H), 7.25 (s, 2H, 3′(4′)-H), 7.63 (d, 2H, $J = 4.0$ Hz, 4(4″)-H). Anal. Calcd for C$_{22}$H$_{26}$N$_2$O$_2$S$_3$: C, 59.16; H, 5.87; N, 6.27; S, 21.53. Found: C, 59.04; H, 5.01; N, 4.88; S, 22.39.

Stetter Reaction to Tetraketone 6 and Its Conversion into PS-11T-PS (7). A mixture of **4** (7.0 g, 1.9 mmol) and NaCN (50 mg, 1.0 mmol) in DMF (20 mL) was stirred under argon for 30 min. Free Mannich base **5** (0.4 g, 0.89 mmol) in DMF (5 mL) was added in 1 h, and stirring was continued overnight. The reaction mixture was dropped in MeOH (400 mL), and the product was isolated, dissolved in THF (50 mL), and precipitated in MeOH (400 mL). The product could be purified to some extent by chromatography on silica gel (1:20, THF/toluene, $R_f = 0.2$). The raw tetraketone **6** (4.0 g) was cyclized using Lawesson's reagent (2 g, 10 equiv) in toluene (300 mL) at 80 °C, for 5 h, under an atmosphere of argon. Evaporation of the solvent and purification by chromatography on silica gel (toluene) yielded PS-11T-PS (**7**) ($R_f = 1$), which was precipitated two times from THF in MeOH and dried under vacuum: yield 2.15 g (0.27 mmol, 30% based on **5**). Anal. Calcd for C$_{580}$H$_{584}$O$_2$S$_{11}$ (7939.67): C, 87.74; H, 7.41; S, 4.44. Found: C, 86.15; H, 7.40; S, 4.54.