Anionic Living Polymerization of 3-(Triethoxysilyl)propyl Isocyanate

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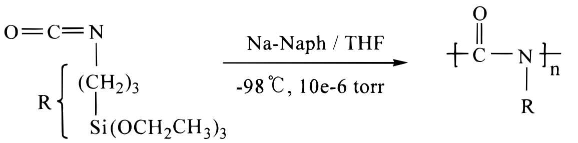
Synthesis of polyisocyanates have been investigated by a number of researchers since 1960[1] because of their unique optical properties and liquid crystalline behavior.[2] Recently, a successful preparation of polyisocyanates via living coordination polymerization with titanium(IV) catalyst was reported by Novak and co-workers.[3] However, no one was able to synthesize polyisocyanates via anionic living polymerization since living anionic chain ends attack carbonyl groups in the main chain, forming trimers: isocyanurates.[4] This made it impossible to control the molecular weight and also to obtain monodispersed polyisocyanates.[5] Although polyisocyanates could be prepared via anionic polymerization,[6] no one was successful in synthesizing polyisocyanates by anionic living polymerization due to the back-biting of the anionic chain ends.

In this study, poly(3-(triethoxysilyl)propyl isocyanate), poly(Si−NCO) (eq 1) which contains cross-linkable alkoxysily groups[7] was synthesized via anionic polymerization as a function of reaction time and temperature. It was also attempted to prevent the formation of trimers by utilizing a complex (Na−15C5) of sodium cation and 15-crown-5 (15C5) as a ligand.[8] The living character of the active anionic chain ends of poly(Si−NCO) was confirmed by preparing block copolymers from poly(Si−NCO) containing Na−15C5, and octyl isocyanate (Oc−NCO) as a second monomer.



$$O{=}C{=}N{-}R,\quad R = (CH_2)_3Si(OCH_2CH_3)_3 \xrightarrow[-98℃,\ 10e\text{-}6\ torr]{Na\text{-}Naph\ /\ THF} \left[\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R}{|}}{N}\right]_n \qquad (1)$$

Experimental Section. Polymerization. All polymerization were carried out under high vacuum in a glass apparatus equipped with break-seals. Polymerization was started by adding the monomer solution to the sodium naphthalenide or sodium naphthalenide−crown ether (Na−15C5) solution in THF. Prior to mixing, the solution temperature was equilibrated to the reaction temperature of −98, −84, −78, −62, or −50 °C as a function of time. The reaction was terminated by adding methanol, and polymers were precipitated into methanol, filtered, and dried. Precipitation was repeated to afford highly pure polymer samples. The resulting polymer was dissolved again in benzene and freeze-dried for characterization. After filtration, methanol soluble parts were analyzed qualitatively by FT-IR and quantitatively by weighing the residue after evaporation of methanol, by ^{1}H NMR, and by SEC to see of there were any unreacted monomer and/or trimers present.

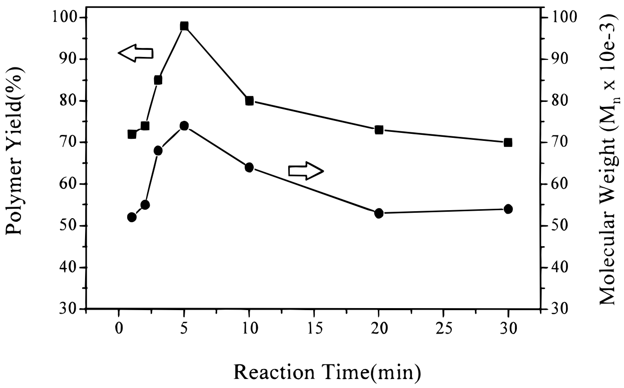


Figure 1. Polymer yields (■) and molecular weights (●) of poly(Si−NCO) with Na−naph (without 15C5) as a function of reaction time at −98 °C (MW was measured by SEC using polystyrene standard in THF at 40 °C).

Polymer was then characterized by size exclusion chromatography (Waters M 77251, M 510), FT-NMR (JEOL JNM-LA300WB), FT-IR (Perkin-Elmer System 2000). Thermal properties were characterized by TGA (TA-2050) and DSC (TA-2010) at 10 °C/min. Size exclusion chromatography (SEC) was carried out with refractive index detector at 40 °C. Molecular weight calibration was performed with polystyrene standards from Scientific Polymer and THF at a flow rate of 1.0 mL/min. Cross-linking of poly(Si−NCO) was characterized by IR after soaking the cast film in 2 N HCl solution at room temperature for 24 h.

^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.6, Si−C$\mathbf{H}_2$ (t, 2H); 1.19, Si−O−CH$_2$−C$\mathbf{H}_3$ (t, 9H); 1.70, CH$_2$−C$\mathbf{H}_2$−CH$_2$ (m, 2H); 3.53, N−C$\mathbf{H}_2$ (t, 2H); 3.76, Si−O−C$\mathbf{H}_2$ (m, 6H). ^{13}C NMR (300 MHz, CDCl$_3$): δ (ppm) 7.5, 18.0, 21.1, 45.1, 58.2, 155.5. IR (thin film): 1100 (s, Si−OCH$_2$-CH$_3$), 1079 (s, SiO−CH$_2$CH$_3$), 1234 (m, Si−CH$_2$), 1697 (s, C═O), 2880 cm^{-1} (s, CH$_2$). TGA onset temperature: 200 °C; residue at 800 °C; 18%. DSC T_g (glass transition temperature): −72 °C. T_m (melting point): 106 °C. T_i (isotropic transition temperature): 127 °C.

Block Copolymerization. One portion of living poly(Si−NCO) solution prepared with Na−15C5 in THF at −98 °C for 5 min was transferred to the attached glassware for characterization. The second monomer, Oc−NCO, in THF, at −98 °C was added to another portion of living poly(Si−NCO) solution, while stirring vigorously and the reaction was allowed to run for 5 min. After the reaction was terminated with methanol, block copolymer solution was poured into a large excess amount of methanol to isolate the polymer. The remainder of poly(Si−NCO) solution was also isolated, as previously described. The polymers were also characterized. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.6, Si−C$\mathbf{H}_2$ (t, 2H); 0.87, C−C$\mathbf{H}_3$ (t, 3H); 1.19, Si−O−CH$_2$−C$\mathbf{H}_3$ (t, 9H); 1.26, (C$\mathbf{H}_2$)$_5$ (m, 10H); 1.54, C$\mathbf{H}_2$−CH$_3$ (m, 2H); 1.70, CH$_2$−C$\mathbf{H}_2$−CH$_2$ (m, 2H); 3.53 N−C$\mathbf{H}_2$ (t, 4H); 3.76, Si−O−C$\mathbf{H}_2$ (m, 6H). ^{13}C NMR (300 MHz, CDCl$_3$): δ (ppm) 7.5, 14.0, 18.0, 22.6, 26.7, 27.8, 29.1, 31.8, 43.0, 58.2, 157.5. TGA onset temperature: 197 °C; residue at 800 °C; 7%.

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Table 1. Poly(3-(triethoxysilyl)propyl isocyanate)s Prepared via Anionic Living Polymerization with Na−15C5 in THF as a Function of Reaction Time at −98 °C

Na−Naph, mmol	15C5, mmol	Si−NCO, mmol	time, min	M_n calcd	M_n obsd[a]	M_w/M_n	yield of polymer,%
0.08	1.01	5.62	1	33 000	28 000	1.55	96
0.16	1.49	5.17	5	15 000	16 000	1.34	93
0.06	1.14	4.92	10	37 000	40 000	1.39	97
0.06	1.04	4.50	30	35 000	32 000	1.39	95
0.07	0.82	5.26	60	34 000	35 000	1.50	96
0.06	0.12	4.92	120	28 000	55 000	1.70	73(26)[b]
0.07[c]	0.14	5.21	5	20 000	40 000	1.60	55(45)[b]
0.07[d]	0.14	5.70	5	6 500	75 000	2.45	15(85)[b]

[a] M_n was measured by SEC using polystyrene standards in THF at 40 °C. [b] The yields of trimer are presented in parentheses. [c,d]The polymerization were carried out at −84 (c) and −78 °C (d), respectively.[10]

Table 2. Block Copolymers by Sequential Polymerization of Si−NCO and Oc−NCO with 15C5 in THF at −98 °C for 5 min in Homo and Block Copolymerization, Respectively

run	Na−Naph, mmol	15C5, mmol	Si−NCO, mmol	Oc−NCO, mmol	homopolymer calcd	homopolymer obsd[a]	block copolymer calcd	block copolymer obsd[a]	M_w/M_n	yield of polymer, %
1 H	0.25	2.71	5.19		10 000	15 000			1.26	94
1 B	0.10	1.09	2.08	4.75			24 000	32 000	1.68	95
2 H	0.08	1.06	4.60		26 000	29 000			1.43	93
2 B	0.05	0.64	2.76	1.37			31 000	34 000	1.56	91
3 H	0.06	1.14	4.92		37 000	40 000			1.39	97
3 B	0.04	0.70	3.00	0.77			42 000	46 000	1.32	90

[a] M_n was measured by SEC using a polystyrene standard in THF at 40 °C.

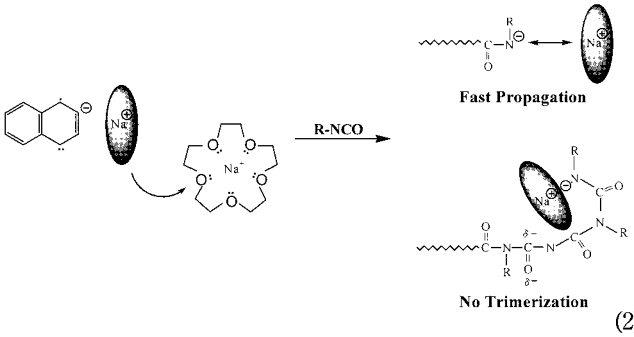
Results and Discussion. Polymerization. Poly(Si−NCO) was synthesized with sodium naphthalenide in THF at −98 °C. As shown in Figure 1, the polymer yield increased with reaction time and approached almost quantitative yield at 5 min. The molecular weight of poly(Si−NCO) also increased with the polymer yield.

As the reaction time increased further, the polymer yield decreased rapidly and then leveled off. Therefore, it can be said that the formation of trimers was successfully inhibited by the very low reaction temperature (−98 °C) at reaction times of less than 5 min.

With reaction times longer than 5 min, trimers and polymers were found in the reaction mixture, but no monomers were detected. For instance, formation 79% of polymer and 20% of trimer were independently analyzed for the case of 10 min reaction time. Therefore, it can be said that propagation was completed and then depolymerization began making it impossible to inhibit trimerization of poly(Si−NCO) even at −98 °C, unless the reaction time is right.

Living Polymerization. A bulky cation−ligand complex such as Na−15C5 was utilized to prevent the depolymerization of poly(Si−NCO). The hole size of 15C5 is 1.7−2.2 Å which can fit into the ionic radius of sodium (1.9 Å).[9]

As shown in eq 2, the bulky cation−ligand complex is expected to inhibit the side reaction (back-biting) of chain ends, where sterically hindered nitrogen anions are unable to attack carbonyl groups, preventing the formation of trimers. In the ligand system, the rate of propagation was enhanced by stretching of ion pair to generate the polymer in 96% yield within 1 min at −98 °C (Table 1). For a rather longer reaction time up to 60 min, almost no trimerization occurred to maintain the high yield of polymer (93−97%), while polymer yield was reduced by back-biting starting at an early stage of the reaction without crown ether (Figure 1). After the polymerization mixture was held at −98 °C for 2 h, the polymer yield decreased (73%) and 26% of trimer was produced (Table 1). At higher temperatures (−84 to −78 °C), low polymer yields and rather higher yields of trimer were observed. Although the ligand system could not perfectly inhibit the back-biting, the bulky complex effectively suppressed the side reaction to afford the living polymer at −98 °C for 1 h.



(2)

Block Copolymerization. ABA triblock copolymers were successfully prepared from octyl isocyanate (Oc−NCO) and poly(Si−NCO) having anionic chain ends, and almost quantitative yields were obtained (Table 2). The composition of the block copolymer determined from the ^{1}H NMR spectrum correlates well with the calculated value.[11] The formation of block copolymer was also confirmed by SEC which showed a curve shifted toward the higher molecular weight region but no peaks from poly(Si−NCO). These results clearly confirm the formation of living poly(Si−NCO) at −98 °C.

Poly(Si−NCO) prepared via anionic living polymerization exhibited a T_g of −72 °C and good solubility in a number of organic solvents such as benzene, hexane, dioxane, and THF. However, poly(propyl isocyante) exhibited poor solubility in these solvents at room temperature. The enhanced solubility may be attributed to the alkoxysilyl groups in the side chain, which can also react with each other to form a network polymer. The cross-linking of poly(Si−NCO) at room temperature in 1 N HCl aqueous solution for 24 h resulted in insoluble poly(Si−NCO).[7] From the FT-IR spectra of poly(Si−NCO), it was speculated that cross-linking reaction occurred among alkoxysilyl groups. Before cross-linking reaction: IR (thin film) 1100 (s, Si−OCH$_2$-CH$_3$), 1079 (s, SiO−CH$_2$CH$_3$), 1234 cm^{-1} (m, Si−CH$_2$). After cross-linking reaction: IR (thin film) 1050, 1107 (s, Si−O−Si), 860 cm^{-1} (s, Si−OH). In thermal degradation study, the decomposition temperature was near 200 °C, similar to that of polyalkylisocyanates reported in other studies.[3a]

It is concluded that polyisocyanates with cross-linkable alkoxysilyl groups were successfully synthesized by anionic living polymerization with crown ether and sodium cation in high vacuum at low temperature (−98 °C). Furthermore, ABA triblock copolymers were also prepared due to the living character of poly(Si−NCO). The utilization of Na−15C5 can be extended to other isocyanate monomers to prepare polymers and block copolymers via anionic living polymerization. Further studies on the synthesis of poly(Si−NCO) under various conditions, together with detailed characterizations of molecular weight and molecular weight distribution of poly(Si−NCO), are now in progress.

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(10) When the polymerization was carried out at −84 or −78 °C for 5 min, only a low yield of polymers was obtained. It means that the formation of trimer occurred around −84 °C even though 15C5 was used as a ligand.

(11) Composition ratio of Si−NCO to Oc−NCO summarized in Table 2 (entry number 2B) was found to be 1:0.55 in ^{1}H NMR (CDCl$_3$) when the feed ratio was 1:0.5. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.6, Si−C**H**$_2$ (t, 2H); 1.19, Si−O−CH$_2$−C**H**$_3$ (t, 9H); 1.70, CH$_2$−C**H**$_2$−CH$_2$ (m, 2H); 3.53, N−C**H**$_2$ (t, 2H); 3.76, Si−O−C**H**$_2$ (q, 6H); 0.87, C−C**H**$_3$ (t, 3H).

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