

Supporting Information

Living Polymerization of Acrylamides catalysed by *N*-Heterocyclic Olefin-Based Lewis Pairs

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1. Stoichiometric NMR reaction of NHO with $\text{AlPh}_3 \cdot \text{OEt}_2$

General procedure for NMR reaction of NHO with $\text{AlPh}_3 \cdot \text{OEt}_2$: A Teflon-valve-sealed J. Young-type NMR tube was charged with NHO (0.02 mmol) and 0.3 mL of C_6D_6 . A solution of $\text{AlPh}_3 \cdot \text{OEt}_2$ (6.6 mg, 0.02 mmol, 0.3 mL C_6D_6) was added to this tube via pipette at ambient temperature, and the mixture was allowed to react for 15 min before analysis by NMR.

a) Stoichiometric NMR reaction of **NHO4** with $\text{AlPh}_3 \cdot \text{OEt}_2$

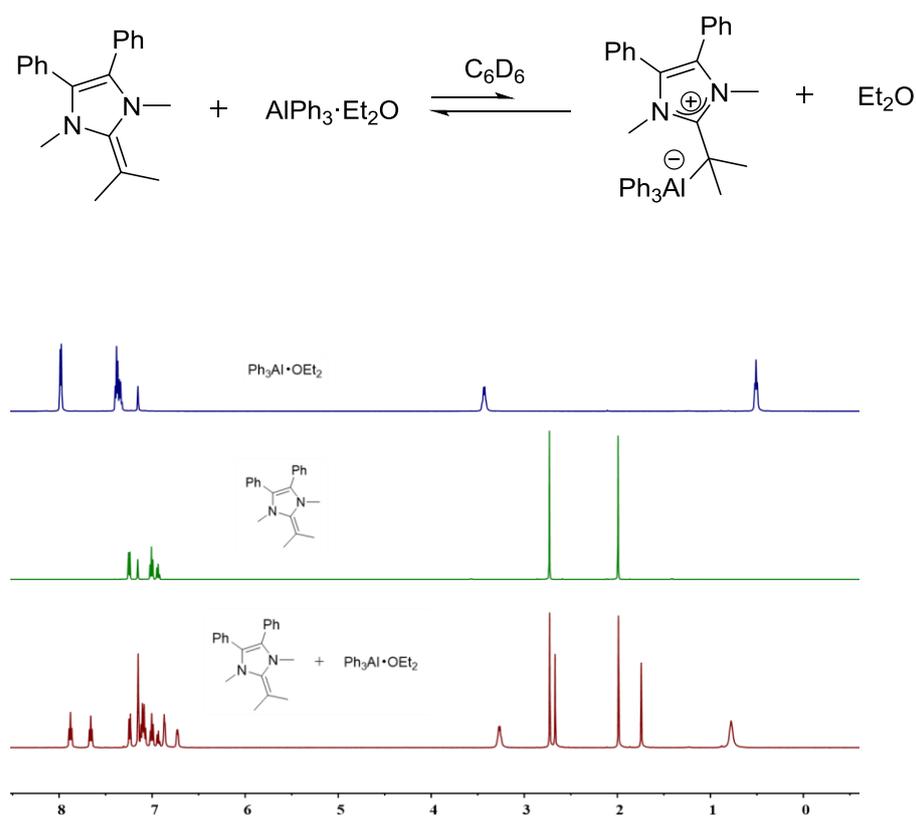


Figure S1. Overlay of ^1H NMR spectra for **NHO4**, $\text{AlPh}_3 \cdot \text{OEt}_2$ and reaction of **NHO4** with $\text{AlPh}_3 \cdot \text{OEt}_2$ (500 MHz, Benzene- d_6)

b) Stoichiometric NMR reaction of **NHO1** with $\text{AlPh}_3 \cdot \text{OEt}_2$

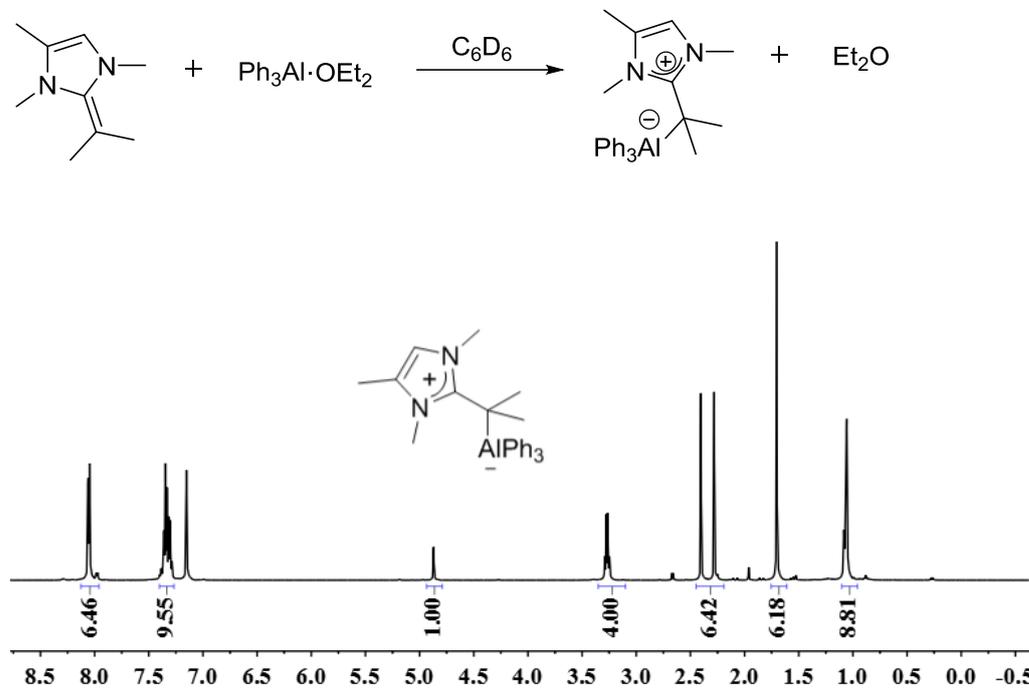
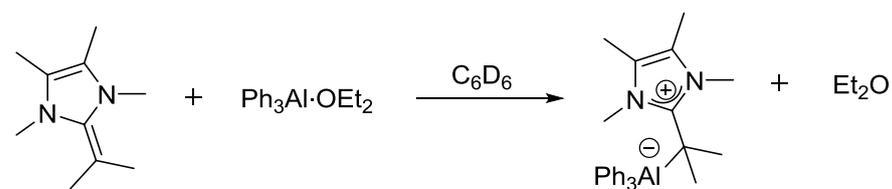


Figure S2. ^1H NMR spectrum for reaction of **NHO1** with $\text{AlPh}_3 \cdot \text{OEt}_2$ (500 MHz, Benzene- d_6)

c) Stoichiometric NMR reaction of **NHO2** with $\text{AlPh}_3 \cdot \text{OEt}_2$



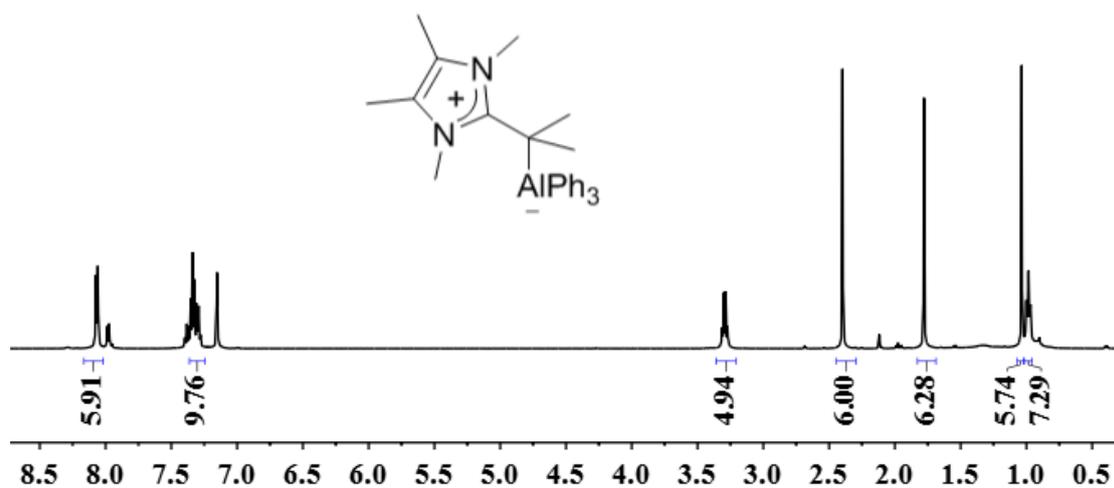


Figure S3. ^1H NMR spectra for reaction of **NHO2** with $\text{AlPh}_3 \cdot \text{OEt}_2$ (500 MHz, Benzene- d_6)

d) Stoichiometric NMR reaction of **NHO3** with $\text{AlPh}_3 \cdot \text{OEt}_2$

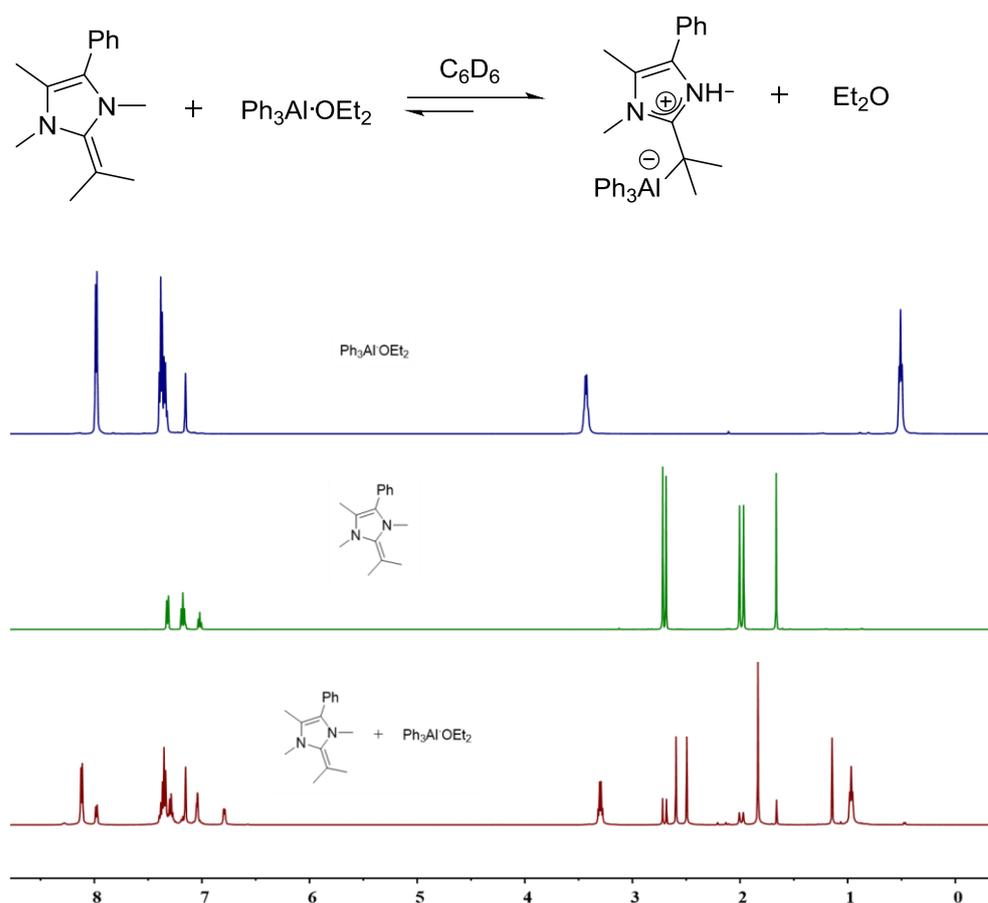


Figure S4. Overlay of ^1H NMR spectra for **NHO3**, $\text{AlPh}_3 \cdot \text{OEt}_2$ and reaction of **NHO3** with $\text{AlPh}_3 \cdot \text{OEt}_2$ (500 MHz, Benzene- d_6)

2. Stoichiometric reactions of NHO4/MeAl(BHT)₂ with DMAA

In an argon-filled glovebox, a Teflon-valve-sealed J. Young-type NMR tube was charged with 5.8 mg (0.02 mmol) of **NHO4** and 0.3 mL of C₆D₆. A 0.3 mL C₆D₆ solution of MeAl(BHT)₂-DMAA (11.6 mg, 0.02 mmol) was slowly added to this tube via pipet at room temperature. The mixture was allowed to react for 15 min at room temperature before the NMR spectra were recorded, which showed the clean formation of the zwitterion as two isomers in a 7:5 ratio.

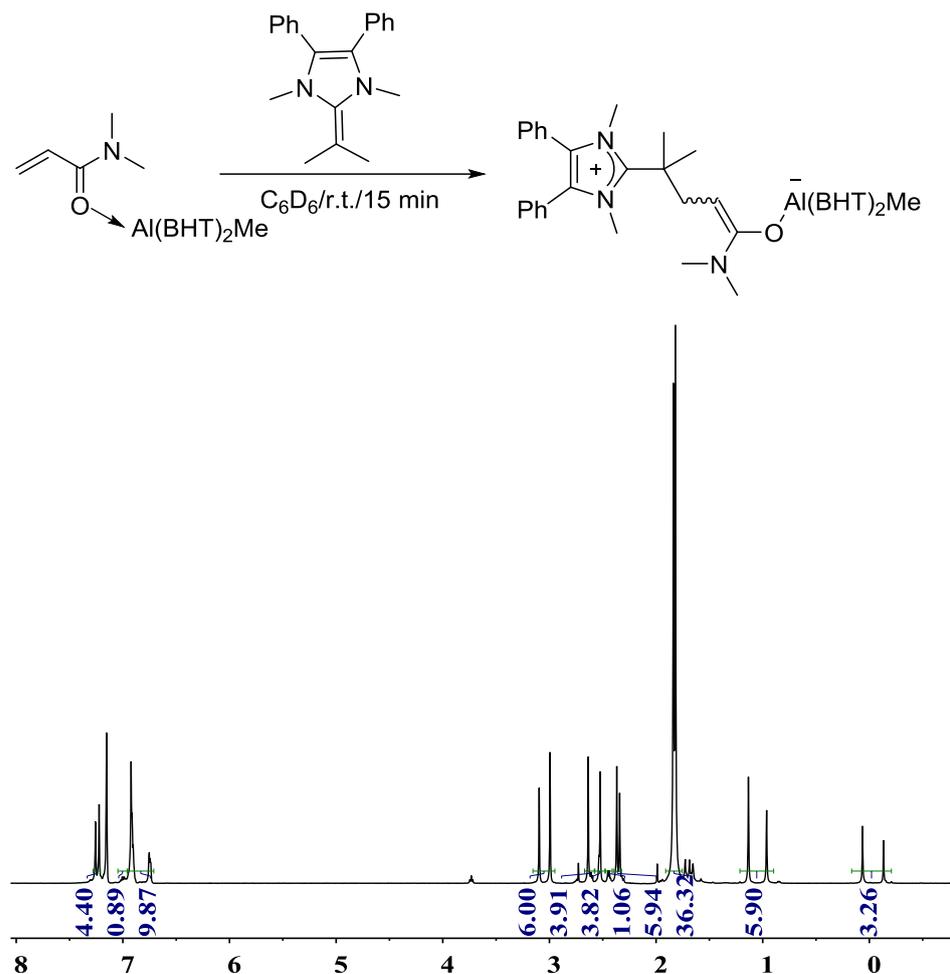


Figure S5. ¹H NMR spectrum obtained for the stoichiometric reaction of **NHO4**/MeAl(BHT)₂ with DMAA

3. Control experiments of DMAA polymerization

Table S1. Results of the polymerization of DMAA by LA alone^a

Entry	LA	M:LA	Time	conv.(%) ^b
1	^t Bu ₃ Al	800:2	1min	68.0
			5min	100
2	AlPh ₃ ·OEt ₂	800:2	30s	0

10min	0
1h	90.6
5h	100

^aCondition: carried out at RT in 4.5 mL of toluene; for a 800DMAA/2LA ratio, [DMAA]₀ = 0.94 M and [LA]₀ = 2.34 mM. ^bMonomer conversions measured by ¹H NMR.

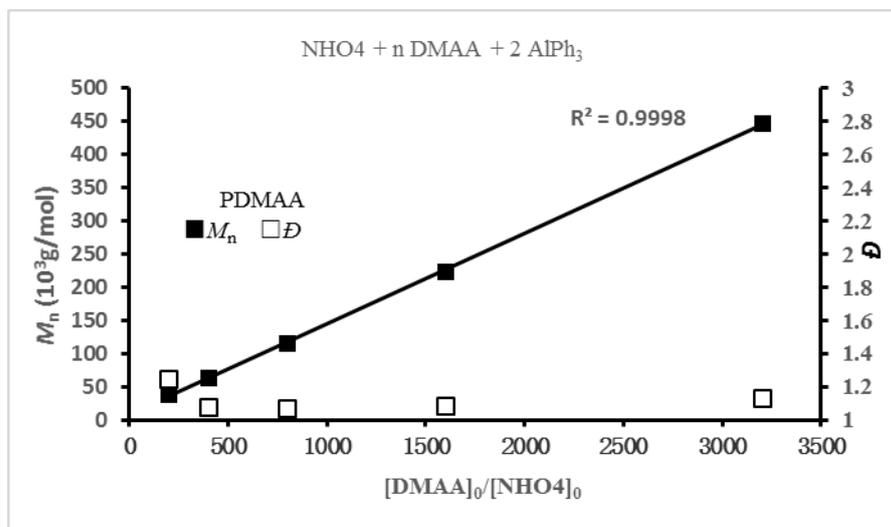
4. DEAA polymerization by NHO based LPs

Table S2. Results of the polymerization of DEAA by NHO based LPs^a

Entry	LB	LA	M:LB:LA	Time	Conv. ^b (%)	M_n^c (kg·mol ⁻¹)	\bar{D}^c (M_w/M_n)	I^d (%)
1	NHO1	MeAl(BHT) ₂	800:1:2	10 h	34.1	n.d.		
2	NHO2	MeAl(BHT) ₂	800:1:2	10 h	30.4	n.d.		
3	NHO3	MeAl(BHT) ₂	800:1:2	10 h	17.9	n.d.		
4	NHO4	MeAl(BHT) ₂	800:1:2	10 h	21.7	n.d.		
5	NHO1	AlPh ₃ ·OEt ₂	800:1:2	30 s	100	85.1	1.09	119
6	NHO2	AlPh ₃ ·OEt ₂	800:1:2	30 s	100	99.4	1.10	102
7	NHO3	AlPh ₃ ·OEt ₂	800:1:2	30 s	100	87.3	1.11	116
8	NHO4	AlPh ₃ ·OEt ₂	800:1:2	30 s	100	90	1.12	113

^aCondition: carried out at RT in 4.5 mL of toluene; for a 800DEAA/1LB/2LA ratio, [DEAA]₀ = 0.94 M and [LA]₀ = 2[LB]₀ = 2.34 mM. ^bMonomer conversions measured by ¹H NMR. ^c M_n and \bar{D} determined by GPC relative to PMMA standards in DMF. ^dInitiation efficiency (I^*)% = $M_n(\text{calcd})/M_n(\text{exptl}) \times 100$, where $M_n(\text{calcd}) = [\text{MW}(\text{DMAA})][[\text{DMAA}]_0 / [\text{I}]_0](\text{conversion}) + \text{MW of chain end groups}$.

5. Plots of M_n and \bar{D} for PDMAA vs [DMAA]₀/[NHO4]₀/ratio



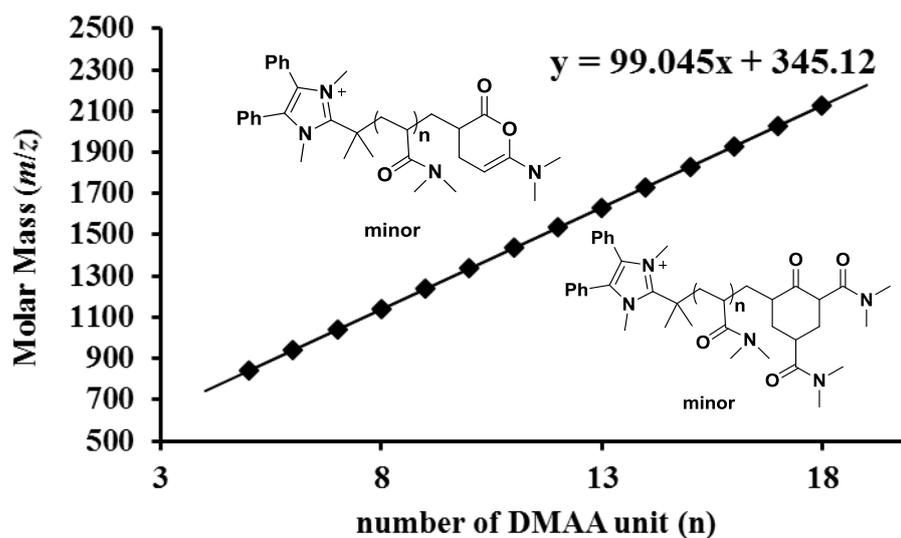


Figure S8. Plot of m/z values from Figure S7 vs the number of DMAA repeat units (n).

7. MALDI-TOF MS spectra of low-MW PDMAA by NHO4/AlMe₃

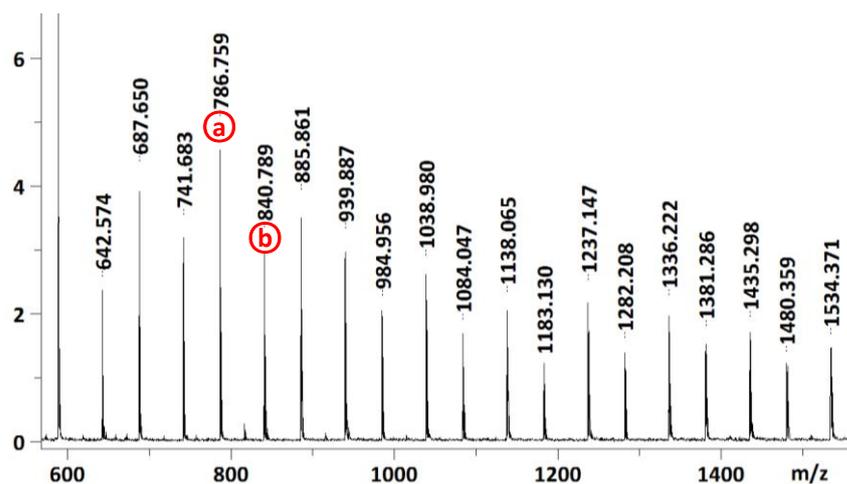


Figure S9. MALDI-TOF mass spectrum of the low-MW PDMAA sample produced by NHO4/AlMe₃ in toluene at RT

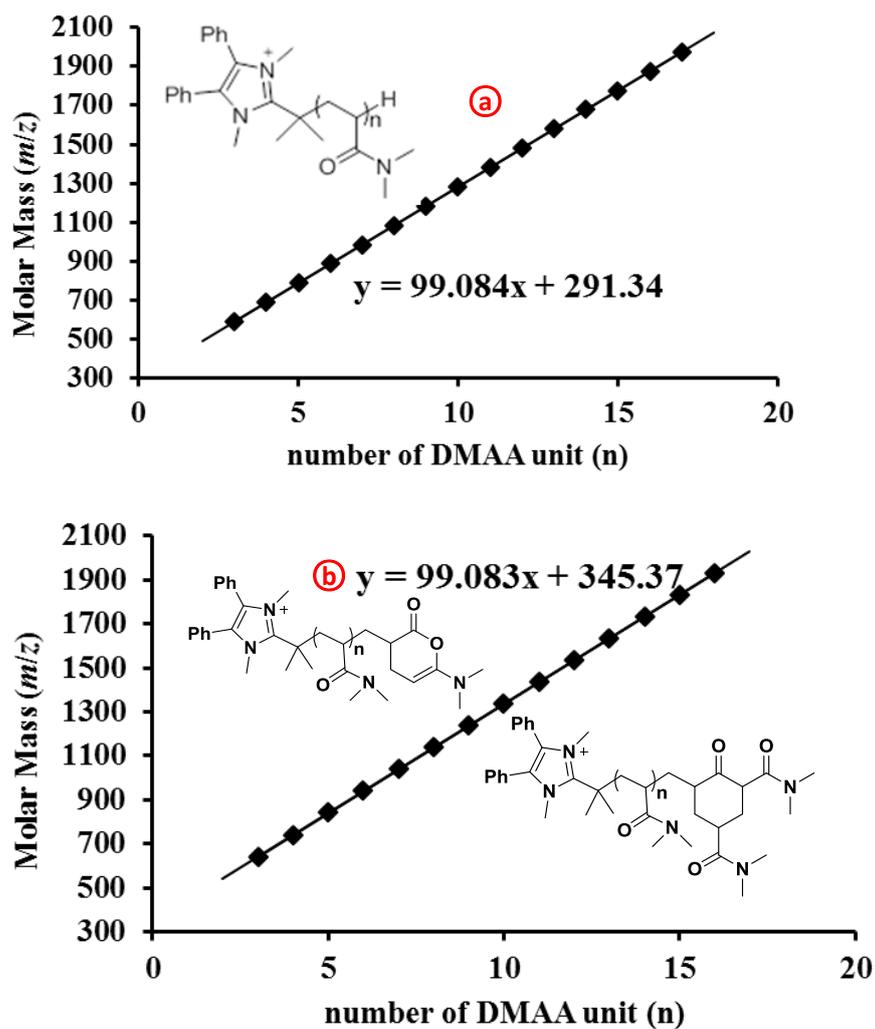


Figure S10. Plot of m/z values from Figure S9 vs the number of DMAA repeat units (n).

8. Chain extension experiments for DMAA Polymerization

Table S3. Chain-extension polymerization of DMAA by $\text{NHO4}/\text{AlPh}_3$ system^a

Entry	M1/M2/M3	Conv. ^b (%)	M_n^c ($\text{kg}\cdot\text{mol}^{-1}$)	\bar{D}^c
1	400DMAA	100	63.9	1.08
2	400/400DMAA	100	114	1.14
3	400/400/400DMAA	100	183	1.13

^a Condition: the first run was carried out with a 400/2/1 DMAA/ AlPh_3 / NHO4 ratio ($[\text{DMAA}]_0 = 0.94 \text{ M}$, $[\text{AlPh}_3]_0 = 2[\text{NHO4}]_0 = 4.68 \text{ mM}$) in 4.50 ml toluene at room temperature. ^b Monomer conversions measured by $^1\text{H NMR}$. ^c M_n and \bar{D} determined by GPC relative to PMMA standards in DMF.

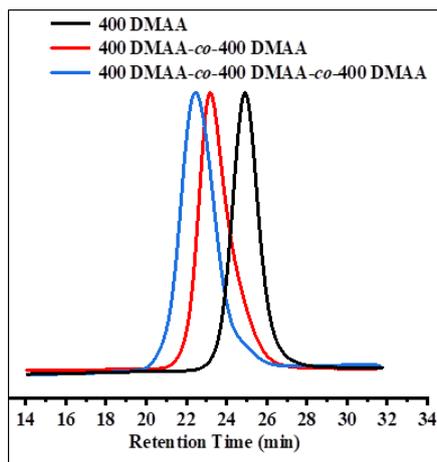


Figure S11. The GPC traces of PDMAA samples obtained from chain extension experiments in toluene at RT.

9. Random and block copolymerization

Table S4. Copolymerization of DMAA and DEAA by NHO₄/AlPh₃ system ^a

Entry	M1/M2/M3	Conv. ^b (%)	M_n^c (kg·mol ⁻¹)	\mathcal{D}^c
1 ^d	400DMAA- <i>ran</i> -400DEAA	DMAA:100 DEAA: 100	103	1.09
2	400DMAA- <i>b</i> -400DEAA	DMAA:100 DEAA: 100	100	1.13
3	400DMAA- <i>b</i> -400DEAA- <i>b</i> -400DMAA	DMAA:100 DEAA: 100	171	1.14
4	400DEAA- <i>b</i> -400DMAA	DMAA:100 DEAA: 100	100	1.21
5	400DEAA- <i>b</i> -400DMAA- <i>b</i> -400DEAA	DMAA:100 DEAA: 100	155	1.14

^a Carried out in 4.50 ml toluene at room temperature, where [DMAA]₀ = [DEAA]₀ = 0.94 M and AlPh₃ was used.

^b Monomer conversions (conv.) measured by ¹H NMR. ^c M_n and \mathcal{D} determined by GPC relative to PMMA standards in DMF. ^d DMAA and DEAA was added at the same time.

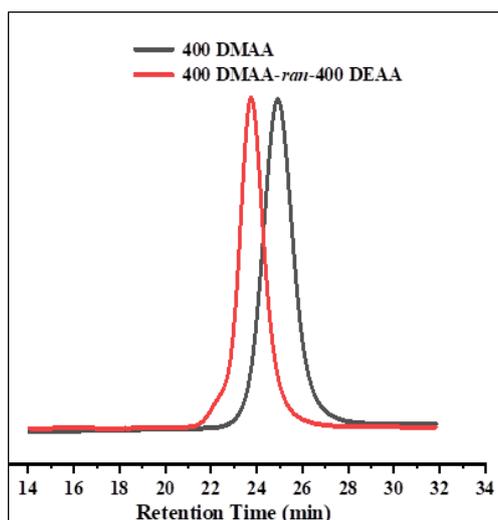


Figure S12. The GPC traces of PDMAA samples obtained from random copolymerization of DMAA and DEAA in toluene at RT.