

Supporting Information

Living Initiator-Transfer Anionic Polymerization of Isocyanates by Sodium Diphenylamide

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S1. Experimental Section

S1.1. Materials

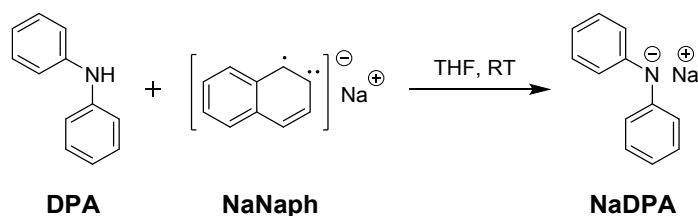
All reagents were purchased from several commercial suppliers (Sigma-Aldrich, TCI, Alfa Aesar, Fisher Scientific, etc.) and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled over sodium naphthalenide (NaNaph) and degassed at room temperature (RT) under 10^{-6} Torr. Sodium tetrphenylborate (NaBPh₄) was dried at 80 °C under 10^{-6} Torr for 12 h. *n*-Hexyl isocyanate (HIC), furfuryl isocyanate (FIC), and allyl isocyanate (AIC) were distilled over calcium hydride (CaH₂) under reduced pressure and then redistilled over CaH₂ under 10^{-6} Torr. NaBPh₄, HIC, FIC, and AIC were appropriately diluted with dry THF and distributed in appropriate numbers of clean glass ampules equipped with break-seals under 10^{-6} Torr. A mixture of an aqueous solution of 37% hydrochloric acid (HCl, 2 mL), methanol (30 mL), and THF (40 mL) was degassed and distributed in twelve clean glass ampules equipped with break-seals under 10^{-6} Torr. A solution of NaNaph in THF was prepared by following the procedure detailed in our previous work.^{S1}

S1.2. Instruments and Analyses

Proton and carbon-13 nuclear magnetic resonance (¹H and ¹³C NMR) spectra were recorded using a JNM-ECX 400 NMR spectrometer (JEOL) in chloroform-*d* (CDCl₃, 99.8 atom% D, contains 0.03 vol% tetramethylsilane (TMS)) or dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, 99.5 atom% D) at 25 °C. Number-average molecular weight (M_n) and dispersity (\mathcal{D}) values of polymers were measured using a size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) instrument equipped with a 515 HPLC pump (Waters), a set of four Styragel columns connected in series (HR 0.5, HR 1, HR 3, and HR 4 with pore sizes of 50, 100, 500, and 1000 Å, respectively,

Waters), a miniDAWN TREOS light scattering detector (Wyatt Technology) and an Optilab T-rEX refractive index detector (Wyatt Technology). The SEC-MALLS was operated in THF:triethylamine (98:2 v:v) with an elution rate of 1.0 mL/min at 40 °C. The refractive index increment (dn/dc) values of polymers were calculated according to the assumption of 100% mass recovery.

S1.3. Preparation of Solutions of Sodium Diphenylamide (NaDPA) and 1:5 NaDPA:NaBPh₄ in THF

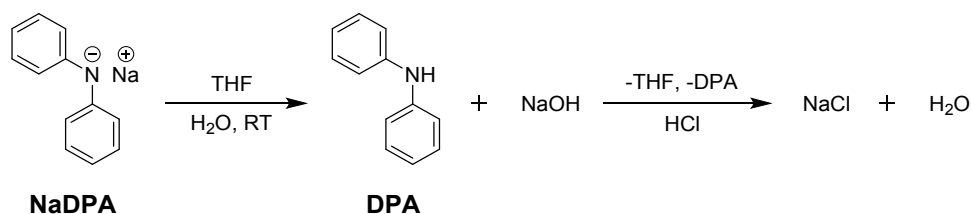


The break-seal technique was performed in a clean glass apparatus at RT under 10^{-6} Torr throughout the process. Diphenylamine (DPA, 1.35 g, 8.0 mmol) was dried for 12 h in a clean glass ampule equipped with a break-seal. DPA was diluted with THF to prepare a 0.316 mol L^{-1} solution and transferred into a new clean glass ampule equipped with a break-seal. Using the break-seal technique, the DPA solution was added to a 0.764 mol L^{-1} solution of NaNaph (8.00 mmol) in THF in a clean glass apparatus. The yellowish solution of sodium diphenylamide (NaDPA) in THF was transferred into a clean glass ampule equipped with a break-seal. The solution was diluted further with THF and distributed in appropriate numbers of clean glass ampules equipped with break-seals. a 0.205 mol L^{-1} solution of NaDPA (3.14 mmol) in THF was mixed with a 0.542 mol L^{-1} solution of NaBPh₄ (15.7 mmol) in THF. The solutions of NaDPA and 1:5 NaDPA:NaBPh₄

were further diluted with THF and distributed in appropriate numbers of clean glass ampoules equipped with break-seals.

DPA: ^1H NMR (DMSO- d_6 , 400 MHz): δ (ppm) 8.12 (s, 1H), 7.19 (t, 4H, $J = 7.6$ Hz), 7.03 (d, 4H, $J = 8.8$ Hz), 6.77 (td, 2H, $J = 7.4, 1.2$ Hz). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ (ppm) 143.94, 129.69, 120.16, 117.22.

S1.4. Acid-Base Titration to Determine the Exact Molar Concentration of NaDPA Solution



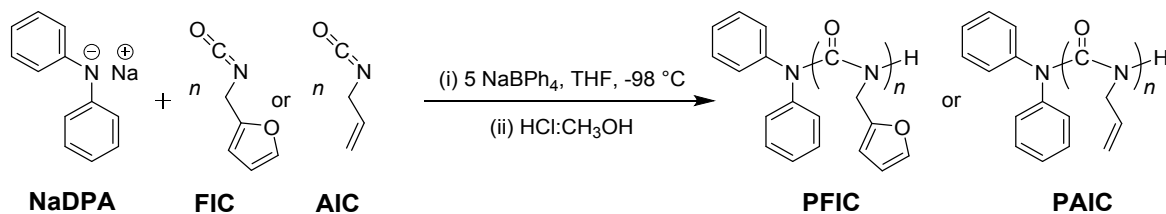
The reaction was carried out using a break-seal technique in a sealed glass reactor under 10^{-6} Torr. Neutral deionized water (pH ≈ 7.0 , 10.0 mL) was slowly added to a 0.103 mol L^{-1} NaDPA solution (10.7 mL; the expected amount of NaDPA = 1.10 mmol) in THF at RT. After the complete reaction, the resultant alkaline solution of NaOH was concentrated under reduced pressure and filtered to remove THF and DPA, respectively. Deionized water was poured into the alkaline solution until the overall volume of the solution became 75 mL. Then, 1 mL of an aqueous solution of 0.20 mol L^{-1} HCl was repeatedly added to the alkaline aqueous solution at RT. The pH of the solution was monitored by a pH meter in real time. The actual molar concentration of NaDPA was found to be 1.01 mmol (91.8%) at the neutralization point. Thus, the molar concentration of NaDPA solution was corrected to a value of the expected molar concentration value multiplied by 0.918.

S.1.5. Anionic Polymerization of HIC for the Kinetic Study

The anionic polymerization was carried out according to the break-seal technique in a clean glass apparatus prewashed with a solution of NaNaph in THF under 10^{-6} Torr. A polymerization bath with -98 °C was prepared from a mixture of methanol and liquid nitrogen. A solution of the initiator (NaDPA or 1:5 NaDPA:NaBPh₄) in THF was transferred into a reaction flask and cooled to -98 °C. The polymerization proceeded by adding a solution of HIC in THF to the initiator solution, in which the $[\text{HIC}]_0$ was close to 0.250 mol L⁻¹. At a particular time (t), the polymerization was terminated by adding a solution of HCl:methanol in THF. The resulting polymer was precipitated in cool methanol, filtered, and dried under vacuum. The conversion to polymer was determined from the gravimetric yield. The methanol-soluble residues were concentrated under reduced pressure and characterized by ¹H NMR to calculate the conversion to cyclotrimer. The anionic polymerization of HIC finally yielded poly(*n*-hexyl isocyanate) (PHIC). The anionic polymerization with $[\text{HIC}]_0$ near to 0.500 mol L⁻¹ was conducted in a bath with -78 °C which was prepared from a mixture of acetone and dry ice.

PHIC with a terminal DPA residue: ¹H NMR (CDCl₃ with 0.03 vol% TMS, 400 MHz): δ (ppm) 7.40–7.15 (br), 4.05–3.30 (br), 1.85–1.40 (br), 1.40–1.05 (br), 0.95–0.75 (br). ¹³C NMR (CDCl₃ with 0.03 vol% TMS, 100 MHz): δ (ppm) 156.83, 129.31, 127.08, 48.62, 31.57, 28.47, 26.30, 22.63, 14.03.

S.1.6. Anionic Polymerization of FIC and AIC

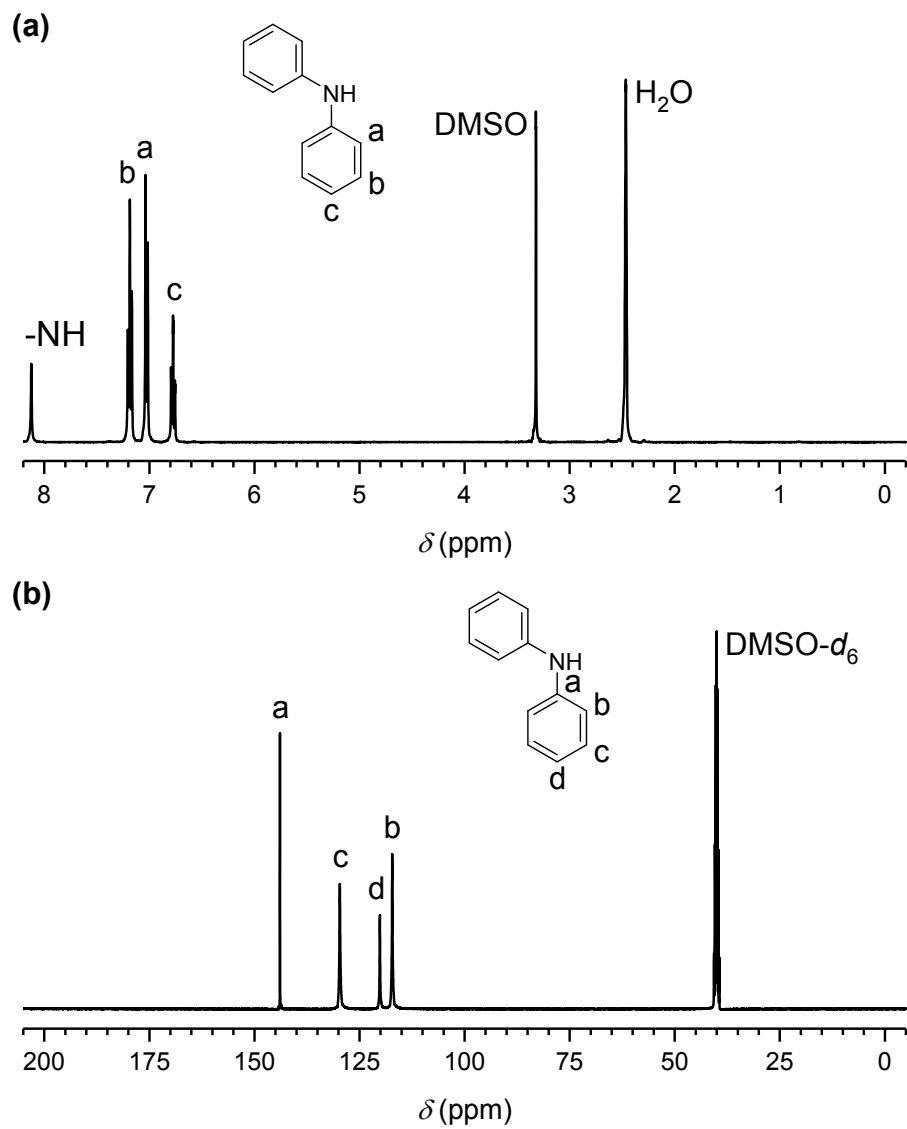


A solution of 1:5 NaPEPPA:NaBPh₄ in THF was transferred into a reaction flask and cooled to -98 °C. The polymerization proceeded by adding a solution of FIC or AIC in THF to the initiator solution, in which the [FIC or AIC]₀ was close to 0.250 mol L⁻¹. At *t*, the polymerization was terminated by adding a solution of HCl:methanol in THF. The resulting polymer was precipitated in cool methanol, filtered, and dried under vacuum. The conversion to polymer was determined from the gravimetric yield. The methanol-soluble residues were concentrated under reduced pressure and characterized by ¹H NMR to calculate the conversion to cyclotrimer. The anionic polymerization of FIC and AIC finally yielded poly(furfuryl isocyanate) (PFIC) and poly(allyl isocyanate) (PAIC).

PFIC with a terminal DPA residue: ¹H NMR (CDCl₃ with 0.03 vol% TMS, 400 MHz): δ (ppm) 7.35–7.15 (br), 6.35–6.12 (br), 5.00–4.55. ¹³C NMR (CDCl₃ with 0.03 vol% TMS, 100 MHz): δ (ppm) 156.67, 153.94, 149.15, 142.04, 128.77, 127.30, 110.52, 108.42, 44.91.

PAIC with a terminal DPA residue: ¹H NMR (CDCl₃ with 0.03 vol% TMS, 400 MHz): δ (ppm) 7.40–7.15 (br), 5.90–5.65 (br), 5.40–5.05 (br), 4.60–4.00 (br). ¹³C NMR (CDCl₃ with 0.03 vol% TMS, 100 MHz): δ (ppm) 159.36, 153.72, 131.93, 129.31, 126.89, 116.99, 50.34.

S2. Supplementary Data



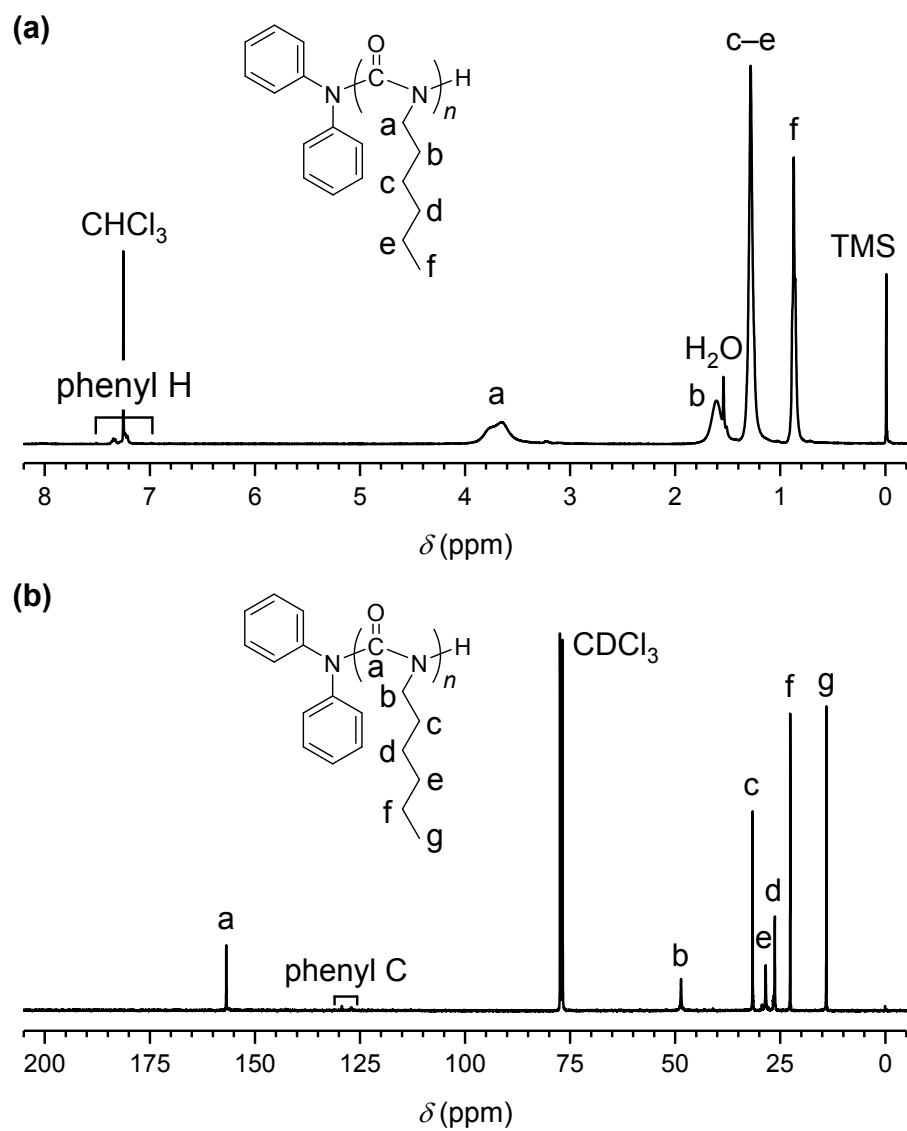


Figure S2. (a) ^1H and (b) ^{13}C NMR of PHIC with a terminal DPA residue in CDCl_3 .

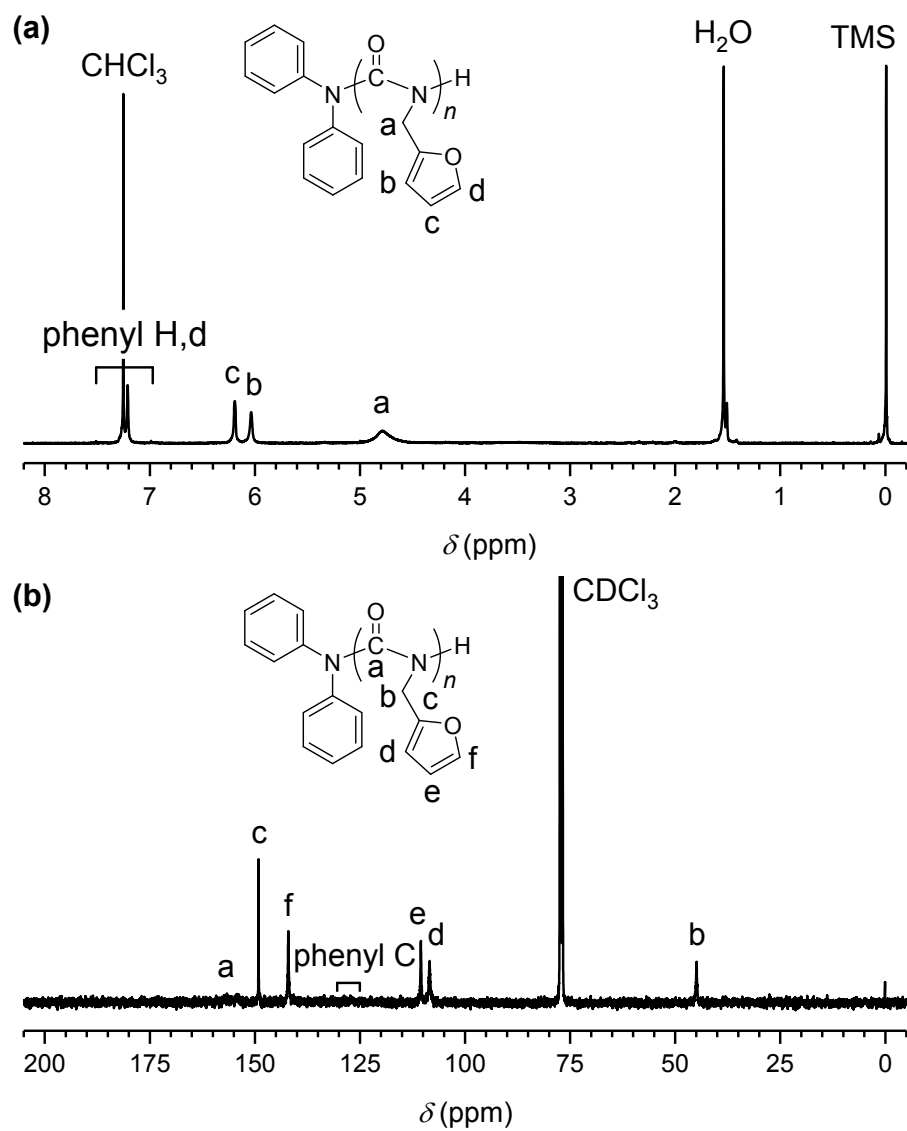


Figure S3. (a) ¹H and (b) ¹³C NMR of PFIC with a terminal DPA residue in CDCl₃.

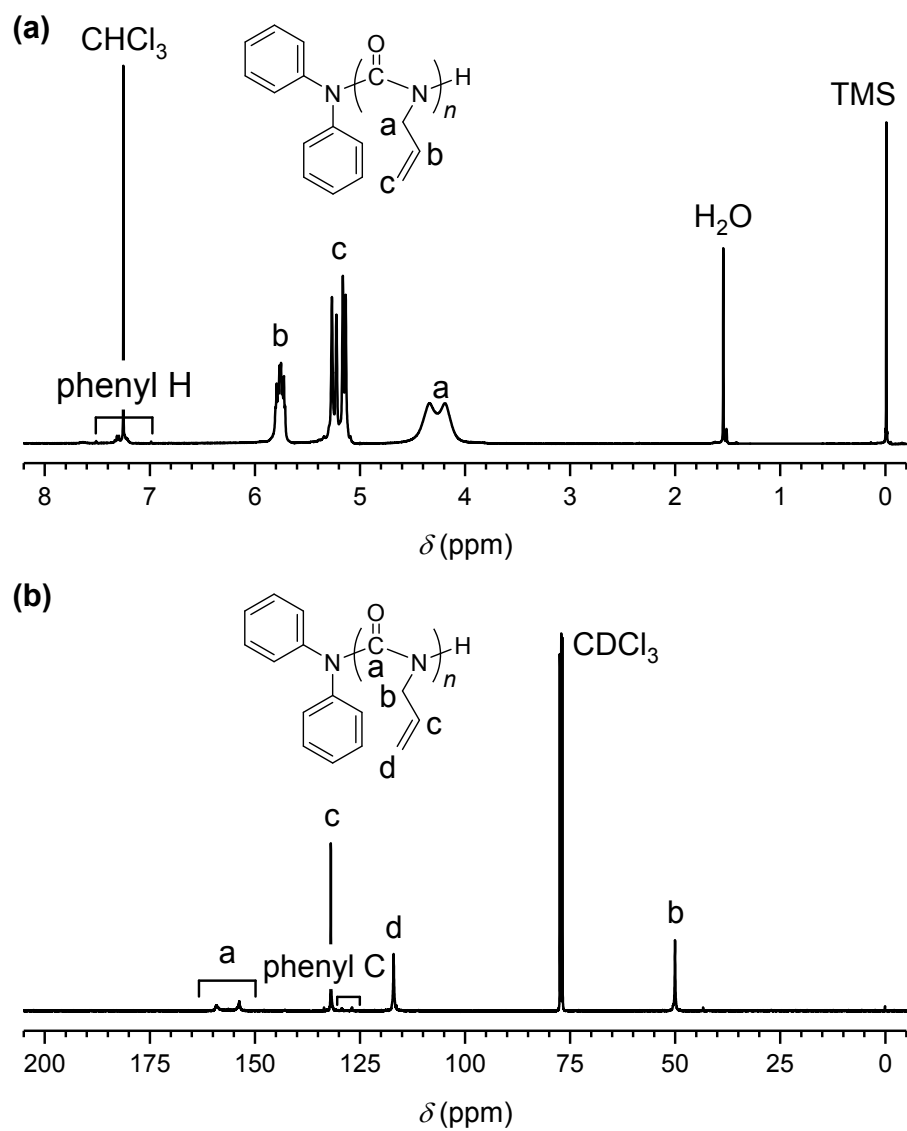


Figure S4. (a) ^1H and (b) ^{13}C NMR of PAIC with a terminal DPA residue in CDCl_3 .

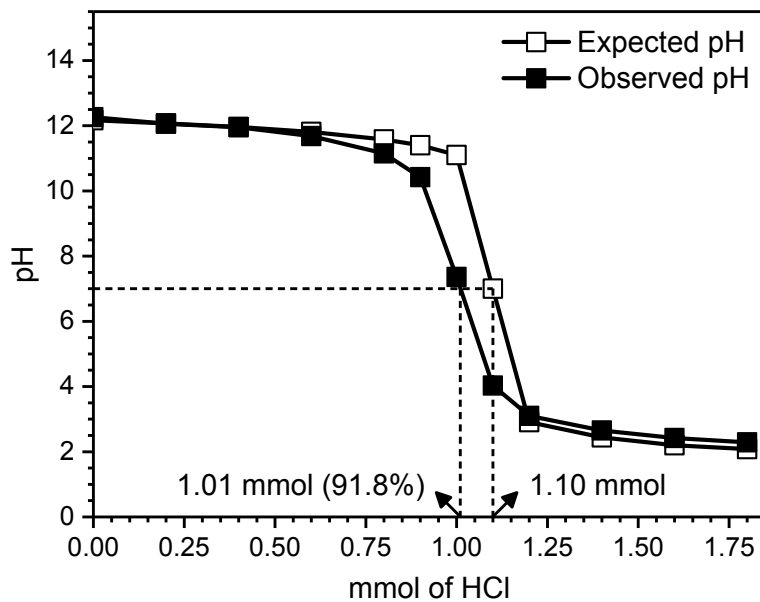


Figure S5. pH profile of aqueous NaOH solution converted from the NaDPA solution in THF after titration with 0.20 mol L^{-1} aqueous HCl solution.

Table S1. Results of the Anionic Polymerization of HIC Initiated by NaDPA in the Absence of NaBPh₄ ([NaBPh₄]₀/[NaDPA]₀ = 0) in THF at -98 °C under 10⁻⁶ Torr

entry	[HIC] ₀ (mol L ⁻¹)	[NaDPA] ₀ (mol L ⁻¹)	[HIC] ₀ / [NaDPA] ₀	<i>t</i> (s)	conv/% P ^a /CT ^b	<i>M</i> _{n,theo} ^c (kDa)	<i>M</i> _n ^d (kDa)	<i>D</i> ^d	<i>f</i> ^e
S1	0.251	10.8 × 10 ⁻³	23.2	60	81.5/0	2.57	4.62	1.15	0.539
S2	0.251	10.8 × 10 ⁻³	23.2	150	95.5/0.1	2.99	4.97	1.16	0.588
S3	0.251	10.8 × 10 ⁻³	23.2	300	98.6/0.3	3.08	5.05	1.17	0.596
S4	0.248	5.39 × 10 ⁻³	46.0	60	73.7/0	4.48	8.85	1.11	0.497
S5	0.248	5.39 × 10 ⁻³	46.0	150	91.8/0	5.54	9.54	1.16	0.573
S6	0.248	5.39 × 10 ⁻³	46.0	300	96.5/0	5.81	9.67	1.17	0.594
S7	0.248	5.39 × 10 ⁻³	46.0	600	98.2/0.1	5.91	9.80	1.17	0.596
S8	0.252	3.10 × 10 ⁻³	81.3	60	62.0/0	6.58	15.1	1.11	0.429
S9	0.252	3.10 × 10 ⁻³	81.3	150	85.6/0	9.02	16.8	1.14	0.532
S10	0.252	3.10 × 10 ⁻³	81.3	300	94.5/0	9.94	17.2	1.13	0.574
S11	0.252	3.10 × 10 ⁻³	81.3	600	97.6/0	10.3	17.3	1.13	0.591
S12	0.252	3.10 × 10 ⁻³	81.3	900	98.0/0	10.3	17.4	1.12	0.588

^aConversion to polymer determined from the gravimetric yield of polymer. ^bConversion to cyclotrimer determined from ¹H NMR. ^c*M*_{n,theo} = MW of DPA + [HIC]₀/[NaDPA]₀ × MW of HIC × conv to polymer/100%. ^dDetermined from SEC-MALLS. ^e*f* = (*M*_{n,theo} of polymer - MW of DPA)/(*M*_n of polymer - MW of DPA).

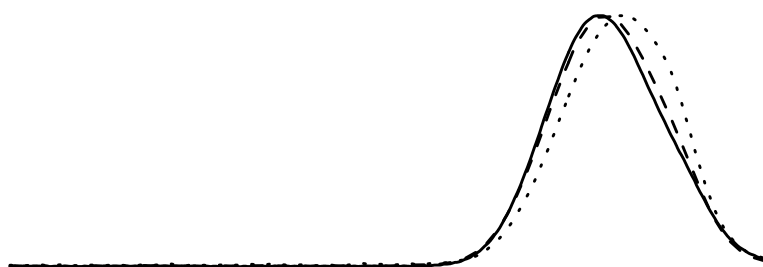
Table S2. Results of the Anionic Polymerization of HIC Initiated by NaDPA in the Presence of NaBPh₄ ([NaBPh₄]₀/[NaDPA]₀ = 5) in THF at -98 °C under 10⁻⁶ Torr

entry	[HIC] ₀ (mol L ⁻¹)	[NaDPA] ₀ (mol L ⁻¹)	[HIC] ₀ / [NaDPA] ₀	<i>t</i> (s)	conv/% P ^a /CT ^b	<i>M</i> _{n,theo} ^c (kDa)	<i>M</i> _n ^d (kDa)	<i>D</i> ^d	<i>f</i> ^e
S18	0.247	10.9 × 10 ⁻³	22.7	300	72.2/0	2.25	4.53	1.06	0.477
S19	0.247	10.9 × 10 ⁻³	22.7	600	92.8/0	2.85	5.77	1.07	0.479
S20	0.247	10.9 × 10 ⁻³	22.7	900	98.1/0	3.00	6.09	1.07	0.478
S21	0.247	5.52 × 10 ⁻³	44.7	300	61.9/0	3.69	7.47	1.14	0.482
S22	0.247	5.52 × 10 ⁻³	44.7	600	84.7/0	4.98	10.0	1.14	0.489
S23	0.247	5.52 × 10 ⁻³	44.7	900	94.4/0	5.54	11.0	1.15	0.496
S24	0.247	5.52 × 10 ⁻³	44.7	1200	97.8/0	5.73	11.4	1.15	0.495
S25	0.258	2.81 × 10 ⁻³	91.8	300	47.0/0	5.66	11.5	1.16	0.485
S26	0.258	2.81 × 10 ⁻³	91.8	600	71.9/0	8.56	17.5	1.11	0.484
S27	0.258	2.81 × 10 ⁻³	91.8	1200	92.3/0	10.9	22.3	1.13	0.485
S28	0.258	2.81 × 10 ⁻³	91.8	1800	97.8/0	11.6	23.6	1.13	0.488
S29	0.248	1.33 × 10 ⁻³	186	600	19.4/0	4.76	23.2	1.55	0.199
S30	0.248	1.33 × 10 ⁻³	186	1200	58.1/0	13.9	41.1	1.11	0.335
S31	0.248	1.33 × 10 ⁻³	186	1800	80.6/0	19.2	56.5	1.11	0.338
S32	0.248	1.33 × 10 ⁻³	186	2400	90.7/0	21.6	63.8	1.16	0.337
S33	0.498	2.68 × 10 ⁻³	186	2400	99.4/0	23.7	47.8	1.16	0.494

^aConversion to polymer determined from the gravimetric yield of polymer. ^bConversion to cyclotrimer determined from ¹H NMR. ^c*M*_{n,theo} = MW of DPA + [HIC]₀/[NaDPA]₀ × MW of HIC × conv to polymer/100%. ^dDetermined from SEC-MALLS. *f* = (*M*_{n,theo} of polymer – MW of DPA)/(*M*_n of polymer – MW of DPA).

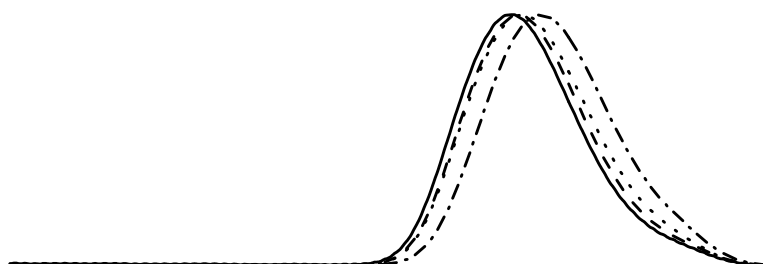
(a) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 23.2$ ($[\text{HIC}]_0 = 0.251 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 10.8 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - - 60 s (81.5%)
- - - 150 s (95.5%)
— 300 s (98.6%)



(b) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 46.0$ ($[\text{HIC}]_0 = 0.248 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 5.39 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - - 60 s (73.7%)
- - - 150 s (91.8%)
- - - 300 s (96.5%)
— 600 s (98.2%)



(c) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 81.3$ ($[\text{HIC}]_0 = 0.252 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 3.10 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - - 60 s (62.0%)
- - - 150 s (85.6%)
- - - 300 s (94.5%)
- - - 600 s (97.6%)
— 900 s (98.0%)

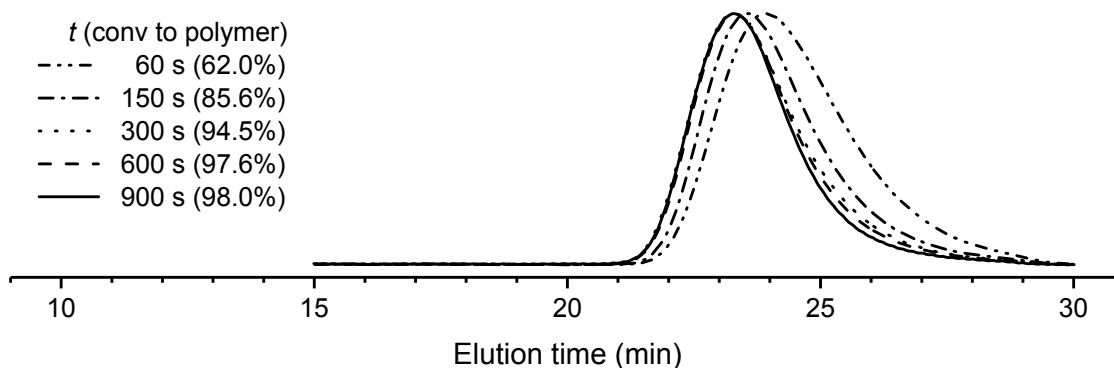
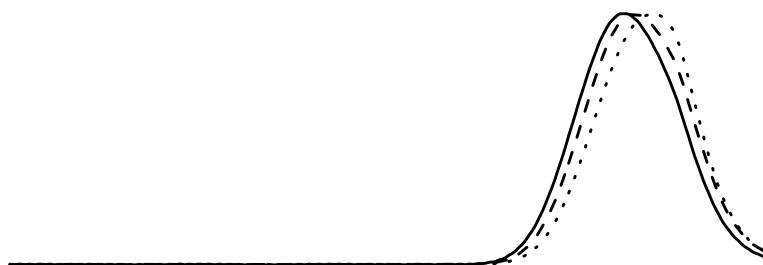


Figure S6. SEC-dRI traces of PHICs yielded from the anionic polymerization of HIC initiated by NaDPA in the absence of NaBPh₄ ($[\text{NaBPh}_4]_0/[\text{NaDPA}]_0 = 0$) in THF at $-98 \text{ }^\circ\text{C}$ under 10^{-6} Torr. $[\text{HIC}]_0/[\text{NaDPA}]_0 =$ (a) 23.2, (b) 46.0, and (c) 81.3.

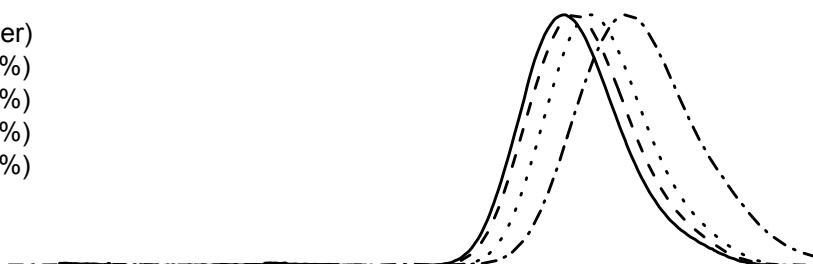
(a) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 22.7$ ($[\text{HIC}]_0 = 0.247 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 10.9 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - 300 s (72.2%)
- - - 600 s (92.8%)
— 900 s (98.1%)



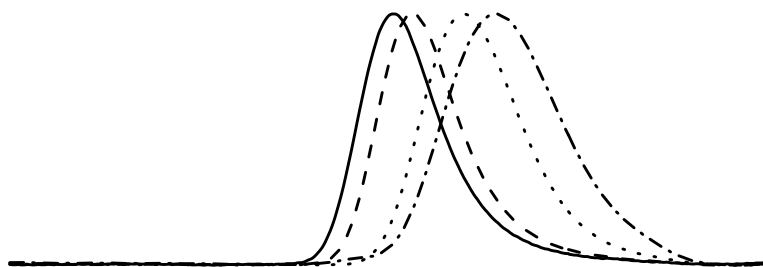
(b) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 44.7$ ($[\text{HIC}]_0 = 0.247 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 5.52 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - 300 s (61.9%)
- - - 600 s (84.7%)
- - - 900 s (94.4%)
— 1200 s (97.8%)



(c) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 91.8$ ($[\text{HIC}]_0 = 0.258 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 2.81 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - 300 s (47.0%)
- - - 600 s (71.9%)
- - - 900 s (92.3%)
— 1200 s (97.8%)



(d) $[\text{HIC}]_0/[\text{NaDPA}]_0 = 186$ ($[\text{HIC}]_0 = 0.248 \text{ mol L}^{-1}$; $[\text{NaDPA}]_0 = 1.33 \times 10^{-3} \text{ mol L}^{-1}$)

t (conv to polymer)
- - - 600 s (19.4%)
- - - 1200 s (58.1%)
- - - 1800 s (80.6%)
— 2400 s (90.7%)

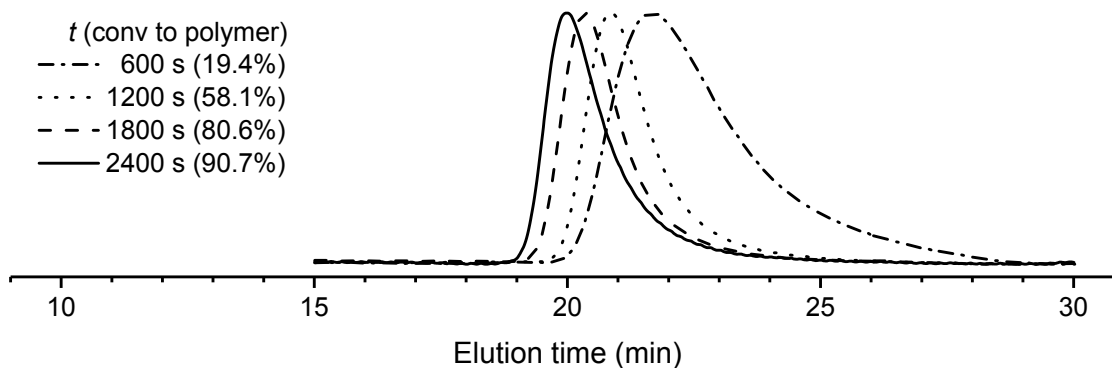


Figure S7. SEC-dRI traces of PHICs yielded from the anionic polymerization of HIC initiated by NaDPA in the presence of NaBPh₄ ($[\text{NaBPh}_4]_0/[\text{NaDPA}]_0 = 5$) in THF at $-98 \text{ }^\circ\text{C}$ under 10^{-6} Torr. $[\text{HIC}]_0/[\text{NaDPA}]_0 =$ (a) 22.7, (b) 44.7, (c) 91.8, and (d) 186.

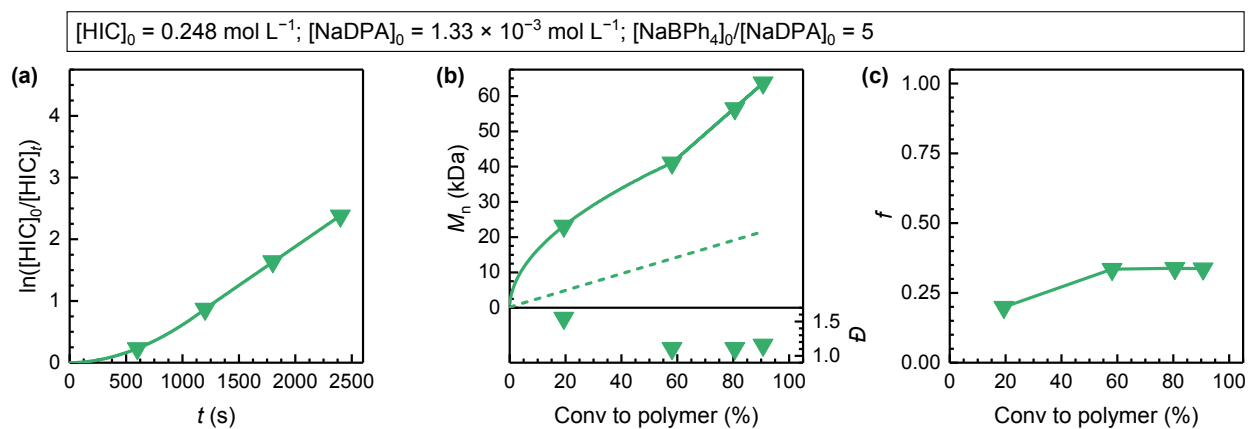


Figure S8. Kinetics profiles for the anionic polymerizations of HIC initiated by NaDPA in the presence of NaBPh₄ ($[\text{NaBPh}_4]_0/[\text{NaDPA}]_0 = 5$) in THF at $-98 \text{ }^\circ\text{C}$ under 10^{-6} Torr: (a) plot of $\ln([\text{HIC}]_0/[\text{HIC}]_t)$ versus t , (b) plots of M_n and D of PHIC versus conversion to polymer (a linear fit of $M_{n,\text{theo}}$ against conversion to polymer is displayed as a dashed line), and (c) plot of f versus conversion to polymer.

Table S3. Free Energy Components in THF at -98 °C (See the Reference S2 for the Equations)

(kcal mol ⁻¹)	$-T\Delta S_{\text{trans}}$	ΔH_{rot}	$-T\Delta S_{\text{rot}}$	$\Delta\Delta G_{0\rightarrow 175\text{K}}$	$\Delta E_{\text{g,OK}}$	ΔG_{solv}	$\Delta G_{\text{THF,175K}}$
	(1)	(2)	(3)	(4) ^a	(5)	(6)	(7) ^b
Na ⁺	-4.3	0.000	0.0	-3.4	-101711.4	-96.8	-101810.6
DPA ⁻	-5.3	0.522	-5.2	-9.1	-325177.3	-42.9	-325228.2
NaDPA	-5.4	0.522	-5.3	-9.3	-427013.6	-27.4	-427049.2
(NaDPA) ₂	-5.8	0.522	-6.0	-10.4	-854070.6	-21.1	-854101.0
(NaDPA) ₃	-6.0	0.522	-6.4	-11.0	-1281119.9	-16.9	-1281146.7
(NaDPA) ₄	-6.1	0.522	-6.7	-11.4	-1708162.4	-25.0	-1708197.8
HIC	-5.2	0.522	-4.9	-8.7	-253937.1	0.2	-253944.5
DPA(HIC)Na	-5.7	0.522	-6.0	-10.2	-680972.3	-23.1	-681004.6
{DPA(HIC)Na} ₂ •(NaDPA)	-5.9	0.522	-6.4	-10.9	-1108032.8	-14.8	-1108057.5

^a(4) = ΔH_{trans} (= 0.87) + (1) + (2) + (3). ^b(7) = (4) + (5) + (6) + $\Delta G_{\text{solv,cor}}$ (= 1.08).

Table S3 (Continued). Equations Used to Calculate Free Energy Changes During the Chemical Transformations Involving (NaDPA)_N (N = 1 to 4), HIC, DPA(HIC)Na, and {DPA(HIC)Na}•(NaDPA) in THF at –98 °C (See Above for ΔG_{THF,175K} Values)

(1) Self-association of NaDPA



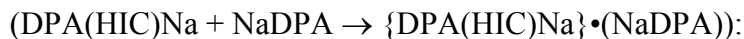
$$\Delta\Delta G_{\text{SA}} = \Delta G_{\text{THF},175\text{K}}((\text{NaDPA})_N) - N \Delta G_{\text{THF},175\text{K}}(\text{NaDPA}) \quad (\text{S1})$$

(2) Initiation reaction of (NaDPA)₂ with HIC



$$\begin{aligned} \Delta\Delta G_{\text{init}} = & \Delta G_{\text{THF},175\text{K}}(\{\text{DPA(HIC)Na}\} \bullet (\text{NaDPA})) \\ & - \Delta G_{\text{THF},175\text{K}}((\text{NaDPA})_2) - \Delta G_{\text{THF},175\text{K}}(\text{HIC}) \end{aligned} \quad (\text{S2})$$

(3) Cross-association of NaDPA with DPA(HIC)Na



$$\begin{aligned} \Delta\Delta G_{\text{CA}} = & \Delta G_{\text{THF},175\text{K}}(\{\text{DPA(HIC)Na}\} \bullet (\text{NaDPA})) \\ & - \Delta G_{\text{THF},175\text{K}}(\text{DPA(HIC)Na}) - \Delta G_{\text{THF},175\text{K}}(\text{NaDPA}) \end{aligned} \quad (\text{S3})$$

Table S4. Final Results of the Anionic Polymerization of Functional Isocyanates Initiated by NaDPA in the Presence of NaBPh₄ ([NaBPh₄]₀/[NaDPA]₀ = 5) in THF at -98 °C under 10⁻⁶ Torr

entry	M	[M] ₀ (mol L ⁻¹)	[NaDPA] ₀ (mol L ⁻¹)	[M] ₀ / [NaDPA] ₀	<i>t</i> (s)	conv/% (P ^a /CT ^b)	<i>M</i> _{n,theo} ^c (kDa)	<i>M</i> _n ^d (kDa)	<i>D</i> ^d	<i>f</i> ^e
6	FIC	0.244	2.25 × 10 ⁻³	108	120	99.7/0	13.4	29.5	1.16	0.451
7	AIC	0.255	3.82 × 10 ⁻³	66.8	600	98.2/0	5.62	10.8	1.04	0.513

^aConversion to polymer determined from the gravimetric yield of polymer. ^bConversion to cyclotrimer determined from ¹H NMR spectroscopy. ^c*M*_{n,theo} = MW of DPA + [M]₀/[NaDPA]₀ × MW of M × conv to polymer/100%. ^dDetermined from SEC-MALLS. ^e*f* = (*M*_{n,theo} of polymer – MW of DPA)/(*M*_n of polymer – MW of DPA).

(a) PFIC ($M_{n,theo} = 13.4$ kDa; $M_n = 29.5$ kDa; $\mathcal{D} = 1.16$)

(b) PAIC ($M_{n,theo} = 5.62$ kDa; $M_n = 10.8$ kDa; $\mathcal{D} = 1.04$)

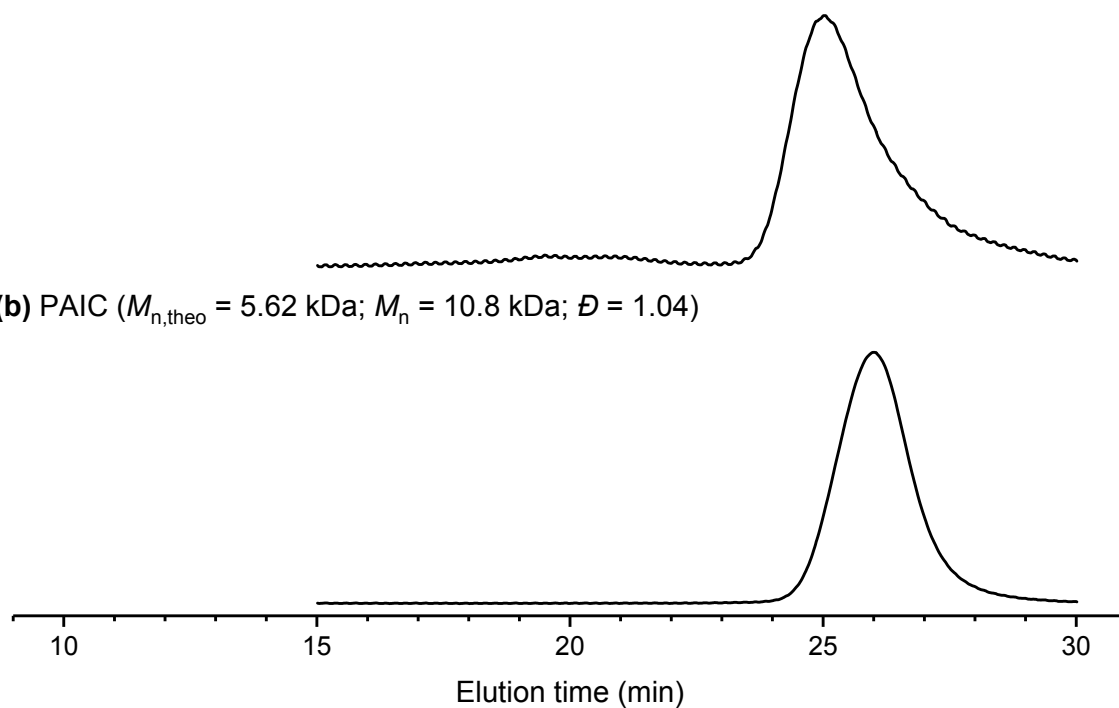


Figure S9. SEC-dRI traces of final (a) PFIC and (b) PAIC from the anionic polymerization of AIC and FIC initiated by NaDPA in the presence of NaBPh₄ ($[\text{NaBPh}_4]_0/[\text{NaDPA}]_0 = 5$) in THF at -98 °C under 10^{-6} Torr.

Table S5. Final Results of the Anionic Polymerization of HIC Initiated by NaDPA in the Presence of NaBPh₄ ([NaBPh₄]₀/[NaDPA]₀ = 5) in THF at -78 °C under 10⁻⁶ Torr

entry	[HIC] ₀ (mol L ⁻¹)	[NaDPA] ₀ (mol L ⁻¹)	[HIC] ₀ / [NaDPA] ₀	<i>t</i> (s)	conv/% (P ^a /CT ^b)	<i>M</i> _{n,theo} ^c (kDa)	<i>M</i> _n ^d (kDa)	<i>D</i> ^d	<i>f</i> ^e
S34	0.575	25.4 × 10 ⁻³	22.6	60	93.8/3.1	2.87	3.68	1.11	0.769
S35	0.513	11.3 × 10 ⁻³	45.4	120	91.6/6.2	5.46	6.40	1.04	0.849
S36	0.545	5.27 × 10 ⁻³	103	120	91.5/2.0	12.2	13.5	1.02	0.902
S47	0.500	2.36 × 10 ⁻³	212	240	91.1/3.0	24.7	24.7	1.03	1.00

^aConversion to polymer determined from the gravimetric yield of PHIC. ^bConversion to cyclotrimer determined from ¹H NMR spectroscopy. ^c*M*_{n,theo} = MW of DPA + [HIC]₀/[NaDPA]₀ × MW of HIC × conv to polymer/100%. ^dDetermined from SEC-MALLS. ^e*f* = (*M*_{n,theo} of polymer – MW of DPA)/(*M*_n of polymer – MW of DPA).

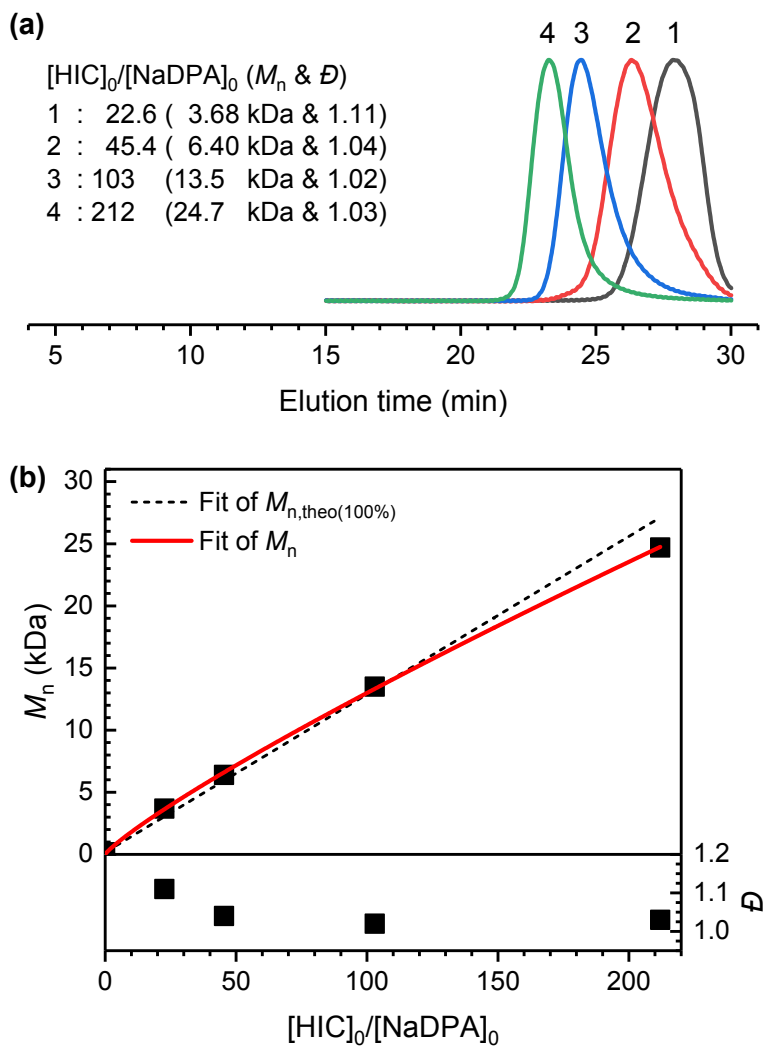


Figure S10. (a) SEC-dRI traces and (b) plots of M_n and \bar{D} versus $[HIC]_0/[NaDPA]_0$ for final PHICs yielded from the anionic polymerization of HIC initiated by NaDPA ($[NaDPA]_0 = 25.4\text{--}2.36 \times 10^{-3} \text{ mol L}^{-1}$) in the presence of NaBPh₄ ($[NaBPh_4]_0/[NaDPA]_0 = 5$) in THF at $-78 \text{ }^\circ\text{C}$ under 10^{-6} Torr.

S3. References

- (S1) Chae, C.-G.; Bak, I.-G.; Lee, J.-S. Propagation-Inspired Initiation of an Aliphatic Sodium Amidate for the Living Anionic Homo- and Copolymerization of Isocyanates: Access to the Multiblocky Sequence Distribution of Binary Comonomers. *Macromolecules* **2018**, *51*, 10083–10094.
- (S2) Jang Y. H.; Lansac, Y.; Kim, J.-K.; Yoo, H.-S.; Chae, C.-G.; Choi, C. H.; Samal, S.; Lee, J.-S. Dual Function of a Living Polymerization Initiator through the Formation of a Chain-End-Protecting Cluster: Density Functional Theory Calculation. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24929–24935.