Synthesis of Poly(*n*-hexyl isocyanate) by Controlled Anionic Polymerization in the Presence of $NaBPh_4$

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Introduction. Polyisocyanates are stiff polymers due to the amide bonds in the polymer main chain, and the polyisocyanate chains are twisted into helical conformations because of steric constraints.[1] Due to these structural properties, polyisocyanates have been studied in many applications such as chiral recognition materials, optical switches, and liquid crystal materials.[2] Since Shashoua and co-workers first reported the polymerization of isocyanates with sodium cyanide in dimethylformamide in 1959,[3] many researchers have studied the synthesis of polyisocyanates.[4] However, living polymerizations of isocyanates were difficult because of depolymerization by the formation of trimer. Despite this difficulty, Novak and co-workers synthesized poly(*n*-hexyl isocyanate) using organotitanium initiators without trimer formation, even though it is a coordination polymerization.[5] Recently, Lee and co-workers succeeded in the synthesis of well-defined poly(3-(triethoxysilyl)propyl isocyanate)) using sodium naphthalene (Na-Naph) and 15-crown-5 (15C5) in THF at −98 °C under high vacuum.[6] The system successfully protected the backbiting of the anionic chain ends using a big countercation, the complex of Na-Naph-15C5. However, that is still unstable due to the greater distance between the active ends and the big ligand in polar solvent.

In this study, poly(*n*-hexyl isocyanate) (PHIC) was synthesized via anionic polymerization as a function of reaction time at −98 °C in THF. We attempted to prevent the formation of trimers by utilizing sodium tetraphenylborate ($NaBPh_4$) as a common ion salt, which stabilizes the active anion by excess counter sodium cations.[7] A postpolymerization was carried out to confirm the living character of the active anionic chain ends of PHIC.

Experimental Section. a. Materials. *n*-Hexyl isocyanate (HIC, Aldrich Chemical Co. Inc., 97%) was dried over CaH_2 for 24 h and distilled under reduced pressure. The resulting monomer was distilled once more from CaH_2 under vacuum. Tetrahydrofuran (THF, Fisher Scientific Co., GR grade) was distilled under N_2 after refluxing over Na for 4 h and stored as Na-Naph solution under vacuum at −30 °C.

b. Anionic Polymerization. All polymerizations were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical polymerization procedure, the initiator solution, Na-Naph (0.10 mmol) in THF, was transferred into the reaction flask through the break-seal followed by 10-fold excess $NaBPh_4$ (0.97 mmol) in THF to the initiator. The solution temperature was equilibrated to the reaction temperature of −98 °C. Polymerization was carried out by adding the HIC (4.53 mmol, 0.57 g) in THF to the initiator solution. The color of the reaction solution changed into slight brown. The polymerization was terminated after 20 min by adding 20-fold excess HCl in methanol to the initiator, and polymer was precipitated into methanol, filtered, and dried in vacuo. Methanol-soluble parts were analyzed quantitatively by weighing the residue after evaporation of methanol and using ^{1}H NMR to check whether there were any unreacted monomers and/or trimers. The yield of polymer was 99%.

c. 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 ($CDCl_3$, 300 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). IR (KBr, cm^{-1}): 3441 (−NH), 2959, 2932, 2860, 1700 (C═O), 1349/1297 (disubstituted amide), 1227, 1175, 1092, 785, 728.

To do the postpolymerization, the first-stage polymerization of HIC (5.95 mmol, 0.76 g) was initiated with Na-Naph (0.10 mmol) in the presence of $NaBPh_4$ (1.00 mmol) in THF at −98 °C in an all-glass apparatus in vacuo. After 15 min, a portion of living polymer was withdrawn to an attached receiver for the characterization of the precursor (0.20 g). The second monomer, HIC (5.90 mmol, 0.75 g), in THF at −98 °C was then added to the residue of the polymer solution with vigorous stirring. The polymerization was terminated after 15 min by adding 20-fold excess HCl in methanol to the initiator, and polymer was precipitated into methanol, filtered, and dried in vacuo. Methanol-soluble parts were analyzed quantitatively by weighing the residue after evaporation of methanol and using ^{1}H NMR to check whether there were any unreacted monomers and/or trimers. The yields of precursor and block polymer were 99% and 96%, respectively. The NMR and IR results of postpolymer were the same as the above results.

d. Measurements. The polymers were characterized by FT-NMR (JEOL JNM-LA300WB) and FT-IR (Perkin-Elmer System 2000). Molecular weights of the poly(HIC)s were calculated from the response of a multi-angle laser light scattering detector system (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). The pore size of the columns is 50, 100, 500, and 1000 Å, respectively. THF was used as the mobile phase at a flow rate of 1.0 mL/min. For the five solutions with different concentrations, the d*n*/d*c* value for PHIC in THF at 35 °C was measured with an LED source (690 nm, Optilab DSP interferometric refractometry 478-009-690, Wyatt Technology). The d*n*/d*c* value was 0.095 ± 0.005 $cm^3\ g^{-1}$. After measuring the d*n*/d*c*, SEC-LS data were gained with refractive index detection at 690 nm and 35 °C. The light scattering of the polymer was detected at 18 angles in the range from 22.5° to 147.0°.

Results and Discussion. a. Anionic Polymerization. The polymerization of HIC was performed with time variable at −98 °C. The optimum conditions for the temperature, −98 °C, and initiator, Na-Naph, were obtained from previous studies and preliminary experi-

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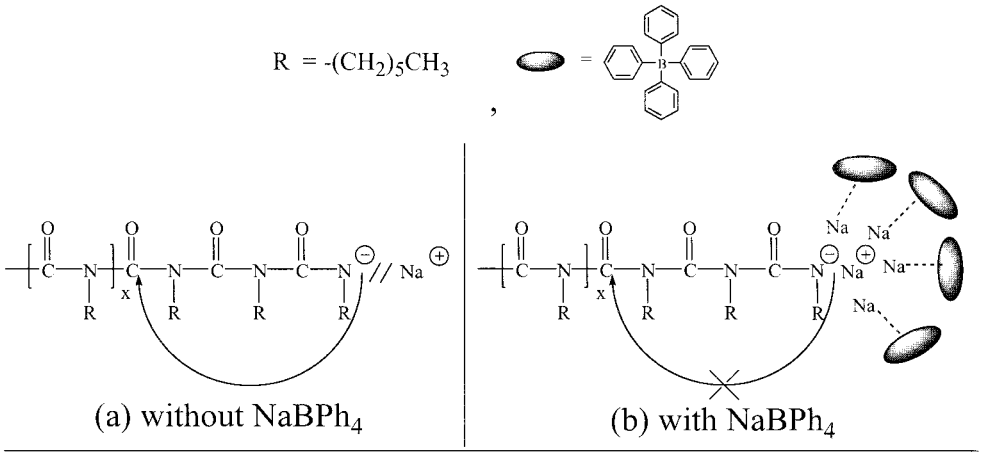
Chart 1



ments.[6] The yield of polymer increased rapidly with reaction time of 2, 5, and 10 min, approaching quantitative yield (100%).[8] As the reaction time passed 10 min, the yield of polymer decreased slowly and trimers formed. This indicates that as long as monomer is present, the growing active chain ends react with it rather than attack the carbonyl carbon in backbone. From these results, we concluded that polymer can be obtained in high yield only with adequate reaction time, temperature, and initiator.

b. Anionic Living Polymerization with $NaBPh_4$. To get a living polymer, an excess of $NaBPh_4$ (10 times larger than initiator) was used for the polymerization of HIC.[9] The addition of $NaBPh_4$ as a common ion salt suppresses the formation of free ions and can result in the formation of inactive species in styrene and methyl methacrylate polymerizations.[7] When the polymerization of (3-triethoxysilyl)propyl isocyanate was performed in the presence of crown ether, the polymerization was finished within 1 min because 15C5 easily formed the metal complex with sodium so that the free ion pairs were made easily due to the stretch between amidate anion and countercation.[6] This indicates that the large countercations, such as the complex of sodium and crown ether, are separated from the amidate anion in polar solvent. However, $NaBPh_4$ forms a tight ion pair with amidate anion and stabilizes the amidate anion with excess sodium cations, so the rate of polymerization decreases, and the polymerization was finished at 20 min as shown in Table 1. To examine whether $NaBPh_4$ attacks HIC or not (see footnote *d* in Table 1), the polymerization was attempted using only $NaBPh_4$ without initiator. The resulting products were only monomers. When both $NaBPh_4$ and an initiator were used, the polymers were obtained in 89% yield in 10 min, even though a 100% yield of PHIC was achieved in polymerization without $NaBPh_4$ in the same time. This means that the polymerization rate decreased presumably, because of formation of tight contact ion pairs with $NaBPh_4$. The calculated molecular weight agreed well with the value observed by SEC-LS. Trimerization was prohibited until the reaction time reached 40 min. This means that the amidate anions were still stable for 40 min without trimerization when $NaBPh_4$ was used in the polymerization.

To investigate the effect of $NaBPh_4$ on the monomers, ^{13}C NMR spectra of HIC and HIC-$NaBPh_4$ solution in *d*-THF were measured. The general peak corresponding to the carbonyl group of HIC in *d*-THF is observed at 123.6 ppm; the peak corresponding to carbonyl group of HIC in HIC-$NaBPh_4$ solution is also observed at 123.6 ppm. The other peaks are also the same. Therefore, $NaBPh_4$ only affects the active chain end without affecting the monomers (see Chart 1). The mechanism indicates that the formation of trimer is suppressed by two factors: the contact ion pairs from the high concentration of sodium cations and the steric hindrance of bulky tetraphenylborate groups.

Table 1. Anionic Polymerization of *n*-Hexyl Isocyanate in the Presence of $NaBPh_4$ in THF at −98 °C

$[NaBPh_4]_0$/ $[Na\text{-}Naph]_0$	$[HIC]_0$/ $[Na\text{-}Naph]_0$	time, min	$M_n \times 10^{-4}$ calcd	$M_n \times 10^{-4}$ obsd[a]	M_w/M_n[a]	yield of polymers, %
48.9	9.9	10	1.10	12.8	1.08	89 (11)[b]
39.0	10.6	20	0.93	10.7	1.11	99
45.3	9.6	20	11.5	11.7	1.09	99
56.4	10.3	20	13.9	14.5	1.07	96
72.4	12.6	20	17.6	16.5	1.10	96
88.2	10.3	20	21.5	22.2	1.11	96
41.3	9.0	30	10.5	11.2	1.10	99
48.0	9.9	40	11.8	12.8	1.12	96
49.6	9.5	60	11.5	10.8	1.13	93 (7)[c]
52.7	11.0	80	11.8	11.0	1.08	87 (13)[c]
55.2	10.0	120	11.4	10.6	1.05	81 (19)[c]
d	*d*	30				0

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 35 °C. [b] The yields of monomer are presented in parentheses. [c] The yields of trimer are presented in parentheses. [d] Polymerization of HIC (5.24 mmol) was performed with $NaBPh_4$ (0.97 mmol) without Na-Naph.

To check the relationship between the molecular weight of polymer and the molar ratio of monomer to initiator, the polymerization of HIC was carried out at varying ratios of monomer and initiator. As shown in Figure 1, each polymer was obtained with narrow molecular weight distribution (around 1.10). Also, the number-average molecular weights observed by SEC-LS obey the expected linear relationship expected from the monomer/initiator ratio.

The postpolymerization of HIC, which may be the most reliable method to confirm living polymerization, was also executed in order to show the living character of polymerization using $NaBPh_4$ as a common ion salt. The precursor (M_n 14 600, M_w/M_n 1.13) and postpolymer (M_n 25 700, M_w/M_n 1.10) were obtained almost quantitatively with relatively sharp MWDs. The peak in SEC-LS spectra clearly shifted toward high molecular weight. The absence of a peak corresponding to the base PHIC indicates that termination and chain transfer reactions are absent.

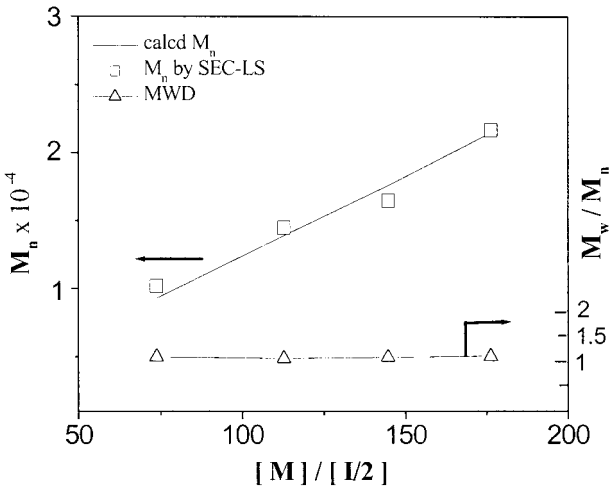


Figure 1. Molecular weight vs the ratio of monomer to initiator of the polymer using $NaBPh_4$ at reaction time of 20 min.

Conclusions. The optimum polymerization condition of HIC was found to be 10 min at the −98 °C in THF in the presence of $NaBPh_4$. The relationship between the molecular weight of polymer and the molar ratio of monomer to initiator was linear, and the molecular weight distributions, M_w/M_n 1.07−1.12, were narrow. Postpolymerization was also possible by using the living character of amidate anion of PHIC with a clear shift between SEC-LS spectra of precursor and postpolymers. The amidate anions are therefore stable and have living character in the polymerization of isocyanate with an initiator system of Na-Naph and $NaBPh_4$.

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(8) The results of the polymerization of HIC without $NaBPh_4$ in THF at −98 °C are listed as following: reaction time (yield of the polymer/monomer/trimer, %), 2 min (74/26/0), 5 min (95/5/0), 10 min (100/0/0), 20 min (92/0/8), 30 min (89/0/11), and 60 min (86/0/14). The entire results will be reported in the full-length paper.
(9) Anionic polymerizations of HIC with changing the concentration of $NaBPh_4$ were also performed, and the results showed that the optimum concentration of $NaBPh_4$ is 10 times larger than that of initiator.

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