

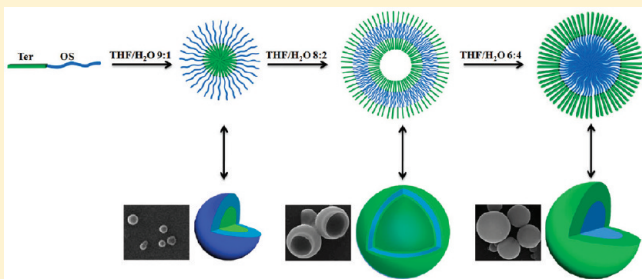
Solvent Mixture Induced Self Assembly of a Terthiophene Based Rod–Coil Block Co-oligomer

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Supporting Information

ABSTRACT: We describe the synthesis and self-assembly of a terthiophene-oligostyrene based block co-oligomer Ter-OSa. While the self-assembly of block copolymers is normally achieved using block-selective solvents, tetrahydrofuran (THF) is a good solvent for both terthiophene and oligostyrene blocks. The self-assembly in this case arises with the nonsolvent (H_2O) in THF/ H_2O mixtures. The absorption spectra showed a blue shift and fluorescence spectra showed quenching of fluorescence with increasing water content indicating that the Ter-OSa self-assembled to form H-aggregates. The morphology was studied using scanning electron microscopy. Depending upon the amount of water the Ter-OSa undergoes morphological transition from hollow to rigid spheres. However at higher water content the Ter-OSa formed large spheres from the fusion of smaller spheres. A mechanism of morphological transition from hollow spheres to rigid spheres is proposed.



INTRODUCTION

Extensive research has been focused on the development of functional soft materials through molecular self-assembly. These materials lead to one-, two-, or three-dimensional assembly of functional molecules and are promising candidates for self-organized devices without a need for extensive processing.¹ Synthesis of block copolymers has attracted much interest in the past three decades due to their ability to undergo self-assembly, its sophisticated tunable built-in structures, and tailored properties.² The most commonly used macromolecules in diblock copolymer synthesis are polystyrene (PS), poly(methyl methacrylate) (PMMA), polyvinylpyridine (PVP), polyisoprene (PI), polybutadiene (PBt), polydimethylsiloxane (PDMS), and poly(ethylene oxide) (PEO). Most of the block copolymers that undergo self-assembly are amphiphilic in nature and when such a molecule is dissolved in a solvent which is suitable for one of the blocks it undergoes self-assembly due to the aggregation of insoluble blocks through hydrogen bonding, π – π , or dipolar interactions.^{3–6} There are also reports on block copolymer self-assembly driven by crystallization.⁷ Self-assembly of block copolymers lead to a wide variety of aggregates which includes vesicles, spheres, rods, nanotubes, etc.^{8–12} The morphology of the aggregates are controlled by several parameters such as block length of copolymers, temperature, solvents or solvent combination, concentration, pH, etc.^{12–14} Among the various morphologies reported, vesicles and spheres are of special interest due to their applications in fields such as drug delivery, catalysis, etc.^{8,15,16}

Block copolymers with a fluorescent moiety have advantages over their nonfluorescent analogues, since it is easy to study the aggregation behavior of the chromophore using spectroscopic techniques. Design and development of self-assembled highly fluorescent structures have attracted attention because of their

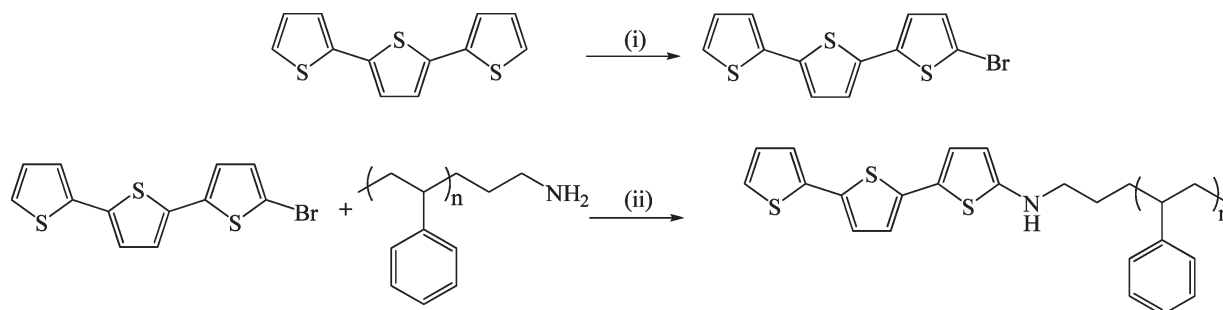
potential applications in a wide variety of areas. For example, conjugated polymer based chemical sensors have recently been used with great success for the detection of a range of analytes from biomolecules to explosives.^{17,18} Introducing fluorescent functionality into block copolymers will extend their use in the preparation of electronic semiconducting materials, photonics, and optoelectronic industry.^{19–21} Oligothiophenes are one such promising and well-studied fluorescent molecules which possesses interesting optical and electronic properties such as fluorescence, semiconductance, and light emission.^{22–25} One of the interesting properties of oligothiophenes is that their fluorescence can be tuned by changing the substituent, and it is possible to obtain emissions in the full visible region.²⁴

A disadvantage of oligothiophenes is their limited solubility in organic solvents. Solubility could be increased by substituting alkyl chains in their α or β positions which also influence the solid state ordering of oligothiophenes.²⁶ Substitution with alkyl chains has been found to impart liquid-crystalline properties, which will further increase the ordering and enhances the charge mobility of the resulting evaporated films.^{26c} Another method to induce solubility is to introduce polymer chains such as polystyrene at the end of molecule and there are only a few reports on this aspect.^{27,28} Recently our group has successfully prepared di- and triblocks of perylene derivatives and PDMS to increase the solubility of the aromatic segment.^{29,30} Micelles and vesicles were observed with the diblock copolymer²⁹ and a nanowire morphology,³⁰ with the triblock copolymer.

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Scheme 1. Synthesis of 5-Bromoterthiophene and Diblock Co-oligomer Ter-OSa



(i) NBS, DMF (ii) Pd_2dba_3 , BINAP, Sodium-*tert*-butoxide and THF at 70 °C

In this paper we discuss the synthesis and self-assembly of terthiophene and oligostyrene based low molecular weight rod-coil diblock co-oligomer which is amphiphilic in nature. We refer to it as block co-oligomer since there are only three thiophene and 9 styrene units in the molecule. It could also be called terthiophene end-capped oligostyrene. The block co-oligomer was synthesized using Buchwald–Harwig coupling reactions. The terthiophene moiety was linked to oligostyrene through an amine linkage. Although oligostyrene would behave as a flexible coil, the terthiophene part of the molecule would function as a rod and self-assemble through π – π interactions. The self-assembly of the polymer was studied by UV–vis absorption and fluorescence measurements and the morphology was characterized with scanning electron microscopy.

EXPERIMENTAL SECTION

Materials. Amino terminated oligostyrene (OSa) ($M_n = 1000$, PDI = 1.18) was purchased from Polymer Source Inc. and was used as received. Tris(dibenzylideneacetone)dipalladium(0) $\text{Pd}_2(\text{dba})_3$, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (\pm BINAP), 2,2′:5′,2′′-terthiophene, *N*-bromo succinimide (NBS), and sodium-*tert*-butoxide were purchased from Sigma-Aldrich and used without further purification. All of the solvents with spectroscopic grade were purchased from Caledon Chemicals Canada.

Characterization. NMR spectra were recorded using a Bruker 300 MHz spectrometer with deuterated chloroform containing tetramethylsilane as an internal standard. A Varian CARY 3 UV–vis spectrophotometer and a Varian Cary Fluorescent spectrofluorometer were used to record the absorption and emission spectra. A TA Instruments 2010 differential scanning calorimeter (DSC) was used for thermal analysis, with a heating rate of 10 °C/min under a nitrogen atmosphere. All of the samples were heated to 175 °C, and the thermograms were recorded in the second scan. Scanning electron microscopy (SEM) images were obtained using a Tescan Vega-II XMU VP scanning electron microscope. The sample preparation for SEM measurements was done by using the following procedure. The glass substrate was cleaned with acetone and then air-dried. The co-oligomer solution in THF and THF/ H_2O with the desired concentrations was drop-cast onto the surface of the glass substrate. It was then allowed to dry at room temperature. The surface of the films was coated with gold and palladium alloy layer before recording the SEM images.

Synthesis of 5-Bromoterthiophene. In a 25 mL two necked RB flask, NBS (0.1075 g, 6.04×10^{-4} mol) in 2.5 mL of DMF was

added to a solution of terthiophene (0.15 g, 6.04×10^{-4} mol) in DMF (2.5 mL). The reaction mixture was stirred for 24 h at room temperature in the absence of light. It was then precipitated into water and extracted with dichloromethane. The organic layer was washed several times with water, dried over Na_2SO_4 , and then concentrated. Yield = 0.17 g (85%).

^1H NMR (300 MHz, CDCl_3 , 25 °C) δ ppm: 7.23 (dd, 1H), 7.15 (dd, 1H), 7.07 (d, 1H), 7.02 (dd, 1H), 7 (d, 1H), 6.97 (d, 1H), 6.88 (d, 1H).

Synthesis of Terthiophene-Oligostyrene block co-oligomer (Ter-OSa). A 25-mL RB flask was charged with $\text{Pd}_2(\text{dba})_3$ (7 mg, 7.639×10^{-6} mol, 5 mol %) and \pm BINAP (10 mg, 1.528×10^{-5} mol, 10 mol %). It was then closed with a rubber septum and the flask was purged with nitrogen for 5 min tetrahydrofuran (2.5 mL) was added and the mixture stirred at room temperature for 10 min until a peach colored suspension formed. The flask was then charged with 5-bromo terthiophene (0.05 g, 1.528×10^{-4} mol, 1 equiv) and amino terminated oligostyrene (0.1528 g, 1.528×10^{-4} mol, 1 equiv). The septum was removed from the flask, and sodium *tert*-butoxide (21 mg, 2.139×10^{-4} mol, 1.4 equiv) was added under a flow of nitrogen. The septum was again placed over the flask, and the flask was purged with nitrogen for 30 s. Additional THF (2.5 mL) was added, and the reaction mixture was immersed in a 70 °C oil bath for 48 h. The mixture was removed from the oil bath and allowed to cool to room temperature. It was then filtered, concentrated, and precipitated in methanol. The material was purified by repeated reprecipitation from THF into methanol until the peach color disappeared. Yield = 0.1421 g.

^1H NMR (300 MHz, CDCl_3 , 25 °C) δ ppm: 7.26–6.24 (b, 12H, aromatic protons of styrene and terthiophene), 2.5–2.41 (b, 2H near to NH), 1.93–1.14 (b, 2H, methylene protons near to aromatic ring), 0.76–0.66 (b, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ ppm: 145.70, 145.23, 130.76, 128.06, 127.66, 125.67, 124.60, 123.97, 43.88, 40.38, 38.17, 31.96, 31.51, 31.27, 29.73, 29.39.

RESULTS AND DISCUSSION

Scheme 1 shows the synthesis method used in this study to prepare terthiophene-*b*-oligostyrene. 5-Bromoterthiophene was prepared by bromination of terthiophene with *N*-bromosuccinimide in the absence of light.³¹ Buchwald coupling reaction was used to prepare the diblock co-oligomer Ter-OSa using $\text{Pd}_2(\text{dba})_3$ catalyst, \pm BINAP ligand and cesium carbonate as well as sodium-*tert*-butoxide as bases for this reaction.³² We found that

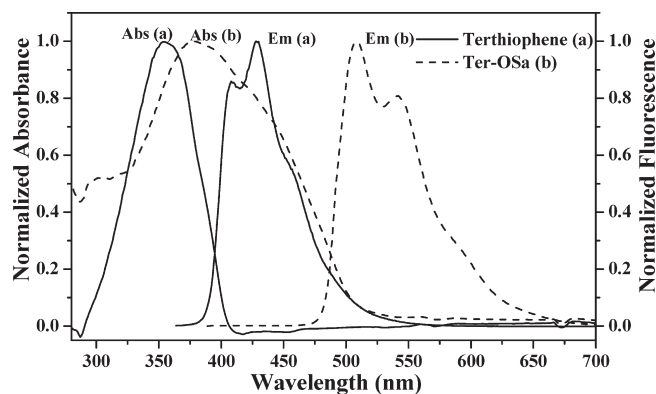


Figure 1. Combined UV–vis and fluorescence spectra of (a) terthiophene and (b) Ter-OSa recorded in tetrahydrofuran (0.1 OD solutions).

the Buchwald coupling of 5-bromoterthiophene with amino terminated oligostyrene using Cs_2CO_3 was less efficient and gives a very low yield (less than 20%). So we carried out the Buchwald coupling of 5-bromoterthiophene using sodium-*tert*-butoxide which gave the best results. Increase in the reaction time also resulted in higher yields. The resulting product was purified by repeated precipitation into methanol. The NMR spectra are shown in Figure S1 (Supporting Information). The formation of product was further confirmed by UV–vis as well as fluorescence spectroscopic methods.

The UV-absorption spectra in Figure 1 indicates a significant change in the electronic structure of the terthiophene. Terthiophene has an absorption maximum (λ_{max}) at 354 nm. The λ_{max} of Ter-OSa was found to be a very broad band with no resolved vibronic structure expected for a molecularly dissolved chromophore and is red-shifted to 379 nm compared to terthiophene. This indicates the effect of amino terminated oligostyrene on the terthiophene moiety. This red shift in the absorption maxima is due to the decrease in the HOMO–LUMO band gap caused by the formation of more extended conjugation system with the lone pair electrons of nitrogen. The emission spectra (Figure 1) of terthiophene showed peaks at 408 and 428 nm, whereas Ter-OSa showed well resolved peaks at 508 and 542 nm corresponding to the 0–0 transition.³³ This also shows that the amino-terminated oligostyrene substitution enhances the conjugation of Ter-OSa by about 75 nm compared to terthiophene. The difference in the fluorescence of terthiophene and Ter-OSa is clearly visible under UV illumination, as shown in Figure 2. The fluorescence of terthiophene is blue and that of Ter-OSa is greenish yellow. The formation of block co-oligomer was further confirmed using DSC measurements. Terthiophene has a melting temperature at 95 °C, and amino-terminated oligostyrene (OSa) has a glass transition temperature at 43 °C. The block co-oligomer Ter-OSa showed a T_g at 70 °C (Figure S2).

The nonsolvent induced aggregation of Ter-OSa was studied by absorption and fluorescence spectroscopies in THF and THF/ H_2O mixtures. These studies were done using 0.1 OD (optical density: the absorbance of an optical medium for a particular wavelength per unit distance) solutions. Measurements were acquired in a 1 cm cuvette with a slit width of 5 nm. It is known that in a good solvent the polymer chains exist as isolated chains and the addition of a nonsolvent can cause aggregation. Varying the solvent/nonsolvent ratio forces the polymer molecules toward aggregate formation. Figure 3 shows the absorption spectra for the co-oligomer in THF and THF/ H_2O

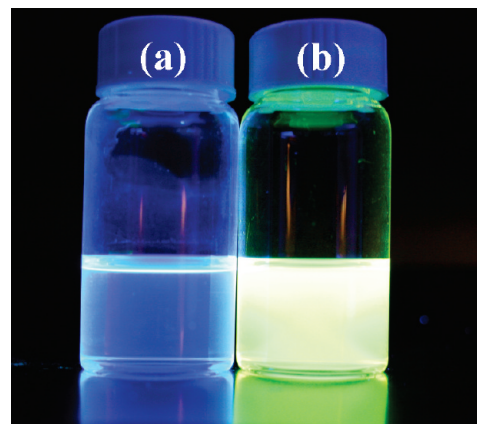


Figure 2. Photograph showing the fluorescence emission in (a) terthiophene and (b) Ter-OSa.

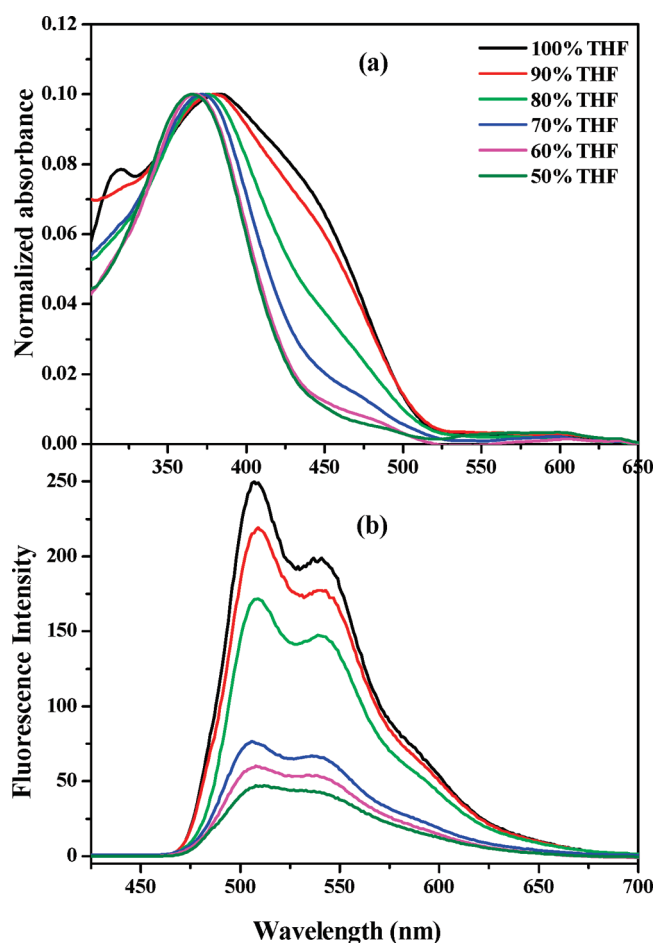


Figure 3. (a) UV–visible absorption spectra and (b) emission spectra (excited at respective absorption maxima) of the Ter-OSa in THF and THF/ H_2O mixtures.

mixtures. The addition of water to the Ter-OSa solution showed drastic changes in the absorption spectra. Two important aspects seen in this figure are that (1) there is a blue shift in the absorption maximum upon adding water and (2) the absorption peak for Ter-OSa becomes sharper and the shoulder at 320 nm vanishes at higher water contents. The absorption spectra for

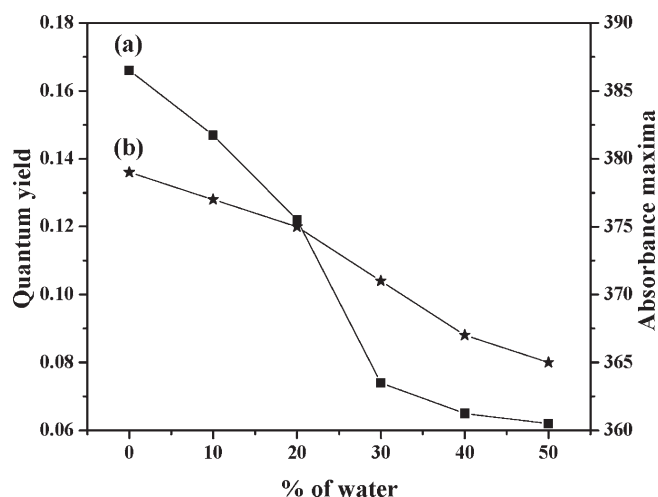


Figure 4. Plot of (a) quantum yield and (b) absorption maxima versus percentage of water in THF/H₂O mixtures.

Ter-OSa in THF showed a broad peak with λ_{max} of 379 nm. With 10% water the λ_{max} shifted to 377 nm along with decrease in the intensity of the shoulder peak. The blue shift increases with water content, with λ_{max} at 375, 371, 367, and 365 nm with 20, 30, 40, and 50% water, respectively, as shown in Figure 4. This phenomenon is well-known for oligothiophenes and is attributed to the formation of H-aggregates in which the oligothiophenes are π -stacked in a parallel manner. The H-aggregate is known to give rise to a high-energy allowed transition and a low-energy forbidden band and in such a case absorption is dominated by the high-energy band, which results in a blue shift relative to the monomer absorption band.³⁴ It was reported that the aggregates of oligothiophenes show a blue-shifted absorption spectrum with respect to the molecularly dissolved state.³⁵ A 14 nm shift of λ_{max} observed here confirms the strong aggregation with higher water content.

Further evidence for parallel face-to-face stacking of the thiophene segment in Ter-OSa was obtained from fluorescence measurements. The emission spectra of Ter-OSa were also recorded in THF and THF/H₂O by exciting at their respective absorption maxima. The fluorescence spectra (Figure 3b) showed characteristic peaks at 508 and 541 nm which are generally observed for oligothiophenes. The high intensity emission spectrum in THF shows that the material is molecularly dissolved. A decrease in the intensity of fluorescence with the amount of water can be attributed to aggregation. In Ter-OSa, the terthiophene unit has strong affinity for π -stacking and the aggregates lead to the quenching of fluorescence intensity. In general, a fluorescence quenching is expected^{36,37} for the H type of aggregates. The formation of H aggregates indicates a close π -stacked arrangement of the molecules.

The fluorescent quantum yields of the Ter-OSa in THF and in different THF/H₂O ratios were calculated using quinine sulfate as the standard^{38,39} ($\Phi_r = 0.546$ in 0.1 M H₂SO₄) and following the equation⁴⁰

$$\Phi_s = \Phi_r [F_s A_r / F_r A_s] (n_s / n_r)^2 \quad (1)$$

where Φ denotes the fluorescence quantum yield, F is the integrated area under the fluorescence spectrum, n is the refractive index of solution, and A is the absorbance at the excitation wavelength. The subscripts r and s denote the reference and the sample, respectively. Terthiophene showed a quantum yield of 0.079 in THF (normal range is 0.06–0.08), and the co-oligomer Ter-OSa, a value of 0.166

(Figure 4 and Table S1). This 2-fold increase in quantum yield for Ter-OSa is attributed to a longer conjugation path compared to terthiophene. Figure 4 shows the decrease in Φ_s with water concentration suggesting that at higher water content the Ter-OSa undergoes strong π – π interactions which lead to the formation of higher order aggregates which in turn results in quenching of fluorescence as evidenced from emission spectra.

Nonsolvent induced self-assembly was further studied using SEM analysis by dissolving terthiophene-oligostyrene block co-oligomer (Ter-OSa) in THF as well as in THF/H₂O mixtures by varying the THF/H₂O ratios ranging from 9:1 to 5:5. The concentration of the solutions was maintained at 1 mg/0.5 mL throughout the study; that is, 1 mg of Ter-OSa was dissolved in THF or THF/H₂O mixtures. Drop-casting is a common technique for studying the morphology of self-assembled systems and is appropriate for device fabrication. In the present study, a drop of each solution was cast onto a clean glass slide and allowed to evaporate at room temperature for 12 h. The SEM images were then recorded. No aggregates were observed for the Ter-OSa in THF alone since THF is a good solvent for both terthiophene and oligostyrene units. This observation is in agreement with the photophysical studies. Aggregation was induced by the addition of a nonsolvent like water.

Figure 5 shows the SEM micrographs of aggregates prepared in different THF/H₂O ratios. It is seen that with THF/H₂O 9:1 ratio Ter-OSa forms spherical aggregates. The average size of these aggregates was found to be $0.391 \pm 0.1 \mu\text{m}$ (Figure 5a). It was also observed that below THF/H₂O 9:1 ratio no aggregation was seen indicating that a minimum of 10% water is needed to induce aggregation. With a further increase in water content (THF/H₂O 8:2) the spherical aggregates transformed into hollow spheres or large vesicles (Figure 5b). It is known that the amount of water in the polymer solution plays an important role in the self-assembly of block copolymers as well as morphological changes.^{13i,j} The hollow nature of the spheres is clearly visible in the SEM image where there is a clear contrast difference between interior and exterior parts. The size of these hollow spheres is $2.15 \pm 0.19 \mu\text{m}$ with an average wall thickness of 54 nm. The average diameter of the holes was found to be $1.53 \pm 0.16 \mu\text{m}$. On further increasing the water content, the solution began turning turbid. The SEM image of Ter-OSa films from THF/H₂O 7:3 shows (Figure 5c) the formation of a cluster of spheres and these spheres are large compared to the ones obtained from THF/H₂O 8:2. It is clear that some of the spheres contain small holes at the surface which indicate that they are hollow in nature. The average size of the spheres was found to be $2.52 \pm 1.4 \mu\text{m}$ with a hole diameter of $0.54 \pm 0.16 \mu\text{m}$. But with THF/H₂O 6:4 the Ter-OSa formed solid spheres with an average diameter of $1.87 \pm 1.05 \mu\text{m}$. These results indicate that the co-oligomer undergoes intermolecular stacking which was enhanced in polar media and this is the driving force for the transformation of vesicle or hollow spheres into micelles or rigid spheres. With THF/H₂O: 5/5 ratio the aggregation becomes uncontrollable which leads to phase separation along with isolated huge spheres formed by the association of smaller spheres (Figure 5e and f).

To further differentiate between hollow and rigid spheres we followed two methods. After the drop-cast solution (THF/H₂O 8:2) dried, we squeezed the surface using another glass slide. In the second method we dipped the cast surface into liquid nitrogen for 10 min and pressed the surface using another glass slide (freeze fracture). The results are shown in the insets of Figure 5b–d. The hollow nature of the microspheres could be concluded from the broken spheres, which clearly shows the hollow interior part. In case of THF/H₂O 7:3 the hole size is

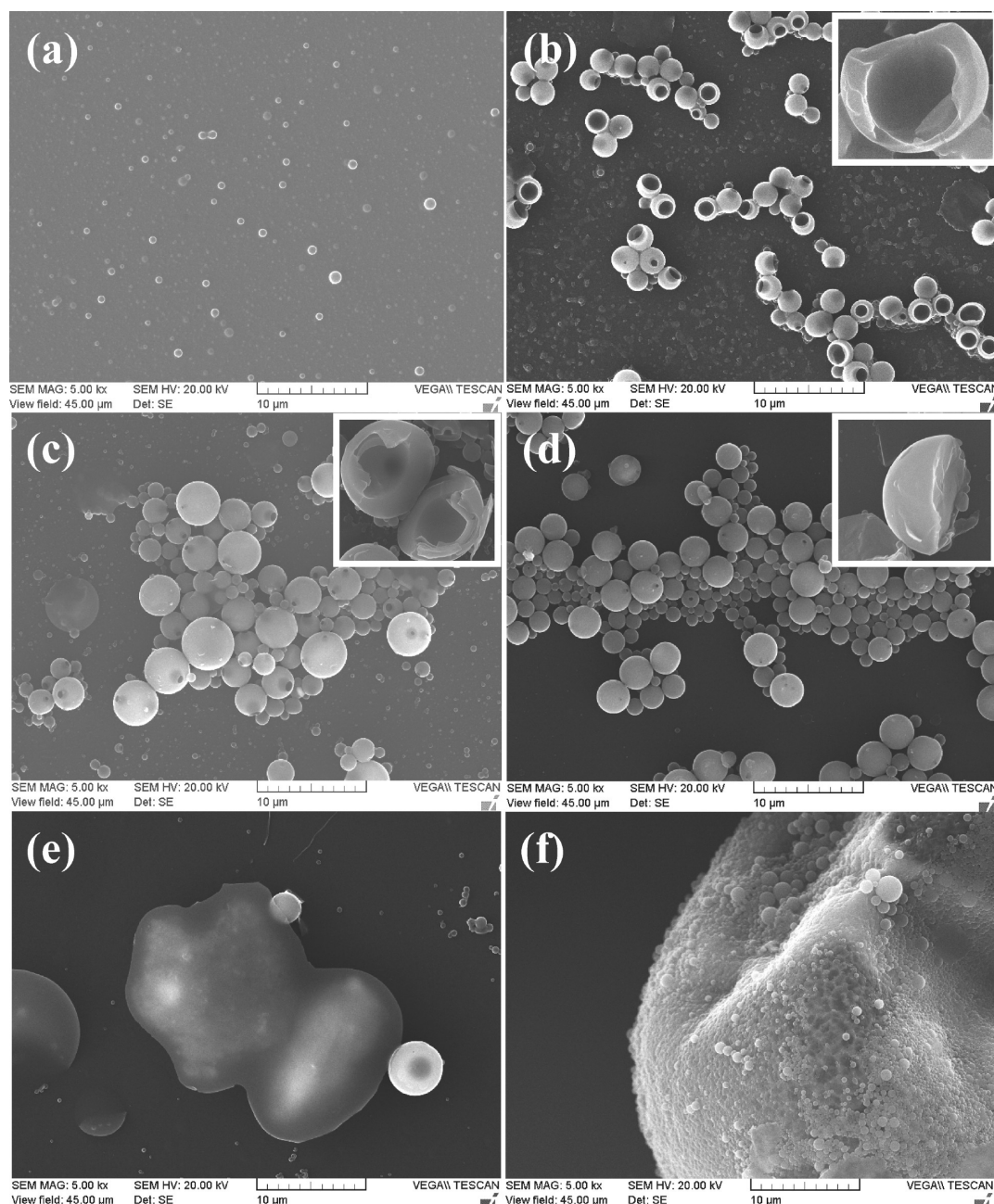


Figure 5. SEM images of drop-cast films of Ter-OSa at different THF/H₂O (1 mg/0.5 mL) ratios (a) 9:1 (b) 8:2 (c) 7:3 (d) 6:4 and (e and f) 5:5.

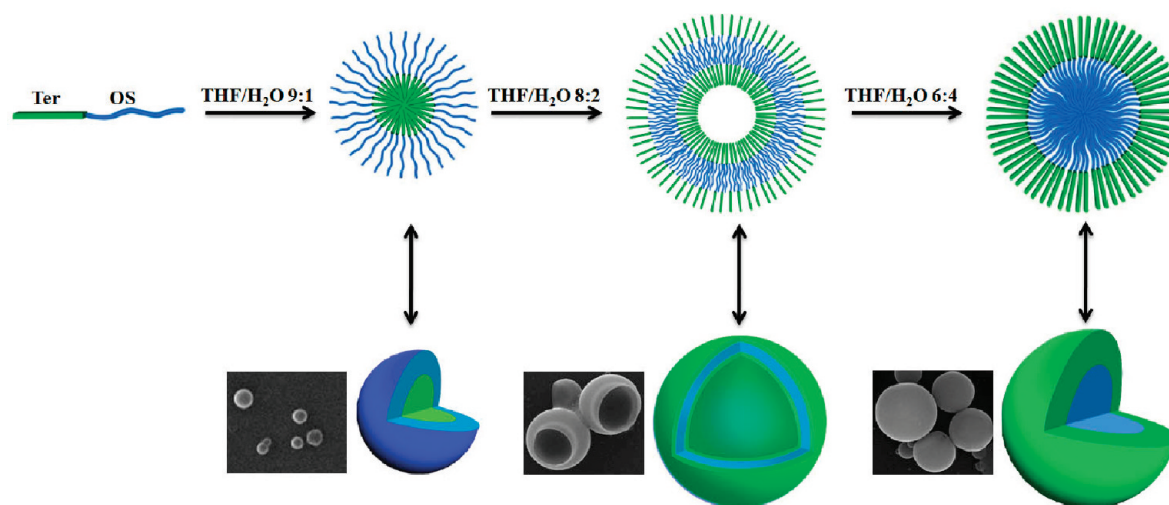
reduced and the wall thickness increased. The spheres obtained from higher water content are rigid in nature as evident from the SEM images. Additional micrographs are shown in Figure S3. Figures S3a and S3b show that even the small spheres of less than 0.5 μm tend to aggregate with one another.

There are only a few reports on oligothiophene and oligostyrene/polystyrene based co-oligomers or co-polymers which use tedious synthetic procedures.^{27,28,41} It should be noted that in some cases such block co-oligomers/polymers failed to produce any special morphology. These authors suggest that this failure is due to the low molecular weight and small volume fraction of the oligothiophene in the system. For example, Hayakawa et al.⁴¹ synthesized sexi and quaterthiophene based block copolymers and out of these the quaterthiophene based polymers were found

to produce porous morphology by breathe figure method which uses humid atmospheres. Our system is different in two aspects: (i) instead of using a single solvent we used a solvent combination for producing spherical morphology or in other words mimicking the humid environment by the addition of water and (ii) even though the Ter-OSa has low molecular weight we were successful in generating spherical morphology.

POSSIBLE MECHANISM FOR THE FORMATION OF VESICLES AND SPHERES

Eisenberg and co-workers used a wide variety of amphiphilic block copolymers to generate different morphologies. According to Eisenberg the formation of any given morphology, including

Scheme 2. Schematic Representation of Formation of Vesicles and Spheres from Ter-OSa^a

^a The blue part represents oligostyrene chains and the green part represents terthiophene group.

vesicles and micelles, is determined by three important factors such as the stretching of the core forming blocks in the core, corona-chain repulsion, and interfacial tension.^{42,43} A polymer will exist isolated when dissolved in a good solvent and will aggregate upon adding a nonsolvent. In the case of Ter-OSa, THF is a good solvent for terthiophene as well as the oligostyrene blocks but more favorable for oligostyrene (the solubility parameter⁴⁴ for oligostyrene and THF is $9.1 \text{ (cal/cm}^3)^{1/2}$). On the other hand, the terthiophene block is more hydrophilic compared to the oligostyrene block. Addition of small amount of water to THF will not change the polarity of the solvent drastically. Hence, upon adding 10% of water the Ter-OSa undergoes aggregation in such a way that the terthiophene blocks point inward and oligostyrene block, outward. But with further addition of water (THF/H₂O 8:2) the solubility of the oligostyrene block decreases which in turn changes the architecture. The oligostyrene has a tendency to stay away from the water molecules so that the molecules undergo a rearrangement. As a result, an interdigitated layer will form between the molecules. A molecular organization of dense packing and low interfacial free energy can be achieved in this way. Terthiophene contains sulfur atoms; therefore, hydrogen atoms from water are attracted to a lone pair of electrons on the negatively polarized sulfur atoms of terthiophene to form a hydrogen bond. In this way the terthiophene part in the block co-oligomer will stabilize the water molecules. It is well-known that the terthiophene units undergo intermolecular stacking through π – π interactions.

The absorption studies showed a blue shift in the absorption maximum up on adding water which supported the presence of intermolecular stacking between the molecules. At higher water contents (THF/H₂O 6:4) the polarity of the solvent changes drastically and the oligostyrene chains lose solubility and try to stay away from water which leads strong association of terthiophene part in the water phase to form spherical solid aggregates. At higher water contents (THF/H₂O 5:5) the solubility of both terthiophene as well as oligostyrene block decreases and the aggregation become uncontrollable, which lead to the formation of huge spheres. The proposed mechanism for the formation of spherical aggregates to hollow spheres and then to rigid spheres is given in Scheme 2. Note that while the wall thickness of 54 nm (Figure 5b) would accord with the organization shown in

Scheme 2, the size of the solid spheres seen in the micrographs are much larger than that depicted in this model. As noted above, even the submicrometer spheres tend to fuse together to form larger ones.

CONCLUSIONS

We have demonstrated the self-assembly of a rod–coil block co-oligomer which was synthesized by a simple Buchwald–Hartwig coupling reaction. While the self-assembly of amphiphilic polymers are usually studied in a block-selective solvent, THF is a solvent for both terthiophene and oligostyrene with the Ter-OSa used here. Self-assembly in this case is induced by the nonsolvent (H₂O). Photophysical studies showed that the Ter-OSa undergoes strong π – π interactions upon adding water which lead to the formation H-aggregates. With drop-cast films, the amount of water was found to have a significant role in the formation of spheres and we observed that a minimum of 10% water is needed for self-assembly. Even though the system is of low molecular weight, we were successful in producing spherical morphology. By simply changing the THF/H₂O ratio the Ter-OSa morphology changed from hollow spheres to rigid spheres. Such hollow spheres can be expected potentially to be use as micro reactors as well as for encapsulation purposes.⁸

ASSOCIATED CONTENT

S Supporting Information. NMR spectra, thermal analysis, additional SEM images and the Table of photophysical properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
- (2) (a) Guarini, K. W.; Black, C. T.; Yeung, S. *Adv. Mater.* **2002**, *14*, 1290. (b) Zhu, H.; Liu, Q.; Chen, Y. *Langmuir* **2007**, *23*, 790. (c) Liu, Y. L.; Chang, Y. H.; Chen, W. H. *Macromolecules* **2008**, *41*, 7857. (d) Dupont, J.; Liu, G.; Niihara, K.; Kimoto, R.; Jinnai, H. *Angew. Chem.* **2009**, *121*, 6260. (e) Cui, H.; Chen, Z.; Wooley, K. L.; Pochan, D. J. *Soft Matter* **2009**, *5*, 1269. (f) Otsuka, I.; Fuchise, K.; Halila, S.; Fort, S.; Aissou, K.; Paintrand, I. P.; Chen, Y.; Narumi, A.; Kakuchi, T.; Borsali, R. *Langmuir* **2010**, *26*, 2325. (g) Azzam, T.; Eisenberg, A. *Langmuir* **2010**, *26*, 10513. (h) Yang, Z.; Wang, X.; Yang, Y.; Liao, Y.; Wei, Y.; Xie, X. *Langmuir* **2010**, *26*, 9386. (i) Mya, K. Y.; Lin, E. M. J.; Gudipati, C. S.; Gose, H. B. A. S.; He, C. J. *Phys. Chem. B* **2010**, *114*, 9128.
- (3) Antonietti, M.; Forster, S. *Adv. Mater.* **2003**, *15*, 1323.
- (4) Forster, S. Polymer Vesicles. In *Encyclopaedia of Polymer Science and Technology*; John Wiley & Sons: New York, 2005.
- (5) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.
- (6) Nagai, A.; Kokado, K.; Miyake, J.; Chujo, Y. *Macromolecules* **2009**, *42*, 5446.
- (7) (a) Portinha, D.; Boue, F.; Bouteiller, L.; Carrot, G.; Chassenieux, C.; Pensec, S.; Reiter, G. *Macromolecules* **2007**, *40*, 4037. (b) Gilroy, J. B.; Gad, T.; Whittell, G. R.; Chabanne, L.; Mitchels, J. M.; Richardson, R. M.; Winnik, M. A.; Mannes, I. *Nature Chem.* **2010**, *2*, 566.
- (8) Vriezema, D. M.; Hoogboom, J.; Velonia, K.; Takazawa, K.; Christianen, P. C. M.; Maan, J. C.; Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 772.
- (9) Xiong, X.; Zou, W.; Yu, Z.; Duan, J.; Liu, X.; Fan, S.; Zhou, H. *Macromolecules* **2009**, *42*, 9351.
- (10) Zhang, W.; Zhang, W.; Zhou, N.; Zhu, J.; Cheng, Z.; Zhu, X. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 6304.
- (11) Grumelard, J.; Taubert, A.; Meier, W. *Chem. Commun.* **2004**, 1462.
- (12) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
- (13) (a) Yu, K.; Zhang, L.; Eisenberg, A. *Langmuir* **1996**, *12*, 5980. (b) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168. (c) Shen, H.; Zhang, L.; Eisenberg, A. *J. Phys. Chem. B* **1997**, *101*, 4697. (d) Yu, Y.; Eisenberg, A. *J. Am. Chem. Soc.* **1997**, *119*, 5980. (e) Yu, Y.; Eisenberg, A. *J. Am. Chem. Soc.* **1997**, *119*, 8383. (f) Yu, Y.; Zhang, L.; Eisenberg, A. *Macromolecules* **1998**, *31*, 1144. (g) Yu, K.; Eisenberg, A. *Macromolecules* **1998**, *31*, 3509. (h) Shen, H.; Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1999**, *121*, 2728. (i) Shen, H.; Eisenberg, A. *J. Phys. Chem. B* **1999**, *103*, 9473. (j) Shen, H.; Eisenberg, A. *Macromolecules* **2000**, *33*, 2561. (k) Terreau, O.; Bartels, C.; Eisenberg, A. *Langmuir* **2004**, *20*, 637.
- (14) Liu, L.; Gao, X.; Cong, Y.; Li, B.; Han, Y. *Macromol. Rapid Commun.* **2006**, *27*, 260.
- (15) Kabanov, A. V.; Batrakov, E. V.; Alakhov, V. Y. *J. Controlled Release* **2002**, *82*, 189.
- (16) Blanz, A.; Armes, S. P.; Ryan, A. J. *Macromol. Rapid Commun.* **2009**, *30*, 267.
- (17) Liu, B.; Bazan, G. C. *Chem. Mater.* **2004**, *16*, 4467.
- (18) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
- (19) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (20) Bao, Z. *Adv. Mater.* **2000**, *12*, 227.
- (21) Yu, G.; Wang, J.; McElvain, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 1431.
- (22) Becker, R. S.; de Melo, J. S.; Maçanita, A. L.; Elisei, F. J. *Phys. Chem.* **1996**, *100*, 18683.
- (23) Radke, K. R.; Ogawa, K.; Rasmussen, S. C. *Org. Lett.* **2005**, *7*, 5253.
- (24) Zambianchi, M.; Maria, F. D.; Cazzato, A.; Gigli, G.; Piacenza, M.; Sala, F. D.; Barbarella, G. *J. Am. Chem. Soc.* **2009**, *131*, 10892.
- (25) Demanze, F.; Cornil, J.; Garnier, F.; Horowitz, G.; Valat, P.; Yassar, A.; Lazzaroni, R.; Bredas, J. L. *J. Phys. Chem. B* **1997**, *101*, 4553.
- (26) (a) Henze, O.; Fransen, M.; Jonkheijm, P.; Meijer, E. W.; Feast, W. J.; Schenning, A. P. H. J. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 1737. (b) Leclère, P.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, F.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Mater.* **2004**, *16*, 4452. (c) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571.
- (27) Li, W.; Maddux, T.; Yu, L. *Macromolecules* **1996**, *29*, 7329.
- (28) Hempenius, M. A.; Langeveld-Voss, B. M. W.; van Haare, J. A. E. H.; Janssen, R. A. J.; Sheiko, S. S.; Spatz, J. P.; Möller, M.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 2798.
- (29) Yao, D.; Tuteja, B.; Sundararajan, P. R. *Macromolecules* **2006**, *39*, 7786.
- (30) Yao, D.; Bender, T. P.; Gerroir, P. J.; Sundararajan, P. R. *Macromolecules* **2005**, *38*, 6972.
- (31) Didier, D.; Sergeyev, S.; Geerts, Y. H. *Tetrahedron* **2007**, *63*, 941.
- (32) Luker, T. J.; Beaton, H. G.; Whiting, M.; Metea, A.; Cheshire, D. R. *Tetrahedron Lett.* **2000**, *41*, 7731.
- (33) Yassar, A.; Horowitz, G.; Valat, P.; Wintgens, V.; Hmyene, M.; Deloffre, F.; Srivastava, P.; Lang, P.; Garnier, F. J. *Phys. Chem.* **1995**, *99*, 9155.
- (34) Whitten, D. G. *Acc. Chem. Res.* **1993**, *26*, 502.
- (35) Hoebe, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.
- (36) Mandal, A. K.; Pal, M. K. *Chem. Phys.* **2000**, *253*, 115.
- (37) Zhu, C.; Zheng, H.; Li, D.; Li, S.; Xu, J. *Spectrochim. Acta Part A* **2004**, *60*, 3173.
- (38) Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahm, D. U.; Birkner, E. *Synth. Met.* **1993**, *60*, 23.
- (39) Garcia, P.; Pernaut, J. M. *J. Phys. Chem.* **1993**, *97*, 513.
- (40) Sunahara, H.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 5597.
- (41) Hayakawa, T.; Yokoyama, H. *Langmuir* **2005**, *21*, 10288.
- (42) Zhang, L.; Eisenberg, A. *Polym. Adv. Technol.* **1998**, *9*, 677.
- (43) Burke, S.; Eisenberg, A. *High Perform. Polym.* **2000**, *12*, 535.
- (44) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; 2nd ed.; CRC Press: Boca Raton, FL, 1991.