Supporting Information

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

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Structure of Anionic Initiators for Polymerization of Isocyanate

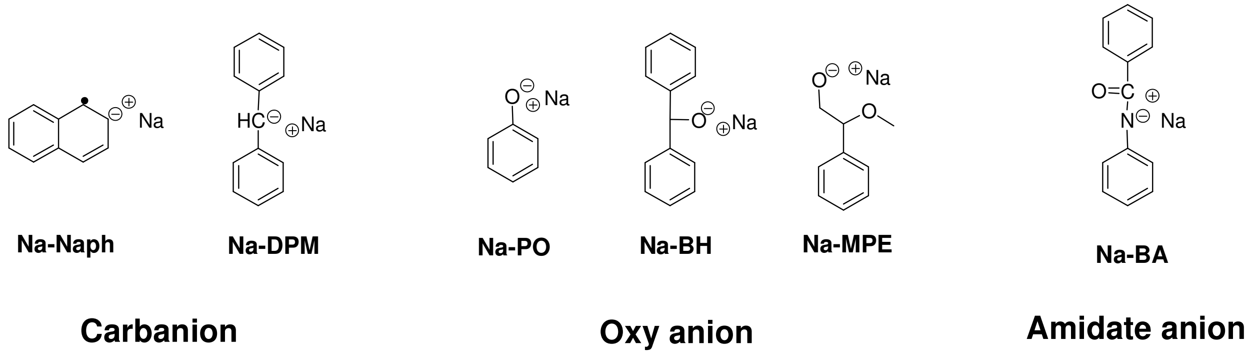
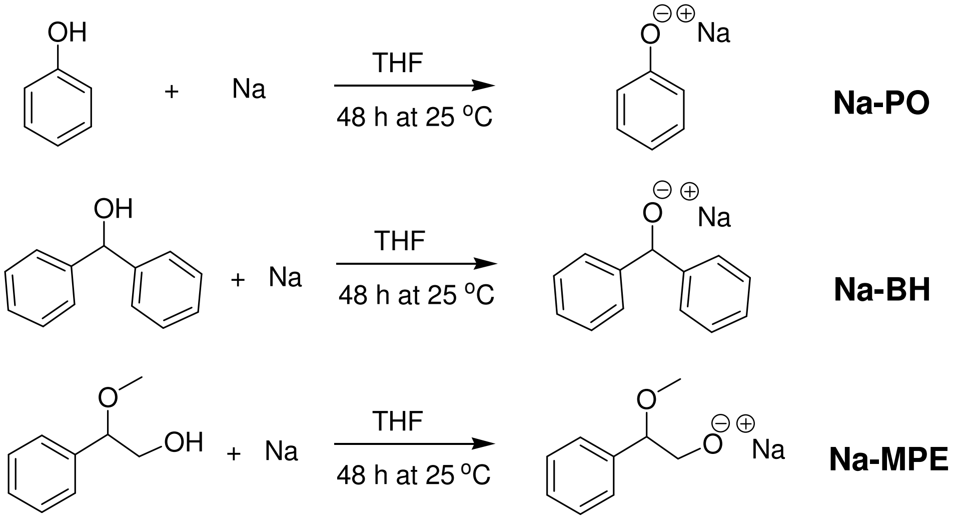


Figure S1. Anionic Initiators for Polymerization of Isocyanate.

Initiators Preparation

It has been reported that Na^+ is the most suitable cationic for the anionic polymerization of HIC among alkali metal counterions such as Li^+, Na^+, and K^+.[11] Sodium benzhydroxide (Na–BH) in THF (50 mL) was prepared by reacting equivalent amounts of benzhydrol (1.20 g, 6.50 mmol) and elemental sodium (0.150 g, 6.50 mmol) at 25 °C for 48 h under high vacuum. After completion of the reaction, the solution was connected to a high vacuum line (10^{-6} torr) and frozen by liquid nitrogen to remove gas. After complete degassing, the obtained initiator was stored in glass ampoules with break seals *in vacuo* at –30 °C. An adequate concentration of initiators was diluted prior to use. Other initiators, i.e., sodium phenoxide (Na–PO) and sodium methoxy-phenylethoxide (Na–MPE), were synthesized following above procedure. (Scheme S1).

Scheme S1. Preparation of oxyinitiators, sodium phenoxide (Na–PO), sodium methoxy-phenylethoxide (Na–MPE) and sodium benzhydroxide (Na–BH)



Estimation of the Oxyanion Content in the Initiators

The estimation of oxyanion in Na−BH is based on the reaction of Na-BH (0.325 g, 1.57 mmol) and CH_3COCl (0.123 g, 1.57 mmol) in the presence of pyridine (0.284 g, 3.60 mmol). The reaction was carried out under high vacuum conditions (10^{-6} torr) in an all-glass apparatus equipped with break-seals. The apparatus was connected to a vacuum line, which was followed by pinhole checks and baking. The apparatus was then sealed and separated from the vacuum line. Na−BH, pyridine and acetyl chloride were mixed, and the resulting mixture was stirred at room temperature for 24 h. After completion of the reaction, the crude mixture was suspended in water and extracted using diethyl ether. After evaporation of ether, the crude benzhydryl acetate was purified by recrystallization. The yield of benzhydryl acetate was ~95%.The structure of the compound was confirmed by ^1H NMR. The anion contents of the other initiators, i.e., Na−PO and Na−MPE, were determined following same procedure. **Benzhydryl acetate.** ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 2.1 (3H, CH_3), 6.0 (1H, $O{-}CH{-}(C_6H_5)_2$), 7.0-7.4 (10H, (C_6H_5)). **Phenyl acetate.** ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 2.1 (3H, CH_3), 7.0-7.4 (5H, (C_6H_5)). **2-Phenylpropyl acetate.** ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 1.3 (3H, $C{-}CH_3$) 2.1 (3H, $O{=}C{-}CH_3$), 3.1 (1H, $CH_3{-}CH{-}(C_6H_5)$), 4.0–4.2 (2H, $O{-}CH_2{-}CH$), 7.0-7.4 (5H, (C_6H_5)).

Anionic Polymerization of HIC using Na−Naph as an Initiator with Na−PO, Na−MPE or Na−BH as an Additive

In a typical polymerization procedure, Na−Naph (9.0 mg, 0.062 mmol) and Na−BH (66.0 mg, 0.320 mmol) in THF were transferred in a reaction flask through a break-seal. The solution was mixed for 5 min and then its temperature was equilibrated to −98 °C in a frozen methanol bath.

The polymerization was initiated by adding HIC (1.00 g, 7.85 mmol) in THF (10 ml) to the mixed solution. The polymerization proceeded for 10 min, and was then terminated by adding a 20-fold excess of HCl in methanol to the reaction solution, and polymer solution was precipitated into a large amount of methanol, filtered, and dried *in vacuo*. The methanol soluble portion was determined quantitatively by weighing the residue after the evaporation of methanol and by using ^{1}H NMR. (Table S1)

Additive Effects of Initators

Polymerization was carried out with a mixture of Na−Naph and each initiator (Na−PO, Na−MPE and Na−BH) to find additive effect. When only Na−Naph as an initiator was used, optimized time was 10 min. After 10 min, yield was slowly decreased and trimerization occurs. When Na−Naph as an initiator and Na−BPh_4 as an additive were used, the polymerization controlled; narrow MWD, predictable MW and 100% yield.

In polymerization with a mixture of Na−Naph and each initiator, Na−Naph played an initiator role, and Na−PO and Na−MPE could not act an additive role except Na−BH case from result Table S1. In Na−BH case, 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).

Table S1. Anionic Polymerization of *n*-Hexyl Isocyanate (HIC) using Sodium Phenoxide (Na−PO), Sodium Methoxy-Phenylethoxide (Na−MPE) and Sodium Benzhyroxide (Na−BH) with Sodium Naphthalenide (Na −Naph) to Confirm Additive Effects

Run	Na−Naph	Na−PO	Na−MPE	Na−BH	HIC	time	M_n × 10^{-3}		PDI[b]	yield
	mmol	mmol	mmol	mmol	mmol	min	calcd	obsd		%
1	0.162	0.242	-	-	7.05	20	9.6[a] /3.2[b]	8.3	1.22	86(14)[c]
2	0.139	-	0.145	-	5.13	20	8.3[a] /4.0[b]	8.6	1.35	88(12)[c]
3	0.057	-	-	0.320	7.59	20	33.7[a] /7.7[b]	34.1	1.06	100
		[Na−BPh4] / [Na−Naph]		[HIC] / [Na−Naph]						
4[d]		-		55.2		10	14.0[a]	36.5	1.21	100
5[d]		-		44.3		20	10.5[a]	29.6	1.26	92(8)[c]
6[d]		9.6		54.5		20	11.5[a]	11.7	1.09	99

[a] M_n is calculated using the relation {([HIC]/[Na−Naph]) × molecular weight of HIC × 2 } × yield of polymer/100. [b] M_n is calculated using the relation {([HIC]/[Na−PO, Na−MPE or Na−BH]) × molecular weight of HIC + molecular weight of H−PO, H−MPE or H−BH } × yield of polymer/100. [c] The yield of trimer is presented in parentheses. [d] These data published (Ahn, J.-H.; Shin, Y.-D.; Kim, S.-Y.; Lee, J.-S. *Polymer* **2003**, 44, 3847)

Suggestion of Polymerization Mechanism using Na−BH

In the polymerization procedure, after HIC is added to the initiator solution, HIC approaches to the Na−BH aggregates and propagation proceeds with efficient chain-end protection. In this aggregate system, Na−BH molecules act as an initiation and reduce reactivity at the growing chain-ends as an additive. Thus, the polymers yield is with ~100% without additional additives in this system.

Scheme S2. Anionic polymerization using Na−BH