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Quantitative in Situ Coupling of Living Diblock Copolymers for the Preparation of Amphiphilic Coil−Rod−Coil Triblock Copolymer Poly(2-vinylpyridine)-*b*-poly(*n*-hexyl isocyanate)-*b*-poly(2-vinylpyridine)

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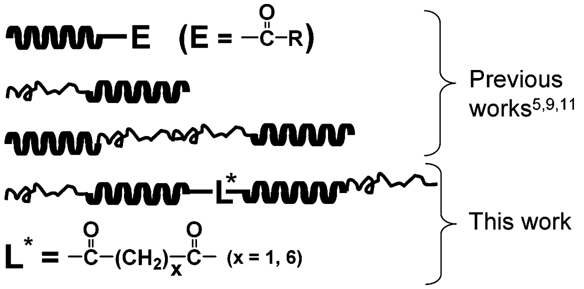
ABSTRACT: A facile approach to synthesis of a series of coil−rod−coil triblock copolymers by in situ coupling of living diblock copolymers is reported. The living diblock copolymer poly(2-vinylpyridine)-*block*-poly(*n*-hexyl isocyanate) (P2VP-*b*-PHIC) synthesized by anionic polymerization was coupled using malonyl chloride or suberoyl chloride in the presence of pyridine. The triblock copolymers were obtained in ∼94−99% yields without the need for fractionation or separation. The copolymers showed narrow molecular weight distribution (MWD = 1.08−1.14) and good agreement between the calculated and observed molecular weights. In a solvent such as tetrahydrofuran (THF), which is common to both the blocks, the copolymers showed characteristics of microphase separation. With high rod volume fractions lamellar phase separation with long-range order was observed.

Introduction

The self-assembly of coil−rod di- and triblock copolymers and the applications of the resulting supramolecular architectures make these materials highly fascinating.[1,2] Tailor-made copolymers of precisely controlled block composition and molecular weight (MW) with narrow molecular weight distribution (MWD) are preferred for such studies. Though a number of coil−rod block copolymers have been synthesized for the purpose, controlled synthesis of coil−rod−coil triblock copolymers have not been realized as yet. Coupling of the rod-functionalized ends of the coil−rod diblock copolymers synthesized by condensation polymerization results in triblock copolymers of uncontrolled MW and broad MWD.[3] Living anionic polymerization is a convenient route to controlled synthesis of homo- and copolymers.[4] Though facile synthesis of coil−rod diblock copolymers have been achieved by this route (Scheme 1),[5] triblock copolymers obtained by coupling of the diblock copolymers are most often contaminated with high percentage of unreacted diblock copolymers even after long reaction time extending to days.[6]

The polyisocyanates are helical polymers with rodlike characteristics[7] and find applications in several fields, such as chiral recognition, optical switches, optical data storage, liquid crystals, and degradable materials.[8] When attached to an amphiphilic coil-like polymer, the resulting coil−rod di- and triblock copolymers are expected to show fascinating properties, owing to their unique self-assembly behavior. We are involved in the controlled synthesis of the polyisocyanate homopolymers[9,10] and their di- and triblock copolymers.[11] For the synthesis of rod−coil−rod triblock copolymers, such as poly(*n*-hexyl isocyanate)-*b*-poly(2-vinylpyridine)-*b*-poly(*n*-hexyl isocyanate) (PHIC-*b*-P2VP-*b*-PHIC), the vinyl monomer is polymerized first using a bidirectional initiator, resulting in P2VP with two reactive ends. Addition of the isocyanate monomer led to the growth of the polyisocyanate rod blocks at the termini of P2VP coil block.

Scheme 1. Schematic Representations of the End-Capped Poly(*n*-hexyl isocyanate) (PHIC) (with ∼100% Yield) and the Coil−Rod, Rod−Coil−Rod, and Coil−Rod−Coil Block Copolymers



The coil−rod−coil triblock copolymers with polyisocyanates as the rod block cannot be synthesized in a similar manner, since the reverse sequence of monomer addition is not allowed. The nucleophilicity of the living polyisocyanate is not strong enough to initiate the polymerization of the vinyl monomers. Recently we discovered a method of 100% end-capping of PHIC anion by reacting it with aliphatic acid chlorides (Scheme 1).[9] Herein, we report controlled synthesis of amphiphilic coil−rod−coil copolymers poly(2-vinylpyridine)-*block*-poly(*n*-hexyl isocyanate)-*block*-poly(2-vinylpyridine) (P2VP-*b*-PHIC-*b*-P2VP) by coupling in situ P2VP-*b*-PHIC diblock copolymers using a number of difunctional carboxylic acid chlorides as the coupling agents.

Experimental Section

Materials. The monomers, 2-vinylpyridine (2VP) (Aldrich, 97%) and *n*-hexyl isocyanate (HIC) (Aldrich, 97%), and the linking reagents, malonyl and suberoyl chlorides (Aldrich, 97%), were dried over CaH_2 and vacuum-distilled. Tetrahydrofuran (THF, Fisher Scientific, GR grade) was distilled under nitrogen after refluxing with sodium for 5 h and distilled again under vacuum from naphthalenide sodium. Calcium hydride (Junsei, 95%), naphthalene (Aldrich, 99%), potassium metal (Aldrich, 98%), sodium tetraphenylborate (Aldrich, 99.5%), triethylamine (Fischer Scientific, 99%), and diphenylmethane (Aldrich, 99%) were used without further purification.

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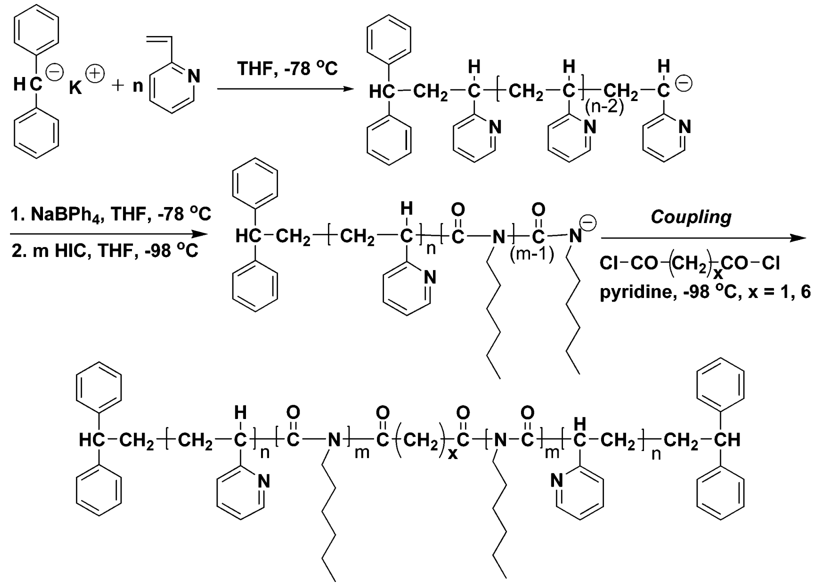
Scheme 2. Synthesis Scheme of Coil−Rod−Coil Copolymers (HIC = *n*-Hexyl Isocyanate, THF = Tetrahydrofuran)



Preparation of the Initiator. For the synthesis of diphenylmethane potassium (DPM-K) initiator, first naphthalenide potassium (Naph-K) was prepared by the reaction of a small excess of naphthalene (5 g, 39 mmol) with potassium (1.50 g, 38 mmol) in THF at room temperature. The reactor was connected to a high-vacuum line (10^{-6} Torr) and degassed by three freeze−pump−thaw cycles. The highly concentrated Naph-K was diluted in THF to portions of desired concentration. The initiator DPM-K was then prepared by the reaction of diphenylmethane (DPM) and Naph-K in THF. In a typical experiment 2 g (11.89 mmol) of DPM was reacted with 0.27 g of Naph-K (7 mmol) under vacuum at room temperature for 3 days. An excess amount of DPM was used to get the one-directional initiator (DPM-K). It was then frozen by liquid nitrogen to remove the dissolved gas by connecting to a high-vacuum line (10^{-6} Torr). After complete degassing, the initiator obtained from this solution was sealed in glass ampules with break-seals in vacuo, and the sealed ampules were stored at −30 °C. The concentrated DPM-K solution in THF was further diluted as required in the same solvent prior to use.

Synthesis of P2VP-*b*-PHIC. 2VP (0.62 g, 5.93 mmol) was first polymerized by using DPM-K (0.029 g, 0.14 mmol) initiator under high-vacuum conditions (10^{-6} Torr) in an all-glass apparatus. Briefly, after the homopolymerization of 2VP for 30 min at −78 °C in 10 mL of THF, an excess of $NaBPh_4$ (0.30 g, 0.87 mmol) in 5 mL of THF was introduced, and the reactor was cooled to −98 °C. The second monomer HIC (0.54 g, 4.23 mmol) in 10 mL of THF was then introduced, and copolymerization was carried out for 20 min by following our reported method.[5] The reaction mixture was then terminated with acidified methanol and precipitated in a large amount of methanol or hexane. The precipitated polymer was filtered and vacuum-dried. Yield = 100%, molecular weight (M_n) = 8200, $f_{PHIC} = 0.46$. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.9 (3H, CH_3), 1.00−2.10 (10H, $(CH_2)_4$ in hexyl group in HIC and CH_2 in vinyl main chain of 2VP), 2.10−2.89 (1H, CH), 3.36−4.14 (2H, $-CH_2-N$ in HIC), 6.11−7.35 (3H, CH in pyridine), 8.02−8.55 (1H, CH in pyridine). ^{13}C NMR ($CDCl_3$,75 MHz), δ (ppm): 13.9 (CH_3), 22.4−31.4 (CH_2 in hexyl group in HIC and CH_2 in vinyl main chain of 2VP), 40.2 (CH), 43 ($-CH_2-N$ in HIC), 156.6 (C=O). FT-IR (KBr, cm^{-1}): 3432 (NH), 3076 (CH, in pyridine ring), 2935 (aliphatic, CH_2-CH in backbone), 1728 (C=O from PHIC), 1590 (C=C), 1474 (C=N).

Synthesis of P2VP-*b*-PHIC-*b*-P2VP. Addition of malonyl chloride (0.011 g, 0.08 mmol) or suberoyl chloride (0.017 g, 0.08 mmol) to the living P2VP-*b*-PHIC (1.18 g, 0.14 mmol) led to linking two living P2VP-*b*-PHIC anions (Scheme 2). The coupling reaction was carried out in situ in the presence of pyridine (0.013 g, 0.16 mmol) at −98 °C for 10−20 min. The coil−rod−coil triblock copolymers were isolated in 96% yield. The reaction mixture was poured into a large amount of hexane or methanol. The choice of the solvent needed for precipitation depends on the block copolymer composition. The precipitated polymer was filtered and dried under vacuum. Dissolution in a good solvent and precipitation using a nonsolvent such as hexane or methanol was repeated to obtain highly pure copolymer samples. The copolymer samples were finally dissolved again in benzene and freeze-dried for 12 h. Solvent-soluble parts were analyzed quantitatively by weighing the residue after evaporation of solvent and using ^{1}H NMR to check whether there were any unreacted monomers or trimers. Molecular weight (M_n) = 16,600, $f_{PHIC} = 0.46$. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (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), 3.36−4.14 (2H, $-CH_2-N$ in HIC), 6.11−7.35 (3H, CH in pyridine), 8.02−8.55 (1H, CH in pyridine). ^{13}C NMR ($CDCl_3$,75 MHz), δ (ppm): 13.9 (CH_3), 22.4−31.4 (CH_2 in hexyl group of HIC and CH_2 in vinyl main chain of 2VP), 40.2 (CH), 43 ($-CH_2-N$ in HIC), 156.6 (C=O). FT-IR (KBr, cm^{-1}): 3432 (NH), 3076 (CH, in pyridine ring), 2935 (aliphatic, CH_2-CH in backbone), 1728 (C=O from linking structure and PHIC), 1590 (C=C), 1474 (C=N).

Phase Separation. Copolymer solutions in THF (5 mg/mL) cast on a carbon-coated copper grid were annealed at 110 °C for 16 h and stained with I_2 vapor for 8 h. Excess I_2 was removed by vacuum, and the samples were examined by transmission electron microscopy (TEM) for phase separation study.

Characterization. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) 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, λ = 690 nm), combined with size exclusion chromatography (SEC) and an OPTI LAB-DSP interferometric refractometer 478-009-690 and a DAWN EOS laser photometer (λ = 690 nm) 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, λ = 690 nm) 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. The phase separation of block copolymers was confirmed from an energy

Table 1. Selected Data for the Poly(2-vinylpyridine)-*b*-poly(*n*-hexyl isocyanate)-*b*-poly(2-vinylpyridine) (P2VP-*b*-PHIC-*b*-P2VP) Triblock Copolymers Synthesized by Using Diphenylmethane−Potassium (DPM-K) Initiator at −98 °C in THF

					diacid chloride (mmol)		$M_n \times 10^{-3}$				
sample	DPM-K (mmol)	2VP (mmol)	$NaBPh_4$ (mmol)	HIC (mmol)	reqd	expt	calcd	obsd[a]	M_w/M_n[a]	total polymer yield (%)	triblock copolymer yield (%)[b]
P2VP	0.17	7.55					4.82[c]	4.7	1.06	100	
P2VP-*b*-PHIC	0.14	5.93	0.87	4.23			8.4[d]	8.2	1.08	100	
1A	0.13	13.13	0.85	5.36	0.065[e]	0.07	31.8[g]	31.4	1.13	100	95
1B	0.14	5.98	0.87	13.91	0.07[e]	0.08	34.3[g]	33.5	1.08	100	94
1C	0.12	1.30	0.81	0.90	0.06[e]	0.07	4.3[g]	4.5	1.08	99	99
2A	0.14	5.93	0.87	4.23	0.07[f]	0.08	16.6[g]	16.1	1.14	100	96
2B	0.12	6.54	0.83	16.64	0.06[f]	0.07	45.6[g]	47.1	1.11	98	94

[a] Molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) in THF/Et_3N at 40 °C. [b] The percentage of yield was estimated by comparing the relative areas of di- and triblock copolymers in the SEC traces. [c] M_n is calculated using the relation M_n = [2VP]/[DPM-K] × molecular weight of 2VP + molecular weight of DPM. [d] M_n is calculated using the relation M_n = [2VP]/[DPM-K] × molecular weight of 2VP + [HIC]/ [DPM-K] × molecular weight of HIC + molecular weight of DPM. [e] Malonyl chloride. [f] Suberoyl chloride. [g] M_n is calculated using the relation M_n = {[2VP]/[DPM-K] × molecular weight of 2VP + [HIC]/ [DPM-K] × molecular weight of HIC + molecular weight of DPM} × 2.

filtering transmission electron microscope (EF-TEM, EM 912 OMEGA).

Results and Discussion

Synthesis of P2VP-*b*-PHIC. The block copolymers of 2VP bear specific importance due to the presence of nitrogen atom on the aromatic ring. But polymerization of 2VP possesses considerable problem as the presence of the heteroatom leads to a number of side reactions, particularly when a strong nucleophile is employed as the initiator.[12] We polymerized 2VP in THF using a relatively low reactive initiator (DPM-K). The polymers isolated with ∼100% yield showed controlled MW and narrow MWD (Table 1).

The polymerization of isocyanates is associated with inherent problems such as trimerization by backbiting.[9,10] Quite often it is not possible to control the MW and MWD.[13] The monomer 2VP was copolymerized with HIC in THF at −98 °C in the presence of $NaBPh_4$ additive. The additive in 5−10 molar excess has been used to prevent the side reaction and trimerization of PHIC.[11] The optimum time for the copolymerization of HIC was 20 min. The block copolymers showed living character and narrow MWD as well as good agreement between calculated and observed MW (Table 1).

Synthesis of P2VP-*b*-PHIC-*b*-P2VP. The coil−rod−coil triblock copolymer P2VP-*b*-PHIC-*b*-P2VP was synthesized by coupling the precursor living diblock copolymer P2VP-*b*-PHIC (Scheme 2). The coil−rod−coil triblock copolymers of 2VP and PHIC cannot be synthesized by sequential copolymerization due to weak reactivity of the living PHIC.[11] The coupling reaction is the only alternative way to synthesis such copolymers. But the triblock copolymers synthesized through coupling reactions are always contaminated from the diblock copolymers. For instance, in the synthesis of a triblock copolymer carried out by coupling of the living diblock copolymer anions or by the addition of living polymers to the end-capped polymers with a heterofunctional agent, the yield was 70−80% even after 24 h of reaction.[6] Several reasons such as method of synthesis of the diblock copolymer, the poor reactivity of the functional ends of diblock copolymers used for coupling, a choice of the initiator, etc., are responsible for the presence of the diblock copolymer impurity in the triblock copolymer. Our target was to significantly shorten the coupling reaction time as well as to ensure high purity of the triblock copolymer.

Balancing the stoichiometry of the coupling reaction is vital to get pure triblock copolymers. Theoretically, the molar ratio of the diblock anion and the coupling agent should be maintained at 2:1. In the anionic polymerization environment maintaining this stoichiometry was a challenging task. Nevertheless, we carried out several experimental runs and found that, when the diblock anion and the coupling agent ratio was 2:0.8, the yield of the triblock copolymer was low (∼80%) and the SEC-LS profile was bimodal (Figure 1a). If the ratio was maintained at the theoretical value (2:1), the yield of the triblock copolymer was also low (∼90%). The SEC-LS profile was broad with visible tailing (Figure 1b). When a little excess (10−

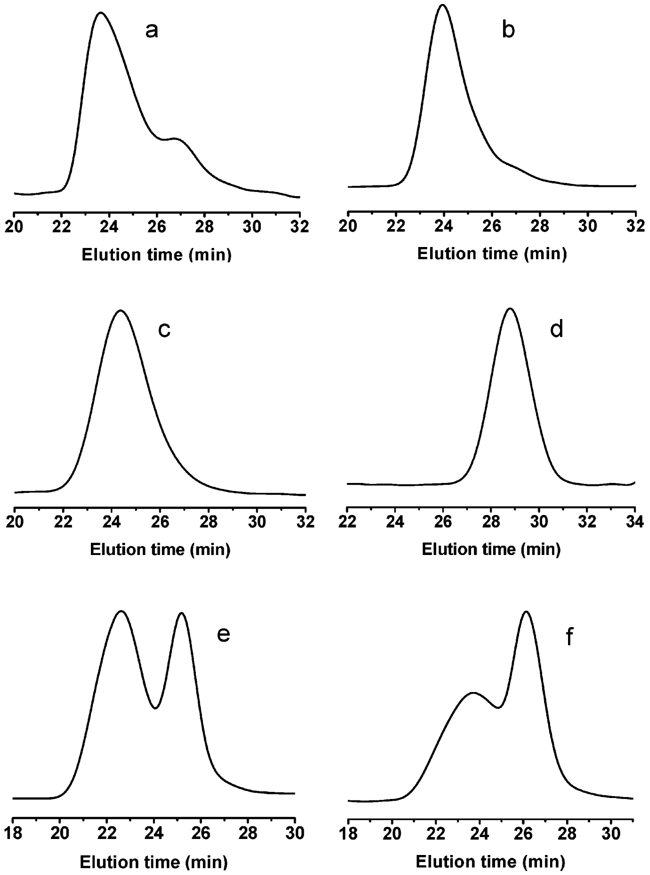


Figure 1. Size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) elution profiles of ABA triblock block copolymers (for the LS response at 90°) obtained with various molar ratios of living AB anions and coupling agent: (a) 2:0.8 (yield ∼80%), (b) 2:1.0 (yield ∼90%), (c) 2:1.08 (**1A** in Table 1, yield ∼95%), (d) 2:1.17 (**1C** in Table 1, yield ∼99%), (e) 2:1.5 (yield ∼50%), and (f) 2:1.7 (yield ∼38%). The presented yields of ABA copolymers are calculated from the SEC traces.

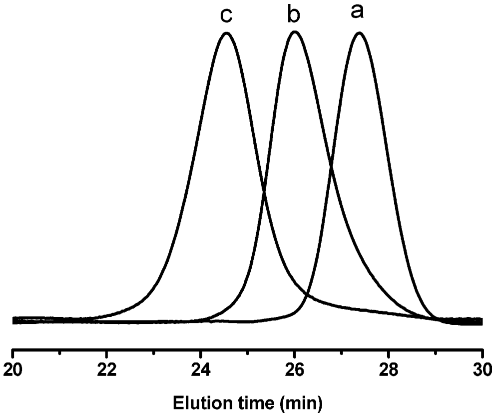


Figure 2. Size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) profiles (for the LS response at 90°) of (a) P2VP, $M_n = 4700$, $M_w/M_n = 1.06$; (b) P2VP-*b*-PHIC, $M_n = 8200$, $M_w/M_n = 1.08$; and (c) P2VP-*b*-PHIC-*b*-P2VP, **2A** in Table 1, $M_n = 16\,100$, $M_w/M_n = 1.14$.

15%) of the dicarboxylic acid chloride was used (molar ratio 2:1.08−1.17), the yield was as high as 94−99% (see Table 1), leading to copolymers of narrow MWD (Figure 2c,d). With a further increase in the concentration of the dicarboxylic acid chloride there was a drastic decrease in the yield (∼50−38%), the SEC-LS profile becoming bimodal again (Figure 1e,f). Thus, a little excess of the coupling agent was suitable to get the triblock copolymers with minimal diblock copolymer impurity. Presumably, during vacuum-sealing of the ampules some amount of the volatile acid chloride was lost such that the desired 2:1 stoichiometry was maintained.

To verify our observation and to study the effect of the molar concentration of AB anions and coupling agent, we have performed a set of controlled experiments (see Table 1). Synthesis of the homopolymer P2VP, the diblock copolymer P2VP-*b*-PHIC, and coupling of the P2VP-*b*-PHIC anion using two different acid chlorides have been carried out. All samples were isolated with controlled MW and narrow MWD. Good agreement between the calculated and observed MW as well as the shift of the SEC-LS profile from the homopolymer through the diblock to the triblock copolymers (Figure 2) indicated that the polymers obtained are indeed of controlled architecture. Furthermore, the synthesis of two types of triblock copolymers, **1A**−**1C** from malonyl and **2A**, **2B** from suberoyl acid chloride linking agents were achieved with controlled MW and narrow MWD. Though we expected ∼100% pure triblock copolymers, contamination from the diblock copolymer could not be entirely prevented. However, it could be considerably minimized to 5% or less by carefully maintaining the molar ratio of living anions and the coupling agent.

Phase Separation. Two samples of the block copolymer **1A** and **1B** (Table 1) of M_n 31 400 and 33 500 with PHIC volume fractions (f_{PHIC}) 0.3 and 0.7, respectively, were chosen to study the phase separation behavior. Parts a and b of Figure 3 show the TEM micrograph of **1A** and **1B**, respectively. THF is a common solvent for both PHIC and P2VP. In this solvent the two blocks phase-separated as expected.[11] The darker regions are the P2VP domains which have been preferentially stained with iodine, and the lighter regions are the unstained PHIC domains. The low molecular weight PHICs are rodlike due to less kinks and phase separation did not lead to long-range order (Figure 3a). As the fraction of the PHIC was increased to 0.7, there was a significant change in morphology. The long PHIC chains are relatively more flexible due to increased number of kinks furnishing the lamellar morphology and a hitherto unknown wavelike pattern extending to several micrometers (Figure 3b). The block copolymers with relatively flexible linker (samples **2A** and **2B)** also show characteristics microphase separation of rod−coil block copolymers.

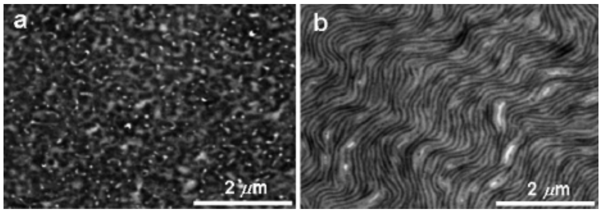


Figure 3. Transmission electron microscope (TEM) image of a bulk thin film cast from THF; the lighter regions are the PHIC domains, and the darker regions are P2VP domains stained with I_2 vapor. (a) **1A** in Table 1, $f_{\mathrm{PHIC}} = 0.3$, $M_n = 31\,400$; (b) **1B** in Table 1, $f_{\mathrm{PHIC}} = 0.7$, $M_n = 33\,500$.

Conclusions

The amphiphilic coil−rod−coil[14] copolymers of PHIC and P2VP with controlled architecture have been synthesized for the first time by quantitative coupling of living diblock copolymers with difunctional agents that eliminated further fractionation or separation. The in-situ coupling method by using diacid chlorides with pyridine is a useful method to prepare the triblock copolymers which cannot be synthesized by sequential polymerization. The amphihpilic coil−rod−coil triblock copolymer with flexible linker shows unique self-assembly behavior in common solvents such as THF. Via coupling it is possible to introduce an active methylene group to the center of the rod block that could be a site for the further functionalization of the block copolymers. Indeed, we are able to attach several pendants such as a fluorescent molecule, a crown ether, and a poly(ethylene glycol) moiety to this active methylene group. With ease of coupling and further functionalization, these amphiphilic reactive block copolymers can be tailor-made for potential applications.

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(14) The product is indeed P2VP-*b*-PHIC-L-PHIC-*b*-P2VP, where L is the linking moiety. However, it is represented as P2VP-*b*-PHIC-*b*-P2VP, as the linking unit is very small compared to the large PHIC rod segments.

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