Enolate Anionic Initiator, Sodium Deoxybenzoin, for Leading Living Natures by Formation of Aggregators at the Growth Chain ends

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ABSTRACT: The living anionic polymerization of *n*-hexyl isocyanate (HIC) using a newly developed initiator forming metal–enolate complex, sodium deoxybenzoin (Na-DB), is reported. For the polymerization of HIC, Na-DB serves the dual functions of providing controlled fast initiation and efficiently protecting the living chain ends. The use of Na-DB has resulted in quantitative polymer yields (~100%), effective control of the polymer's molecular weights, and low polydispersity index. To examine the living nature of poly(*n*-hexyl isocyanate) (PHIC), block copolymerization of HIC with another isocyanate monomer, 3-(triethoxysilyl)propyl isocyanate (TESPI), was carried out. The resulting block copolymer, poly(*n*-hexyl isocyanate)-*b*-poly(3-(triethoxysilyl)propyl isocyanate) (PHIC-*b*-PTESPI) was synthesized successfully via living anionic polymerization using Na-DB with quantitative yield and controlled molecular weight. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1742–1748

KEYWORDS: anionic polymerization; block copolymers; dual functional initiator; living polymerization; polyisocyanate; sodium deoxybenzoin

INTRODUCTION Polyisocyanates and their block copolymers are of considerable interest due to their structural properties being helical conformation caused by their stiff amide backbones and steric constraints.[1] Because of their unique properties generated from their structural characteristics,[2] polyisocyanates have been used in various materials, including optical switches, liquid crystals, degradable materials, composites, chiral recognition substrates, and templates for open-pored inorganic nanoparticles.[3] The synthesis of well-controlled polyisocyanate has been a major challenge for many researchers. The living polymerization of isocyanate is difficult because trimer formation can cause depolymerization. Numerous strategies to avoid depolymerization during the polymerization of isocyanate have been investigated.[4–13]

Shashoua groups were the first to report the anionic polymerization of isocyanates, using *N*,*N*-dimethylformamide and sodium cyanide (NaCN) as the solvent and the initiator, respectively.[4] Initiators such as NaCN, metal alkyl derivatives, and metal naphthalenide are typical used for anionic polymerization of isocyanates.[4,5] The polymerizations reactions using such initiators produced polyisocyanates with low polydispersity indices (PDIs) and a disparity between the calculated and observed molecular weights. These problems resulted from the formation of cyclic trimer by back-biting.

Okamoto groups carried out the polymerization of aromatic isocyanates using lithium amides and lithium alkoxides,[6] and Fukuwatari groups used lanthanoid isopropoxide as the initiator for the anionic polymerization of isocyanates.[7] A relatively high yield of the polyisocyanates could be obtained using lanthanoid isopropoxide rather than NaCN as initiators. The above cases, however, the polymerization of isocyanates did not show living natures due to depolymerization by trimerization even though the development of polymerization yield.

Introduction of several additives has been reported to prevent depolymerization. Endo groups used samarium iodide as an additive for the polymerization of isocyanates.[8] The use of samarium iodide drastically suppressed trimer formation during polymerization with alkyllithiums in tetrahydrofuran (THF) at −78 °C, resulting in polymer with a higher molecular weight. Because balance between initiation rate and propagation rate was not matched, the PDI was relatively high, in the range of 2.4–3.5. The samarium iodide was not considered a satisfactory additive because it did not react effectively with the alkyl lithium initiator.

We have reported the successful synthesis of polyisocyanates via living anionic polymerization with sodium naphthalenide (Na-Naph) as an initiator with several additives, such as 15-crown-5[9] and sodium tetraphenylborate (Na-Ph_4B).[10,11] These additives made metal complex at the growing chain ends and effectively suppressed formation of trimers by steric hindrance effects. Effects of structures and reactivity

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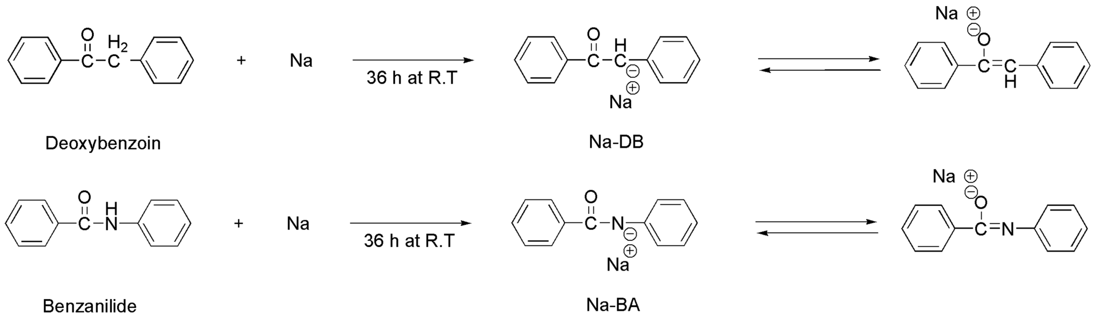


SCHEME 1 Preparation of sodium deoxybenzoin (Na-DB) and sodium benzanalide (Na-BA).

among oxy anionic initiators as following aromatic, secondary, and primary oxy anion for living anionic polymerization were studied. We found the relation between structures and reactive effects.[12]

In addition, we have developed a unique initiator for the living anionic polymerization of isocyanates, sodium benzanilide (Na-BA), which has dual functions, controlled initiation, and efficiently prevention of trimerization reaction. The Na-BA has a same amide bond like main back bone of polyisocyanate. The amide has an isomer structure, imidic acid, in certain condition by tautomerism. Thus, Na-BA coexist sodium-amide complex conformation and sodium-imidic acid complex conformation. These initiators can make bulky aggregates and help to prevent trimerization. Thus, when using Na-BA, the use of an additive is eliminated completely.[13]

In this article, we introduced new sodium of enolate anionic initiator, sodium deoxybenzoin (Na-DB) which has keto-enol isomers by tautomerism, for the living anionic polymerization of *n*-hexyl isocyanates. Change of aggregation of initiators and polymerization condition was studied, when "N" on Na-BA changed to "C" on Na-DB. We compared reactivity of initiators and number of initiators forming aggregators to Na-DB and Na-BA. Living natures of anionic polymerization was confirmed by synthesizing controlled polyisocyanates and block copolymers in Na-DB initiation system similar with Na-BA initiation system.

EXPRIMENTAL

Materials

n-Hexyl isocyanate (Aldrich, 97%) and 3-(triethoxysilyl)-propyl isocyanate (Aldrich, 95%) were dried over calcium hydride (CaH_2) and then vacuum distilled. Tetrahydrofuran (Fisher Scientific, GR grade) was distilled under N_2 after refluxing with sodium for 5 h and was then distilled again under vacuum from a sodium naphthalenide solution. Sodium (Na, Aldrich, 99%), calcium hydride (Junsei, 95%), naphthalene (Naph, Aldrich, 99%), and deoxybenzoin (DB, Aldrich, 97%) were used without further purification. The glass (Iwaki Glass PYREX®) used for the glass apparatus was rinsed with tap water and followed by triple-distilled water before being oven-dried. Freshly distilled THF was mixed with Na-Naph under high vacuum conditions with repetition of degassing procedures and. The THF was distilled from vacuum line before use.

Preparation of Na-DB Initiator

Na^+ has been reported to be the most suitable cation for the anionic polymerization of HIC among the alkali metals including Li^+, Na^+, and K^+.[10] We used Na^+ as the counter ion for the synthesis of the initiator. Na-DB in THF (50 mL) was prepared from the reaction of equivalent amounts of DB (1.22 g, 6.20 mmol) and elemental sodium (0.140 g, 6.20 mmol) at room temperature for 36 h under nitrogen (Scheme 1).

The color of reaction mixture turned light yellow, and dissolved gas was removed by freezing the reaction mixture in liquid nitrogen followed by subjection to high vacuum (10^{-6} torr). After complete degassing, the initiator obtained from this solution was stored at −30 °C in glass ampoules with break seals *in vacuo*. The ampoules contents were diluted to the desired concentration of Na-DB before use.

Estimation of DB Anion Content in Na-DB

The estimation of the DB anion content in Na-DB was carried out using a reaction of Na-DB (0.266 g, 1.22 mmol) and acetyl chloride (0.096 g, 1.22 mmol), in the presence of pyridine (0.122 g, 1.54 mmol) at room temperature for 24 h, which yielded 1,2-diphenylbutane-1,3-dione (acetyl deoxybenzoin). The reaction was carried out under high vacuum (10^{-6} torr) in an all-glass apparatus equipped with break seals. The apparatus was connected to the vacuum line followed by pinhole check and baking, and it was then sealed and separated from the vacuum line. Na-DB, acetyl chloride, and pyridine were mixed, and the reaction mixture was allowed to stir at room temperature for 24 h under nitrogen. After completion of the reaction, the crude product was suspended in water, and the organic layer was extracted with diethyl ether. The crude product was purified by recrystallization after evaporation of ether. The product (2-diphenylbutane-1,3-dione) was obtained 0.28 g, and yield was ~97%. The structure of the compound was confirmed by ^1H NMR studies.

2-Diphenylbutane-1,3-dione

^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 2.2 (3H, CH_3), 4.8 (3H, CH), 7.0–7.3 (5H, $—C—(C_6H_5)$), 7.4–8.0 (5H, $O{=}C—$ (C_6H_5)).

Anionic Polymerization of HIC Using Na-DB

All polymerizations reactions were carried out under high vacuum in a glass apparatus equipped with break seals. The reactors were always prewashed with THF solution containing the active anion after being sealed off from the vacuum line. In a typical polymerization reaction, the initiator solution, Na-DB (0.059 g, 0.271 mmol) in THF (10 mL), was transferred into the reaction flask through a break seal, and the solution temperature was then equilibrated at −98 °C in a frozen methanol bath. The polymerization was initiated by adding the monomer, HIC (0.693 g, 5.45 mmol) in THF (10 mL), to the initiator solution. The polymerization was terminated after 10 min by adding a 20-fold excess of HCl in methanol to the reaction solution. The polymer was precipitated using a large amount of methanol, filtered, and dried *in vacuo*. The yield of methanol–soluble polymer was determined quantitatively by weighing the residue after evaporation of the methanol; ^{1}H NMR was used to determine whether or not any unreacted monomers and/or trimers were present. The yield of the polymer was 100%.

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—), 7.3–7.7 (aromatic). ^{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). FTIR (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 Na-Naph with Na-DB as an Additive

In a typical isocyanate polymerization reaction using the additive system, the initiator solution, Na-Naph (0.011 g, 0.070 mmol) in THF (10 mL), was transferred into a reaction flask through a break seal, and then Na-DB (0.032 g, 0.148 mmol) was added as an additive to the initiator solution instead of Na-BPh_4. The solution was allowed stirred for 5 min, and then the temperature was equilibrated at the −98 °C in a frozen methanol bath. The polymerization was initiated by adding the monomer, HIC (0.687 g, 5.41 mmol) in THF (10 mL), to the initiator solution. The polymerization was terminated after 20 min. Further treatment was performed in the same manners as above. The yield of the polymer was 100%.

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). FTIR (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 TESPI Using Na-DB

PTESPI was prepared by procedures similar to that described above in "Anionic Polymerization of HIC Using Na-DB" section. The polymerization was initiated by adding TESPI, instead of HIC, to the initiator solution, and the reaction was terminated by addition of methanol without HCl to the reaction solution. The yield of the polymer was 97%.

PTESPI

^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.6 (2H, Si—CH_2), 1.21 (9H, Si—O—CH_2—CH_3), 1.73 (2H, CH_2—CH_2—CH_2), 3.55 (2H, N—CH_2), 3.77 (6H, Si—O—CH_2), 7.3–7.7 (aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 7.5 (Si—CH_2—), 18.0 (CH_3), 21.1 (CH_2), 45.1 (N—CH_2—), 58.2 (O—CH_2—), 155.5 (C=O). FTIR (KBr, cm^{-1}): 2860 (CH_2), 1700 (C=O), 1234 (Si—CH_2), 1100 (s, Si—OCH_2—CH_3), 1079 (s, Si—OCH_2—CH_3).

Block Copolymerization of HIC with TESPI

In a typical block copolymerization procedure, HIC (0.616 g, 4.84 mmol) was first polymerized and polymerization of TESPI was subsequently performed with Na-DB (0.051 g, 0.235 mmol), in a glass apparatus under high vacuum, at −98 °C. After 10 min, TESPI (0.933 g, 3.77 mmol), the second monomer, was added, and copolymerization was carried out for 8 min under the same condition as were used previously. The reaction was terminated by adding methanol, and the polymer was precipitated with methanol, filtered, and dried *in vacuo*. The reverse order of monomer feeding was also carried out. The TESPI (1.19 g, 4.81 mmol) was homopolymerized first using Na-DB (0.056 g, 0.255 mmol) at −98 °C in THF. After 8 min, HIC (0.628 g, 4.94 mmol), the second monomer, was added and the copolymerization reaction continued for 10 min. Further treatment was performed in the same manners for HIC polymerization. The yield of PHIC-*b*-PTESPI was 98%.

PHIC-b-PTESPI

^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.6 (2H, Si—CH_2—), 0.9 (3H, CH_3), 1.21 (9H, Si— $(OCH_2CH_3)_3$), 1.0–2.0 (8H, $(CH_2)_4$), 3.7 (4H, N—(CH_2)—), 3.81 (6H, Si—O—CH_2—), 7.3–7.7 (aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 7.6 (CH_2—SiO), 13.9 (CH_3), 18.2 (SiO—CH_2—CH_3), 21.2 (CH_2), 22.5 (CH_2), 26.2 (CH_2), 28.5 (CH_2), 31.5 (CH_2), 45.3, 48.6 (N—CH_2—), 58.4 (SiOCH_2), 156.7 (C=O). FTIR (KBr, cm^{-1}): 3441 (—NH), 2959, 2932, 2860, 1700 (C=O), 1349/1297 (disubstituted amide), 1234 (Si—CH_2), 1227, 1175, 1100 (s, Si—OCH_2 —CH_3), 1092, 1079 (s, Si—OCH_2—CH_3), 785, 728 (CH_2).

Characterization

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-LA300WB spectrometer using $CDCl_3$ as the solvent. ^{1}H NMR chemical shifts were calculated with respect to tetramethylsilane (TMS) at 0 ppm, and ^{13}C NMR chemical shifts were calculated with respect to deuterated chloroform at 77.0 ppm. FTIR spectra were obtained on a Perkin-Elmer System 2000 using KBr pellets. The molecular weights of the polymers were determined using a multi-angle laser light scattering detector system (MALLS), SEC-LS, (OPTI LAB-DSP Interferometric Refractometry 478-009-690 and DAWN EOS Laser Photometer 113-E, Wyatt Technology) with four columns (HR 0.5, HR 1, HR 3 and HR 4, Waters Styragel columns run in series with column pore sizes 50, 100, 500 and 1,000 Å, respectively). THF containing triethylamine was used as the mobile phase at a flow rate of 1.0 mL/min. The dn/dc values in THF at 40 °C were measured

TABLE 1 Anionic Polymerization of *n*-Hexyl Isocyanate (HIC) and 3-(Triethoxysilyl)propyl Isocyanate (TESPI) Using Sodium Deoxybenzoin (Na-DB) in Tetrahydrofuran at −98 °C

Entries	Na-Naph (mmol)	Na-DB (mmol)	Na-BA (mmol)	HIC (mmol)	TESPI	Time (min)	$M_n \times 10^{-3}$		PDI[b]	Yield (%)
							Calcd[a]	Obsd[b]		
1	–	0.244	–	5.18	–	5	2.58	8.30	1.17	89 (11)[c]
2	–	0.254	–	5.06	–	8	2.65	8.87	1.10	97
3	–	0.271	–	5.45	–	10	2.75	8.71	1.09	100
4	–	0.272	–	8.64	–	10	4.24	11.5	1.08	100
5	–	0.253	–	12.3	–	10	6.33	19.1	1.03	99
6	–	0.270	–	17.8	–	10	8.39	24.5	1.05	98
7	–	0.231	–	22.4	–	10	12.3	35.3	1.07	98
8	–	0.262	–	5.11	–	12	2.62	8.23	1.19	98
9	–	0.277	–	5.31	–	15	2.53	8.77	1.09	96 (4)[d]
10	0.070	0.148	–	5.41	–	10	19.8[e]	18.8	1.05	100
							4.64[f]			
11	0.071	0.145	–	5.84	–	20	21.0[e]	19.7	1.04	100
							5.12[f]			
12[g]	0.090	–	–	4.97	–	10	14.0	67.5	1.04	100
13[g]	0.100	–	–	4.70	–	30	10.5	100	1.26	89 (11)[d]
14	–	0.259	0.281	6.09	–	60	3.03[h] 2.75[i]	9.03	1.02	100
15	–	0.242	–	–	3.83	5	2.84	10.4	1.13	69 (31)[c]
16	–	0.242	–	–	3.83	8	3.99	10.7	1.11	97
17	–	0.244	–	–	3.97	10	3.80	11.3	1.11	90 (10)[d]
18	–	0.245	–	–	3.69	12	3.14	10.7	1.12	80 (20)[d]

[a] M_n is calculated using the relation {([monomer]/[Na-DB]) × molecular weight of monomer ??? molecular weight of DB} × yield of polymer/100.

[b] M_n and PDI were measured by SEC-LS in THF at 40 °C.

[c] The amount of unreacted monomer is presented in parentheses.

[d] The yield of trimer is presented in parentheses.

[e] The calculated molecular weight based on Na-Naph as an initiator.

[f] The calculated molecular weight based on Na-DB as an initiator.

[g] Data from the reference: Kim, S. Y.; Ahn, J. H.; Shin, Y. D.; Lee, J. S. *Polym. Prepr.* **2000**, *41(2)*, 1211.

[h] The calculated molecular weight based on Na-DB as an initiator.

[i] The calculated molecular weight based on Na-BA as an initiator.

with an LED (Optilab DSP) source. The d*n*/d*c* values of polyisocyanate were measured to 0.090 for preparation of five different concentration polymer samples, and then SEC-LS data were obtained using refractive index detection at 40 °C.

RESULTS AND DISCUSSION

Living Anionic Polymerization of HIC Using Na-DB

The yield of PHIC increased with the increasing reaction time of 5, 8, and maximum yield was reached after 10 min (Table 1, entries 1–3). If the reaction time exceeded 10 min, however, then the yield of polymer dropped slowly and the formation of the trimer was observed at 12 and 15 min (Table 1, entries 8–9). These results show that as long as monomer is present in the reaction mixture, the active growing chain ends prefer reaction with the monomer to attack the carbonyl carbon in the backbone in 10 min.[10,11]

To examine the living nature of the system, the polymerization of HIC was carried out changing various molar ratios of the monomer to the initiator, which resulted in PHIC samples with molecular weights in the range of 8700–35,000 (Table 1, entries 3–7). The results show a linear relationship between the monomer-to-initiator ratio and the observed molecular weight determined using SEC-MALLS; the polymers also had low PDIs (Fig. 1).

When Na-DB was used as an initiator, anionic polymerization of *n*-hexyl isocyanate showed living natures, such as narrow MWD, controlled molecular weight, and high yield. Na-DB could play both initiation function and additive function like Na-BA. Difference between Na-DB and Na-BA during polymerization is reaction time. Reaction time required 10 min to reach complete polymerization was faster than for the polymerization using Na-BA (60–70 min).[13] Because reactivity on growth chain ends in Na-DB initiation system is stronger than that of Na-BA, optimized reaction time is shorten. In short, Na-DB can make aggregators which can prevent trimerization on growth chain ends, and the number molecules forming aggregators is smaller than Na-BA.

In substance, the calculated molecular weight did not match the observed molecular weights. The formula used to determine the molecular weight (Table 1) suggests that either the concentration of the Na-DB initiator is not accurate, or that the efficiency of the initiator is three times lower than we expected.

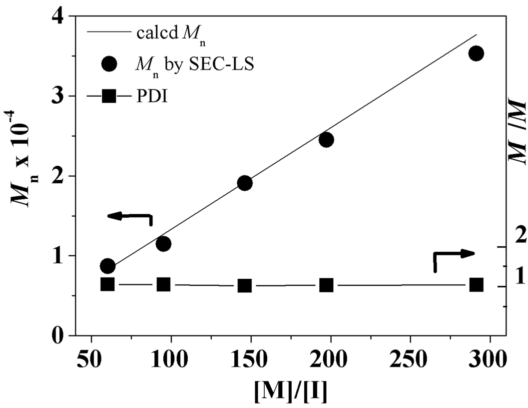


FIGURE 1 Number average molecular weight (M_n) versus the molar ratio of *n*-hexyl isocyanate (HIC) to sodium deoxybenzoin (Na-DB) initiator for anionic polymerization in tetrahydrofuran at −98 °C.

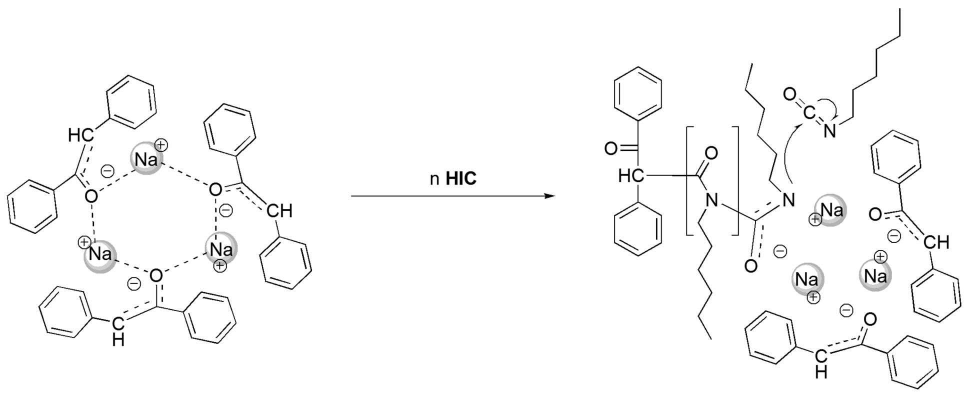
We propose that three of Na-DB molecules self-aggregate. In the polymerization procedure, after HIC is added to the initiator solution, it reacts with the Na-DB aggregate and propagation proceeds with efficient chain end protection. In the aggregate system, one Na-DB molecule is consumed for the initiation and the other two molecules protect the growing chain ends. This action results in ~100% polymer yields without the need for an additional additive (Scheme 2). The calculated molecular weight using about 33 (±4)% of the initiator concentration showed the good agreement with the observed molecular weight, thus indicating that the new initiator Na-DB has dual functions; not only does it initiate the reaction, but it also protects the chain ends.

To account for the above discrepancy, we estimated the proportion of active DB^- anion in the Na-DB initiator using a model reaction of the Na-DB with an acid chloride, which led to the formation acetyl deoxybenzoin with a ~98% yield. This result suggests that a large percentage of initiator molecules are available to polymerize HIC. To confirm that Na-DB plays the role as other additive, the polymerization of HIC was carried out using a mixture of Na-Naph and Na-DB (twofold excess). It is highly probable that some of the Na-DB act as an additive to protect the chain ends in coinitiation system because additives like Na-Ph_4B.[10,11] For the polymerization of isocyanate using Na-Naph without any other additive, the back-biting reaction occurred at long reaction times, which resulted in low polymer yields and disagreement between observed molecular weight and the calculated molecular weight.[10]

In the cases of the Na-Naph and Na-DB mixture, however, all obtained polymers showed good accordance between the observed and calculated molecular weights with 100% yields, and no trimer based on Na-Naph as an initiator (Table 1, entries 10–13). In addition, aromatic proton signals were not observed in the ^{1}H NMR spectra of PHICs obtained from the initiator mixture but were observed in PHICs obtained when using Na-DB as the initiator (Table 1, entries 1–9).

These results indicate that some of the initiator molecules have an additional function as an additive to protect the growing chain ends, thus preventing the back-biting reaction. Self-aggregated Na-DB also plays both functions as an initiation effect and an additive effect like Na-BA. Na-BA can form a certain clusters including five-membered molecules and play a dual function like initiators to attack monomers and additives to prevent trimerization. The system using the unique initiator Na-BA was first proposed by our groups.[13]

Additionally, we proposed that trimeric aggregated Na-DB system is also supported firmly by the fact that the rate of HIC polymerization is faster when using Na-DB in comparison to using Na-BA. The relative reactivity of a Na-DB (pKHA = 17.7 in DMSO)[14] is as low as that of a Na-BA (pKHA = 18.8 in DMSO).[15] We try to polymerize HIC with coinitiators, Na-DB and Na-BA, to compare reactivity between Na-DB and Na-BA. However, the reactivity of initiators was changed by aggregation of the initiator molecules during polymerization. From the result, the obtained polymer showed 100% yields, narrow PDI value and good accordance between the observed and calculated molecular weights based on Na-DB as an initiator (Table 1, entries 14). In addition, the propagation was stable for 60 min. It means that a single initiator among Na-DB aggregates attacked monomers and other Na-DB molecules and all Na-BA molecules prevent trimerization by forming clusters at the growing chain ends. Because less aggregated initiators have high reactivity in comparison to more highly aggregated ones,[16] Na-DB molecules like



SCHEME 2 Dual function of controlled initiation and efficient protection of living chain ends.

TABLE 2 Block Copolymerization of *n*-Hexyl Isocyanate (HIC) with 3-(Triethoxysilyl)propyl Isocyanate (TESPI) Using Sodium Deoxybenzoin (Na-DB) in Tetrahydrofuran at −98 °C

Entries	Na-DB (mmol)	First Monomer (mmol)	Second Monomer (mmol)	Time (min)	$M_n \times 10^{-3}$		PDI[b]	Polymer Yield (%)	Composition
					Calcd[a]	Obsd[b]			
		HIC	TESPI						
19	0.235	4.84	3.77	10/8	6.46	22.1	1.15	98	1.27:1
		TESPI	HIC						
20	0.255	4.81	4.94	8/10	7.18	19.3	1.23	98	1:1.06

[a] M_n is calculated using the relation {([HIC]/[Na-DB]) × molecular weight of HIC + ([TESPI]/[Na-DB]) × molecular weight of TESPI + molecular weight of DB} × yield of polymer/100.

[b] M_n and PDI were measured by SEC-LS in THF at 40 °C.

trimeric structures are less aggregated than Na-BA molecules which form pentameric structures.[13]

We anticipate that the trimeric macroring is formed by weak $C^{\delta-}$ --- Na^+ --- $O^{\delta-}$ interactions between the Na-DB molecules. Furthermore, the carbanion in the $C^{\delta-}$ --- Na^+ --- $O^{\delta-}$ has a comparatively smaller atomic volume than the amidate anion in the $N^{\delta-}$ --- Na^+ --- $O^{\delta-}$ interaction, which may allow the initiator molecules to form compact trimeric structures.

Living Anionic Polymerization of TESPI Using Na-DB

The yield of PTESPI increased with the increasing reaction time of 5 and 8 min using Na-DB in THF at −98 °C, and a quantitative yield of polymer with a low PDI and the predicted molecular weight was approached at 8 min. As the reaction time exceeded 8 min, however, the yield of the polymer dropped and formation of the trimer was observed at 10 and 12 min (Table 1, entries 15–18). The result shows that the initiator can be used for polymerization of another isocyanate monomer. For the polymerization of TESPI, it was also found out that the initiator has an initiating efficiency of about 33%, and can therefore be considered an aggregate system.

Block Copolymerization of HIC with TESPI

Block copolymerization is the most reliable method to confirm living nature of polymerization. Thus, we carried out block copolymerization of HIC with TESPI using Na-DB (Table 2, entries 19–20). PHIC-*b*-PTESPI was produced nearly quantitatively with a low PDI (M_n = 22,100 g/mol, PDI = 1.15). The composition ratio of HIC to TESPI, summarized in Table 2, was found to be 1.27:1 by ^{1}H NMR analysis for the feed ratio of 1.28:1. Therefore, the ^{1}H NMR analysis result for the block copolymer was in good agreement with the monomer feed ratio. When PTESPI and PHIC were used as the first and second polymer, respectively, poly(3-(triethoxysilyl)propyl isocyanate)-*b*-poly(*n*-hexyl isocyanate) was also obtained as desired. The chain-length of each block could be controlled effectively by the monomer/initiator feed ratios, which supported the living character of the polymerization.

The peak in the SEC-LS spectrum was clearly shifted toward high molecular weight without tailing (Fig. 2). The absence of the peak corresponding to the first polymer, PHIC, indicated the absence of termination or chain transfer reactions.

CONCLUSIONS

Na-DB does not only make keton-enol isomers by tautomerism but also make a trimeric cluster similar with Na-BA which forms amide and imidic acid isomers and pentamaric clusters. Na-DB has been shown to be an appropriate initiator for the living anionic polymerization of isocyanates, and it results in predictable molecular weight, a narrow MWD, and possible for block copolymerization with PHIC and PTESPI. Interestingly, it was found out that the initiator has an initiation efficiency of about 33% in the anionic polymerization of isocyanates. We, thus, hypothesized that three Na-DB molecules self-associate to form a trimeric structure through weak $C^{\delta-}$ --- Na^+ --- $O^{\delta-}$ interactions between the molecules. In the polymerization reaction, one of the Na-DB molecules is consumed for the initiation and the others

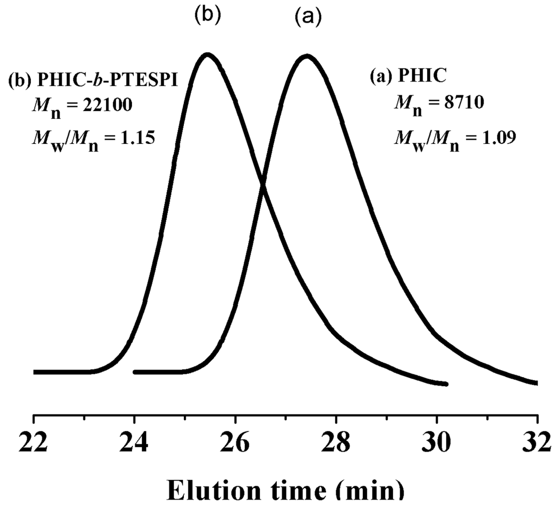


FIGURE 2 Size-exclusion chromatography and multiangle laser light scattering (SEC-MALLS) curves of poly(*n*-hexyl isocyanate) (PHIC) and poly(*n*-hexyl isocyanate)-*b*-poly(3-(triethoxysilyl)propyl isocyanate) (PHIC-*b*-PTESPI) in tetrahydrofuran at 40 °C. The homopolymerization and block copolymerizations reactions were carried out using sodium deoxybenzoin (Na-DB) as an initiator in tetrahydrofuran at −98 °C.

protect the growing chain ends, which prevents undesired back-biting reaction. Because of the trimeric association, the reactivity of the Na-DB initiator is increased, which results in rapid polymerization in comparison to that using pentameric Na-BA.

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