Synthesis of Amphiphilic Miktoarm Star Copolymers of Poly(*n*-hexyl isocyanate) and Poly(ethylene glycol) through Reaction with the Active Methylene Group

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ABSTRACT: Coupling of the living poly(*n*-hexyl isocyanate) (PHIC) with malonyl chloride in the presence of pyridine resulted in a well-defined polymer PHIC-COCH$_2$CO-PHIC in ~95% yields. The active methylene group in the center of the polymer is a site for the introduction of suitable functionalities so as to impart additional attributes to the polymer. Poly(ethylene glycol) was anchored to the polymer center using monomethacrylate poly(ethylene glycol) (PEG1) by Michael addition reaction leading to the amphiphilc copolymer (PHIC)$_2$-PEG1. Two molecules of PHIC-COCH$_2$CO-PHIC were linked with a dimethacrylate poly(ethylene glycol) (PEG2) leading to (PHIC)$_2$-PEG2-(PHIC)$_2$. These miktoarm star copolymers of A$_2$B and A$_2$BA$_2$ architecture, where A is the hydrophobic PHIC and B is the hydrophilic and biocompatible PEG, were isolated in ~90% yields with controlled molecular weight and narrow molecular weight distribution (1.08−1.14). The amphiphilic A$_2$B-type copolymers formed solid micelles in CHCl$_3$ and vesicles in THF:C$_2$H$_5$OH (1:9 v/v) mixed solvent.

Introduction

Copolymers with complex molecular architectures, such as, star, ring, and comb, are fascinating materials. Especially, miktoarm star copolymers have attracted a lot of attention in recent years in view of their distinctive properties. Hirao and co-workers designed miktoarm[1] and ABCD-type star copolymer.[2] A series of well-defined 3-, 4-, and 6-miktoarm star copolymers are reported by Hadjichristidis et al.[3−5] Recently, a number of miktoarm star copolymers of diverse architectures have been synthesized.[6−9] Hydrophilic AB4 miktoarm star for micellization studies[10] and theoretical works on microphase separation of AB2 miktoarm star copolymers[11] have also been made.

Unlike the above miktoarm star polymers with coil-like arms, those with a rod arm are rare. An amphiphilic water-soluble stimuli-responsive rod−coil AB2 miktoarm star copolymers have been prepared by atom transfer radical polymerization.[12] Synthesis of amphiphilic miktoarm star polymer with a rod component is of considerable significance particularly because the rod−coil mutiblock copolymers have many fascinating properties.[13] Amphiphilic block copolymers form micelles and hollow spheres having unique characteristics, such as nanosize, core−shell architecture, and low critical micelle concentration, and find potential applications as nanoreactors, nanoreservoirs, gene delivery vehicles, and reaction media for biocatalysis.[14] Such copolymers having polyisocyanate blocks could be still more attractive, since polyisocyanates exhibit proven applications in several fields, such as chiral recognition, optical switches, optical data storage, liquid crystals, and degradable materials.[15,16] However, synthesis of such copolymers with controlled molecular architecture has remained a major challenge.

Copolymers, particularly those synthesized via living and controlled/living polymerizations, are of well-defined macromolecular architecture and narrow molecular weight distribution.[17] We synthesized a number of linear di- and triblock copolymers with polyisocyanates as the rod block by living anionic polymerization adopting the sequential polymerization process.[18,19] In this approach, first the vinyl monomers are polymerized at low temperature (−78 °C), and then the isocyanates are added as the second monomer at a still lower temperature (−98 °C). However, the similar protocol is not permissible for the synthesis of coil−rod copolymers of poly(ethylene glycol) (PEG) and poly(*n*-hexyl isocyanate) (PHIC). Besides, we observed that ethylene glycol monomer gets precipitated at −78 °C. The first attempt toward synthesis of the linear copolymers of PEG with PHIC was made by coordination polymerization.[13] But the copolymers were of uncontrolled molecular weight distribution often with very low PEG content ($M_n = 550$). As the molecular weight of PEG increased, the PEG macroinitiator lost its activity due to low solubility of PEG in toluene at 0 °C. As of now, the controlled synthesis of linear or star block copolymers of PEG and PHIC has not been successful.

Recently, we achieved ~100% end-capping of living PHIC with a number of acid chlorides in the presence of pyridine.[20,21] As a sequel to this, the living PHIC was reacted with malonyl chloride which led to coupling of the PHIC blocks with the introduction of an active methylene group to the center of the polymer. This opened up new avenues of introducing functional groups to the center of the rod block. The active methylene groups are known to undergo a variety of reactions, such as, alkylation, Michael addition, and Bingel reaction.[22−26] In the present study, we describe the synthesis of the rod−coil amphiphilic miktoarm star copolymers by introducing PEG into the center of the PHIC rod block via Michael addition reaction of the active methylene group and PEG methacrylates.

Experimental Section

Materials. *n*-Hexyl isocyanate (HIC) (Aldrich, 97%) and the linking molecule, malonyl chloride (Aldrich, 97%), were dried over

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Scheme 1. Synthesis of PHIC-COCH$_2$CO-PHIC and Amphiphilic Miktoarm Star Polymer from Coupled PHIC with Monomethacrylate Poly(ethylene glycol) (PEG1) and Dimethacrylate Poly(ethylene glycol) (PEG2)

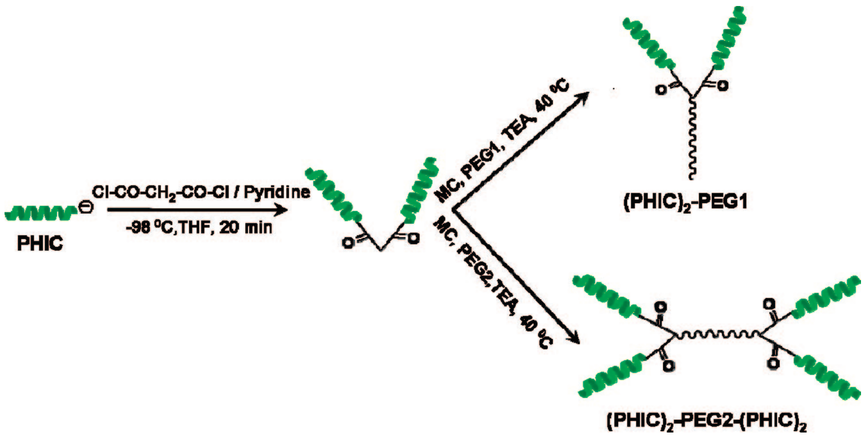

Table 1. Synthesis Results of the Coupled PHIC, A$_2$B, and A$_2$BA$_2$ Type Miktoarm Star Copolymers of PHIC and PEG

sample	polymers	M_n[a]	M_n[b]	MWD[b]	yield (%)[c]	f_{PHIC}[c]
1	PHIC-COCH$_2$CO-PHIC		5500	1.13	94	1.0
2	PHIC-COCH$_2$CO-PHIC		7500	1.08	95	1.0
3	PHIC-COCH$_2$CO-PHIC		9300	1.12	95	1.0
4	(PHIC)$_2$-PEG1	7500	7600	1.08	93	0.73
5	(PHIC)$_2$-PEG1	9500	9400	1.13	91	0.78
6	(PHIC)$_2$-PEG2-(PHIC)$_2$	10700	10900	1.14	84	0.68
7	(PHIC)$_2$-PEG2-(PHIC)$_2$	12500	12400	1.13	81	0.72

[a] Calculated molecular weight. Sample **4**: M_n of sample **1** (5500) + M_n of PEG1 (2000). Sample **5**: M_n of sample **2** (7500) + M_n of PEG1 (2000). Sample **6**: M_n of sample **2** (7500) + M_n of PEG2 (3200). Sample **7**: M_n of sample **3** (9300) + M_n of PEG2 (3200). [b] M_n and MWD were measured by SEC-LS at 40 °C in THF. [c] Yield and volume fraction of PHIC were measured by ^{1}H NMR.

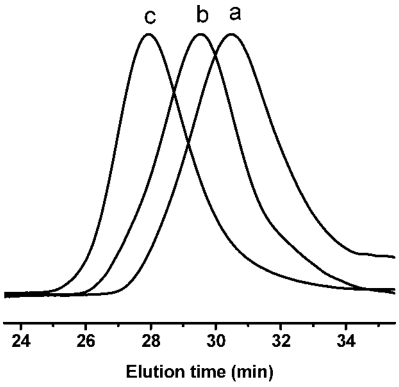

Figure 1. SEC-LS profile of (a) PHIC-CO-CH$_2$-CO-PHIC, M_n = 7500, MWD = 1.08; (b) (PHIC)$_2$-PEG1, M_n = 9400, MWD = 1.13; and (c) (PHIC)$_2$-PEG2-(PHIC)$_2$, M_n = 10 900, MWD = 1.14.

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, monomethacrylate poly(ethylene glycol) (PEG1) (M_n = 2000) and dimethacrylate poly(ethylene glycol) (PEG2) (M_n = 3200) (Aldrich), calcium hydride (Junsei, 95%), sodium (Aldrich, 99%), benzanilide (Aldrich, 98%), triethylamine (Fischer Scientific, 99%), and naphthalene (Aldrich, 99%) were used without further purification.

Synthesis of PHIC-COCH$_2$CO-PHIC. The homopolymerization of HIC was carried out at −98 °C for 50 min in THF using sodium benzanilide (Na-BA) as the initiator[20] in an all-glass apparatus under high-vacuum conditions (10^{-6} Torr). The reaction mixture was terminated with malonyl chloride in the presence of pyridine which resulted in coupling of two living PHIC blocks. After 10−15 min, the coupled polymer was precipitated in an excess amount of methanol and filtered and then dried in vacuum. PHIC-COCH$_2$CO-PHIC ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 0.9 CH_3, 1.00−2.10 (CH_2)$_4$ in hexyl group of HIC, 2.8−2.9 CH_2 in malonyl, 3.66 −CH_2−N in HIC.

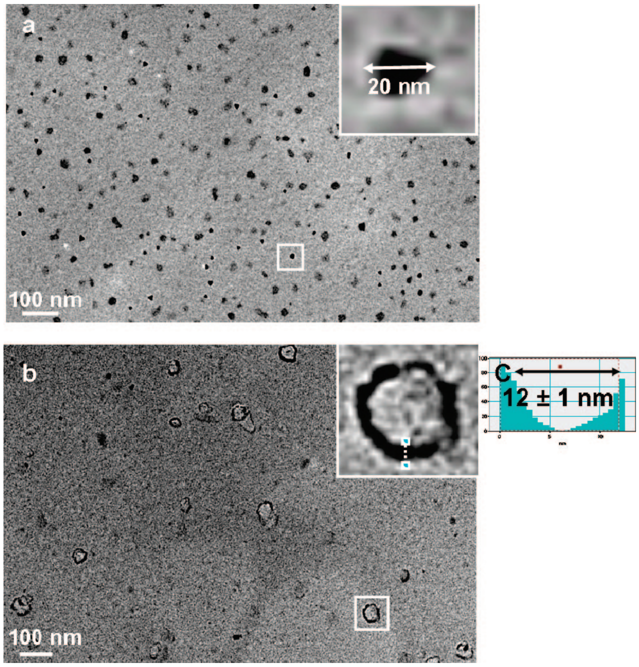

Figure 2. TEM image of (a) solid micelles of A$_2$B in CHCl$_3$ with PEG core and PHIC shell, unstained PHIC shell is not visible in the micrograph. (b) Vesicles of A$_2$B in THF:C$_2$H$_5$OH (1:9 v/v) with PHIC constituting the interior part and PEG as the exterior part of the bilayer. (c) Intensity profile of the inset in (b), showing 12 ± 1 nm thickness of the bilayer. The dark regions are PEG blocks which was selectively stained with I$_2$ vapor.

Synthesis of (PHIC)$_2$-PEG1 (A$_2$B). PEG was introduced to the center of PHIC-COCH$_2$CO-PHIC via Michael addition reaction. In a typical procedure, the polymer sample (0.2 g, 0.036 mM) was dissolved in 20 mL of dichloromethane, and then PEG1 (0.15 g, 0.054 mM) was added in the presence of 0.006 g (0.059 mM) of triethylamine (TEA) (Scheme 1). The reaction mixture was stirred for 7 h at 40 °C. The product was precipitated in methanol and then filtered. The crude polymer sample was repeatedly dissolved in a small amount of THF and reprecipitated in methanol to remove unreacted PEG. The sample was then dried in vacuum at 40 °C for characterization and morphology study. (PHIC)$_2$-PEG1. ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 0.9 CH_3, 1.00−2.10 (CH_2)$_4$ in hexyl group

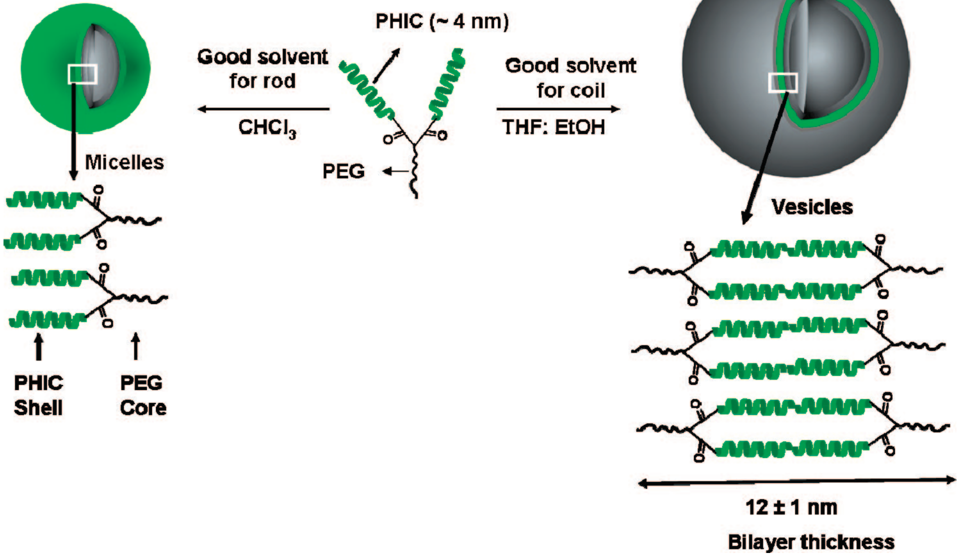

Figure 3. Schematic representation of the A_2B type amphiphilic miktoarm star block copolymer self-assembly showing the PHIC (green) and PEG (gray) blocks.

of HIC, 3.0−3.2 C*H* in malonyl, 3.4−4.0 $-CH_2-N$ in HIC, and $-CH_2$ in PEG1.

Synthesis of (PHIC)$_2$-PEG2-(PHIC)$_2$ (A_2BA_2). The reaction between the coupled PHIC and the difunctional PEG2 was performed at 40 °C for 7 h in the presence of TEA (TEA) (Scheme 1). In a typical procedure, 0.4 g (0.054 mM) of the polymer sample was dissolved in dicloromethane (20 mL), and then 0.14 g (0.04 mM) of PEG2 was added in the presence of 0.005 g (0.049 mM) of triethylamine. The product was precipitated in methanol solution and then filtered. The crude polymer sample was repeatedly dissolved in a small amount of THF and reprecipitated in methanol to remove unreacted PEG. The sample was then dried in vacuum at 40 °C. (PHIC)$_2$-PEG2-(PHIC)$_2$. ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 0.9−1.2 C*H*$_3$ in HIC and PEG2, 1.00−2.10 (C*H*$_2$)$_4$ in hexyl group of HIC, 2.12−2.16 C*H*$_2$ in PEG2, 2.4−2.5 C*H* in PEG$_2$, 3.0−3.2 (C*H* in malonyl, 3.4−4.0 $-CH_2-N$ in HIC and $-CH_2$ in PEG2.

Micellization. The micellization of the block copolymers was studied in CHCl$_3$ as well as THF:C$_2$H$_5$OH mixed solvent. The sample concentration was maintained at 5 mg/mL. The sample solutions in select solvents were cast on carbon-coated copper grid and stained with I$_2$ vapor for morphological studies by transmission electron microscope (TEM).

Characterization. ^{1}H NMR spectra were measured using a JEOL JNMLA300WB with CDCl$_3$ as the solvent. Chemical shifts were examined by comparing with tetramethylsilane (TMS) at 0 ppm. Molecular weights were determined on the basis of the response of a multiangle laser light scattering detector system (MALLS), SEC-LS (OPTI LABORATORY-DSP interferometric refractometer 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 4% of triethylamine (for the prevention of adsorption of hydrophilic polymer in the column) was used as a mobile phase at flow rate 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 of each polymer sample, SEC-LS data were expressed as refractive index detection at 40 °C. The micelles of block copolymers were confirmed by morphological examination performed with an energy filtering transmission electron microscope (EF-TEM, EM 912 OMEGA).

Results and Discussion

Synthesis of PHIC-COCH$_2$CO-PHIC. Isocyanates are a class of interesting monomers that have been extensively studied in the anionic polymerization process. Since the polymerization of highly reactive monomer *n*-hexyl isocyanate is not easily obtainable due to the formation of trimers or side reactions,[19] we carried out the anionic polymerization of HIC using a Na-BA initiator in THF at −98 °C.[21] Na-BA is a unique initiator for the polymerization of isocyanates since it serves the dual functions of controlled initiation and efficient protection of the living chain ends. After 50 min, there was no unreacted monomer left and the living properties persisted until about 70 min. The long reaction time and living nature of PHIC made it possible to introduce reactive center to polymer using a simple protocol. Two living PHIC blocks were coupled by terminating the reaction with malonyl chloride in the presence of pyridine. This furnished the coupled PHIC having an active methylene group in its center in ~95% yield. The polymer samples have defined molecular weight and narrow molecular weight distribution. The molecular weight and MWD determined by SEC-LS are summarized in Table 1.

Synthesis of (PHIC)$_2$-PEG1. The Michael addition reaction between the active methylene group of PHIC-COCH$_2$CO-PHIC and monofunctional PEG in the presence of TEA led to the amphiphilic miktoarm star copolymers of A_2B type (where A is PHIC and B is PEG1) in ~90% yields. The M_n of A_2B copolymer (sample **4**) was 7600, which matched with the calculated M_n (7500) (PHIC: 5500, PEG1: 2000) (Table 1). For another sample (sample **5**) the experimental M_n of 9600 also matched with the calculated M_n (9500) (PHIC: 7500, PEG1: 2000). Copolymers with narrow MWD and with predictable molecular weight indicated that the miktoarm copolymers of PHIC and PEG have been successfully synthesized.

Synthesis of (PHIC)$_2$-PEG2-(PHIC)$_2$. The A_2BA_2 miktoarm star copolymers of PHIC and PEG2 were synthesized by the Michael addition reaction of coupled PHIC and the difunctional PEG2. The copolymers were isolated in ~80% yields. Agreements between the calculated and observed molecular weights were also seen for samples **6** and **7** (Table 1). Narrow MWD and gradual shift of the SEC-LS profile (Figure 1) from the coupled PHIC through the miktoarm copolymer A_2B to A_2BA_2 indicated that the block copolymers were indeed of controlled architecture.

Aggregation Behavior. The amphiphilic block copolymers having different solubility parameter between its blocks, formed normal micelles, reverse micelles, and vesicles[27] in selective solvents. The sample for the TEM analysis was $(PHIC)_2$-PEG1 (sample **4**, M_w 7600, f_{PHIC} 0.73) dissolved in $CHCl_3$. The TEM results (Figure 2a) showed black dots of about 20 nm diameter (inset Figure 2a). For sampling, iodine was used as the staining agent. Since iodine preferentially stains PEG, $(PHIC)_2$-PEG1 in $CHCl_3$ formed core−shell type micelles with PEG as the core and PHIC as the shell. $CHCl_3$ is the solvent of choice for the PHIC rod block. The flexible PEG blocks aggregated in $CHCl_3$, while PHIC remained fully extended. This led to the formation of well-defined spherical solid micelles with PEG core and PHIC shell.

The same sample of $(PHIC)_2$-PEG1 was dissolved in THF/ethanol (1/9 v/v) solvent mixture. Since the copolymer has a high rod fraction (f_{PHIC} 0.73), it is not soluble in ethanol. A small amount of THF, a common solvent that dissolves both PEG and PHIC blocks, was used to first dissolve the copolymer. The effect of addition of ethanol, the nonsolvent for the rod block, was studied. Various solvent ratios were investigated, and a 10−20% of common solvent (THF) with 80−90% nonsolvent (ethanol) resulted in bilayer vesicles of average size 50 ± 10 nm (Figure 2b). The $(PHIC)_2$-PEG1 sample contained ~45 units of HIC in its two PHIC arms and 40 units of ethylene glycol (EG). One unit of HIC is ~0.18 nm long.[28] Hence, total length of the PHIC rod block for this copolymer is ~4.05 nm. Considering that a unit length of EG is equal to the carbon−carbon−oxygen single bond length, the fully extended length of the PEG1 is ~11 nm. The average thickness of the vesicle bilayer is in the range of 12 ± 1 nm (Figure 2c). This suggests that the architecture of the vesicles is bilayer in nature with the PHIC block forming the interior and PEG block as the exterior of the vesicle. The inset TEM image of Figure 2a suggests that PEG block collapses on the PHIC block.

Figure 3 shows the schematic representation of the formation of micelles and vesicles by $(PHIC)_2$-PEG1 in the selective solvents. The simple method for the generation of the solid micelles and bilayer vesicles from an amphiphilic copolymer with easily degradable PHIC blocks could have implications in various applications, such as nanocontainers for controlled drug release.

Conclusions

Coupling of living PHIC in situ is very effective in the presence of pyridine. The reaction afforded a PHIC polymer with an active methylene group in its center. The active methylene group facilitated further functionalization of the rod block, thus expanding the scope of PHIC chemistry. It was possible to introduce PEG to PHIC center very efficiently, leading to amphiphilic miktoarm copolymers of A_2B and A_2BA_2 architecture with PHIC and PEG blocks. The copolymers formed solid core−shell or hollow spherical micelles by simply changing the solvent.

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