

Supporting Information

Unprecedented Control Over Polymerization of *n*-Hexyl Isocyanate Using an Anionic Initiator Having Synchronized Function of Chain-End Protection

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Experimental

Materials. *n*-Hexyl isocyanate (Aldrich, 97%) was dried over CaH₂ and vacuum distilled. Tetrahydrofuran (THF, Fisher Scientific, GR grade) was distilled under N₂ after refluxing with sodium for 5 h and distilled again under vacuum from Na-Naph solution. The acid halides and pyridine of high purity were dried over CaH₂, and distilled under vacuum before use. Sodium (Aldrich, 99%), potassium (Aldrich, 98%), lithium (Aldrich, 99.9%), calcium hydride (Junsei, 95%), naphthalene (Naph, Aldrich, 99%), diphenylmethane (DPM, Aldrich, 99%), and benzanilide (Aldrich, 99.5%) were used

without further purification. Glass (Iwaki Glass Co. PYREX[®]), used for the glass apparatus, was rinsed with tap water and finally with triply distilled water and then oven-dried.

Initiators. Na-DPM was prepared from the reaction of equivalent amounts of DPM (0.223 g, 1.33 mmol) and Na-Naph (0.810 mmol) in THF (70 mL) at room temperature for 24 h. The exchange of Naph by DPM through alkali metal transfer mechanism is indicated by a change in color of the reaction mixture to red. Na-BA in THF (50 mL) was prepared from the reaction of equivalent amounts of benzanilide (8.70 g, 0.043 mol) and elemental sodium (1.00 g, 0.043 mol) at room temperature. When the color of reaction mixture turned light yellow, it was frozen by liquid nitrogen to remove dissolved gas by connecting to a high vacuum line (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*. An adequate concentration of Na-DPM and Na-BA was diluted prior to use. Li-BA and K-BA were synthesized by the same method as described above for Na-BA.

Estimation of BA anion content in the initiator Na-BA. The estimation of Na-BA is based on a reaction of Na-BA (2.20 g, 11.7 mmol) and CH_3COCl (1.75 g, 22.3 mmol), in the presence of pyridine (2.42 g, 30.5 mmol) at room temperature for three days, furnishing *N*-acetyl benzanilide. 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 the vacuum line followed by pinholes checks and baking. It was then sealed and separated from the vacuum line. Na-BA, pyridine and acetyl chloride were mixed and the mixture stirred at room temperature for 3 days. After completion of the

reaction the crude was suspended in water, and the organic layer extracted using diethyl ether. The crude *N*-acetyl benzanilide sample after evaporation of ether was purified by recrystallization, yield ~90%. The structure of the compound was confirmed from GC-MS and ¹H NMR studies.

Anionic polymerization of HIC. The polymerization reactions were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical procedure, the initiator solution, Na-BA (0.013 g, 0.066 mmol) in THF, was transferred into the reaction flask through the break-seal and the solution temperature was then equilibrated to the reaction temperature of -98 °C. The polymerization was effected by adding the HIC (0.753 g, 5.93 mmol) in THF to the initiator solution. At this point, the color of the reaction solution changed to light yellow. The reaction was terminated after 60 min by adding a 20-fold excess HCl in methanol when poly(*n*-hexyl isocyanate) (PHIC) was precipitated, which was filtered off, and dried *in vacuo*. The methanol soluble portion was determined quantitatively by weighing the residue after evaporation of methanol and using ¹H NMR to determine whether any unreacted monomers and/or trimers were present. The yield of the polymer was 99%. The procedure for polymerizations by the initiators Na-DPM was same as described for Na-BA.

PHIC. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 0.9 (3H, CH₃), 1.0-2.0 (8H, (CH₂)₄), 3.7 (2H, N-CH₂-). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 14.5 (CH₃), 22.5 (CH₂), 26.2 (CH₂), 28.5 (CH₂), 31.5 (CH₂), 48.6 (N-CH₂-), 156.8 (C=O). IR (KBr, cm⁻¹): 3441 (-NH), 2959, 2932, 2860 (CH₂), 1700 (C=O), 1349/1297 (disubstituted amide), 1227, 1175, 1092, 785, 728 (CH₂).

End-capping reaction. The PHIC end-capping was carried out reacting the living PHIC polymer with the acid halides in the presence of pyridine. The acid halide concentration is 20% molar excess of the initiator concentration. After 50 minutes of HIC polymerization by Na-BA, the acid halide in pyridine (1:1 molar ratio in 10 ml THF) was added, and the reaction mixture stirred at $-98\text{ }^{\circ}\text{C}$ for 10-20 minutes. The reaction takes place with a visual change in color from light yellow to a clear transparent solution. Without pyridine there was no change in color, and the polymer degrades with time to cyclic trimer. In a typical anionic polymerization experiment, to Na-BA (0.53 mmol in 10 mL THF), HIC (4.37 mmol in 6.5 mL THF) were reacted at $-98\text{ }^{\circ}\text{C}$ for 50 minutes. Then a mixture of the end-capping acid chloride, (s)-(-) acetoxypropionyl chloride (s(-)APC, 0.64 mmol in 5 mL THF) and pyridine (0.64 mmol) was added under high vacuum. The mixture was stirred at $-98\text{ }^{\circ}\text{C}$ for 20 minutes. The vacuum was broken and the reaction mixture was poured into excess methanol (200 mL). The precipitated polymer was purified by repeated dissolution and reprecipitation. Yield 98%. From ^1H NMR the efficiency of end-capping was determined. A comparison of the peak areas of the terminal $-\text{CH}_3$ with the $-\text{N}(\text{CH}_2-\text{C}_5\text{H}_{11})-$ protons shows an end-capping efficiency of $\sim 100\%$.

Structure of the initiator and suggested mechanism of polymerization. Benzanilide exists exclusively in the *trans* conformation both in the crystal and in solution, whereas *N*-methylbenzanilide exists predominately in *cis* structure.¹ The temperature dependent conformational studies indicate that at 233 K, *N*-methylbenzanilide exists exclusively in *cis* form.² Na-BA can exist in *trans* or *cis* conformation as seen from the energy minimized structures (Figure S1).

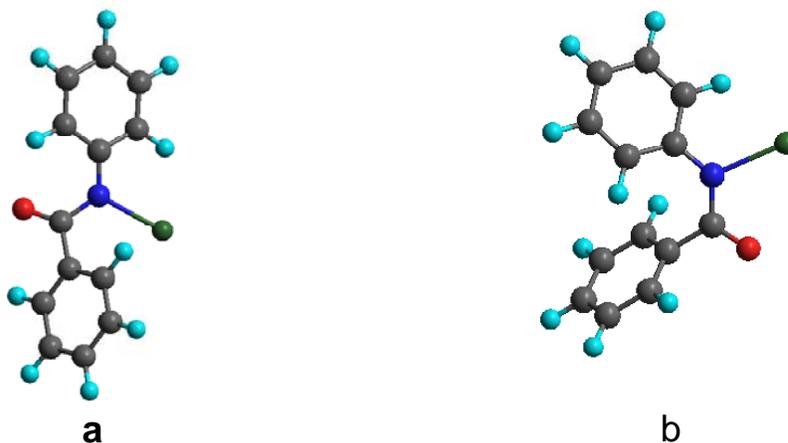


Figure S1. Optimized conformations of Na-BA from MM2 energy minimization (Chem3D Ultra 7.0): (a) *trans*, (b) *cis*. Color scheme: nitrogen – blue, oxygen – red, sodium – deep green, carbon – grey, hydrogen – bluish green.

Thus, the N --- Na⁺ bond in Na-BA, though predominantly ionic it should have some covalent character due to polarization effect. We propose a self-assembled cluster of five Na-BA molecules to form a macroring generated from weak interactions between Na⁺ of one molecule with the carbonyl oxygen of a neighboring molecule (Figure S2). Pentameric macrorings utilizing weak interactions are known to exist in solution as well as in solid state.³ The cavity of the model macroring (Figure S2b) shows that the nitrogen centers are accessible to the monomer (HIC). Bearing in mind that the schematic structure is labile as being held together by weak forces, addition of HIC can lead to a host of events. We visualize the initiation process as follows: (1) a molecule of HIC approaches the Na-BA pentameric cluster. (2) Since there is an equal probability of reaction with any of the Na-BA nitrogens, it ends up in reacting with one. (3) With the transfer of the negative charge on nitrogen in Na-BA to the isocyanate nitrogen, the

monomer occupies the place of the Na-BA molecule it covalently binds. (4) The negatively charged nitrogen of the HIC in the ring is more nucleophilic compared to other nitrogens resonating with the aromatic ring. Hence this nitrogen has the higher probability of attacking the second HIC molecule. This thought process is schematically presented in Figure S3.

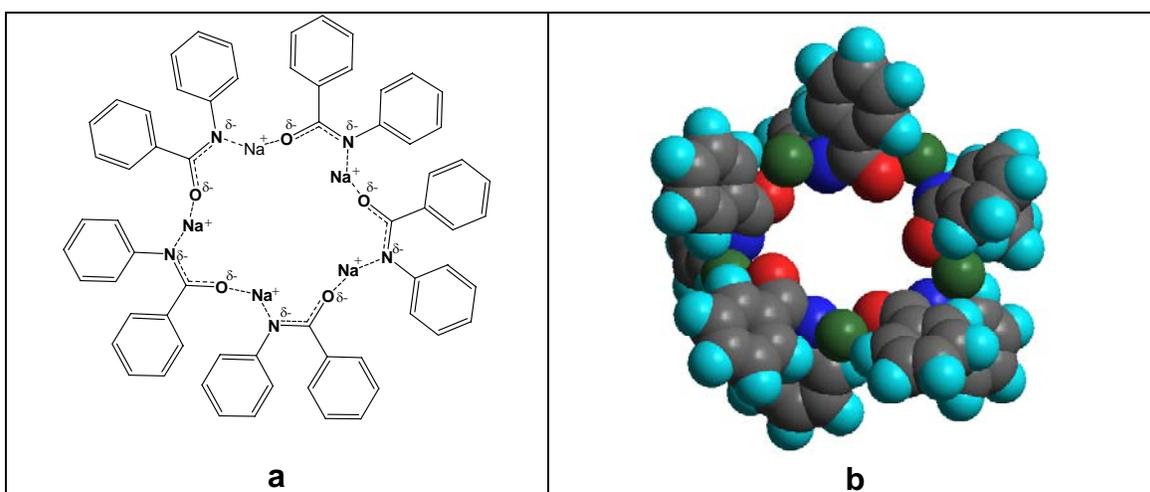


Figure S2. Structural models of Na-BA forming the pentameric macroring: (a) line drawing showing formation of the macroring utilizing weak $N^{\delta-} \cdots Na^+ \cdots O^{\delta-}$ interactions. (b) Energy minimized (MM2) structure of the macroring, space-filling model, top view. Color scheme: nitrogen – blue, oxygen – red, sodium – deep green, carbon – grey, hydrogen – bluish green.

Measurements. 1H and ^{13}C nuclear magnetic resonance (NMR) spectra were run using a JEOL JNM-LA300WB. All FT-NMR spectra were run in $CDCl_3$. 1H NMR chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm, ^{13}C NMR chemical shifts were referenced to deuterated chloroform at 77.0 ppm. IR spectra were obtained using KBr pellets by the Perkin Elmer System 2000. Molecular weights of the polymers

were calculated from the response of a multi-angle laser light scattering detector (Wyatt Technology) that was connected to a size exclusion chromatograph (MALLS/SEC). THF was used as the mobile phase at a flow rate of 1.0 mL/min. The dn/dc value for PHIC in THF at 40 °C was measured with an LED (Optilab DSP) source. After dn/dc was measured for 5 different concentrations for one polymer sample, SEC-LS data were acquired with refractive index detection at 40 °C.

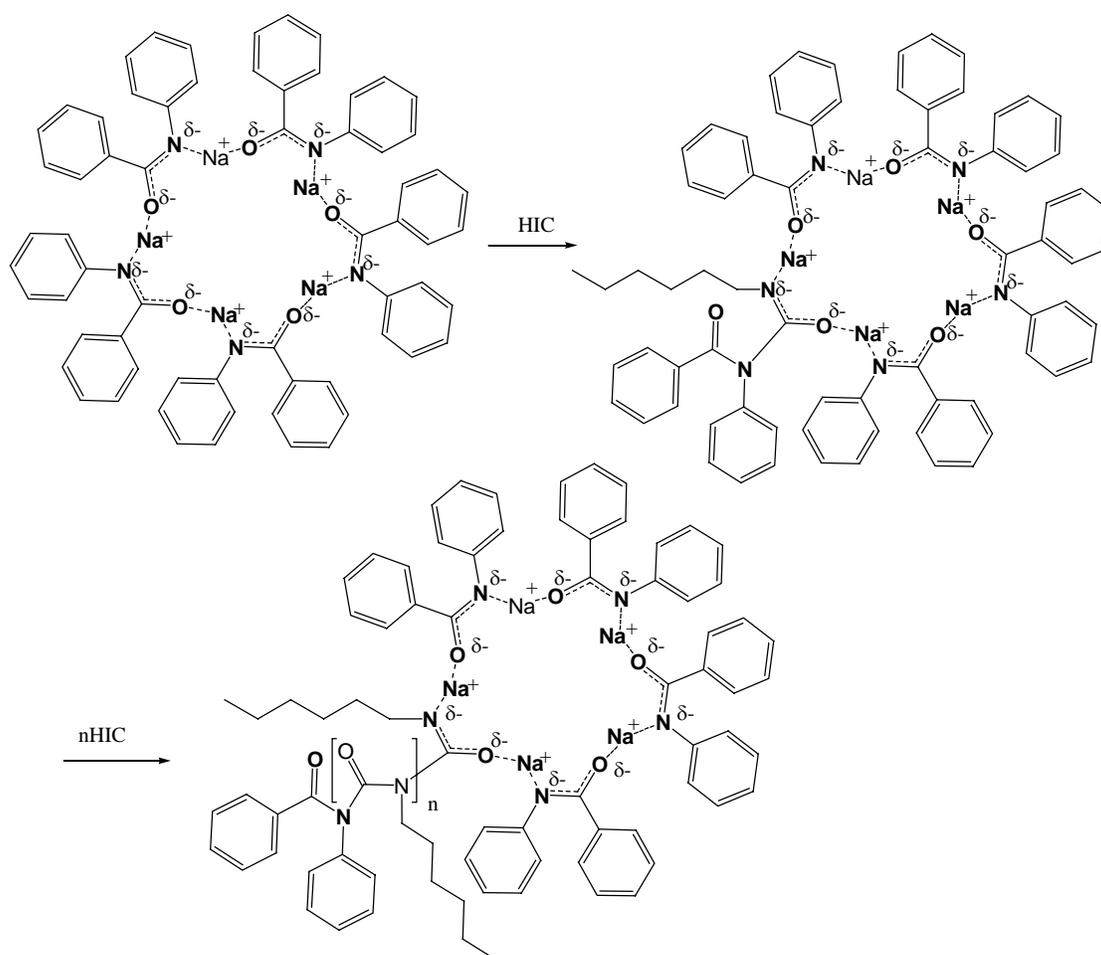


Figure S3. Interaction of the macroring with the monomer in the initiation and propagation steps.

Table S1. Anionic polymerization of HIC using Na-BA in THF at $-98\text{ }^{\circ}\text{C}$.

Na-Naph, mmol	Na-BA, mmol	HIC, mmol	time, min	$M_n \times 10^{-3}$		M_w/M_n^b	yield of polymer, %
				calcd ^a	obsd ^b		
-	0.175	5.34	10	1.6	10.4	1.08	40(60) ^c
-	0.160	5.15	20	2.8	15.1	1.07	68(32) ^c
-	0.225	5.21	30	2.5	13.5	1.09	85(15) ^c
-	0.205	5.07	40	2.8	14.6	1.10	94(6) ^c
-	0.310	5.54	50	2.2	11.7	1.10	97(3) ^c
-	0.330	5.93	60	2.3	12.0	1.09	99
-	0.390	8.24	60	2.7	13.6	1.09	100
-	0.340	8.64	60	3.2	16.8	1.11	100
-	0.350	13.3	60	4.8	22.1	1.12	99
-	0.380	18.0	70	5.9	30.5	1.08	98
-	0.265	17.6	70	8.2	40.8	1.16	97
-	0.415	7.24	80	1.9	8.9	1.16	92(8) ^d
-	0.445	7.34	100	1.7	10.1	1.12	81(19) ^d
0.090 ^e	-	4.97	10	14.0	67.5	1.26	100
0.100 ^e	-	4.70	30	10.5	100	1.12	89(11) ^d
0.100 ^e	-	4.82	60	10.5	73.5	1.24	86(14) ^d
0.075	0.201	6.69	10	22.7	19.7	1.15	100
0.079	0.206	6.28	30	20.3	21.5	1.18	100
0.082	0.200	6.53	60	20.2	21.1	1.11	100

^aCalculated M_n is computed by $\{([HIC]/[M-BA]) \times \text{molecular weight of HIC} + \text{molecular weight of BA}\} \times \text{yield of polymer}/100$. ^b M_n and M_w/M_n were measured by SEC-LS in THF at $40\text{ }^{\circ}\text{C}$. ^cThe unreacted monomer are presented in parentheses. ^dThe yields of trimer are presented in parentheses. ^eData from the reference: Kim, S. Y.; Ahn, J. H.; Shin, Y. D.; Lee, J. S. *Polym. Prepr.* **2000**, 41(2), 1211.

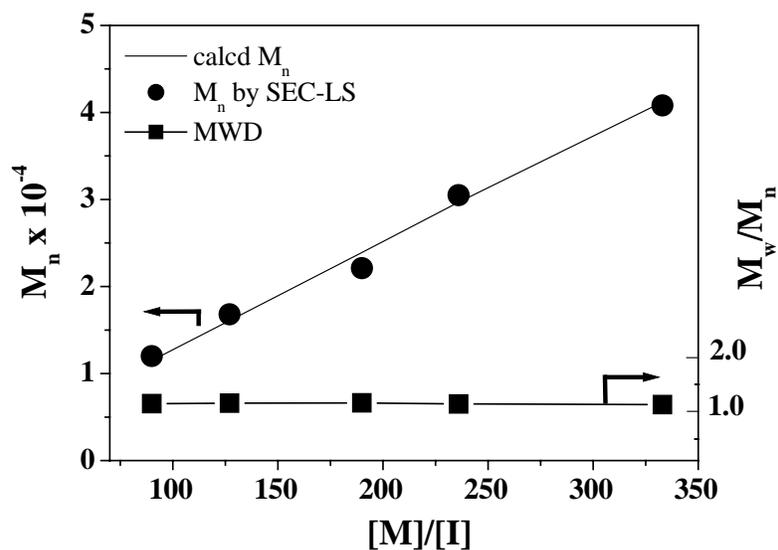


Figure S4. Molecular weight and molecular weight distribution vs. the feed ratio of HIC(M) to Na-BA (I).

References

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