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# Synthesis and Self-Assembly Studies of Amphiphilic Poly(*n*-hexyl isocyanate)-*block*-poly(2-vinylpyridine)-*block*-poly(*n*-hexyl isocyanate) Rod−Coil−Rod Triblock Copolymer

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ABSTRACT: Rod−coil−rod triblock copolymers of 2-vinylpyridine (2VP) and *n*-hexyl isocyanate (HIC) were synthesized by living anionic polymerization. The homopolymerization of 2VP was carried out at −78 °C in THF by using bidirectional initiators sodium naphthalenide (Na−Naph) and potassium naphthalenide (K−Naph). Block copolymerization with HIC was performed at −98 °C in the presence of sodium tetraphenylborate additive. While K−Naph yields copolymers of broad molecular weight distribution, Na−Naph was quite effective in facilitating a high degree of control over the copolymerization. The block copolymers containing higher rod volume fraction showed lamellar microphase separation in THF, a common solvent for both the rod and the coil blocks. The self-organization of the copolymer in solvents selective for one block was quite fascinating in that in $CHCl_3$ solid micelles of ∼20 nm were formed, whereas large hollow micelles of ∼200 nm were generated in $CH_3OH$.

## Introduction

Rod−coil block copolymers have attracted an increasing interest due to their typical self-assembly behavior forming various supramolecular structures.[1,2] The inherent immiscibility between different blocks and the competing thermodynamic effects give rise to spherical, lamellar, and gyroid molecular architectures depending on the volume fraction, chemical composition, segmental interaction, and molecular weight of block copolymers.[3] Micelles and hollow spheres of the amphiphilic block copolymers generated in solvents selective for a specific block have numerous applications as nanoreactors, nanoreservoirs, gene delivery vehicles, phase transfer catalysts, templates for nanostructured hybrids, and reaction media for biocatalysis.[4−10] For many of these applications, it is desirable that the molecular weight and molecular weight distribution of the block copolymers be controlled and defined.

Living anionic polymerization is the proven technique for synthesis of a wide variety of di-, tri-, and multiblock copolymers of well-defined structure.[11] Among the several block copolymers studied, those with 2VP bear specific significance due to the nitrogen atom on the aromatic ring. But polymerization of 2VP possesses considerable problems as the presence of the heteroatom leads to a number of side reactions, particularly when a strong nucleophile is employed as the initiator.[12] Another family of interesting monomers that has been extensively studied by living anionic polymerization is the isocyanates. Owing to the typical structural features,[13] the polyisocyanates find applications in several fields, such as chiral recognition, optical switches, optical data storage, liquid crystals, and degradable materials.[14] The polymerization of isocyanates is associated with inherent problem such as trimerization by backbiting. Quite often it is not possible to control the molecular weight and molecular weight distribution (MWD). Hence, the synthesis of a block copolymer of 2VP with an isocyanate monomer of defined architecture is of considerable challenge.

Copolymers of vinyl monomers with a number of isocyanates have been reported, but the molecular weight of the block copolymer could not be controlled.[15] Our group is involved in the controlled synthesis of polyisocyanates and its copolymers. We succeeded in preventing backbiting in isocyanate polymerization using additives such as 15-crown-5 and sodium tetraphenylborate.[16] Recently, we achieved a perfect control over polymerization of HIC using sodium benzanilide that does the dual function of initiation as well as chain-end protection.[17] Furthermore, we have developed novel synthetic protocols toward rod−coil diblock copolymers of 2VP and rod−coil−rod triblock copolymers of isoprene, styrene, and isocyanate by anionic polymerization.[18]

The synthesis of rod−coil−rod triblock copolymers with poly(2-vinylpyridine) (P2VP) as the midblock has some added limitations. Polymerization of 2VP using a bidirectional initiator leads to carbanions at the termini of the growing polymer chain, which can initiate the polymerization of monomers like *tert*-butyl acrylate,[19] but fails to polymerize many vinyl monomers like styrene and isoprene. Consequently, only a very few triblock copolymers with P2VP as the midblock prepared by sequential addition of monomers are known. Interestingly, we observed that the living P2VP anion obtained by potassium diphenylmethane (K−DPM), an unidirectional initiator, could polymerize HIC, leading to the first poly(2-vinylpyridine)-*block*-poly(*n*-hexyl isocyanate) (P2VP-*b*-PHIC) coil−rod diblock copolymer.[18a] To achieve better control over the polymerization of living P2VP with HIC monomer, we used $NaBPh_4$ to exchange the $K^+$ countercation with $Na^+$.

Since P2VP is a reactive polymer with its nitrogen heteroatom being responsible for a number of potential applications,[20] we thought it worthwhile to synthesize poly(*n*-hexyl isocyanate)-*block*-poly(2-vinylpyridine)-*block*-poly(*n*-hexyl isocyanate) (PHIC-*b*-P2VP-*b*-PHIC) rod−coil−rod triblock copolymer. Herein, we report the controlled synthesis of this copolymer by living anionic polymerization using the bidirectional initiators, Na−Naph and K−Naph, in the presence of $NaBPh_4$ as the additive along with the phase separation and self-assembly of the block copolymers by TEM, AFM, and SEM studies.

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**Table 1. Results of the Synthesis of PHIC-*b*-P2VP-*b*-PHIC Triblock Copolymers**

| entry | initiator (mmol) | 2VP (mmol) | $NaBPh_4$ (mmol) | HIC (mmol) | time/temp (min/°C) | $M_n \times 10^{-3}$ calcd | $M_n \times 10^{-3}$ obsd[c] | MWD $M_w/M_n$[c] | polymer yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | Na−Naph | | | | | | | | |
| RH1 | 0.12 | 7.70 | | | 30/−78 | 13.4[a] | 13.0 | 1.08 | 100 |
| RB1[d] | 0.10 | 6.52 | 0.76 | 3.48 | 20/−98 | 22.5[b] | 23.3 | 1.12 | 98 |
| RH2 | 0.13 | 7.80 | | | 30/−78 | 12.6[a] | 12.3 | 1.07 | 100 |
| RB2[d] | 0.11 | 6.56 | 0.99 | 6.06 | 20/−98 | 26.5[b] | 27.0 | 1.08 | 98 |
| RH3 | 0.13 | 7.76 | | | 30/−78 | 12.5[a] | 12.8 | 1.07 | 100 |
| RB3[d] | 0.11 | 6.54 | 1.02 | 15.01 | 20/−98 | 47.1[b] | 49.0 | 1.10 | 99 |
| | K−Naph | | | | | | | | |
| RH4 | 0.14 | 7.77 | | | 30/−78 | 11.6[a] | 8.8 | 1.62 | 98 |
| RB4 | 0.11 | 6.46 | 1.11 | 2.0 | 20/−98 | 16.9[b] | 10.5 | 1.37 | 95 |
| RH5 | 0.16 | 6.15 | | | 30/−78 | 8.1[a] | 6.7 | 1.22 | 99 |
| RB5 | 0.12 | 4.63 | 1.18 | 4.25 | 20/−98 | 17.1[b] | 9.9 | 1.43 | 97 |

[a] $M_n$ is calculated using the relation $M_n = \{[2VP]/[M\text{-}Naph] \times$ molecular weight of 2VP$\} \times 2$. [b] $M_n$ is calculated using the relation $M_n = \{[2VP]/[M\text{-}Naph] \times$ molecular weight of 2VP $+$ $[HIC]/[M\text{-}Naph] \times$ molecular weight of HIC$\} \times 2$. [c] $M_n$ and $M_w/M_n$ were measured by SEC-LS in THF/$Et_3N$ at 40 °C. [d] Molar composition of HIC/2VP block copolymers determined from $^1H$ NMR.

## Experimental Section

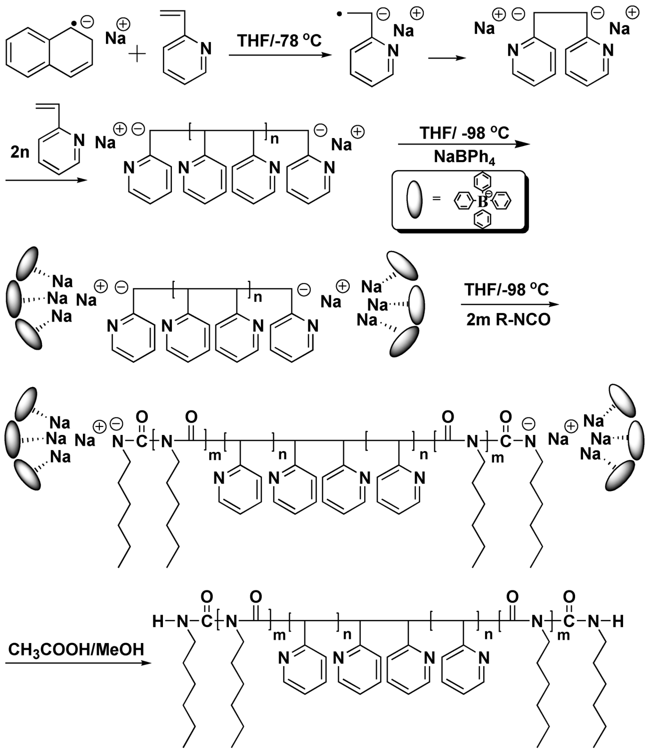
**Materials.** 2-Vinylpyridine (Aldrich, 97%) and *n*-hexyl isocyanate (Aldrich, 97%) were dried over $CaH_2$ and vacuum-distilled. Tetrahydrofuran (Fisher Scientific, GR grade) (THF) was distilled under $N_2$ after refluxing with sodium for 5 h and distilled again under vacuum from sodium naphthalenide solution. Calcium hydride (Junsei, 95%), naphthalene (Aldrich, 99%), sodium (Aldrich, 99%), potassium (Aldrich, 98%), sodium tetraphenylborate (Aldrich, 99.5%), triethylamine (Fischer Scientific, 99%), and octyl alcohol (Duksan Pharmaceutical Co., First grade) were used without further purification.

**Initiators.** Na−Naph and K−Naph initiators were prepared by the reaction of a small excess of naphthalene with sodium or potassium in THF at room temperature. The reactor was connected to a high-vacuum line ($10^{-6}$ Torr) and degassed by freeze−thaw cycles for 2−3 times. The highly concentrated initiator was divided into predetermined concentration for use in the anionic polymerization under vacuum.

**Synthesis of PHIC-*b*-P2VP-*b*-PHIC.** The bidirectional initiators Na−Naph and K−Naph were used to synthesize rod−coil−rod triblock copolymer of PHIC-*b*-P2VP-*b*-PHIC (Scheme 1) under high-vacuum conditions ($10^{-6}$ Torr) in an all-glass apparatus following standard procedure.[21] In a typical procedure for the block copolymerization, homopolymerization of 2VP (0.81 g, 7.70 mmol) was carried out with Na−Naph (0.018 g, 0.12 mmol) as the initiator in THF (10 mL) in a break-seal glass apparatus under high vacuum at −78 °C using a frozen acetone bath. The color of the reaction mixture turned dark red, indicating the formation of the carbanion. After the homopolymerization of 2VP for 30 min at −78 °C, an excess of $NaBPh_4$ (0.256 g, 0.75 mmol) was introduced, and the reactor was cooled to −98 °C. The second monomer HIC (0.392 g, 3.48 mmol) was then introduced, and copolymerization was carried out for 20 min. The reaction was terminated with a $CH_3COOH$/methanol mixture. The reaction mixture was poured into a large amount of hexane or methanol according to the block composition of the polymer. The precipitated polymer was filtered and dried. Dissolution in solvent and precipitation was repeated to obtain highly pure polymer sample, which was dissolved again in benzene and freeze-dried for characterization. Solvent-soluble parts were analyzed quantitatively by weighing the residue after evaporation of solvent and using $^1H$ NMR to check whether there were any unreacted monomers or trimers. PHIC-*b*-P2VP-*b*-PHIC. $^1H$ NMR ($CDCl_3$, 300 MHz), (ppm): 0.9 (3H, $CH_3$), 1.00−2.10 (10H, $(CH_2)_4$ in hexyl group of HIC and $CH_2$ in vinyl main chain of 2VP), 2.10−2.89 (1H, CH), 3.66 (2H, $-CH_2-N$ in HIC), 6.11−7.35 (3H, CH in pyridine), 8.02−8.55 (1H, CH in pyridine). FT-IR (KBr, $cm^{-1}$): 3442 (NH) 3080 (CH, in pyridine ring), 2935 (aliphatic, $CH_2-CH$ in backbone), 1700 (C═O), 1593 (C═C), 1475 (C═N).

**Phase Separation and Micellization.** Copolymer solutions in THF (5 mg/mL) on carbon-coated copper grid were annealed at 110 °C for 16 h and stained with $I_2$ vapor for 8 h. The excess $I_2$ was removed by vacuum, and the samples were examined by TEM. The micellization of the block copolymers was studied in $CHCl_3$ and $CH_3OH$ (5 mg/mL). The sample solutions were spin-cast on silicon wafer and dried at room temperature for AFM and SEM studies.

**Scheme 1. Synthesis Scheme of Rod−Coil−Rod Triblock Copolymer**



**Characterization.** The $^1H$ and $^{13}C$ NMR spectra were measured using a JEOL JNMLA300WB using $CDCl_3$ as the solvent. Chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm. Molecular weights were determined from the response of a multiangle laser light scattering detector system (MALLS), SEC-LS, (OPTI LAB-DSP interferometric refractometry 478-009-690 and DAWN EOS laser photometer 113-E, Wyatt Technology) with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series with column pore sizes 50, 100, 500, and 1000 Å, respectively). THF with triethylamine (for the prevention of adsorption of hydrophilic polymer in the column) was used as the mobile phase at a flow rate of 1.0 mL/min. The d*n*/d*c* values for block copolymers in THF at 40 °C were measured with an LED (Optilab DSP) source. After d*n*/d*c* was measured for five different concentrations for each polymer sample, SEC-LS data were gained with refractive index detection at 40 °C. FTIR spectra were run in a Perkin-Elmer System 2000 using KBr pellets. The phase

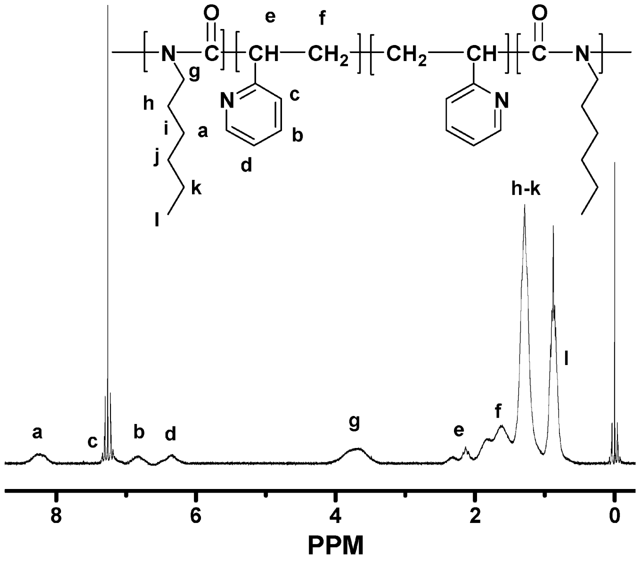


**Figure 1.** $^1$H NMR of PHIC-*b*-P2VP-*b*-PHIC triblock copolymer.

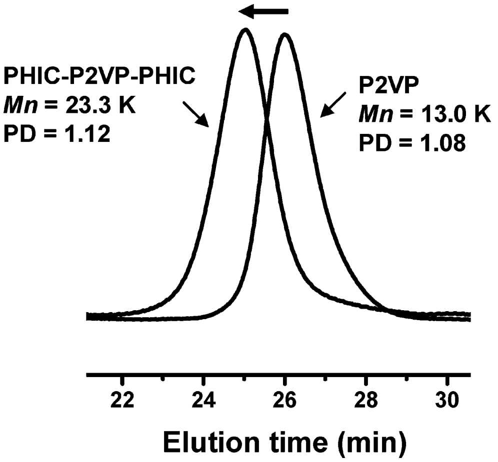


**Figure 2.** SEC-LS profile of P2VP homopolymer and PHIC-*b*-P2VP-*b*-PHIC block copolymer.

separation and micelles of block copolymers were confirmed from an energy filtering transmission electron microscope (EF-TEM, EM 912 OMEGA). Micelles were characterized by a multimode atomic force microscope (model MMAFMLN), a PISA advance probe microscope, and a field emission scanning electron microscope (FE-SEM, model s-4700, Hitachi).

## Results and Discussion

**Homopolymerization of 2VP.** The anionic initiators M−Naph (M = Li, Na, K) have been studied earlier for the copolymerization of styrene with HIC, and it was reported that K−Naph is the most suitable initiator for polymerization of styrene.[18b] Relatively low reactive initiator is needed for the polymerization of 2VP, as the pyridine ring is susceptible to nucleophilic attack. We carried out the anionic polymerization of 2VP by using Na−Naph and K−Naph as initiators in THF at −78 °C. When 2VP was introduced into the initiator, the reaction mixture turned dark red, indicating the formation of carbanion. After 30 min, there was no unreacted monomer left and the yield of the polymer was ~100%. When Na−Naph was used as the initiator for the polymerization of 2VP, the calculated and observed molecular weights agreed well, and the MWDs were narrow compared to the previous reports.[22] On the other hand, polymerization of 2VP by K−Naph provided P2VP of broad MWD (Table 1). These results have been explained in terms of the difference in the rates of initiation and propagation as well as the disparity in the solvation energy. Generally, the propagation rate is affected by the nature of the countercations. For example, in the case of anionic polymerization of styrene in THF, the propagation rate constant followed the order $Li^+ > Na^+ > K^+ > Cs^+$.[23] This was attributed to the progressive decrease in the degree of solvation of the alkali cations. K−Naph furnishes a high concentration of naphthalenide anion that initiates polymerization of 2VP at a rapid rate. The less solvated ion pair generated in the initiation step is also very reactive, leading to competing side reactions through nucleophilic attack on the pyridine rings. On the other hand, the rate of initiation by Na−Naph is relatively slower. The ion pairs after the initiation step are comparatively more solvated and hence less reactive. Thus, with this initiator the polymerization ensues at a moderate rate and the probability of side reactions get dampened.

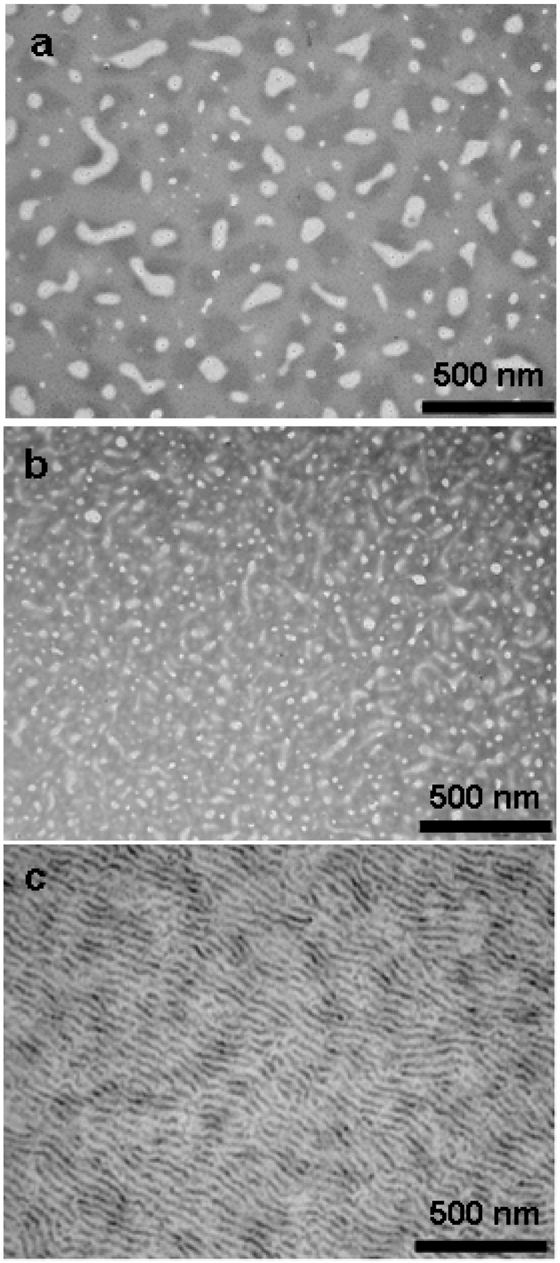


**Figure 3.** FE-TEM image of PHIC-*b*-P2VP-*b*-PHIC block copolymers in THF, annealed at 110 °C for 16 h. $f_{PHIC}$: (a) 0.3, (b) 0.5, (c) 0.7. Sample concentration 5 mg/mL. Dark region are P2VP, selectively stained with $I_2$ vapor.

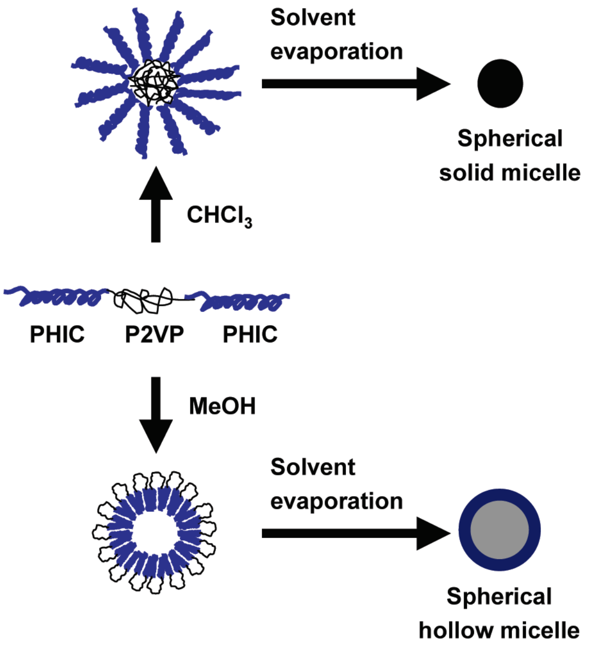


**Figure 4.** Schematic representation of the formation of solid micelles and hollow micelles.

**Block Copolymerization of PHIC-*b*-P2VP-*b*-PHIC.** For the polymerization of HIC by K−Naph, K$^+$ counterion was exchanged by Na$^+$ before copolymerization with HIC. It was suggested that Na$^+$ is the best counterion due to the favorable distance between amidate anion and Na$^+$.[18b] If Na−Naph is used as the initiator, copolymerization with HIC was facilitated without a need for the counterion exchange procedure. Hence, we used this initiator to carry out the copolymerization of 2VP with HIC, so as to get a rod−coil−rod triblock copolymer. A 5−10-fold excess of NaBPh$_4$ was used before addition of HIC to protect the backbiting. After adding HIC, the reaction mixture turned light yellow, indicating the formation of the amidate anion. The optimum condition of polymerization of HIC is 20 min at −98 °C. The feed ratio of the monomers was confirmed from $^1$H NMR. The broad N−C$H_2$ peak at 3.66 ppm in Figure 1 from the main chain of the rigid PHIC ensures that the synthesis of the block copolymer was successful. The molecular weights determined by MALLS/SEC are summarized in Table 1. In Figure 2 the P2VP homopolymer peak is clearly shifted to higher molecular weight region without tailing, indicating that the block copolymers were indeed synthesized. Excellent agreement between the calculated and the observed molecular weights as well as narrow MWD (Figure 2) also proved that the synthesis of block copolymers was quantitative.

**Phase Separation.** The synthesized block copolymers with different block composition were utilized to study their phase separation behaviors. The phase separation of block copolymers depends on several factors such as the solvent used for polymer

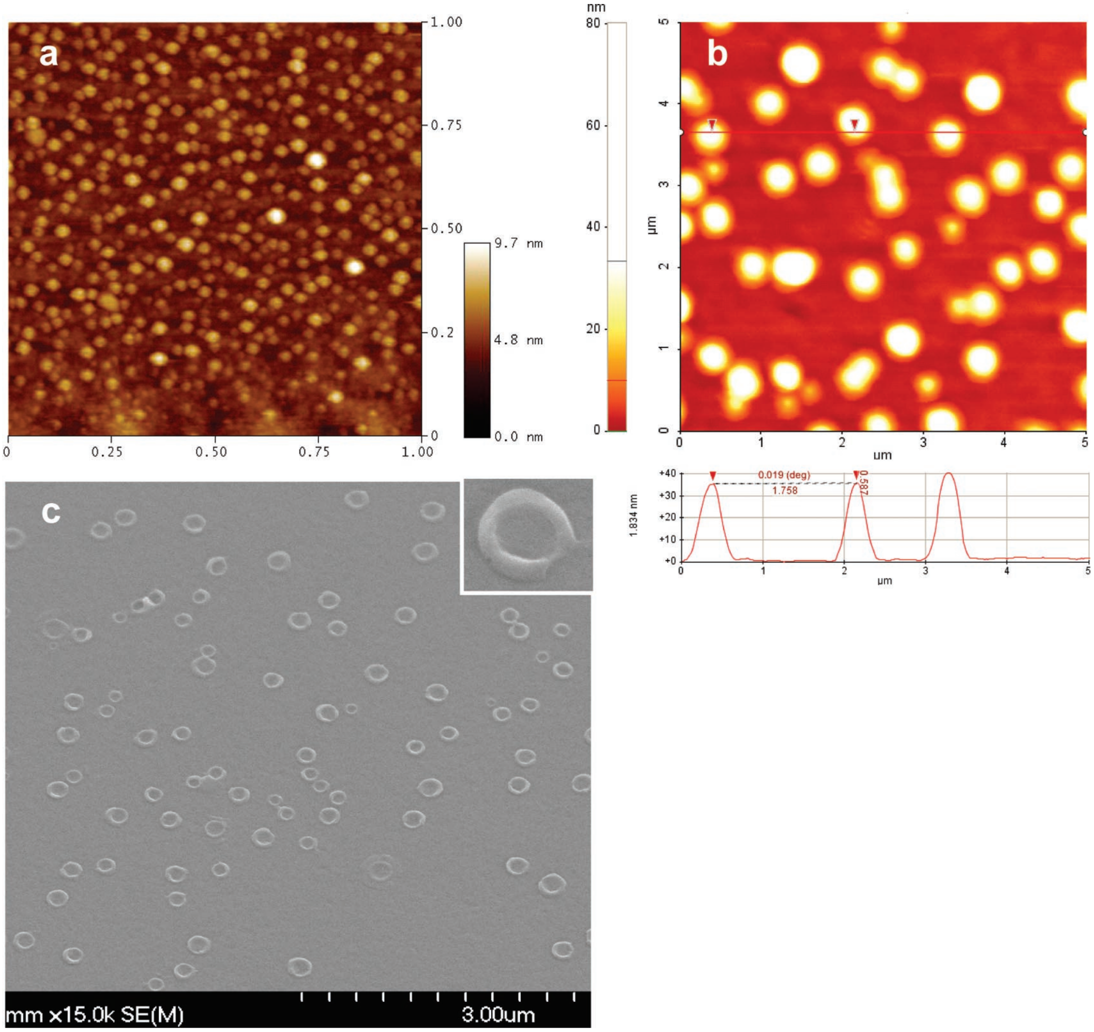


**Figure 5.** AFM height images (a) micelles in CHCl$_3$, (b) a ∼12-fold increase in size of the micelles in CH$_3$OH, and (c) 2D SEM image of (b) showing that the micelles in CH$_3$OH are hollow. The sample used is RB-2 (Table 1); concentration of the copolymer in all cases is 5 mg/mL.

film casting, molecular weight, molecular weight distribution, block composition, and sample treatment.[24] Figure 3 shows the TEM micrograph obtained from bulk sample of PHIC-*b*-P2VP-*b*-PHIC cast from THF, a common solvent for both blocks and annealed at 110 °C for 16 h. The dark regions are the P2VP domains, which have been selectively stained with $I_2$ vapor and the lighter regions are the unstained PHIC domains. The micrographs clearly show the periodic lamellar phase separation as the volume fraction of PHIC increased. The lamellar spacing and width of the PHIC domain were determined, and it was observed that the width of the PHIC domain is ~24 nm with a lamellar spacing of ~18 nm.

**Micellization.** The self-assembly of block copolymers composed of two distinct blocks having different solubility in selective solvents led to micelles and reverse micelles.[25−27] The formation of micelles and reverse micelles is schematically shown in Figure 4. The specific triblock copolymer we have studied contains equimolar rod and coil blocks. In $CHCl_3$, which is the solvent selective for the rod block, the flexible P2VP block aggregated while PHIC remained fully extended resulting in well-defined spherical micelles. Figure 5a shows AFM height image of the uniformly distributed spherical micelles with average size of ~20 nm.

Polymeric hollow spheres have received special attention due to the high efficiency of encapsulation of large-size molecules.[27a,28] For block copolymers composed of a cross-linkable block and degradable block, micellization, cross-linking the shell block, and finally removing the core block by degradation chemically or biologically is the common route to produce hollow spheres.[29] The self-organization of a rod−coil block copolymer in selective solvent have been also shown to form hollow spherical micelles.[27] However, the size of these hollow micelles was in the micrometer range. In the present study, we observed the hollow spherical micelles from PHIC-*b*- P2VP-*b*-PHIC in $CH_3OH$, which is the solvent selective for the coil block. In this solvent the PHIC blocks associate by hydrophobic interaction. After solvent evaporation the hydrophilic P2VP blocks collapsed on the hydrophobic PHIC, generating well-defined hollow spheres with average diameter of ~200 nm. The AFM image (Figure 5b) and the section analysis show the surface morphology of the block copolymer of equimolar rod and coil blocks cast in $CH_3OH$. 2D FE-SEM image (Figure 5c) also clearly shows the hollow spherical micelles.

The ease of formation of the lamellar phase, the generation of the solid and hollow micelles by simply changing the solvent and the block composition, should lead to many interesting applications, such as nanofabrication and nanoreactor for synthesis of quantum dots and other such interesting applications based on the reactivity of the P2VP block.

## Conclusions

The synthesis of well-defined P2VP by using Na−Naph bidirectional initiator is quantitative which facilitates the controlled synthesis of rod−coil−rod triblock copolymer PHIC-*b*-P2VP-*b*-PHIC. K−Naph leads to such polymerization but affords polymers of broad molecular weight distribution. This was ascribed to differences in the degree of polarization and solvation of the countercations. In THF the triblock copolymer self-assembled into lamellar phase and in $CHCl_3$ and $CH_3OH$ furnished solid and hollow micelles, respectively, with greatly varying sizes.

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