Chemoselective polymerization of polar divinyl monomers with rare-earth/phosphine Lewis pairs

Pengfei Xu [1], Lei Wu [1], Liqiu Dong [1,2] and Xin Xu [1,]*

[1] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China;

[2] Suzhou International Academy, BFSU, Suzhou 215200, P. R. China

** Correspondence: xinxu@suda.edu.cn; Tel.: +86-512-65882921*

Supporting Information

NMR data of complex 5:

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{1}H = 7.04 / 6.50 (*m*-O*Ar* / *p*-O*Ar*), 5.84 / 5.08 (OCH_2CH=CH_2 / OCH_2CH=CH_2), 5.84 / 4.32 (OCH_2CH=CH_2 / OCH_2CH=CH_2), 2.05 / 1.25 (PCH_2CH_3 / PCH_2CH_3).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.04 / 125.1 (*m*-O*Ar*), 6.50 / 115.8 (*p*-O*Ar*), 5.84 / 135.6 (OCH_2CH=CH_2), 5.08 / 116.8 (OCH_2CH=CH_2), 4.32 / 68.3 (OCH_2CH=CH_2), 2.88 / 24.1 (CH_2C=), 2.05 / 12.5 (PCH_2CH_3), 1.52 / 18.5 (CH_3C=), 1.42 / 32.7 ($C(CH_3)_3$), 1.25 / 6.0 (PCH_2CH_3).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) [selected traces]: δ^{1}H / δ^{13}C = 7.04 / 163.4, 35.8 (*m*-O*Ar* / *i*-O*Ar*, $C(CH_3)_3$), 6.50 / 139.0 (*p*-O*Ar* / *o*-O*Ar*), 4.32 / 135.6, 116.8 (OCH_2CH=CH_2 / OCH_2CH=CH_2, OCH_2CH=CH_2), 2.88 / 159.5, 67.2, 18.5, 12.5 (CH_2C= / O*C*=, CH_2C=, CH_3C=, PCH_2CH_3).

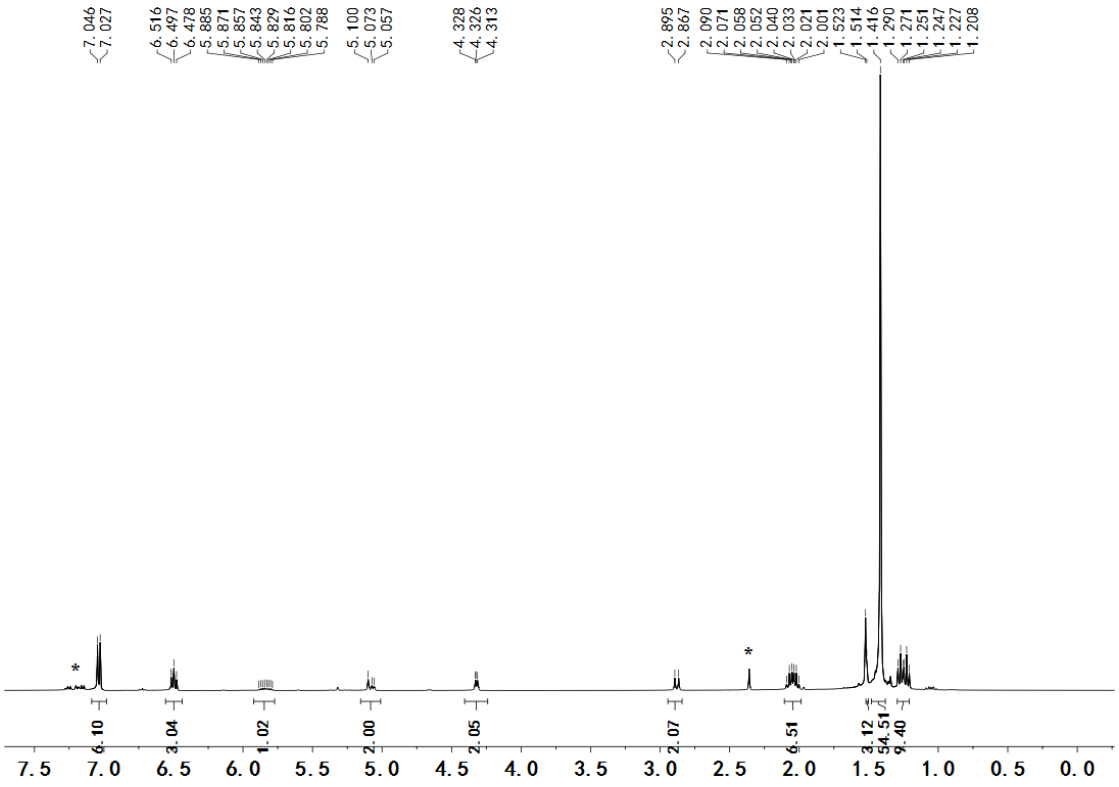

Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) [*: Toluene]

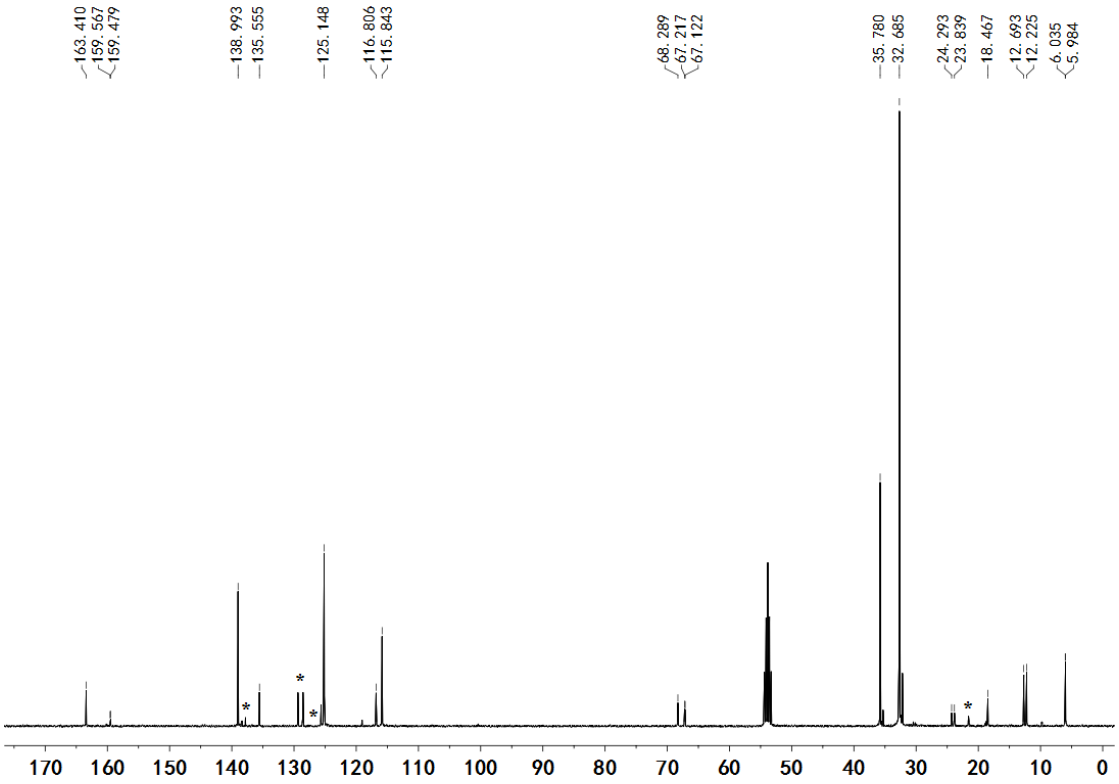

Figure S2. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) [*: Toluene]

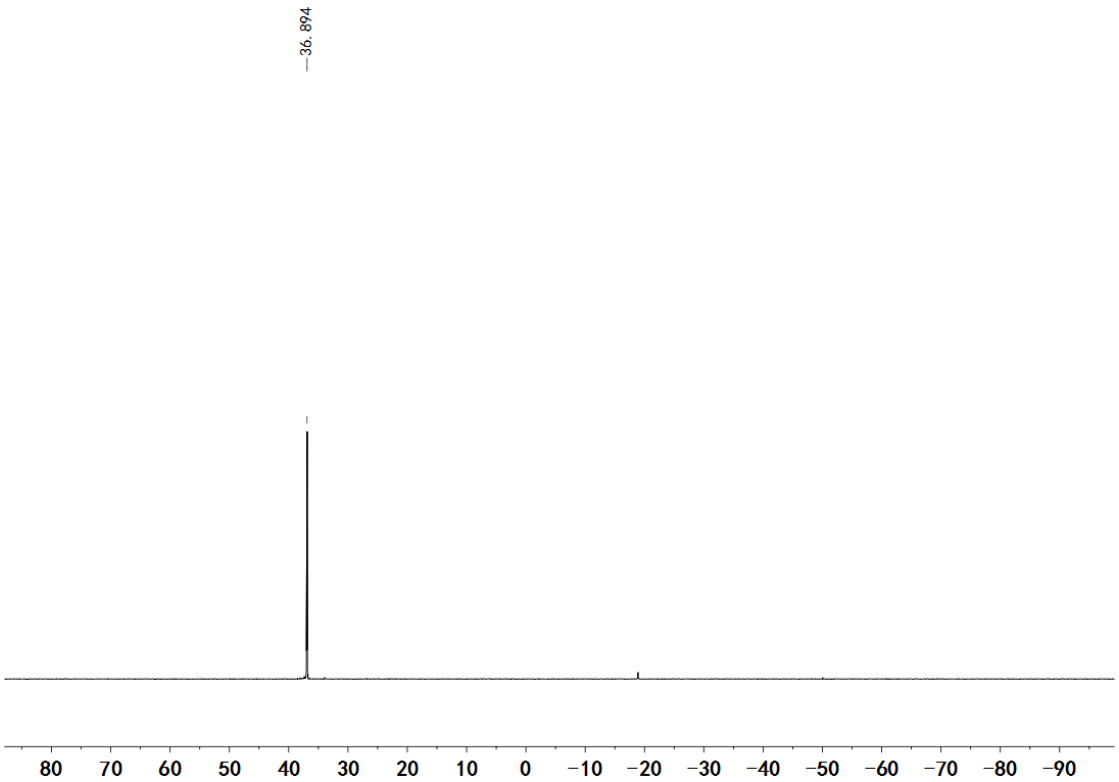

Figure S3. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K).

NMR data of complex 6:

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{1}H = 7.05 / 6.51 (*m*-O*Ar* / *p*-O*Ar*), 6.98 / 4.36, 3.99 (OC*H*=CH_2 / OCH=C*H*$_2$), 2.07 / 1.28 (PC*H*$_2$$CH_3$ / PCH_2C*H*$_3$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.05 / 125.1 (*m*-O*Ar*), 6.98 / 148.1 (O*CH*=CH_2), 6.51 / 116.0 (*p*-O*Ar*), 4.36, 3.99 / 89.8 (OCH=*CH*$_2$), 2.90 / 23.4 (*CH*$_2$C=), 2.07 / 12.4 (P*CH*$_2$$CH_3$), 1.48 / 18.2 (*CH*$_3$C=), 1.41 / 32.6 (C(*CH*$_3$)$_3$), 1.28 / 6.0 ($PCH_2$*CH*$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) [selected traces]: δ^{1}H / δ^{13}C = 7.05 / 163.3, 35.7 (*m*-O*Ar* / *i*-O*Ar*, *C*$(CH_3)_3$), 6.51 / 139.0 (*p*-O*Ar* / *o*-O*Ar*), 4.36, 3.99 / 148.1 (OCH=C*H*$_2$ / O*C*H=CH_2), 2.90 / 157.3, 68.4, 18.2, 12.4 (C*H*$_2$C= / O*C*=, CH_2*C*=, *C*H_3C=, P*C*H_2CH_3).

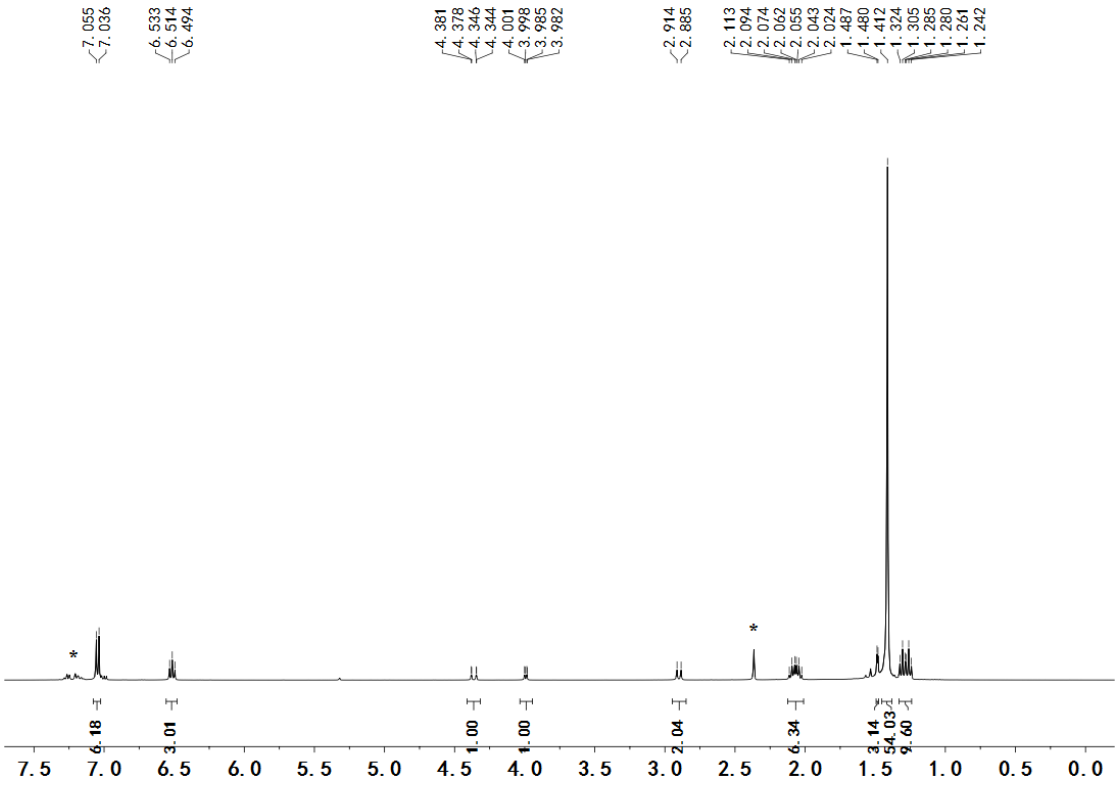

Figure S4. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) [*: Toluene]

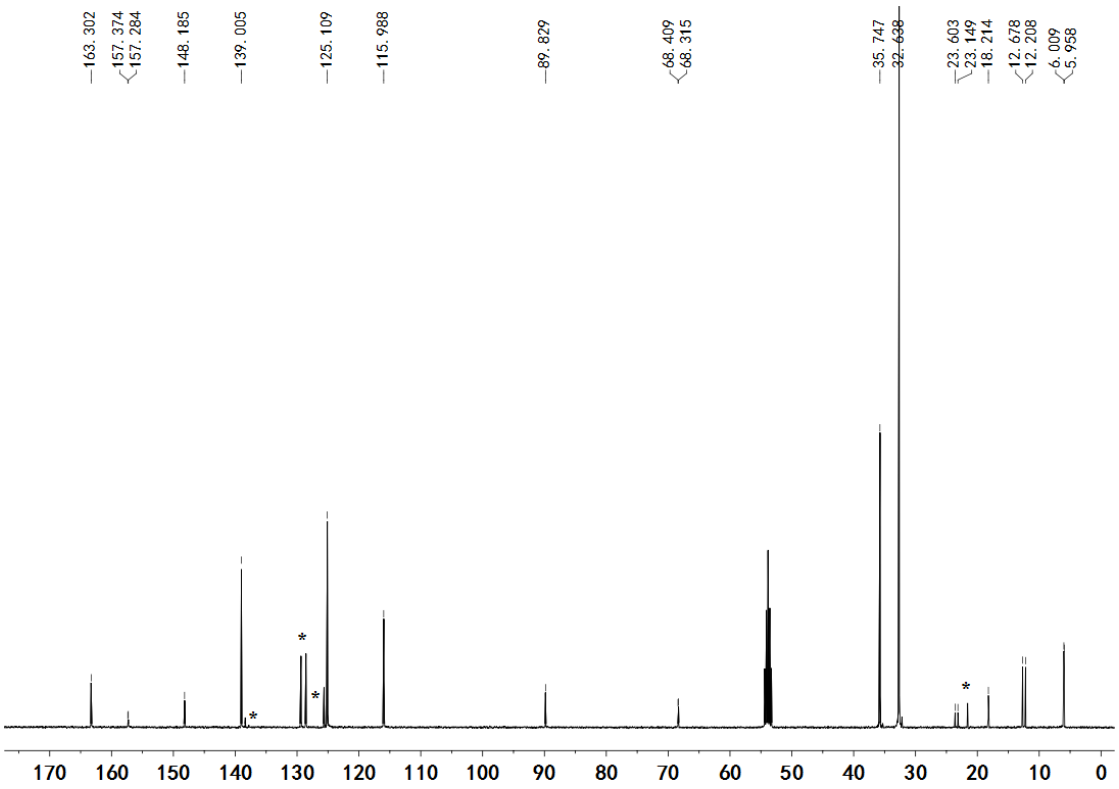

Figure S5. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) [*: Toluene]

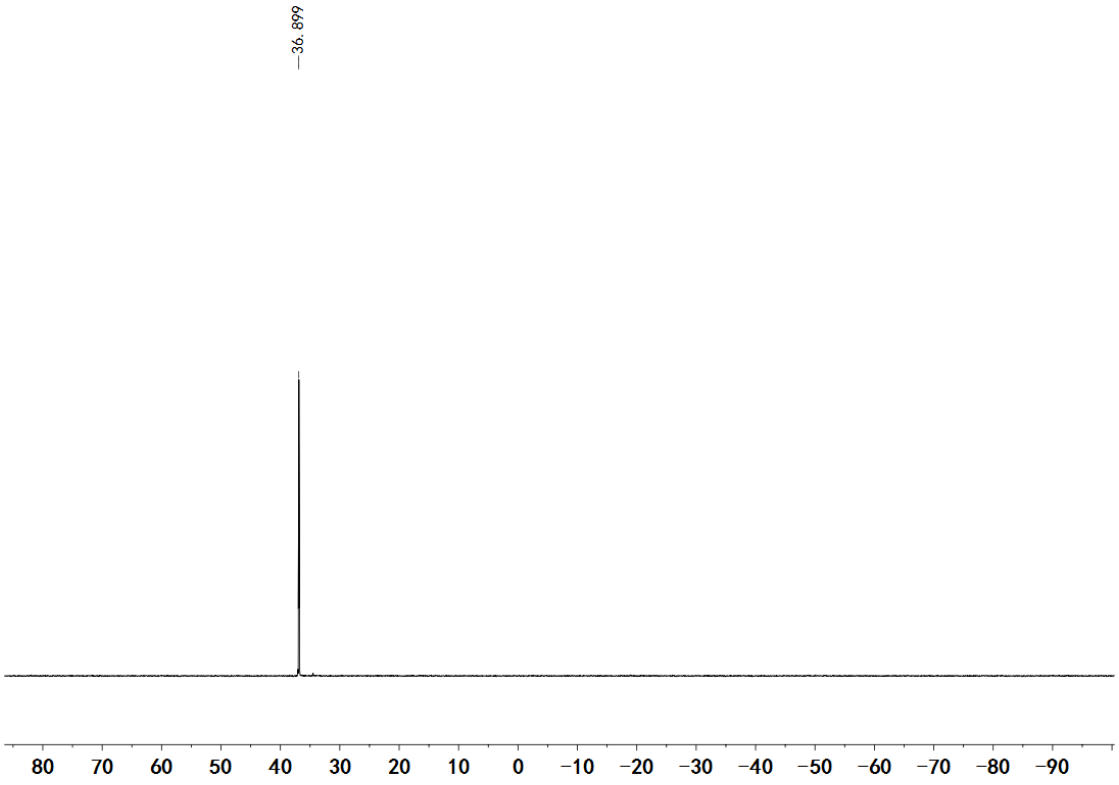

Figure S6. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K)

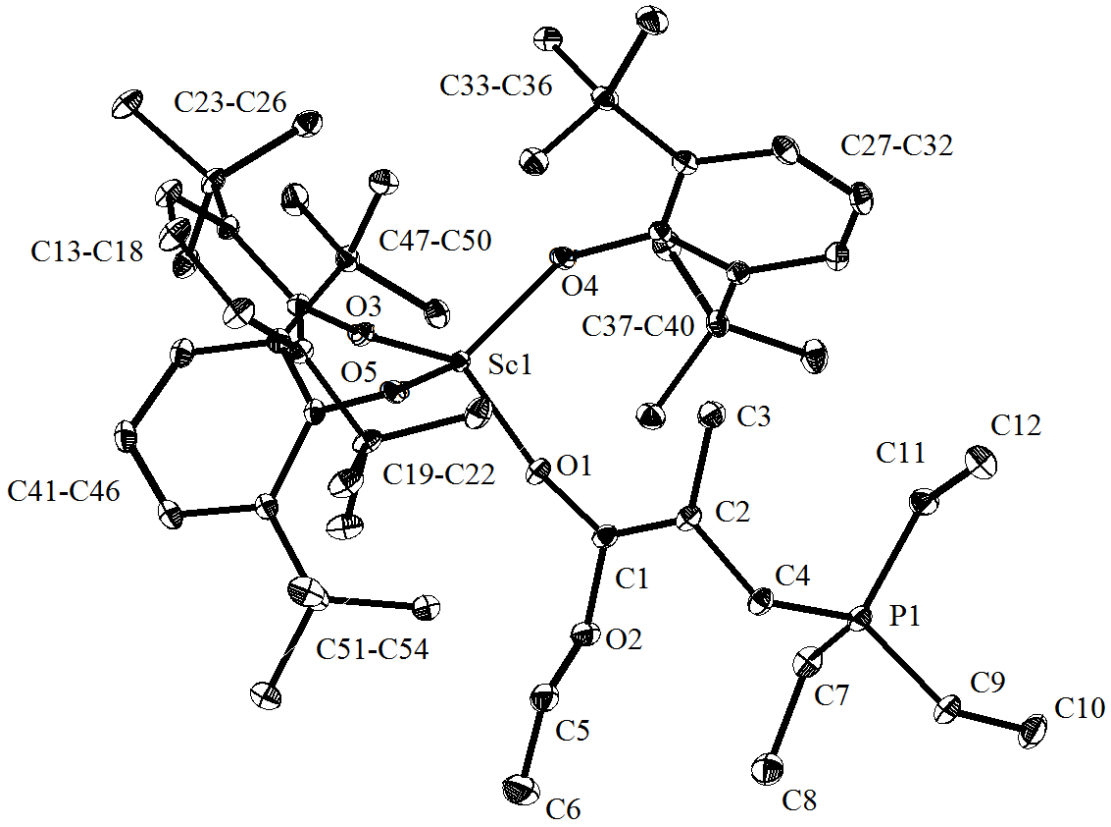

Figure S7. Molecular structure of complex **6**.

Reaction of complex 1 with PEt_3 and AMA in 2:1:1 stoichiometric ratio.

A Teflon-valve-sealed J. Young-type NMR tube was charged with $Sc(OAr)_3$ (26.4 mg, 0.04 mmol), AMA (2.5 mg, 0.02 mmol), and 0.3 mL of CD_2Cl_2. A solution of PEt_3 (2.4 mg, 0.02 mmol, 0.3 mL CD_2Cl_2) was added to this NMR tube via pipette at ambient temperature, and the colorless mixture was allowed to react for 30 min before NMR analysis, which showed the formation of complex **5** and unreacted $Sc(OAr)_3$ in a 1:1 molar ratio.

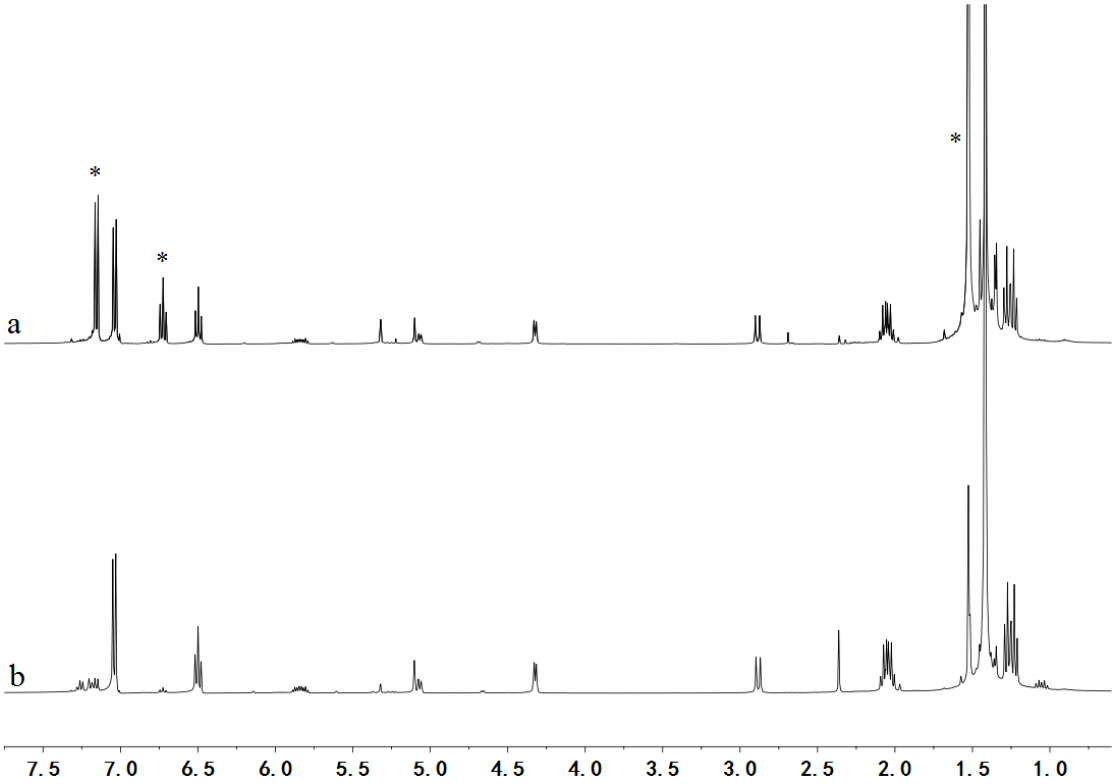

Figure S8. a: **^{1}H NMR** (400M, CD_2Cl_2, 298 K) of reaction of complex **1** with PEt_3 and AMA in 2:1:1 stoichiometric ratio. [*: complex **1**]; b: **^{1}H NMR** (400M, CD_2Cl_2, 298 K) of complex **5**.

Reaction of complex 1 with PEt_3 and VMA in 2:1:1 stoichiometric ratio.

Following the procedure described for AMA, reaction of $Sc(OAr)_3$ (26.4 mg, 0.04 mmol), VMA (2.2 mg, 0.02 mmol), and PEt_3 (2.4 mg, 0.02 mmol) showed the formation of complex **6** and unreacted $Sc(OAr)_3$ in a 1:1 molar ratio.

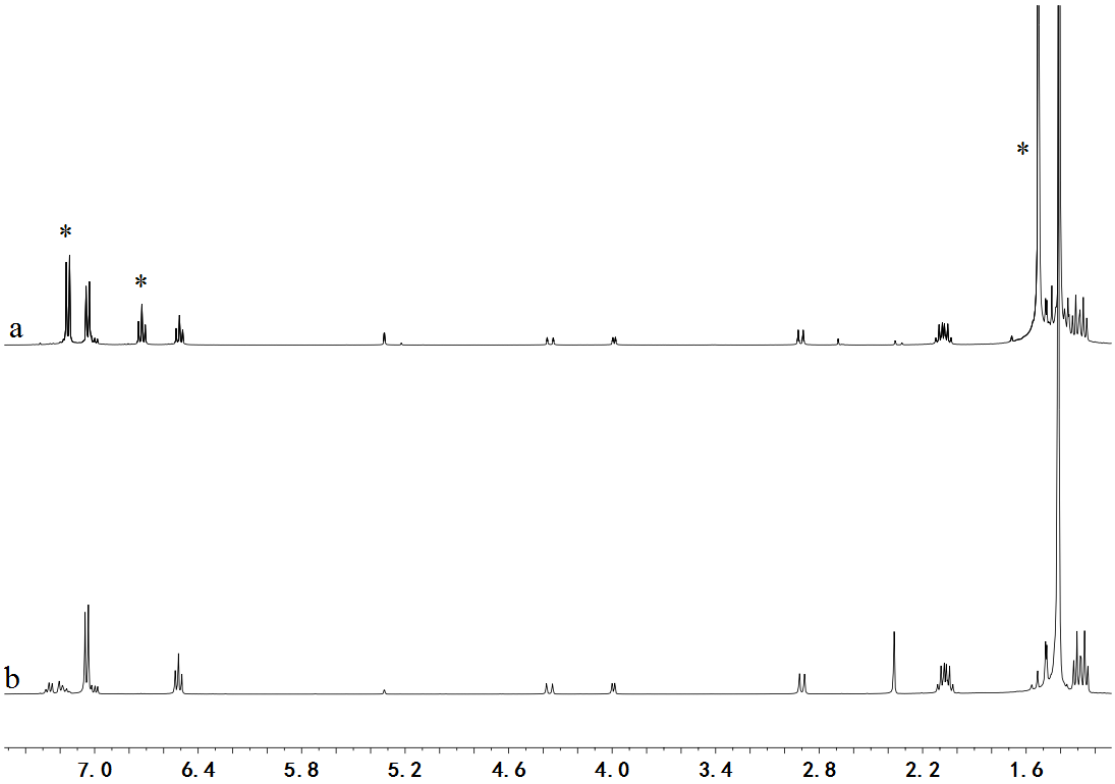

Figure S9. a: **^{1}H NMR** (400M, CD_2Cl_2, 298 K) of reaction of complex **1** with PEt_3 and VMA in 2:1:1 stoichiometric ratio. [*: complex **1**]; b: **^{1}H NMR** (400M, CD_2Cl_2, 298 K) of complex **6**.

Table S1. Results of chemoselective polymerization of polar divinyl monomers with homoleptic rare-earth aryloxides based LPs.[a]

Entry	Monomer	LA	LB	[M]/[LB]	t [min]	Conv. [%]	M_n [10^4 g/mol]	PDI [M_w/M_n]	*rr* [%]	*mr* [%]	*mm* [%]
1	AMA	**1**	PPh_3	200	1440	0	-	-	-	-	-
2[b]	AMA	**1**	PPh_3	200	1440	0	-	-	-	-	-
3	AMA	**1**	PCy_3	200	25	100	12.3	1.33	79.8	19.6	0.6
4	AMA	**1**	PEt_3	200	15	100	5.03	1.23	79.9	19.5	0.6
5[b]	AMA	**1**	PEt_3	200	40	100	5.20	1.40	80.2	18.9	0.9
6[c]	AMA	**1**	PEt_3	200	1440	75	10.8	1.38	87.8	11.4	0.8
7	AMA	**1**	PMe_3	200	30	90	5.09	1.23	79.2	20.0	0.8
8	AMA	**2**	PEt_3	200	3	100	8.57	1.41	75.3	23.5	1.2
9	AMA	**3**	PEt_3	200	1	100	9.16	1.34	75.0	23.7	1.7
10	AMA	**4**	PEt_3	200	<1	100	10.0	1.42	72.5	26.0	1.5

11	AMA	**4**	PEt_3	400	5	100	15.3	1.76	72.8	25.4	1.8
12	AMA	**1**	-	200	1440	0	-	-	-	-	-
13	AMA	**4**	-	200	1440	0	-	-	-	-	-
14	VMA	**1**	PEt_3	100	10	100	5.62	1.36	75.6	22.6	1.8
15	VMA	**1**	PMe_3	100	10	100	7.59	1.31	76.8	21.6	1.6
16	VMA	**4**	PEt_3	100	1	100	4.74	1.76	69.3	29.1	1.6
17[b]	VMA	**4**	PEt_3	100	1	100	6.08	1.43	70.1	28.7	1.2
18	VMA	**1**	-	100	1440	0	-	-	-	-	-
19	VMA	**4**	-	100	1440	0	-	-	-	-	-
20	VBMA	**1**	PEt_3	100	45	100	2.55	1.87	75.0	22.5	2.5
21[b]	VBMA	**1**	PEt_3	100	90	100	2.34	1.73	76.1	20.7	3.2
22	VBMA	**1**	PMe_3	100	45	100	2.42	1.99	76.2	22.8	1.0
23[b]	VBMA	**1**	PMe_3	100	90	100	2.87	2.04	76.2	21.3	2.5
24	VBMA	**4**	PEt_3	100	5	100	2.92	2.00	72.1	26.3	1.6
25[b]	VBMA	**4**	PEt_3	100	1440	0	-	-	-	-	-
26	VBMA	**1**	-	100	1440	0	-	-	-	-	-
27	VBMA	**4**	-	100	1440	0	-	-	-	-	-
28[b]	AMA	**5**	-	100	1440	32	2.12	1.45	75.3	21.5	3.2
29[d]	AMA	**5**	-	100	20	100	4.23	1.42	78.4	19.6	2.0
30[b]	VMA	**6**	-	100	1440	0	-	-	-	-	-
31[d]	VMA	**6**	-	100	20	100	4.89	1.42	77.4	21.7	0.9

[a]Conditions: polymerizations were conducted at room temperature in toluene ($V_{monomer}/V_{solvent}$: 1:2) and a LA/LB ratio of 2, where $n_{[LA]}$ = 40 μmol. Monomer conversions were determined by ^{1}H NMR spectroscopy and confirmed by gravimetric methods, *rr*, *mr*, *mm* measured by ^{1}H NMR spectroscopy. M_n and PDI were determined by GPC in DMF relative to PMMA standards. [b]Polymerization was conducted in CH_2Cl_2. [c]Polymerization was conducted at -30 ^oC. [d]Polymerization was conducted in CH_2Cl_2 in the presence of 1 eqiv. **1**.

Procedure for the post-functionalization of PVBMA: AIBN (55 mg, 0.33 mmol) was added to a solution of PVBMA (202 mg) and $PhCH_2SH$ (5 g, 40 mmol) in 15 mL of THF. After stirring for 24 h at 70°C, the reaction mixture was filtered and the volatiles were removed under reduced pressure. The produced crude product was further purified by precipitation in THF/petroleum ether mixture and then dried in a vacuum oven at 50 °C overnight to a constant weight.

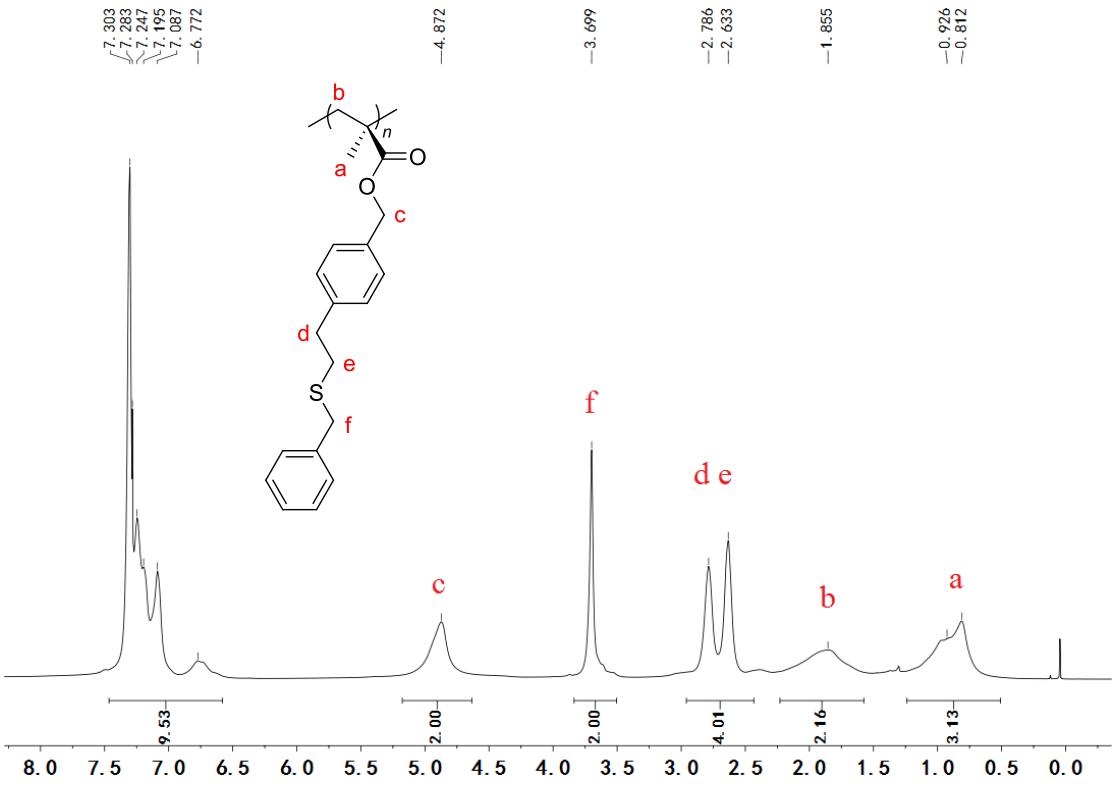

Figure S10.

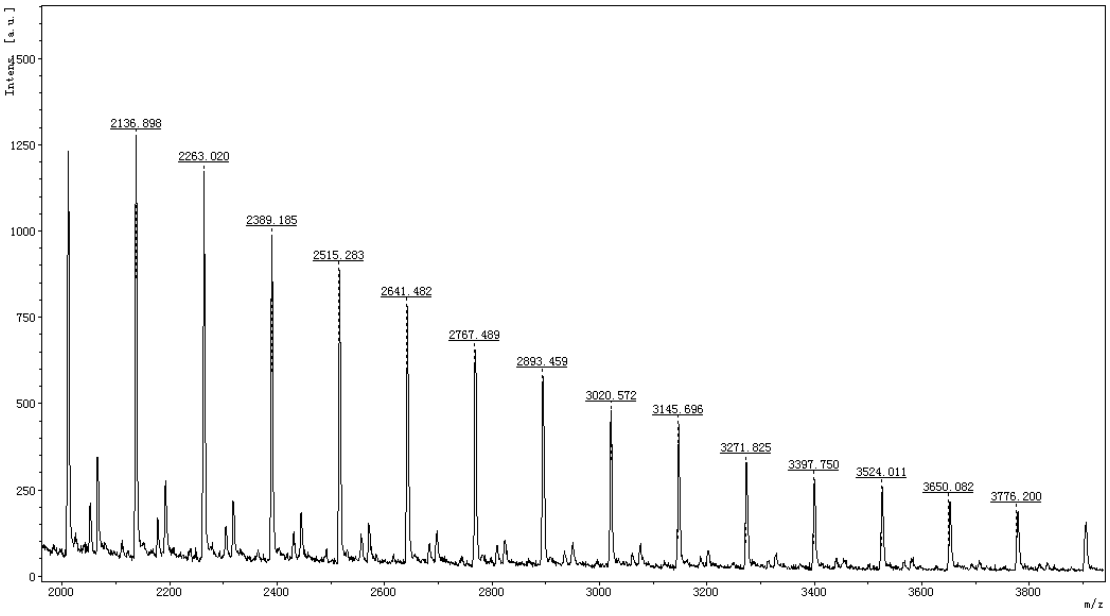

Figure S11. MALDI-TOF MS spectrum of low molecular weight AMA oligomers produced by **1**/PEt_3 at RT with [M]/[LB] = 20:1.

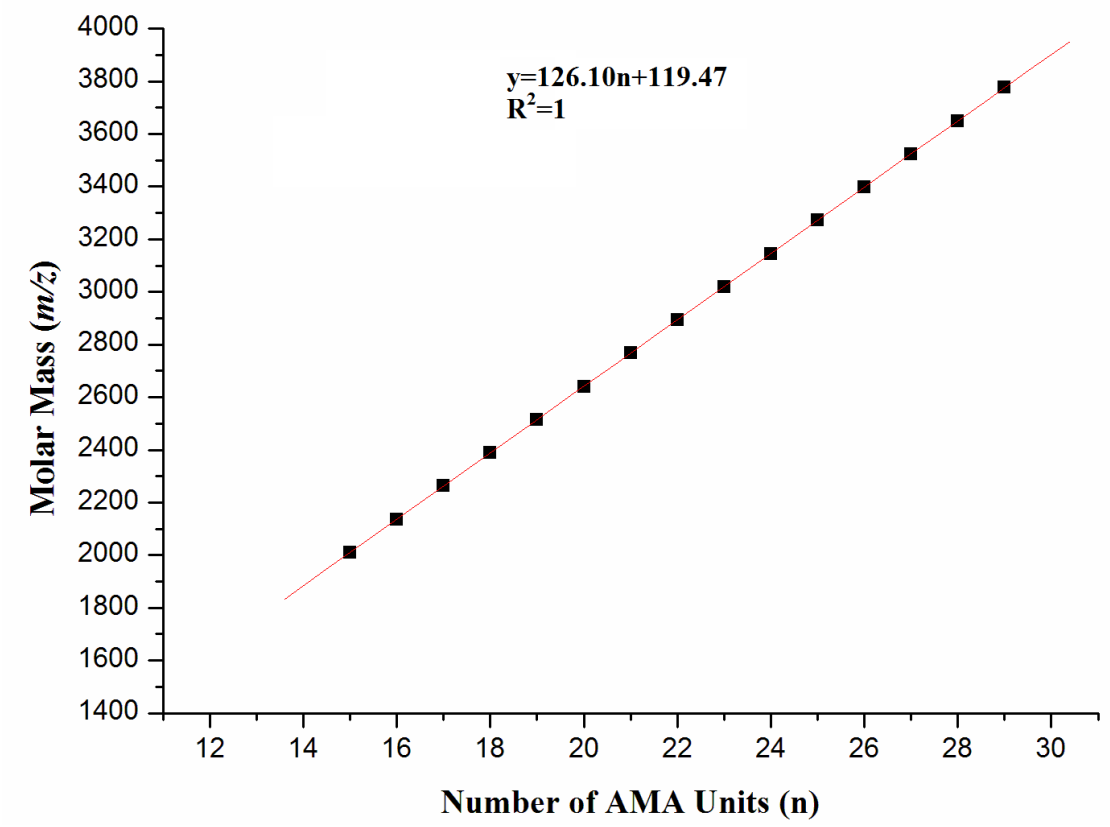

Figure S12. Plot of *m*/*z* values *vs* the number of AMA repeat units (*n*).

^{1}H NMR spectra of PAMA:

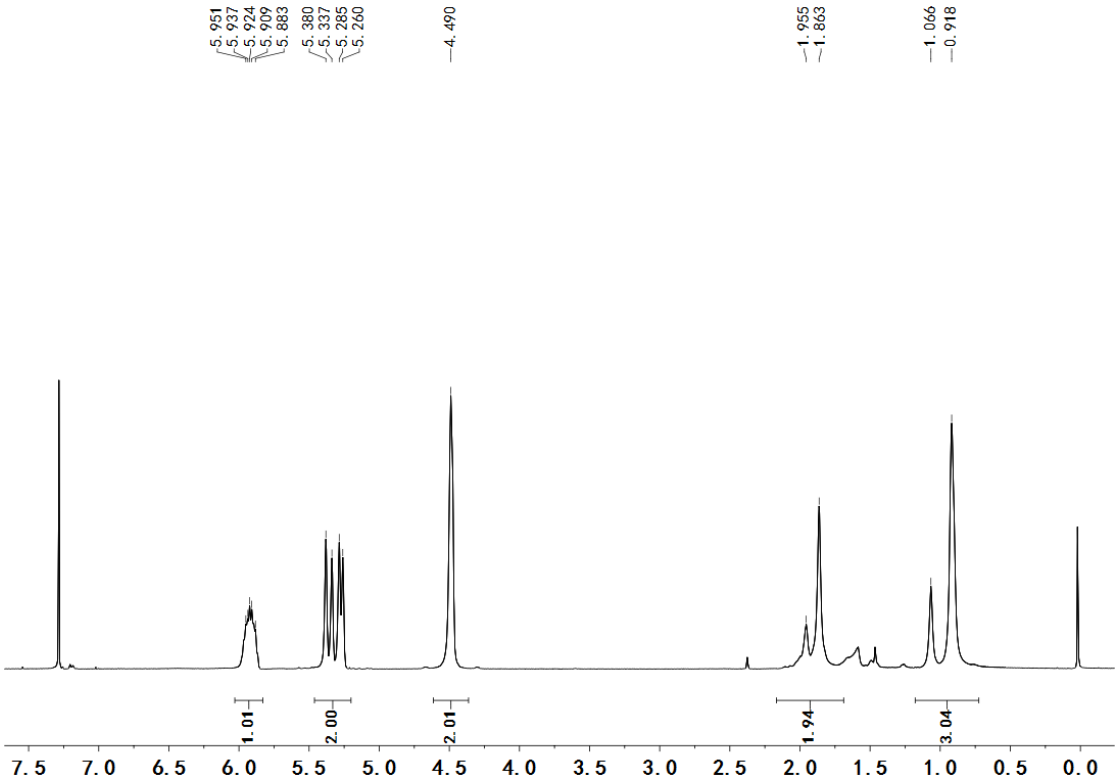

Figure S13. ^{1}H NMR (400M, $CDCl_3$, 298 K) of the PAMA produced by the **1**/PEt_3 pair in toluene at RT with [AMA]/[PEt_3] = 200:1. (*rr* = 79.9%)

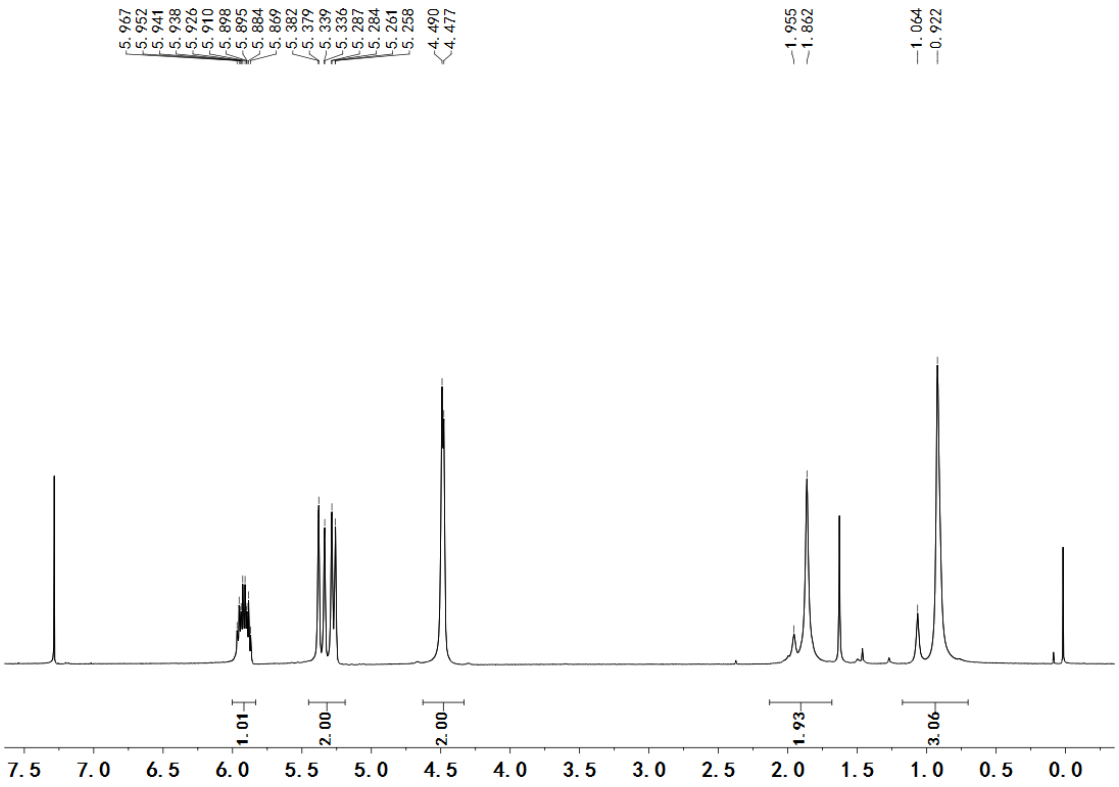

Figure S14. ^{1}H NMR (400M, $CDCl_3$, 298 K) of the PAMA produced by the **1**/PEt_3

pair in toluene at -30°C with [AMA]/[PEt_3] = 200:1. (*rr* = 87.8%)

^{1}H NMR spectra of PVMA:

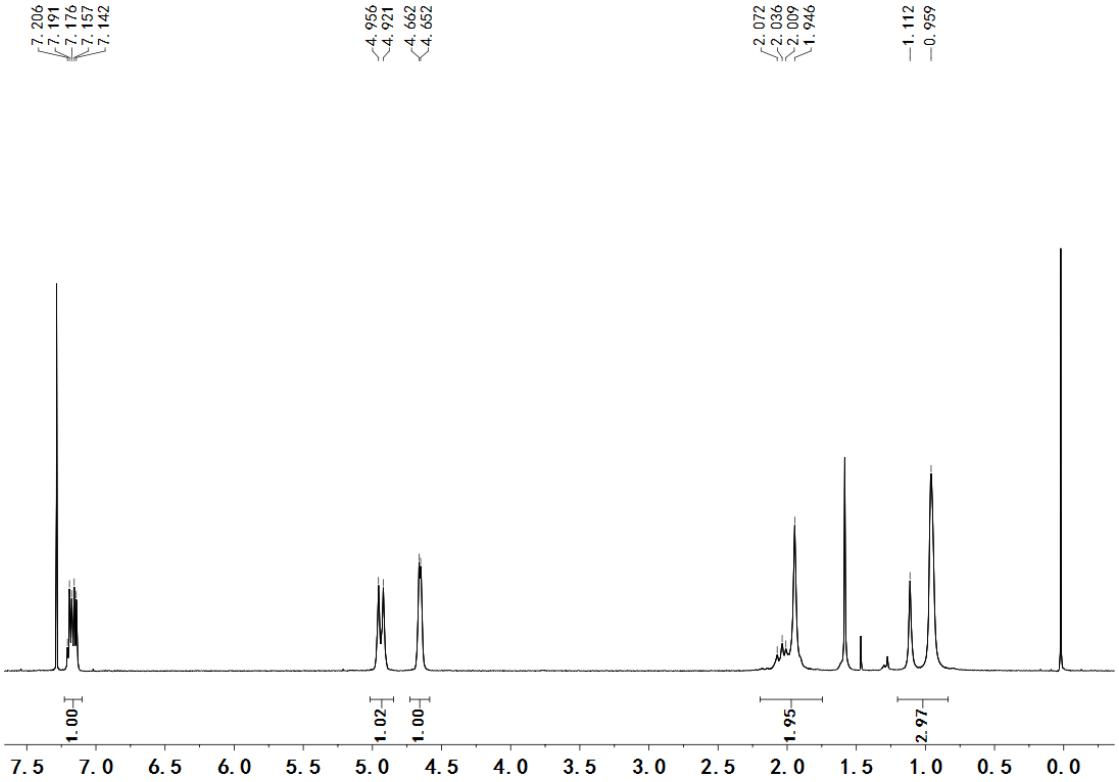

Figure S15. ^{1}H NMR (400M, $CDCl_3$, 298 K) of the PVMA produced by the **1**/PEt_3 pair in toluene at RT with [VMA]/[PEt_3] = 100:1. (*rr* = 75.6%)

^{1}H NMR spectra of PVBMA:

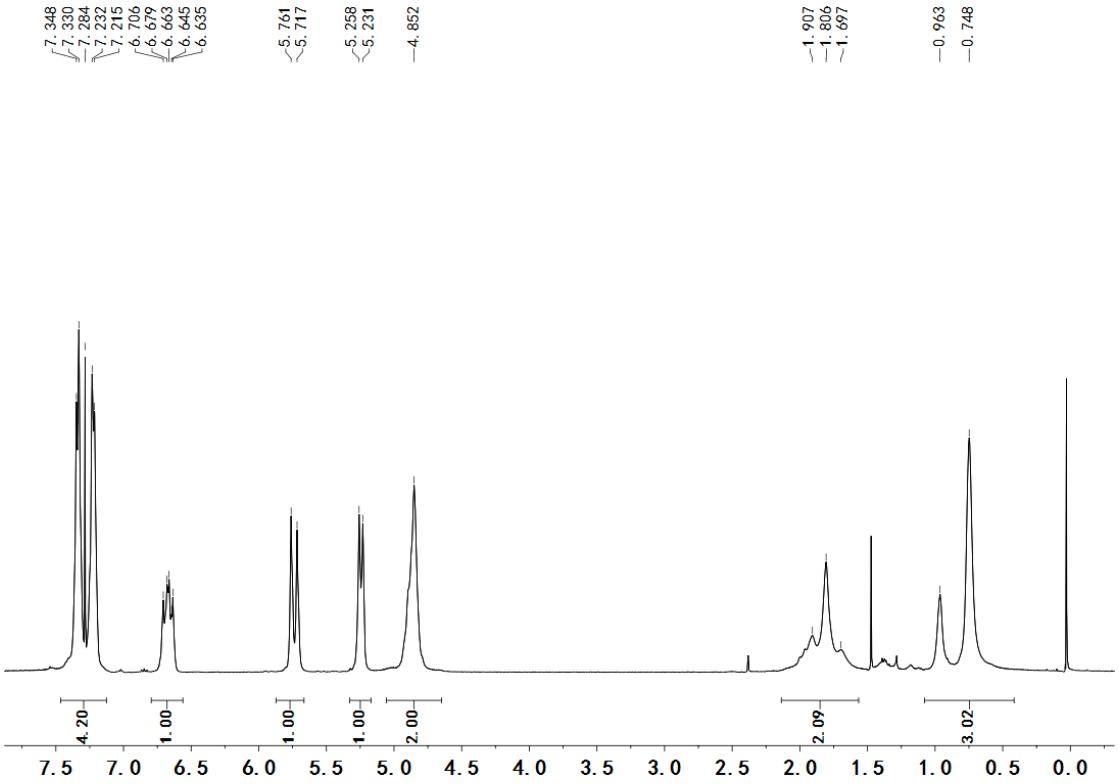

Figure S16. ^{1}H NMR (400M, $CDCl_3$, 298 K) of the PVBMA produced by the **4**/PEt_3 pair in toluene at RT with [VBMA]/[PEt_3] = 100:1. (*rr* = 72.1%)

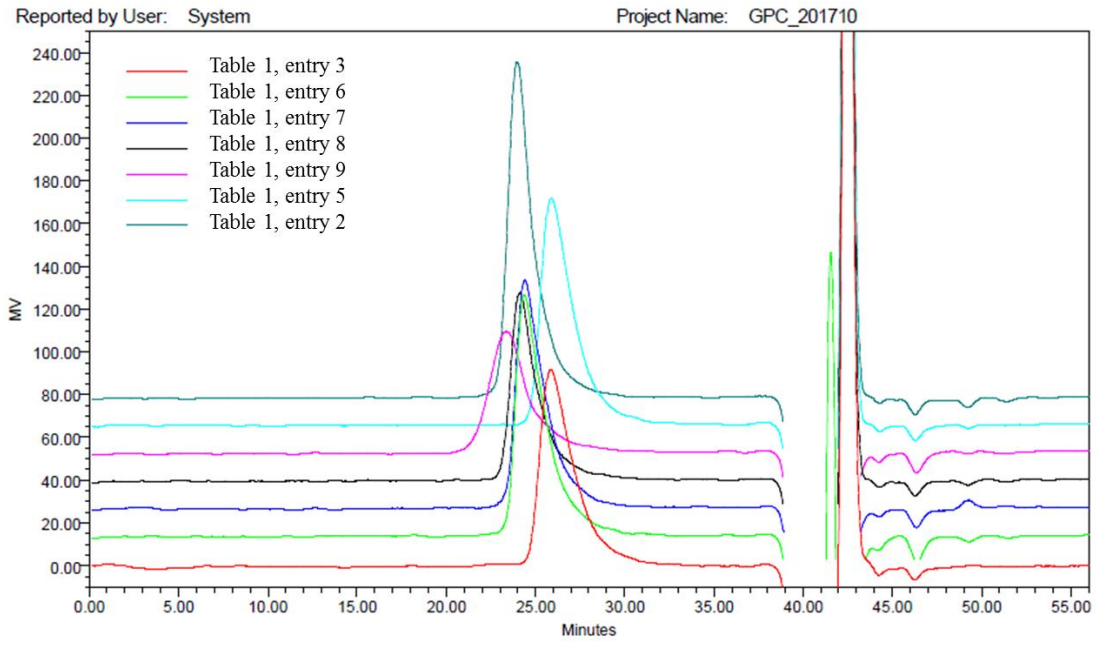

Figure S17. Typical GPC curves of current polymerization.