Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 3927–3932 **3927**
DOI: 10.1021/ma900197g

Living Anionic Polymerization of Isocyanate Containing a Reactive Carbamate Group

M. Shahinur Rahman,† Hee-Soo Yoo, Mohammad Changez, and Jae-Suk Lee*

Department of Materials Science and Engineering and Department of Nanobio Materials and Electronics, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro (Oryong-dong), Buk-gu, Gwangju 500-712, Korea. † *Current address: Department of Chemistry, University of Tennessee, Knoxville, TN 37996*

Received January 29, 2009; Revised Manuscript Received April 1, 2009

ABSTRACT: Anionic polymerization of *n*-alkoxycarbonylaminohexyl isocyanates was carried out using a sodium benzanilide (Na-BA) as an initiator without additives in tetrahydrofuran (THF) at −98 °C under high vacuum (10^{-6} Torr). The polymerization of methoxycarbonylaminohexyl isocyanate (MAHI) resulted in an insoluble material. However, the polymerization of *n*-propyloxycarbonylaminohexyl isocyanate (PAHI) with propyl side chain was moderately controlled and gave high yields (∼98%) of the polymers with polydispersity index (PDI 1.18−1.22). The results of the polymerization were improved significantly when *n*-pentanoxycarbonylaminohexyl isocyanate (PEAHI) with pentyl side chain was used. Poly(*n*-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI) was isolated in ∼99% yields, controlled molecular weight, and a narrow PDI (1.08−1.14). The living nature of PPEAHI was indicated from the linear plot of the molar ratio of the monomer to the initiator versus the number-average molecular weight (M_n) in addition to the successful block copolymerization of PEAHI with another isocyanate monomer, *n*-hexyl isocyanate (HIC). Furthermore, the hydrogen bonding between the active hydrogen of the carbamate group of the PPEAHI and the nitrogen atom of the poly(2-vinylpyridine) formed a vesicle-like morphology in methanol.

Introduction

Polyisocyanates possess a helical main chain conformation in the crystalline state.[1] Polyisocyanates with functional side chains also possess a helical conformation in the crystalline state as well as in solution.[2−5] Because of this unique characteristic and structural feature, polyisocyanates have been studied extensively and have potential applications as materials for chiral recognition, optical switches, liquid crystals, and degradable materials.[6] Side-chain-functionalized polyisocyanates with ether, ester, or ketone groups were reported to form miscible blends with hydrogen-bonding donor random coil polymers.[5] However, such blends do not form with poly(*n*-hexyl isocyanate) (PHIC) and a random donor coil polymer even though PHIC does have a hydrogen-bonding acceptor group in its backbone. Functional polyisocyanates with active hydrogen side groups, such as −OH, $-NH_2$, −COOH, or −NHCOOR, could strongly influence the helical structure of the polymer chain through polar interactions and are also useful for appending a variety of molecules through the side chain. However, the synthesis of functional polyisocyanates having active hydrogen in the side chain without proper protective groups is not straightforward due to efficient proton abstraction and chain transfer reactions.[7] Much attention has thus been paid to the synthesis of polyisocyanates from commercially available alkyl isocyanate monomers. However, relatively few studies have focused on functional polyisocyanates due to the difficulty of their synthesis.

An attempt at the anionic polymerization of functional isocyanate using a NaCN initiator at −78 °C in toluene was carried out by Khatri and co-workers.[5] However, the resulting polymers showed an uncontrolled PDI with low yield. Zentel and co-workers also synthesized optically active polyisocyanates with azobenzene side chains. Nevertheless, the yield of the polymer was low with a broad PDI.[8] Okamoto and co-workers reported the anionic polymerization of isocyanates with an active hydrogen in the side chain bearing a carbamate group (−NHCOOR, R = achiral or chiral alkyl group) using various achiral and chiral initiators in THF at −98 °C. A moderately controlled polymer can be achieved by this method.[7] Unluckily, high molecular weight oligomers were also obtained due to the intramolecular transfer of the propagation end to the carbamate group in the side chain during the initial stage of the polymerization.

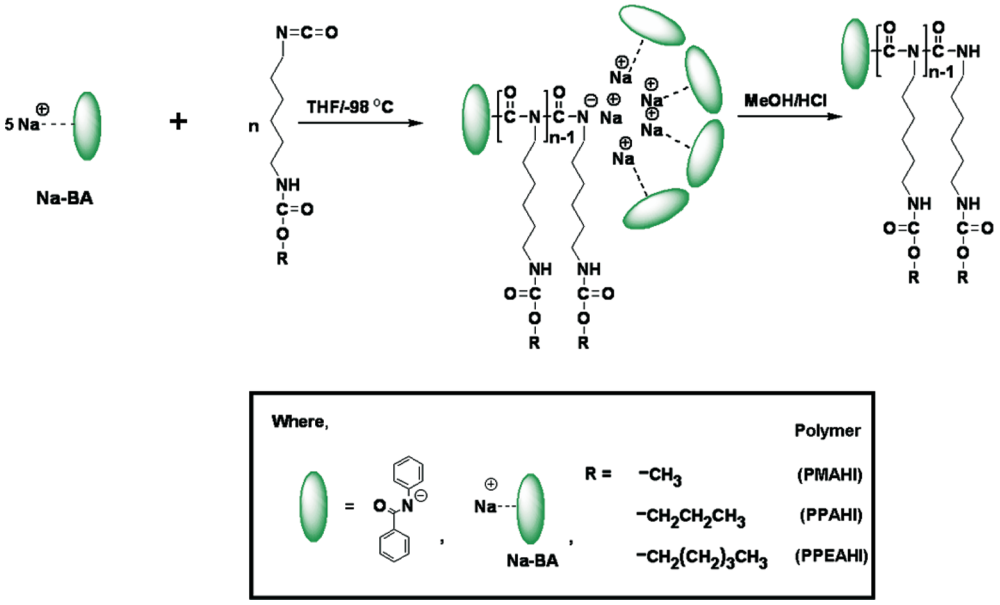
We are involved in the controlled synthesis of polyisocyanates[9−12] and also reported the polymerization of isocyanate monomers with bulky molecule *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (Disperse Red1 or DR1) using sodium napthalenide (Na-Naph) as an initiator in the presence of 15C5 crown ether in THF at −98 °C.[13] The bulky DR1 group on the side chain in the presence of the 15C5 crown ether was found to effectively prevent chain transfer. In addition, synthesis of chiral poly(6-{1[(*S*)-(−)-2-methylbutyal]oxycarbonylamino}hexyl isocyanate) using sodium diphhenylmethamide (Na-DPM) or Na-Naph initiator with sodium tetraphenylborate ($NaBPh_4$) as an additive was successfully carried out without side reaction. However, the PDI was broad.[14]

Also, we have observed that chain length of the simple alkyl side chain played an important role in the anionic polymerization of functional isocyanate with a carbamate group using a Na-Naph initiator and 15C5 or $NaBPh_4$ as an additive.[15] However, compared to the PDI from the true living anionic polymerization of monomers like *n*-hexyl isocyanate (HIC), the PDI of the functional polyisocyanates with carbamate group was broad, and the calculated molecular weight was not in accord with the observed molecular weight. Thus, the controlled synthesis of functional polyisocyanates with carbamate group remains a challenge.

*Corresponding author: e-mail jslee@gist.ac.kr; Tel + 82 62 970 2306; Fax + 82 62 970 2304.

Published on Web 05/14/2009

Scheme 1. Anionic Polymerization of Methoxycarbonylaminohexyl Isocyanate (MAHI), *n*-Propyloxycarbonylaminohexyl Isocyanate (PAHI), and *n*-Pentanoxycarbonylaminohexyl Isocyanate (PPEAHI) in Tetrahydrofuran at −98 °C Using a Sodium Benzanilide (Na-BA) Initiator



Recently, we found a unique low reactive dual functional sodium benzanilide (Na-BA) initiator for the polymerization of hexyl isocyanate (HIC).[9] Na-BA seems to be an appropriate initiator for the synthesis of functional polyisocyanates bearing a carbamate linkage in the side chain. Herein, we report the controlled synthesis of such functional polyisocyanates with carbamate linkage using a Na-BA initiator in THF at −98 °C. Furthermore, the presence of an active hydrogen of the carbamate group in the polyisocyanate was investigated by formation of hydrogen bonding with poly(2-vinylpyridine) (P2VP).

Experimental Section

Materials. Methanol, *n*-propanaol, and *n*-pentanol (Aldrich) were used as received. 1,6-Diisocyanatohexane (98%, Aldrich) and monomer 2-vinylpyridine (2VP, Aldrich, 97%) were stirred with CaH_2 overnight and distilled under reduced pressure. Tetrahydrofuran (Fisher, GR grade) was stirred with sodium overnight under reflux and then distilled. Sodium (Aldrich, 99%), diphenylmethane (Aldrich, 99%), naphthalene (Naph, Aldrich, 99%), and benzanilide (Aldrich, 99.5%) were used without further purification. Glass (Iwaki Glass Co. Pyrex), used for the glass apparatus, was rinsed with tap water and finally with triply distilled water before being oven-dried. Freshly distilled THF was stirred with Na-Naph solution in THF under high-vacuum conditions with repetition of degassing procedures and was distilled again prior to use.

Preparation of Initiators. The Na-BA initiator in THF (50 mL) was prepared via the reaction of equivalent amounts of benzanilide (8.70 g, 0.043 mol) and elemental sodium (1.00 g, 0.043 mol) at room temperature. When the color of the reaction mixture turned light yellow, it was frozen in liquid nitrogen to remove dissolved gas by connecting it to a high-vacuum line (10^{-6} Torr). After complete degassing, the initiator obtained from this solution was stored at −30 °C in glass ampules with break-seals in vacuo. Na-BA was diluted to the appropriate concentration prior to use. The diphenylmethane potassium (DPM-K) initiator was prepared by following the procedure of previously reported paper.[12]

Synthesis of Monomers. Three monomers, methoxycarbonylaminohexyl isocyanate (MAHI), *n*-propyloxycarbonylaminohexyl isocyanate (PAHI), and *n*-pentanoxycarbonylaminohexyl isocyanate (PEAHI), were prepared from the reaction between 1,6-diisocyanatohexane and a corresponding alcohol, methanol, propanol, or pentanol, respectively. The details of the synthetic procedures were reported by us in our previous contribution.[15]

Anionic Polymerization of Monomers. All of the polymerizations were carried out in a glass apparatus equipped with break-seals under high vacuum (10^{-6} Torr) as a function of time at −98 °C (Scheme 1). The reactors were always prewashed with the initiator solutions after being sealed off from a vacuum line. The initiator was introduced to the reactor and cooled to −98 °C in a frozen methanol bath. Polymerization was initiated by adding the monomer to the initiator solution. The reaction was terminated with the addition of acidified methanol to the reaction solution. The mixture was then poured into a large amount of methanol, and the precipitated polymer was filtered and dried under reduced pressure. To check the weight of the unreacted monomers or trimers, the methanol soluble portion was concentrated by evaporation under reduced pressure and then drying in vacuo.

In a typical polymerization procedure, PEAHI (1.22 g, 4.77 mmol) was polymerized using a Na-BA (0.13 g, 0.60 mmol) initiator for 70 min at −98 °C. The living PPEAHI was then quenched by adding degassed acidified methanol. The reaction mixture was precipitated in a large amount of methanol, filtered, and then dried under reduced pressure. PPEAHI (M_n = 26 200 g/mol, PDI = 1.08, and yield = 98%). ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.88−0.92 (3H, $-CH_3$), 1.30−1.46 (6H, $-(CH_2)-$), 1.47−1.56 (2H, $-CH_2-$), 1.59−1.68 (2H, $-CH_2-$), 3.13−3.31 (2H, $-CH_2-NH-$), 3.6−3.7 (2H, $-CH_2-NCO$), 4.01−4.06 (3H, CH_3-O-), 5.3 (1H, −NH−). FT-IR (KBr, cm^{-1}): 3432 (NH), 2276 (N=C=O), 1701 (C=O).

The 2VP monomer was polymerized (M_n = 19 000 g/mol, PDI = 1.07, and yield = 98%) by using DPM-K initiator under high-vacuum conditions (10^{-6} Torr) in an all-glass apparatus for 30 min at −78 °C in THF (10 mL) and characterized by ^{1}H NMR, FT-IR, and gel permeation chromatography (GPC).[12]

Block Copolymerization of PEAHI with HIC. In a typical block copolymerization procedure, the homopolymerization of PEAHI (1.63 g, 6.37 mmol) as the first polymer to initiate subsequent polymerization of HIC was performed with Na-BA (0.061 g, 0.278 mmol) as an initiator in THF, in a glass apparatus under high vacuum at −98 °C. After 70 min, HIC (0.940 g, 7.39 mmol), the second monomer, was added, and copolymerization was carried out for 60 min under the same conditions as were used previously. The reaction was terminated by adding

Table 1. Anionic Polymerization of Methoxycarbonylaminohexyl Isocyanate (MAHI), *n*-Propyloxycarbonylaminohexyl Isocyanate (PAHI), and *n*-Pentanoxycarbonylaminohexyl Isocyanate (PEAHI) in Tetrahydrofuran at −98 °C Using a Sodium Benzanilide (Na-BA) Initiator

				$M_n \times 10^{-3}$			
monomer	Na-BA[a] (mmol)	monomer (mmol)	time (min)	calcd[b]	obsd[c]	M_w/M_n[c]	yield[d] (%)
MAHI	0.11	6.50	40	10.7			
PAHI	0.12	6.92	60	14.5	16.4	1.18	98
	0.11	6.15	60	14.0	19.8	1.22	95
PEAHI	0.12	4.77	70	10.7	10.9	1.14	98
	0.12	5.40	70	12.1	12.5	1.11	99
	0.13	9.66	70	19.9	19.1	1.13	98
	0.13	11.6	70	24.5	26.2	1.08	98

[a] The concentration of Na-BA is 20% of the actual concentration (ref 9). [b] Number-average molecular weight (M_n) was calculated using the relation {([monomer]/[Na-BA]) × (molecular weight of monomer) + (molecular weight of benzanilide)} × (yield of polymer)/100. [c] M_n and polydispersity index (M_w/M_n) were measured by size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) for the LS response at 90° in tetrahydrofuran at 40 °C. [d] Yield was calculated gravimetrically.

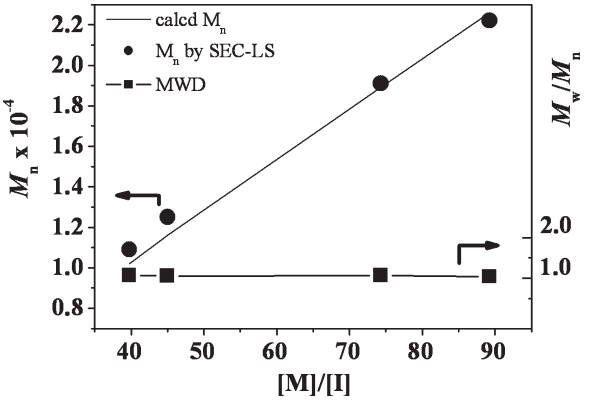


Figure 1. Number-average molecular weight (M_n) vs the molar ratio of *n*-pentanoxycarbonylaminohexyl isocyanate (PEAHI) to sodium benzanilide (Na-BA) initiator for anionic polymerization in tetrahydrofuran at −98 °C.

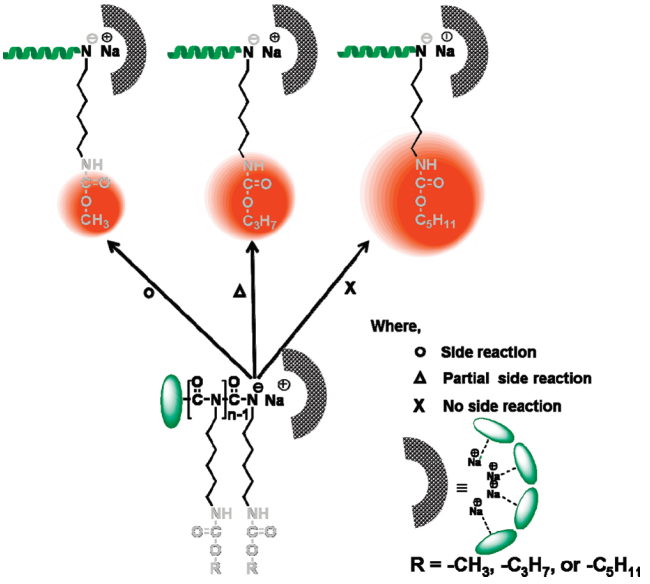


Figure 2. Model for possible side reactions during the synthesis of poly (methoxycarbonylaminohexyl isocyanate) (PMAHI), poly(*n*-propyloxycarbonylaminohexyl isocyanate) (PPAHI), and poly(*n*-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI).

methanol, and the polymer was precipitated into methanol, filtered, and then dried in vacuo (M_n = 47 900 g/mol, PDI = 1.25, and yield = 97%). The reverse order of monomer feeding was also carried out. The homopolymerization of HIC (0.870 g, 6.84 mmol) as the first polymer to initiate the HIC sequence was used with Na-BA (0.068 g, 0.312 mmol) as an initiator at −98 °C in THF. After 60 min, PEAHI (1.62 g, 6.32 mmol), the second monomer, was added, and copolymerization continued for 70 min. Further treatment was performed in the same manner as above. PPEAHI-*b*-PHIC: ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.88−0.92 (6H, $-CH_3$ of PEAHI and HIC), 1.30−1.46 (12H, $-(CH_2-)$, 1.47−1.56 (4H, $-CH_2-$), 1.59−1.68 (4H, $-CH_2-$), 3.13−3.31 (2H, $-CH_2-NH-$), 3.6−3.7 (4H, $-CH_2-NCO$), 4.01−4.06 (3H, CH_3-O-), 5.3 (1H, −NH−). FT-IR (KBr, cm^{-1}): 3432 (NH), 2276 (N=C=O), 1701 (C=O).

Blending of PPEAHI with P2VP. The blending of the PPEAHI and P2VP was carried out in MeOH using an equimolar ratio of PPEAHI and P2VP (5 mg/mL) to assess the ability of the carbamate group to form hydrogen bonds.

Characterization. The ^{1}H NMR (300 MHz) spectra were measured using a JEOL JNMLA300WB with $CDCl_3$ 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 (λ = 690 nm) (MALLS SEC-LS, OPTI LAB-DSP interferometric refractometry 478-009-690 (λ = 690 nm) 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). To prevent the adsorption of the hydrophilic polymer in the column, THF with triethylamine (2% v/v) was used as the mobile phase at a flow rate of 1.0 mL/min at 40 °C. The dn/dc values for the block copolymers in THF at 40 °C were measured with an LED (Optilab DSP) source. After dn/dc was measured for five different concentrations of each polymer sample, SEC-LS data were obtained with refractive index detection at 40 °C. The morphology of the blend of PPEAHI and P2VP was studied by atomic force microscope (AFM, Nanoscope IIIa Multimode AFM (Digital Instruments) (operating under tapping mode), field emission scanning electron microscope (FE-SEM, Hitachi S-4700, Japan), and transmission electron microscopy (TEM, JEOL 2010, Japan). For AFM and SEM analysis, samples of the PPEAHI and P2VP blend were prepared on silica substrate by spin-coating (rpm = 2000, t = 30 s). For TEM observation, 5 μL aliquot of polymer blend was deposited on a 400-mesh lacey carbon film coated copper grid, dried in a desiccators, and stained by iodine vapors for 10 h. The polymer blend was platinum-coated for FE-SEM analysis.

Results and Discussion

Polymerization of MAHI. The three monomers MAHI, PAHI, and PEAHI were polymerized using Na-BA as the initiator in THF at −98 °C, and the results of their anionic polymerization are summarized in Table 1. In the polymerization of MAHI, the major part of the product was the

Table 2. Block Copolymerization of *n*-Pentanoxycarbonylaminohexyl Isocyanate (PEAHI) with *n*-Hexyl Isocyanate (HIC) Using Sodium benzanilide (Na-BA) Initiator in Tetrahydrofuran at −98 °C

				$M_n \times 10^{-3}$				
Na-BA[a] (mmol)	1st monomer (mmol)	2nd monomer (mmol)	time (min)	calcd[b]	obsd[c]	M_w/M_n[c]	yield[d] (%)	composition ratio[e]
	PEAHI	HIC						
0.056	6.37	7.39	70/60	45.9	47.9	1.25	97	1:1.18
	HIC	PEAHI						
0.062	6.84	6.32	60/70	40.1	41.2	1.22	98	1.08:1

[a] The concentration of NA-BA is 20% of the actual concentration (ref 9). [b] Number-average molecular weight (M_n) was calculated using the relation {([monomer]/[Na-BA]) × (molecular weight of monomer) + (molecular weight of benzanilide)} × (yield of polymer)/100. [c] M_n and polydispersity index (M_w/M_n) were measured by size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) for the LS response at 90° in tetrahydrofuran at 40 °C. [d] Yield was calculated gravimetrically. [e] The composition ratio of PEAHI to HIC was evaluated by using ^{1}H NMR.

insoluble polymer; the methanol-soluble part contained the unreacted monomer. The methoxy group on the carbamate moiety presumably failed to prevent both chain transfer from the main chain to the side chain and the cross-linking reaction with the other chain. The initiation, propagation, and prevention of the side reaction using the low reactive dual functional initiator Na-BA probably occurred more slowly than the intra- and intermolecular chain transfer reactions[7] during the polymerization of MAHI. The results were very similar to the case of polymerization of MAHI in the presence of additives such as 15C5 and $NaBPh_4$, as previously reported.[11]

Polymerization of PAHI. The results of the polymerization of PAHI, which contains a slightly longer alkyl side chain, showed significant improvement. The conversion of PAHI was ~98%, using Na-BA as the initiator and a reaction time of 60 min beyond the point where trimerization occurred. The calculated molecular weight (MW) was closer to the observed M_n (Table 1) and showed a relatively narrow PDI (1.18−1.22) as compared to the PPAHI (PDI ≤ 1.75) synthesized using the Na-Naph initiator in the presence of additives.[15] These results indicate the effectiveness of Na-BA in preventing backbiting and interchain cross-linking as well as controlled initiation as the length of side chain of the monomer increased.

Polymerization of PEAHI. For the polymerization of PEAHI with longer alkyl side chain, the yield of the polymer was ~100% even at 70 min of reaction time. The results of the polymerization are summarized in Table 1. In the case of the polymerization of HIC using a Na-BA initiator, the observed M_n was about 5 times the calculated M_n since 20% of the initiator takes part in initiation and 80% acts as an additive to protect the living chain end.[9] Using a similar expression, the calculated M_n of PPEAHI was computed in Table 1 (see footnote). The good agreement between the calculated and observed M_n as well as the narrow PDI confirms the successful polymerization of a functional PEAHI monomer such as HIC. Thus, Na-BA is found to be effective in preventing backbiting as well as leading to the controlled initiation of the functional monomer having a longer side chain.

To examine the living nature, the polymerization of PEAHI was carried out using various molar ratios of the monomer to the initiator to yield PPEAHI samples in the M_n range of 10 000−26 000 g/mol. A good linear relationship between [monomer]/[initiator] and MW was observed as shown in Figure 1, which supports the living character of PPEAHI in the anionic polymerization.

Mechanism for Protection of Side Reaction. Sodium benzanilide is a relatively weak nucleophile, leading to a low probability of side reactions and a slow initiation of the polymerization.[9] It also mimics the amidate anion of the polyisocyanate and establishes propagation rates similar to the initiation rate and formation of sodium benzanilide

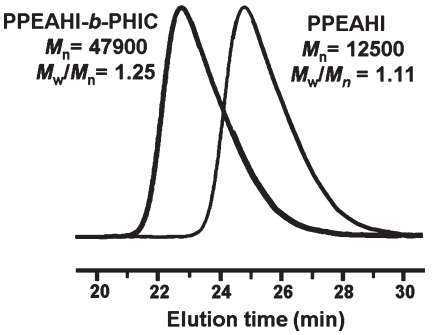


Figure 3. Size-exclusion chromatography, multiangle laser light scattering (SEC-MALLS) (for the LS response at 90°) curves of poly (*n*-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI) and poly(*n*-pentanoxycarbonylaminohexyl isocyanate-*block*-*n*-hexyl isocyanate) (PPEAHI-*b*-PHIC) in tetrahydrofuran at 40 °C. The homopolymerization and block copolymerization was carried out using sodium benzanilide (Na-BA) as an initiator in tetrahydrofuran at −98 °C.

clusters; therefore, it not only protects the growing chain-end for backbiting but also protects the chain transfer reaction. Our approach for dealing with the high reactivity of the carbamate hydrogen moiety or carbonyl group with the amidate anion was to prevent the amidate anions from attacking the active hydrogen of the carbamate or carbonyl group by increasing the steric hindrance around the reactive sites.

For this purpose, the alkyl chain length was increased from methyl to pentyl (Scheme 1 and Figure 2) at the carbamate group. The side reactions were observed during the synthesis of PMAHI, and a relatively elevated PDI (1.18−1.22) was observed for PPAHI. However, PPEAHI with the bulky pentyl group at the carbamate group, which may form kinks during molecular dynamics around the carbamate hydrogen or carbonyl group, increased the steric hindrance (Figure 2) and reduced the possibility of the terminal chain approaching a reactive site. Therefore, PPEAHI was successfully synthesized without side reactions.

Block Copolymerization of PEAHI with HIC. Block copolymerization is the most reliable method to confirm living polymerization. To confirm the living nature in the system under study, block copolymerization of PEAHI and HIC was carried out using Na-BA (Table 2). Poly(*n*-pentanoxycarbonylaminohexyl isocyanate)-*b*-poly(*n*-hexyl isocyanate) (PPEAHI-*b*-PHIC) was successfully synthesized with high yield (M_n = 47 900 g/mol, M_w/M_n = 1.25). The composition ratio of PEAHI to HIC, summarized in Table 2, was found to be 1:1.18 by ^{1}H NMR for the feed ratio of 1:1.16. When the first polymer was changed to PHIC, poly(*n*-hexyl isocyanate)-*b*-poly(*n*-pentanoxycarbonylaminohexyl isocyanate) was also obtained as desired (Table 2). Thus, ^{1}H NMR analysis of the block copolymer was also in good agreement with the feed ratio of the monomers. The chain

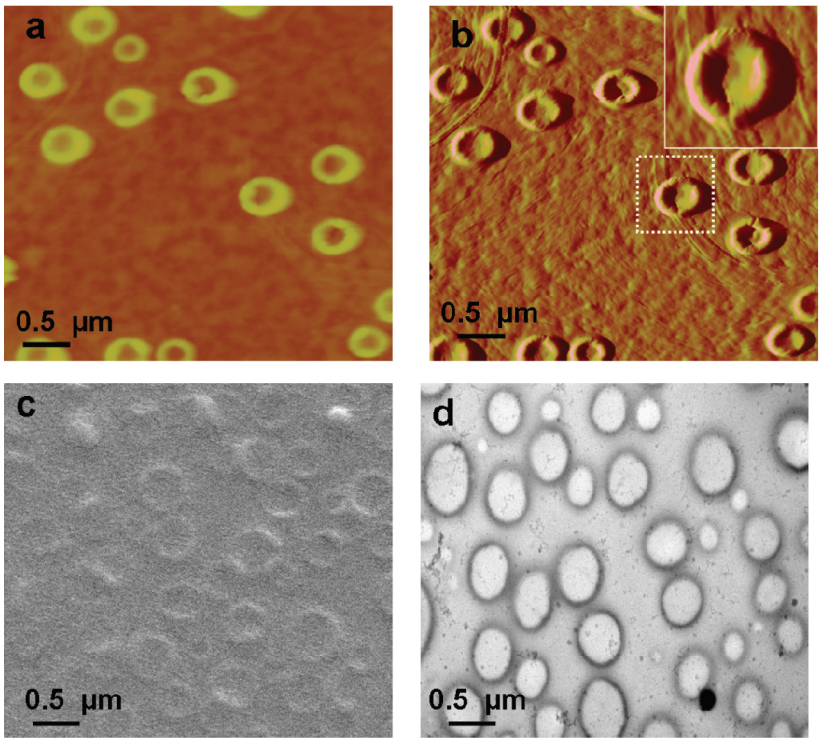


Figure 4. (a) Height and (b) phase contrast atomic force microscope (AFM, tapping mode), (c) field emission scanning electron microscope (FE-SEM), and (d) transmission electron microscope (TEM) image of poly(*n*-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI) and poly(2-vinylpyridine) (P2VP) blend.

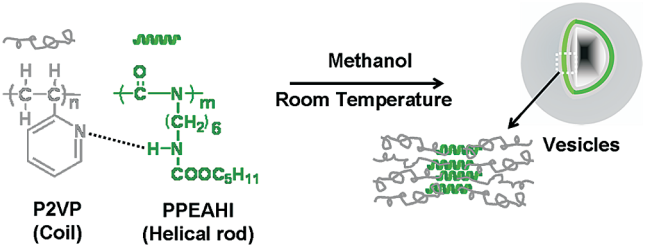
length of each block could be effectively controlled by the monomer/initiator feed ratios, supporting the living character of the polymerization.

The peak in the SEC-LS spectrum was clearly shifted toward high molecular weight without tailing (Figure 3). The absence of the peak corresponding to the first polymer, PPEAHI, indicated the absence of termination or chain transfer reactions.

Blending of PPEAHI and P2VP. Recently, great progress has been made in the use of specific interactions as the main driving forces to construct block copolymer-free strategies to form a variety of assemblies with two- or three-dimensional regularities.[16,17] Nevertheless, because of the flexible and long-chain nature of most synthetic polymers, the specific interactions between them usually occur in an uncontrollable way and, as a result, lead to irregular structures.[18]

The blending ability of the homopolymer PPEAHI (M_n = 19 100 g/mol and PDI = 1.13) and P2VP (M_n = 19 000 g/mol and PDI = 1.07) was studied in methanol (MeOH). MeOH is a good solvent for P2VP, and PPEAHI is insoluble in MeOH. However, mixing of the PPEAHI in P2VP solution in methanol formed a transparent solution. Figure 4a shows the AFM image of the polymer blend of the PPEAHI and P2VP. The PPEAHI has 74 repeating units, which corresponds to a ~15 nm helical rod (the length of the repeating unit is considered to be 0.2 nm),[19] and each repeating unit contains a hexyl side chain with a carbamate, which is capable of forming hydrogen bonds. Considering the total bond length of the side chain, the diameter of PPEAHI is roughly 4 nm.[20] The width of the wall of the aggregates observed from FE-SEM (Figure 4c) and TEM (Figure 4d) is much longer than the length of the PPEAHI rod. Therefore, possibility of the monolayer morphology of the aggregates wall is diminished and provides a background for the bilayer vesicles characteristic of the aggregates. The PPEAHI chains in the intermediate layer may be connected at the top and bottom with P2VP blocks through hydrogen bonding as shown in the schematic representation for the formation of the vesicles (Scheme 2).

Scheme 2. Schematic Representation of the Self-Assembly of the Blend of Poly(*n*-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI) and Poly(2-vinylpyridine) (P2VP)



Conclusions

The effect of an alkyl side chain in preventing chain transfer in the polymerization of three aliphatic isocyanates obtained from the reaction of diisocyanates and aliphatic alcohols was investigated. The anionic polymerization of the carbamate isocyanate bearing the methyl group undergoes cross-linking and results in insoluble polymers. However, steric hindrance at the carbamate group due to a longer alkyl group and the considerable effectiveness of the weak reactive initiator Na-BA in the prevention of backbiting as well as controlled initiation resulted in the formation of PPEAHI polymers with high yields as well as narrow PDI. The active hydrogen of the carbamate linkage was found to be intact, which is confirmed by the complex formation through hydrogen bonding with P2VP and blend formed vesicles in methanol. This procedure can synthesis various polyisocyanates containing a carbamate group which form from the reaction between isocyanate and a hydroxyl group with various bulky side chains, either aliphatic or aromatic, via living anionic polymerization.

Acknowledgment. Financial help from the Program for Integrated Molecular Systems (PIMS) and World Class University (WCU) program is appreciated. The authors also thank the Korean Basic Science Institute (KBSI) for transmission electron microscope (TEM) observation.

References and Notes

(1) (a) Lifson, S.; Felder, C. E.; Green, M. M. *Macromolecules* **1992**, *25*, 4142–4148. (b) Alemán, C.; Green, M. M. *Macromol. Theory Simul.* **2001**, *10*, 100–107.
(2) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727–746.
(3) Cook, R. *Macromolecules* **1987**, *20*, 1961–1964.
(4) Bur, A. J.; Roberts, D. J. *J. Chem. Phys.* **1969**, *51*, 406–420.
(5) Khatri, C. A.; Vaidya, M. M.; Levon, K.; Jha, S. K.; Green, M. M. *Macromolecules* **1995**, *28*, 4719–4728.
(6) (a) Vogl, O.; Jaycox, G. D. *Polymer* **1987**, *28*, 2179–2182. (b) Wulff, G. *Angew. Chem., Int. Ed.* **1989**, *28*, 21–37. (c) Mayer, S.; Zentel, R. *Prog. Polym. Sci.* **2001**, *26*, 1973–2013. (d) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349–372.
(7) Maeda, K.; Matsunaga, M.; Yamada, H.; Okamoto, Y. *Polym. J* **1997**, *29*, 333–338.
(8) (a) Muller, M.; Zentel, R. *Macromolecules* **1994**, *27*, 4404–4406. (b) Muller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609–1617.
(9) Ahn, J.-H.; Shin, Y.-D.; Nath, G. Y.; Park, S.-Y.; Rahman, M. S.; Samal, S.; Lee, J.-S. *J. Am. Chem. Soc.* **2005**, *127*, 4132–4133.
(10) Shin, Y.-D.; Kim, S.-Y.; Ahn, J. -H.; Lee, J.-S. *Macromolecules* **2001**, *34*, 2408–2410.
(11) Lee, J.-S.; Ryu, S.-W. *Macromolecules* **1999**, *32*, 2085–2087.
(12) Rahman, M. S.; Samal, S.; Lee, J.-S. *Macromolecules* **2007**, *40*, 9279–9283.
(13) Shin, Y.-D.; Ahn, J.-H.; Lee, J.-S. *Polymers* **2001**, *42*, 7979–7985.
(14) Shin, Y.-D.; Ahn, J.-H.; Lee, J.-S. *Macromol. Rapid Commun.* **2001**, *22*, 1041–1046.
(15) Shin, Y.-D.; Rahman, M. S.; Samal, S.; Lee, J.-S. *Macromol. Symp.* **2006**, *240*, 151–156.
(16) (a) Zemb, T.; Dubois, M.; Deme, B.; Gulik-Krzywicki, T. *Science* **1999**, *283*, 816–819. (b) Cui, H. G.; Chen, Z. Y.; Zhong, S.; Wooley, K. L.; Pochan, D. J. *Science* **2007**, *317*, 647–650. (c) Jung, H. T.; Lee, S. Y.; Kaler, E. W.; Coldren, B.; Zasadzinski, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15318–15322. (d) Waggoner, T. A.; Last, J. A.; Kotula, P. G.; Sasaki, D. Y. *J. Am. Chem. Soc.* **2001**, *123*, 496–497. (e) Kim, J. K.; Lee, J. I.; Lee, D. H. *Macromol. Res.* **2008**, *16*, 267–292.
(17) (a) Shimizu, L. S. *Polym. Int.* **2007**, *56*, 444. (b) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9–21.
(18) Chen, D. Y.; Jiang, M. *Acc. Chem. Res.* **2005**, *38*, 494–502.
(19) (a) Wu, J.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **2002**, *35*, 1791–1796. (b) Fetters, L. J.; Yu, H. *Macromolecules* **1971**, *4*, 385–389.
(20) Ohkita, M.; Higuchi, M.; Kawaguchi, M. *J. Colloid Interface Sci.* **2005**, *292*, 300–303.