Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

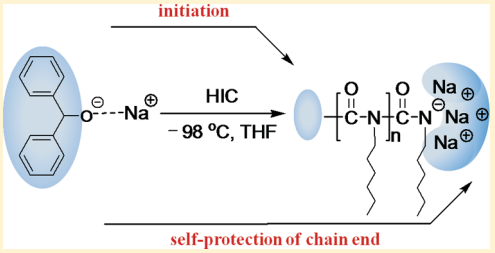
Effects of Different Reactive Oxyanionic Initiators on the Anionic Polymerizaition of *n*-Hexyl Isocyanate

Joonkeun Min, Priyank N. Shah, Jun-Hwan Ahn, and Jae-Suk Lee*

Department of Nanobio Materials and Electronics and School of Material Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, Korea

Supporting Information

ABSTRACT: Poly(*n*-hexyl isocyanate) was synthesized by anionic polymerization using various oxy-initiators, including sodium phenoxide (Na-PO), sodium benzhydroxide (Na-BH), and sodium methoxyphenylethoxide (Na-MPE). We optimized polymerization conditions. To confirm the living natures of the polymerization, we carried out various polymerizations changing mole ratio between monomers and initiators and a postpolymerization by sequential monomer addition method. Our results indicated that the anionic polymerization of *n*-hexyl isocyanate was not controlled using Na-PO and Na-MPE. However, Na-BH as an initiator is favorable for the living anionic polymerization of *n*-hexyl isocyanate because it has a dual function in the initiation and in the efficient prevetion of trimerization by reducing the reactivity at the growth chain ends. Polymers were thus synthesized with predictable molecular weights (MW), narrow molecular weight distributions (MWD), and high yields.



INTRODUCTION

Polyisocyanates have a stiff and helical structure[1] that result from the partially double-bonded nature of the amide backbone in their main chain. Because of this unique structure, polyisocyanates and their block copolymers are of considerable interest in various fields and emerging technologies, including optical switches, chiral recognition, liquid crystals, and nanomaterials.[2] Of particular interest are rod−coil block copolymers containing polyisocyanate, in which the rodlike liquid crystalline character of polyisocyanates leads to a unique self-assembly.[3] To apply polyisocyanates and block copolymers in the above-mentioned fields, a living method to synthesize well-controlled polymers needs to be developed.

Synthesis of polyisocyanates is usually carried out by anionic polymerization. However, this polymerization method is difficult to control as the propagating anionic chain ends can attack the carbonyl carbons due to their partial positive charge and form a trimer.[4] Many groups have attempted to solve the trimerization problem. For instance, different cosolvent systems,[5] diverse initiators,[5,6] and ligand systems[7] have all been studied. As a result of these studies, yield of the polymer could be increased and trimer formation could be suppressed. However, all the characteristics that are important for a living polymerization could not be optimized at the same time.

Passing only 30 years after the first synthesis of polyisocyanate,[4] the controlled polymerization of iscyanate was possible through coordination polymerization. Novak and co-workers have reported the living coordination polymerization of alkyl isocyanates using organo-titanium(IV) compounds as catalysts,[8] which form stable bonds between chain ends and the catalyst to prevent side reactions.

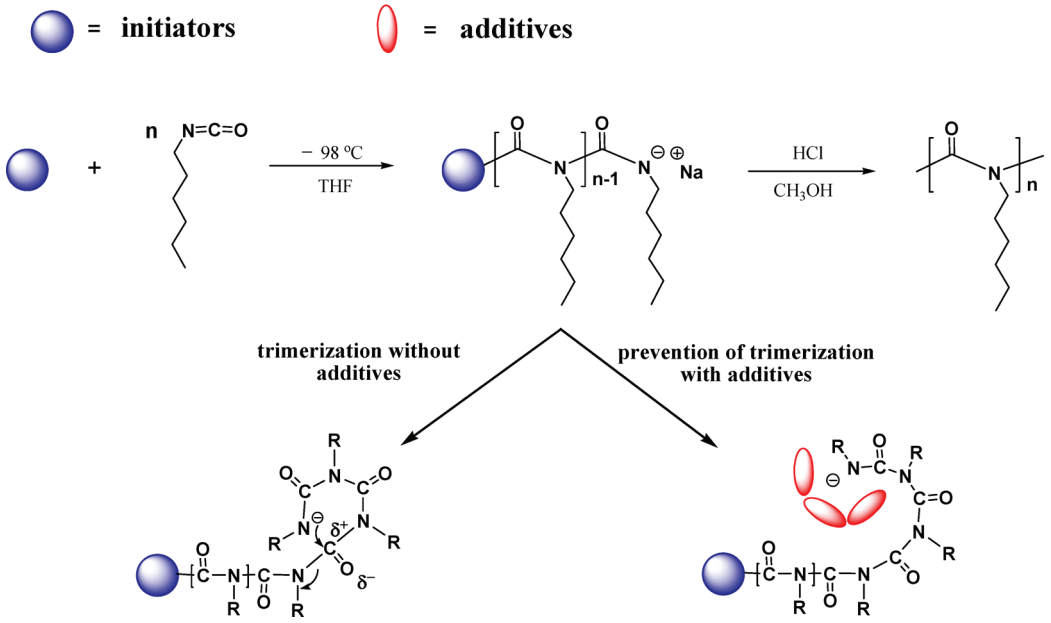
The synthesis of living polyisocyanate by anionic polymerization was impossible only few years ago. We have successfully synthesized well-controlled polyisocyanates by living anionic polymeriztion using additives, such as 15-crown-5[9] and sodium tetraphenylborate (Na-BPh_4)[10,11] (Scheme 1).

Recently, an initiator of low reactivity forming aggregators, sodium benzanilide (Na-BA),[12] was reported in the living anionic polymerization of *n*-hexyl isocyanates. Na-BA structure is a same amidate anion like propagating polyisocyanate anion. By structural features, the reactivity of the amidate anion on Na-BA is reduced due to resonance effects and sharing electrons in their aggregators.[12] When *n*-hexyl isocyanate (HIC) is added to the aggregated Na-BA initiator solution, a single molecule of the aggregated Na-BA solution initiates a monomer and propagation proceeds efficiently; the amidate anion of the growth chain ends with the remaining Na-BA aggregated molecules is stabilized. As a result, Na-BA plays dual roles in the controlled initiation and chain-end protection. The addition of an additive is thus not required for the controlled polymerization. Poly(hexyl isocyanate) could be obtained in quantitative yields with controlled MW and narrow MWD. The Lee group discovered that low reactive initiators are more suitable for a living anionic polymerization of isocyanate than highly reactive initiators, such as sodium naphthalenide (Na-Naph)[9] and sodium diphenylmethylene (Na-DPM)[13] (Figure S1).

In this work, we introduced low reactive carboxy anionic initiators, less reactive than C^- (carbaion) or N^- (amide anion), to evaluate the suitability of oxy-initiators based on their reactivity.

Received: February 22, 2011
Revised: April 4, 2011
Published: April 14, 2011

Scheme 1. General Anionic Polymerization of HIC



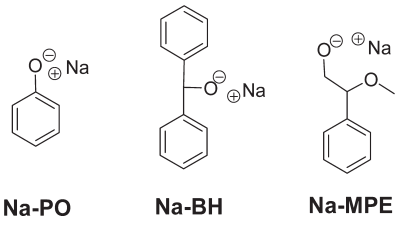


Figure 1. Various carboxy-initiators, namely, sodium phenoxide (Na-PO), sodium benzhydroxide (Na-BH), and sodium methoxyphenylethoxide (Na-MPE).

The reactivity of carboxy anionic initiators are generally as follows by steric hindrance: aromatic carboxy anion < tertiary carboxy anion < secondary carboxy anion < primary carboxy anion.[14,15] To identify trends among carboxy-initiators for the anionic polymerization of *n*-hexyl isocyanate (HIC), we decided to use three types of carboxy-initiators: (a) primary carboxy anion (e.g., sodium methoxyphenylethoxide), (b) secondary carboxyanion (e.g., sodium benzhydroxide), and (c) aromatic carboxy anion (e.g., sodium phenoxide)[14,15] (Figure 1).

EXPERIMENTAL DETAILS

Materials. *n*-Hexyl isocyanate (Aldrich, 97%) was dried over calcium hydride (CaH_2) and distilled under vacuum. Tetrahydrofuran (Fisher Scientific, GR grade) was distilled under N_2 after refluxing with sodium for 5 h and then distilled again under vacuum from a sodium naphthalenide solution. Sodium (Na, Aldrich, 99%), calcium hydride (Junsei, 95%), naphthalene (Naph, Aldrich, 99%), phenol (PO, Aldrich, 99%), (*R*)-(−)-2-methoxy-2-phenylethanol (MPE, Aldrich, 99.5%), and benzhydrol (BH, Aldrich, 97%) were used without further purification. The glassware (Iwaki Glass Co. Pyrex) used for the glass apparatus was rinsed with tap water and with triply distilled water before being oven-dried. Freshly distilled THF was stirred with a Na-Naph solution under high-vacuum conditions with repeated degassing and was distilled again prior to use.

Anionic Polymerization of HIC Using Oxy-initiators. The polymerizations using oxy-initiators, Na-PO, Na-MPE, or Na-BH, were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical polymerization procedure, Na-BH solution (40.0 mg, 0.195 mmol) was transferred into the reaction flask through the break-seal, and the solution temperature was equilibrated to −98 °C. The polymerization was then started by adding a solution of HIC (1.20 g, 9.45 mmol) in THF (10 mL) to the initiator solution. At this point, the viscosity of the solution increased. After completion of the reaction (10 min), a 20-fold excess of HCl in methanol was added. The polymer was precipitated in methanol and was then filtered and dried *in vacuo*. The methanol-soluble portion was analyzed quantitatively by weighing the residue after evaporation of methanol and by using ^{1}H NMR to determine whether there were unreacted monomers, trimers, or both. Polymerization with Na-PO and Na-MPE was the same as the above procedure. PHIC: ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.9 (3H, CH_3), 1.0−2.0 (8H, $(CH_2)_4$), 3.7 (2H, N−(CH_2)−). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 14.5 (CH_3), 22.5 (CH_2), 26.2 (CH_2), 28.5 (CH_2), 31.5 (CH_2), 48.6 (N−CH_2−), 156.8 (*C*═O). FT-IR (KBr, cm^{-1}): 3441 (−NH), 2959, 2932, 2860 (CH_2), 1700 (C═O), 1349/1297 (disubstituted amide), 1227, 1175, 1092, 785, 728 (CH_2).

Anionic Polymerization of HIC Using Oxy-initiators with Na-BPh_4. Polymerizations using oxy-initiators, Na-PO or Na-MPE, in the presence of an additive (Na-BPh_4) were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical polymerization procedure, Na-PO solution (9.0 mg, 0.078 mmol) and Na-BPh_4 (0.150 g, 0.437 mmol) were transferred into the reaction flask through the break-seal. The solution was mixed for 5 min, and then the solution temperature was equilibrated to −98 °C in a frozen methanol bath. The polymerization was started by adding the HIC (0.90 g, 6.71 mmol) in THF (10 mL) to the mixed solution. At this point, the viscosity of the reaction solution increased. After completion of reaction (40 min), the polymerization was terminated by adding a 20-fold excess of HCl in methanol (Scheme 2). Polymer was precipitated in methanol, then filtered, and dried *in vacuo*. The methanol-soluble portion was

dx.doi.org/10.1021/ma200414f |*Macromolecules* 2011, 44, 3211–3216

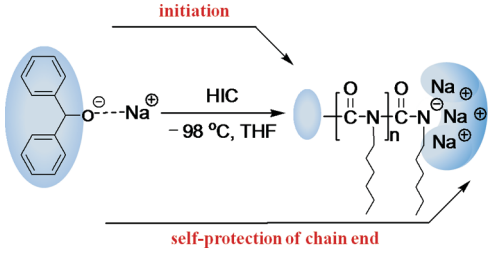
analyzed quantitatively by weighing the residue after evaporation of methanol and by using ^{1}H NMR to determine whether there were unreacted monomers, trimers, or both. Polymerization with Na-MPE and Na-BPh$_4$ was the same as the previous procedure.

Characterization. ^{1}H and ^{13}C NMR spectra were measured by a JEOL JNM-LA300WB using $CDCl_3$ as the solvent. ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm, and ^{13}C NMR chemical shifts were referenced to deuterated chloroform at 77.0 ppm. FT-IR spectra were obtained using KBr pellets and a Perkin-Elmer System 2000. The molecular weights of the polymers were determined from the response of a multiangle laser light scattering detector system (MALLS), SEC-LS (OPTI LAB-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 of 50, 100, 500, and 1000 Å, respectively). THF with triethylamine (for the prevention of adsorption of hydrophilic polymer on the column) was used as the mobile phase at a flow rate of 1.0 mL/min. dn/dc values (0.090) for the polymers in THF at 40 °C were measured for five different concentrations, and then SEC-MALLS data were gained with refractive index detection at 40 °C.

RESULTS AND DISCUSSION

Anionic Polymerization of HIC in the Presence of Na-PO. The results showed that some unreacted monomers remain before 5 min when Na-PO was used as an initiator. Trimerization occurred during propagation at 10 min, including the coexistence of monomers and trimers. As the reaction time was increased to over 10 min, the yield of PHIC decreased and the formation of trimers rose (Table 1, runs 1−3). The control of polymerization with only Na-PO as an initiator was unsuccessful, even though the reactivity of Na-PO is similar to that of Na-BA.[14] Contrary to Na-BA, molecules of Na-PO did not reduce reactivity of the chain end, so we can assume that the Na-PO molecules were not aggregated at the end of chains. Therefore, the relationship between [monomer]/[initiator] and molecular weight is not matched, and the molecular weight distribution (MWD) was broad.

Scheme 2. Dual Function of Na-BH: Initiation and Self-Protection System of the Living Chain Ends



Sodium phenoxide (Na-PO) crystallizes the four-membered ring in the solvent-free. In addition, Na-PO crystallizes in THF with the formation of a Na_6OPh_6 core, consisting of two face-fused heterocubes.[16] When isocyanate monomer solution is added to this initiator solution, a single Na-PO among crystalline structures is initiate monomers. After initiation, oxo ligands (−PO) prefer interacting with each other to interacting with amidate anion. Thus, ∼25% of Na-PO molecules can initiate monomers, and the others remain self-aggregated crystalline forms (Table 1, runs 1−3).

We measured the initiation efficiency by model reaction which is conducted by reaction with acid chloride and Na-PO to clarify aggregation effects. Product yield was ∼95% (Supporting Information). In addition, one more polymerization carried out with mixed initiators, Na-Naph and Na-PO (Table S1). Reactivity of Na-Naph is stronger than that of Na-PO. In this case, Na-Naph played an initiator role and Na-PO did not play any role. These results suggest that Na-PO molecules may prefer forming an aggregate each other by structural feature rather than to initiating monomer during propagation.

To control polymerization, we used an additive, sodium tetraphenylborate (Na-BPh$_4$), which is a common ion salt with a bulky counteranion ($^-$BPh$_4$), and HIC was polymerized with Na-PO and various Na-BPh$_4$ portion as well as by changing reaction time (Table 1, runs 4−7). However, addition of Na-BPh$_4$ could not also prevent trimerization. Na-BPh$_4$ could interact with Na-PO molecules in solution as initiation efficiency changes (Table 2). As a result, Na-PO did not act additive effect and did not control living anionic polymerization of *n*-hexyl isocyanate using Na-PO with Na-BPh$_4$.

Table 1. Anionic Polymerization of *n*-Hexyl Isocyanate (HIC) Using Sodium Phenoxide (Na-PO) and Sodium Methoxyphenylethoxide (Na-MPE) in Tetrahydrofuran at −98 °C

						$M_n \times 10^{-3}$			
run	Na-PO (mmol)	Na-MPE (mmol)	Na-BPh$_4$ (mmol)	HIC (mmol)	time (min)	calcd[a]	obsd[b]	PDI[b]	yield (%)
1	0.103			4.87	5	5.25	20.1	1.15	86(14)[c]
2	0.135			4.23	10	3.50	13.4	1.24	86(14)[c,d]
3	0.160			7.15	20	4.50	15.0	1.51	78(22)[d]
4	0.141		0.543	6.53	30	2.92	7.10	1.19	49(51)[c]
5	0.078		0.437	6.71	40	8.81	23.3	1.13	80(20)[c,d]
6	0.074		0.667	4.51	50	6.19	18.0	1.07	79(21)[c,d]
7	0.069		0.630	6.03	60	6.72	17.3	1.08	60(40)[d]
8		0.034		5.34	5	17.5	19.0	1.23	87(13)[c]
9		0.038		7.53	10	25.0	24.8	1.20	99
10		0.032		6.04	20	19.5	25.0	1.21	81(19)[d]
11		0.033	0.106	4.02	20	14.7	10.8	1.20	94(6)[c]
12		0.034	0.088	3.42	30	12.5	12.3	1.10	97
13		0.034	0.107	6.52	40	24.0	24.5	1.10	98
14		0.048	0.091	5.07	60	12.3	11.7	1.12	91(9)[d]

[a] M_n is calculated using the relation {([HIC]/[Na-PO, Na-MPE]) × molecular weight of HIC + molecular weight of H-PO, H-MPE} × yield of polymer/100. [b] M_n and PDI were measured by SEC-MALLS (size exclusion chromatography − multiangle laser light scattering) in THF at 40 °C. [c] The amount of unreacted HIC is presented in parentheses. [d] The yield of trimer is presented in parentheses.

dx.doi.org/10.1021/ma200414f |*Macromolecules* 2011, 44, 3211–3216

Table 2. Efficiency of Initiators, Sodium Phenoxide (Na-PO), Sodium Methoxyphenylethoxide (Na-MPE), and Sodium Benzhydroxide (Na-BH)[a]

	Na-PO	Na-PO/ Na-BPh_4	Na-MPE	Na-MPE/ Na-BPh_4	Na-BH
efficiency (%)	25[b]	40[b]	100	100	40

[a] Efficiency was estimated approximately by calculating calcd M_n/obsd $M_n \times 100$. [b] Efficiency of an initiator is not correct. Trimerization was not prevented during propagation due to heterogeneous solution. Therefore, this polymerization is not controlled quantitatively, and efficiency of an initiator cannot be calculated correctly.

Anionic Polymerization of HIC in the Presence of Na-MPE. After the reaction time was increased from 5 to 10 min, the yield of PHIC increased when Na-MPE, the most reactive of the three oxy-initiators, was used.[14,15] The yield was almost quantitative after10 min of reaction, and a relatively broad MWD, 1.20, was obtained (Table 1, runs 8−10). Longer reactions resulted in trimerization, and the polymer yield was found to be lower.

These results indicated that the growing active chain ends reacted with the monomer as long as the monomer existed in the reaction rather than attacking the carbonyl carbon in the backbone. The yield is 99% at optimized condition without trimers and monomers. However, MWD is broad because of unbalanced reaction rate between initiation and propagation; propagation rate might be equal to or slower than initiation rate. Partially, it shows the possibility for anionic polymerization of HIC.[9−11]

To solve this unbalance between initiation rate and propagation rate, 3 times Na-BPh_4 as high as Na-MPE was used as an additive (Table 1, runs 11−14). As expected, the PHIC was quantitatively synthesized for 30−40 min with narrow MWD. Amidate anion on growth end could be interacted with ion pair of Na-BPh_4.This is to say that Na-BPh_4 molecules could be assembled at the chain end, and these made aggregators. The aggregators could reduce reactivity of amidate anion of growing polyisocyanate, and bulky structures of themselves could help prevention of the trimerization by steric hindrance effects.

Living Anionic Polymerization of HIC in the Presence of Na-BH. PHIC was synthesized using Na-BH and by increasing the reaction times. A maximum yield of ∼100% was obtained. Trimerization was suppressed in 10−12 min (Table 3, runs 1−7). At longer reaction times, the yield of the polymer decreased slowly and formation of trimers was observed. From results, PHIC could be obtained in quantitative yields and an effective control over the molecular weight and narrow MWD could be achieved. The polymerization of HIC was also carried out by changing the molar ratios of the monomer to the initiator to examine the living nature of the Na-BH initiation system (8000−40 000 g mol^{-1}). The results show a good consensus between observed MW and calculated MW by changing the ratio between monomer and initiator (Figure 2).

The value for the calculated molecular weight is relatively different from the observed value; the observed molecular weight is 2.5 times higher than the calculated one. This means 40% of initiator molecules can initiate HIC. Since the controlled anionic polymerization of HIC without additives is practically impossible, it can be assumed that some parts of the initiator molecules act as additives to stabilize the anion of the growth chain ends by self-assembly. To confirm efficiency of Na-BH more clearly, we determined the number of active BH^- anions in the Na-BH initiator by a model reaction of Na-BH with acid chloride, which leads to a yield of ∼95%. Most of the initiator molecules are available to initiate HIC

Table 3. Anionic Polymerization of *n*-Hexyl Isocyanate (HIC) Using Sodium Benzhydroxide (Na-BH) in Tetrahydrofuran at −98 °C

				$M_n \times 10^{-3}$			
run	Na-BH (mmol)	HIC (mmol)	time (min)	calcd[a]	obsd[b]	PDI[b]	yield (%)
1	0.207	9.74	5	5.5	14.3	1.07	89(11)[c]
2	0.194	4.29	10	2.9	8.4	1.11	96
3	0.195	9.45	10	6.2	14.6	1.04	97
4	0.181	14.5	10	10.2	26.6	1.10	98
5	0.205	27.0	10	16.4	38.2	1.14	97
6	0.197	8.67	12	5.6	13.9	1.17	97
7	0.213	9.84	15	5.7	16.8	1.10	93(7)[d]
8	0.191	6.65	10	4.4	11.1	1.07	98
9[e]	0.191	$6.65^{1st}/5.36^{2nd}$	10/10	7.7	20.0	1.11	96

[a] M_n is calculated using the relation {([HIC]/[Na-BH]) × molecular weight of HIC + molecular weight of H-BH} × yield of polymer/100. [b] M_n and PDI were measured by SEC-MALLS (size exclusion chromatography − multiangle laser light scattering) in THF at 40 °C. [c] The amount of unreacted HIC is presented in parentheses. [d] The yield of trimer is presented in parentheses. [e] Postpolymerization by sequential monomer addition method conducted to show molecular weight shift for confirming living characters (Figure 3).

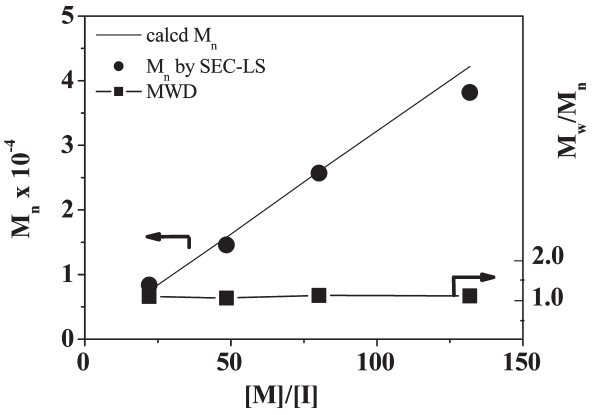


Figure 2. Number-average molecular weight (M_n) vs the molar ratio of *n*-hexyl isocyanate (HIC) to sodium benzhydroxide (Na-BH) initiator for anionic polymerization in tetrahydrofuran at −98 °C.

monomers. From the result, Na-BH can be expected to play two roles, initiation and prevention of trimerization as an additive.

Polymerization of HIC was carried out with a mixture of Na-Naph as an initiator and Na-BH (5-fold excess) to better assess the additive effects of Na-BH like Na-BA.[12] In general, backbiting reaction occurs during the polymerization of isocyanate using Na-Naph in the absence of additional additives. If Na-BH could not play an additive role, trimerization occurs during polymerization. However, there is a quite good accordance between the observed and calculated molecular weights based on Na-Naph as an initiator and no trimer (Table S1). In addition, the ^1H NMR spectra of the PHIC do not show the aromatic proton peaks that were observed in the PHIC obtained using Na-BH as an initiator. According to the result, Na-BH can act as an additive by self-assembled at growth chain ends.

Additionally, Na-BH molecules form a hexagonal crystalline structure in free solvent. By, structural effects, Na-BH molecules can be expected that they make a certain bulky self-aggregated

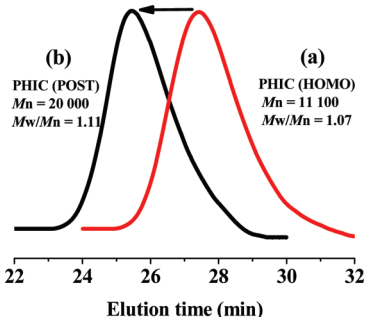


Figure 3. SEC curves of poly(*n*-hexyl isocyanate) obtained from (a) homopolymerization and (b) postpolymerization by sequential monomer addition method using sodium benzhydroxide (Na-BH).

complex in THF solvent, cyclobutane-type structure.[18] Unstable aggregators among Na-BH aggregators like butyllithium clusters[17] may initiate monomers, and then other Na-BH molecules can interact with amidate anion at growth chain ends. Reactivity of amidate anion was reduced, and trimerization was effectively prevented.

In other words, after HIC is introduced to the initiator solution, it approaches the Na-BH aggregators in the polymerization procedure. A single Na-BH molecule in an aggregator is used for the initiation, and the other molecules aggregated at the end of the chains to prevent trimerization (Scheme 2 and Scheme S2). As a result, these aggregators can help to stabilize the end of the chains during propagation. Therefore, it makes a good balance between the propagation and initiation rates. This results in a yield of ~100% without addition of any additives, and it was close correspondence between the calculated molecular weight by using about 40 ± 5% of the initiator concentration and the observed one (Table 3).

To confirm the living nature of the Na-BH initiation system, we carried out a postpolymerization by sequential HIC addition. Poly(*n*-hexyl isocyanate)-*b*-poly(*n*-hexyl isocyanate) was nearly quantitatively produced with a narrow MWD (M_n = 20 000, M_w/M_n = 1.11) with ~100% yield. However, sampling of the first polymer was impossible. The trimerization of the first monomer occurred in the receiver during the propagation of the second monomer because the polymerization was progressed in sealed vacuum conditions. A model reaction was then conducted to show shifts toward high molecular weight in the SEC-LS spectrum. The homopolymerization and the postpolymerization by sequential monomer addition method were conducted in different baths using exactly the same amount of initiators and monomers (Table 3, runs 8 and 9); the SEC-LS spectrum curves were obtained and compared (Figure 3).

CONCLUSIONS

On the basis of previous studies on Na-BA, we found initiator of low reactivity is suitable for the living anionic polymerization of isocyanate. To study the effects of different oxy-initiators of low reactivity on the polymerization, we prepared aromatic and aliphatic oxy-initiators with the following reactivity: Na-PO < Na-BH < Na-MPE. Synthesis of poly(*n*-hexyl isocyanate) by anionic polymerization could not be controlled when Na-PO was used as an initiator, even though Na-PO is the most similar to Na-BA in terms of reactivity. It does not prevent trimerization during the propagation because Na-PO cannot stabilize growing amidate anions at the end of chains. Na-MPE proved to be effective for the polymerization. However, it did not lead to a good control of the anionic polymerization because Na-MPE could not be self-assembled to reduce propagation rate and prevent trimerization. The reaction rate between initiation and propagation was unbalanced, and thus the MWD was a little broad. Na-BH prevents trimerization as it reduces the reactivity of the living chain by being self-aggregated easily at the growth chain ends. This leads to the well-controlled living polymerization of isocyanate without additional additives being necessary. The role of Na-BH as an additive was proved by determining as an initiation efficiency and polymerization of HIC using the co-initiator system. The main factor determining the possibility of a living anionic polymerization of HIC is the formation of aggregators and self-protection at growth chain ends, as seen with Na-BH, to reduce the propagation rate, even though reactivity of initiators has been also important.

ASSOCIATED CONTENT

Supporting Information. Detailed preparation process of initiators; initiator structures; detailed polymerization mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel +82-62-970-2306, Fax +82-62-970-2304, e-mail jslee@gist.ac.kr.

ACKNOWLEDGMENT

This work was supported by the Program for Integrated Molecular System (PIMS) and the World Class University (WCU) program (Project No. R31-20008-000-10026-0).

REFERENCES

(1) (a) Wulff, G. *Angew. Chem., Int. Ed.* **1989**, *28*, 21–37. (b) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727–746. (c) Yashima, E.; Katsuhiro, M.; Hiroki, I.; Yoshio, F.; Kanji, N. *Chem. Rev.* **2009**, *109*, 6102–6211.

(2) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866. (b) Kim, J.-H.; Rahman, M. S.; Lee, J.-S.; Park, J.-W. *J. Am. Chem. Soc.* **2007**, *129*, 7756–7757. (c) Maeda, K.; Okamoto, Y. *Macromolecules* **1998**, *31*, 1046–1052. (d) Stig, A. *Chirality* **2003**, *15*, 409–422. (e) Rahman, M. S.; Kim, H.-D. *Macromol. Res.* **2006**, *14*, 634–639. (f) Kim, S.-H.; Kim, B.-K.; Lim, H. *Macromol. Res.* **2008**, *16*, 467–472. (g) Mayer, S.; Zentel, R. *Prog. Polym. Sci.* **2001**, *26*, 1973–2013. (h) Han, S. H.; Wu, J. W.; Kang, J.-W.; Shin, Y.-D.; Lee, J.-S.; Kim, J.-J. *J. Opt. Soc. Am. B* **2001**, *18*, 298–301. (i) Nath, G. Y.; Samal, S.; Park, S.-Y.; Murthy, C. N.; Lee, J.-S. *Macromolecules* **2006**, *39*, 5965–5966.

(3) (a) Chen, J. T.; Thomas, E. L.; Ober, C. K.; Hwang, S. S. *Macromolecules* **1995**, *28*, 1688–1697. (b) Chen, J. T.; Thomas, E. L.; Ober, C. K.; Mao, G. *Science* **1996**, *273*, 343–346. (c) Park, J.-W.; Thomas, E. L. *J. Am. Chem. Soc.* **2002**, *124*, 514–515. (d) Park, J.-W.; Thomas, E. L. *Macromolecules* **2006**, *39*, 4650–4653. (e) Rahman, M. S.; Changez, M.; Min, J.; Shah, P. N.; Samal, S.; Lee, J.-S. *Polymer* **2011**10.1016/j.polymer.2011.03.011.

(4) (a) Shashoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3156–3156. (b) Shashoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866–873.

(5) (a) Okamoto, Y.; Nagamura, Y.; Hatada, K.; Khatri, C.; Green, M. M. *Macromolecules* **1992**, *25*, 5536–5538. (b) Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 309–315. (c) Maeda, K.; Okamoto, Y. *Macromolecules* **1999**, *32*, 974–980.

(6) (a) Fukuwatari, N.; Sugimoto, H.; Inoue, S. *Macromol. Rapid Commun.* **1996**, *17*, 1–7. (b) Ikeda, T.; Sugimoto, H.; Inoue, S. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A* (34), 1907–1920.

(7) (a) Wang, J.; Nomura, R.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 869–872. (b) Wang, J.; Nomura, R.; Endo, T. *Macromolecules* **1996**, *29*, 2707–2708.

(8) (a) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 5065–5066. (b) Petten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436–439. (c) Hoff, S. M.; Novak, B. M. *Macromolecules* **1993**, *26*, 4067–4069. (d) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906–1916. (e) Patten, T. E.; Novak, B. M. *Macromolecules* **1996**, *29*, 5882–5892. (f) Goodson, S. H.; Novak, B. M. *Macromolecules* **2001**, *34*, 3849–3855.

(9) Lee, J.-S.; Ryu, S.-W. *Macromolecules* **1999**, *32*, 2085–2087.

(10) (a) Shin, Y.-D.; Kim, S.-Y.; Ahn, J.-H.; Lee, J.-S. *Macromolecules* **2001**, *34*, 2408–2410. (b) Ahn, J.-H.; Lee, J.-S. *Macromol. Rapid Commun.* **2003**, *24*, 571–575. (c) Ahn, J.-H.; Lee, C.-H.; Shin, Y.-D.; Lee, J.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 933–940.

(11) Ahn, J.-H.; Shin, Y.-D.; Kim, S.-Y.; Lee, J.-S. *Polymer* **2003**, *44*, 3847–3854.

(12) 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.

(13) Shin, Y.-D.; Ahn, J.-H.; Lee, J.-S. *Macromol. Rapid Commun.* **2001**, *22*, 1041–1045.

(14) Bordwell, F. G.; Ji, G. Z. *J. Am. Chem. Soc.* **1991**, *113*, 8398–8401.

(15) Andrieux, C. P.; Gamby, J.; Hapiot, P.; Saveant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 10119–10124.

(16) Kunert, M.; Dinjus, E.; Nauck, M.; Sieler, J. *Chem. Ber.* **2006**, *130*, 1461–1465.

(17) (a) Nichols, M. A.; Williard, P. C. *J. Am. Chem. Soc.* **1993**, *115*, 1568–1572. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principle and practical Application*; Marcel Dekker: New York, 1996; p 132.

(18) Geier, J.; Ruegger, H.; Grutzmacher, H. *Dalton Trans.* **2006**, 129–133.