

Electronic supplementary information (ESI)

**Alternating Radical Copolymerization of α -Styrylboronic Acid
Pinacol Ester with Electron-Deficient Olefins**

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1) General

All polymerization reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. Toluene for polymerization was distilled with sodium-benzophenone under nitrogen atmosphere before use. All reagents, unless otherwise noted, are purified by distillation or column chromatography.

The following reagents were used after distillation: *n*-butyl acrylate (**nBA**) (99%, Aladdin), *N,N*-dimethylacrylamide (**DMAA**) (97%, Konosience), acrylonitrile (**AN**) (99%, Energy), α -methylstyrene (**α -MS**) (99%, Aladdin), methyl methacrylate (**MMA**) (99%, Energy), vinyl acetate (**VA**) (98%, Energy), 2-methyl-1-(vinylloxy)propane (**MVOP**) (98%, Adams). The following reagents were used after chromatography: α -styryl boronate pinacol ester (**StBpin**) (95%, Bidepham), *N*-ethylmaleimide (**EMI**) (98%, Meryer). For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. All other chemicals were purchased from Beijing Chemical Reagent Co. Ltd.

¹H NMR spectra were recorded on Bruker ARX 400 (400 MHz); ¹³C NMR spectra were recorded on Bruker ARX 400 (101 MHz). Chemical shifts were reported in ppm with tetramethylsilane (TMS) as the internal standard. Monomers described in the literature were characterized by comparing their ¹H and/or ¹³C NMR spectra with previously reported data.

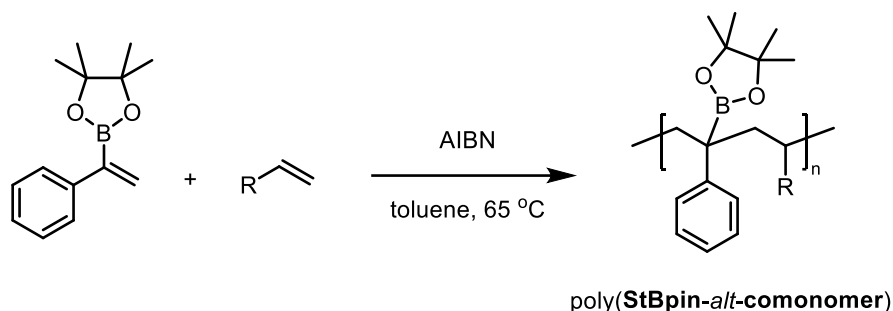
Size exclusion chromatography (SEC) for the analysis of number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers was carried out with Waters 515 Gel permeation chromatography. The instrument was calibrated with narrow-dispersity polystyrene standards. All runs were performed at 1.0 mL/min THF flow rate and 30 °C. Molecular weights (MW) were calculated using Chemstation GPC data analysis software based on the refractive index signals.

Thermal gravimetric analysis (TGA) was conducted on a Q600-SDT thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere of 100 mL/min. Differential scanning calorimetry (DSC) was performed on a Q2000 differential scanning calorimeter at a heating rate of 10 °C/min under a nitrogen atmosphere of 50 mL/min. Data of the endothermic thermograms were recorded from the second scan and analyzed with a TA Universal Analysis software.

MALDI-TOF MS analysis was performed with a Bruker ULTRAFLEX mass spectrometer. For MALDI MS analysis, mass spectra were acquired with a SmartBeam laser (355 nm) operating at 100 Hz, a laser focus of 50 μ m. The device parameters for MALDI MS were chosen as follows: plate offset voltage, 19 kV; deflector detector voltage, 20 kV. Data were processed using DataAnalysis 3.0 (Bruker Daltonics). The preparation of samples followed the treatment method below: DCTB was solved in THF (15 mg/ mL) followed by blending with the solution of testing polymers (1 mg·mL⁻¹) with the same volume. Then 1 μ L mixed solution was pipetted on the stainless-steel target. After dried under room temperature, the target was loaded into the ion-source to be analyzed.

2) General procedure for the copolymerization

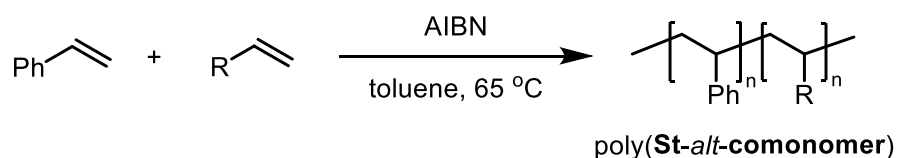
1. General procedure for the copolymerization of **StBpin** and copolymers



Scheme S1. Copolymerization of **StBpin** and comonomers

StBpin (920.6 mg, 4.0 mmol, 2.0 equiv) and initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) (6.56 mg, 0.04 mmol, 0.02 equiv) were added into 4 mL vial with PTFE cap. Comonomer (2.0 mmol, 1.0 equiv) and toluene (400 μ L) were added to the vial under N_2 atmosphere. The vial was warmed to 65 $^{\circ}C$ for 96 h and a pale-yellow sticky solution formed. The polymerization was quenched by cooling to room temperature. When copolymers were *n*-butyl acrylate (**nBA**) and *N,N*-dimethylacrylamide (**DMAA**), the reaction mixture was diluted by chloroform and purified by preparative gel permeation chromatography. When copolymers are acrylonitrile (**AN**) and *N*-ethylmaleimide (**EMI**), the reaction mixture was dissolved in 1 mL dichloromethane and precipitated in methanol at room temperature. The precipitates were isolated by centrifuge and dried in *vacuo* to afford the products for determining the yields. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (GPC). The precipitates were further purified by precipitation to afford the sample for 1H and ^{13}C NMR spectra.

2. General procedure for the copolymerization of styrene (**St**) and copolymers



Scheme S2. Copolymerization of styrene (**St**) and comonomers

Styrene (**St**) (208.1 mg, 2 mmol, 1.0 equiv) and initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) (6.56 mg, 0.04 mmol, 0.02 equiv) were added into 4 mL vial with PTFE cap. Comonomer (2.0 mmol, 1.0 equiv) and toluene (400 μ L) were added to the vial under N_2 atmosphere. The vial was warmed to 65 $^{\circ}C$ for 40 h and a pale-yellow sticky solution formed. The polymerization was quenched by cooling to

room temperature. When copolymers are *n*-butyl acrylate (**nBA**) and *N,N*-dimethylacrylamide (**DMAA**), the reaction mixture was diluted by chloroform and purified by preparative gel permeation chromatography. When copolymers were acrylonitrile (**AN**) and *N*-ethylmaleimide (**EMI**), the reaction mixture was dissolved in 2 mL dichloromethane and precipitated in methanol at room temperature. The precipitate was isolated by centrifuge and dried in *vacuo* to afford the products for determining the yields. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (GPC). The precipitate was further purified by precipitation to afford the sample for ^1H and ^{13}C NMR spectra.

Table S1. Results of styrene (St) and comonomers copolymerization

entry	comonomer	M_n (kDa)	M_w/M_n	yield (%)
1	nBA	21.1	1.79	88
2	DMAA	12.1	1.89	98
3	AN	23.9	1.86	99
4	EMI	16.5	1.89	99

3. Procedure to determine monomer reactivity ratios¹

According to Mayo and Lewis, the behavior of two monomers can be described as the following equation.²

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])}$$

$[M_1]$ or $[M_2]$: concentration of M_1 or M_2 ; r_1 or r_2 : the reactivity ratio of M_1 or M_2 .

When the monomer consumptions are small enough, Mayo-Lewis equation can be approximated as:

$$\frac{\Delta[M_1]}{\Delta[M_2]} = \frac{[M_1]_0(r_1[M_1]_0 + [M_2]_0)}{[M_2]_0(r_2[M_2]_0 + [M_1]_0)}$$

$[M_1]_0$ or $[M_2]_0$: Initial concentration of M_1 or M_2 ; $\Delta[M_1]$ or $\Delta[M_2]$: the consumption of M_1 or M_2 during reaction.

Define $F_1 = \Delta[M_1]/(\Delta[M_1] + \Delta[M_2])$, $F_2 = \Delta[M_2]/(\Delta[M_1] + \Delta[M_2])$, and $f_1 = [M_1]_0/([M_1]_0 + [M_2]_0)$, $f_2 = [M_2]_0/([M_1]_0 + [M_2]_0)$, equation shown above can be expressed as below:

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2}$$

Based on the equation shown above and experimental result f_1 and F_1 ,

nonlinear curve fitting of f_1 and F_1 was performed by OriginPro 2019b.

Copolymerization of **StBpin** and comonomers were initiated by AIBN. The feed ratio changed for different reactions ($[\text{StBpin}]_0 : [\text{comonomer}]_0 = 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, \text{ and } 10:90$). The actual feed ratio and consumption of monomers were determined by $^1\text{H NMR}$ (CDCl_3). Typical procedure of copolymerization showed below. **StBpin** (115.1 mg, 0.5 mmol, 1.0 equiv) and initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) (1.64 mg, 0.01 mmol, 0.01 equiv) were added into 4 mL vial with PTFE cap. Comonomer (0.5 mmol, 1.0 equiv), toluene (100 μL), and Tetralin (68 μL , 0.5 mmol, internal standard) were added into vial under N_2 atmosphere at room temperature (50:50 feed ratio condition). The vial was warmed to 65 $^\circ\text{C}$ for 5 h. The reaction was terminated by cooling in a freezer. F_{StBpin} was determined by monomer conversion ratio [$F_{\text{StBpin}} = \text{conv.}_{\text{StBpin}} / (\text{conv.}_{\text{StBpin}} + \text{conv.}_{\text{comonomer}})$] by $^1\text{H NMR}$ (CDCl_3) with tetralin as an internal standard. The actual feed ratio f_{StBpin} and consumption of monomers were determined by $^1\text{H NMR}$ (CDCl_3) before reaction. According to F_{StBpin} and f_{StBpin} , r_{StBpin} and $r_{\text{comonomer}}$ can be obtained by fitting. The monomer conversion of copolymerization showed in the table below.

Table S2. Copolymerization of **StBpin** with *n*-butyl acrylate (**nBA**) for determination of the monomer reactivity ratios^a

f^b	time (h)	conv. StBpin (%) ^c	conv. nBA (%) ^c	F
0.07	5	25.8	8.0	0.21
0.17	5	17.6	6.7	0.37
0.29	5	11.9	6.3	0.44
0.39	7	12.9	8.8	0.49
0.50	7	9.0	9.9	0.47
0.61	7	6.8	9.8	0.52
0.70	9	6.3	12.9	0.53
0.81	9	4.2	9.8	0.64
0.90	9	2.7	9.5	0.71

^a $[\text{StBpin} + \text{M}_1]_0 : [\text{AIBN}]_0 = 1000:10$ mM in toluene at 65 $^\circ\text{C}$. ^bDetermined by $^1\text{H NMR}$ (CDCl_3) before reaction. ^cDetermined by $^1\text{H NMR}$ (CDCl_3) after reaction

Table S3. Copolymerization of **StBpin** with *N,N*-dimethylacrylamide (**DMAA**) for the determination of the monomer reactivity ratios^a

f^b	time (h)	conv. StBpin (%) ^c	conv. DMAA (%) ^c	F
0.08	5	48.7	10.3	0.33
0.18	5	24.4	6.8	0.46
0.28	5	13.7	4.6	0.55
0.38	7	13.5	6.3	0.58

0.48	7	8.3	6.5	0.55
0.60	7	7.1	7.2	0.60
0.69	9	5.8	9.0	0.59
0.79	9	5.7	10.6	0.66
0.91	9	2.8	10.0	0.73

^a[StBpin+M₂]₀: [AIBN]₀ = 1000:10 mM in toluene at 65 °C. ^bDetermined by ¹H NMR (CDCl₃) before reaction. ^cDetermined by ¹H NMR (CDCl₃) after reaction

Table S4. Copolymerization of **StBpin** with acrylonitrile (**AN**) for the determination of the monomer reactivity ratios^a

<i>f</i> ^b	time (h)	conv. StBpin (%) ^c	conv. AN (%) ^c	F
0.10	3	46.5	12.3	0.33
0.22	3	31.1	11.0	0.47
0.33	3	16.3	12.2	0.40
0.43	3	11.6	12.7	0.40
0.54	3	9.0	12.9	0.44
0.64	3	6.3	14.9	0.42
0.73	3	3.9	12.7	0.44
0.82	3	2.1	10.3	0.47
0.91	4	1.9	19.0	0.47

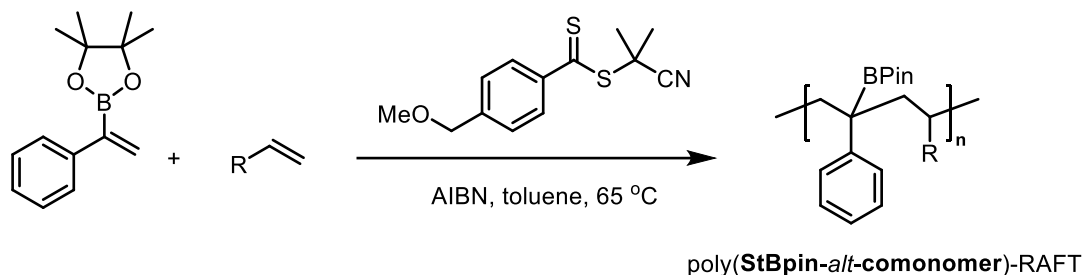
^a[StBpin+M₃]₀: [AIBN]₀ = 1000:10 mM in toluene at 65 °C. ^bDetermined by ¹H NMR (CDCl₃) before reaction. ^cDetermined by ¹H NMR (CDCl₃) after reaction

Table S5. Copolymerization of **StBpin** with *N*-ethylmaleimide (**EMI**) for the determination of the monomer reactivity ratios^a

<i>f</i> ^b	time (min)	conv. StBpin (%) ^c	conv. EMI (%) ^c	F
0.09	8	25.6	4.4	0.38
0.19	8	17.3	6.0	0.41
0.29	8	13.2	6.2	0.47
0.39	8	14.2	10.2	0.48
0.50	8	7.8	7.8	0.50
0.60	8	5.3	7.3	0.52
0.70	8	3.5	7.3	0.53
0.80	10	3.0	8.3	0.59
0.90	10	2.1	5.0	0.80

^a[StBpin+M₄]₀: [AIBN]₀ = 1000:10 mM in toluene at 65 °C. ^bDetermined by ¹H NMR (CDCl₃) before reaction. ^cDetermined by ¹H NMR (CDCl₃) after reaction

4. General procedure of copolymerization with RAFT reagent



Scheme S3 . Copolymerization with RAFT reagent

StBpin (230.15 mg, 1 mmol, 1 equiv), initiator 2,2'-azobis(2-methylpropanitrile) (AIBN) (4.1 mg, 0.025 mmol, 0.025 equiv) and 2-cyanopropan-2-yl 4-(methoxymethyl) benzodithioate (CMBD) (11.0 mg, 0.05 mmol, 0.05 equiv) were added into 4 mL vial with PTFE cap. **Comonomer** (0.5 mmol, 0.5 equiv) and toluene (200 μ L) were added into vial under N_2 atmosphere. The vial was warmed to 65 $^{\circ}C$ for 48 h and a pink sticky solution formed. The reaction was quenched by cooled to room temperature. Then the reaction mixture was diluted by chloroform and purified by preparative gel permeation chromatography. The resultant polymers were dried in *vacuo* to afford the yield. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (GPC). The precipitate was further purified by precipitation to afford the sample for 1H and ^{13}C NMR spectra.

Table S6. Result of **StBpin** and **M1-M4** copolymerization with RAFT reagent

entry	comonomer	yield (%)	M_n (kDa)	M_w/M_n
1	nBA	63	1.4	1.36
2	DMAA	52	1.1	1.23
3	AN	73	1.4	1.27
4	EMI	89	1.8	1.53

3) Characterization data of the polymer products

poly(**StBpin-*alt*-ⁿBA**): yield: 68%, ¹H NMR (400 MHz, CD₂Cl₂): δ 7.52 – 6.68 (m, 5H), 3.56 – 0.62 (m, 26H). ¹³C NMR (151 MHz, CD₂Cl₂): δ 175.88, 143.09, 128.88, 127.31, 125.01, 83.28, 63.69, 43.54, 39.84, 34.52, 30.24, 25.02, 20.23, 13.87.

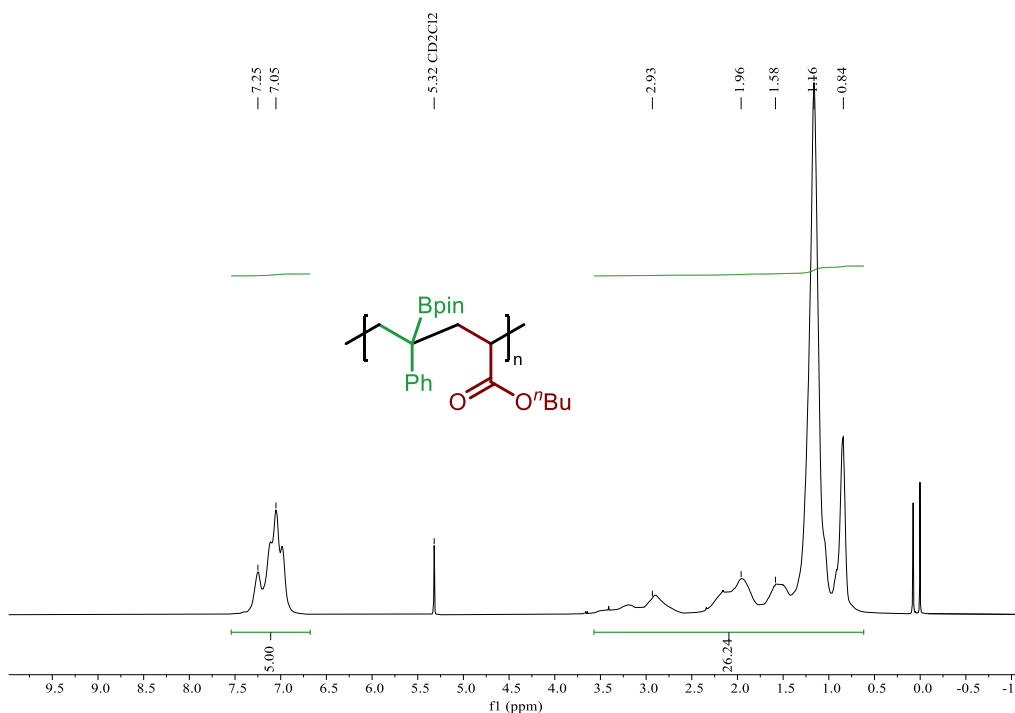


Figure S1. ¹H NMR (400 MHz) spectra of poly(**StBpin-*alt*-ⁿBA**)-RAFT

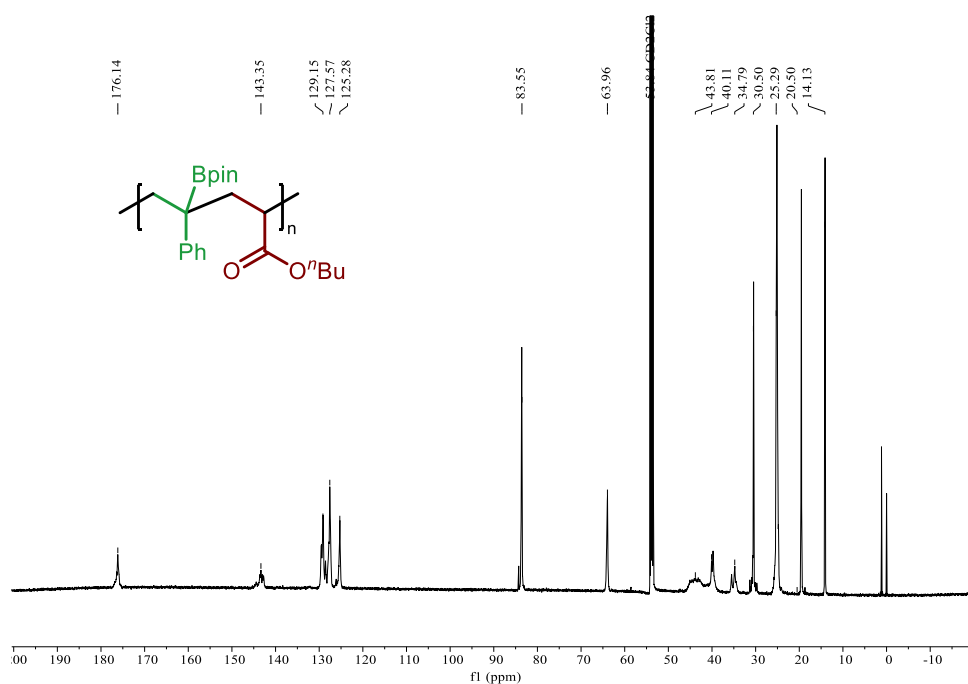


Figure S2. ¹³C NMR spectra (151 MHz) of poly(**StBpin-*alt*-ⁿBA**)-RAFT

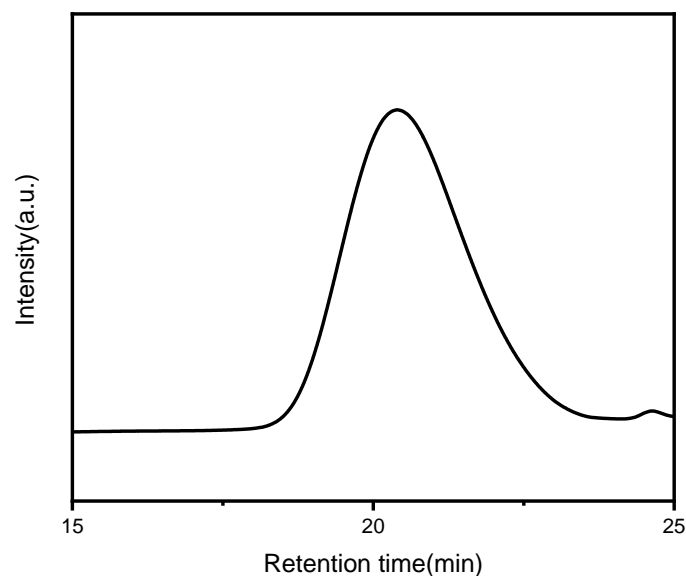


Figure S3. Size exclusion chromatograms of poly(**StBpin-*alt*-ⁿBA**)
SEC condition : eluent = THF

poly(**StBpin-*alt*-DMAA**): yield: 46%, ¹H NMR (400 MHz, CD₂Cl₂): δ 7.06 (br, 5H), 2.95 – 0.80 (m, 23H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 175.32, 144.15, 129.46, 127.38, 125.20, 83.13, 46.47, 36.83, 35.58, 25.61.

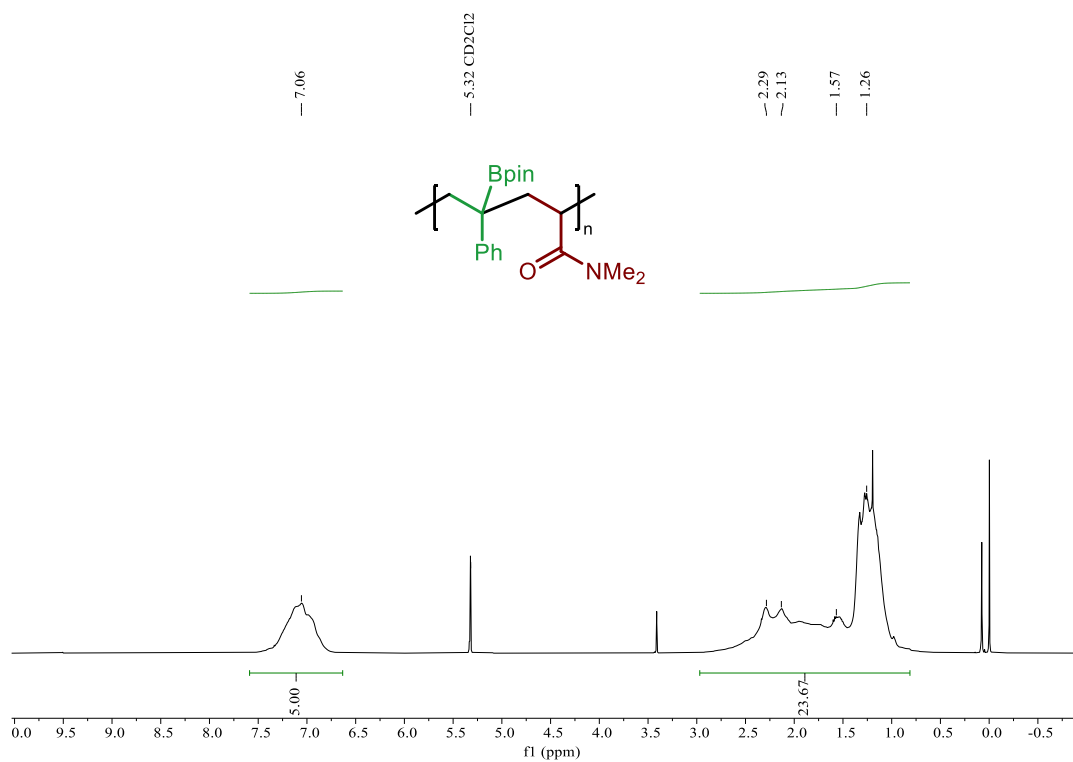


Figure S4. ¹H NMR spectra (400 MHz) of poly(**StBpin-*alt*-DMAA**)

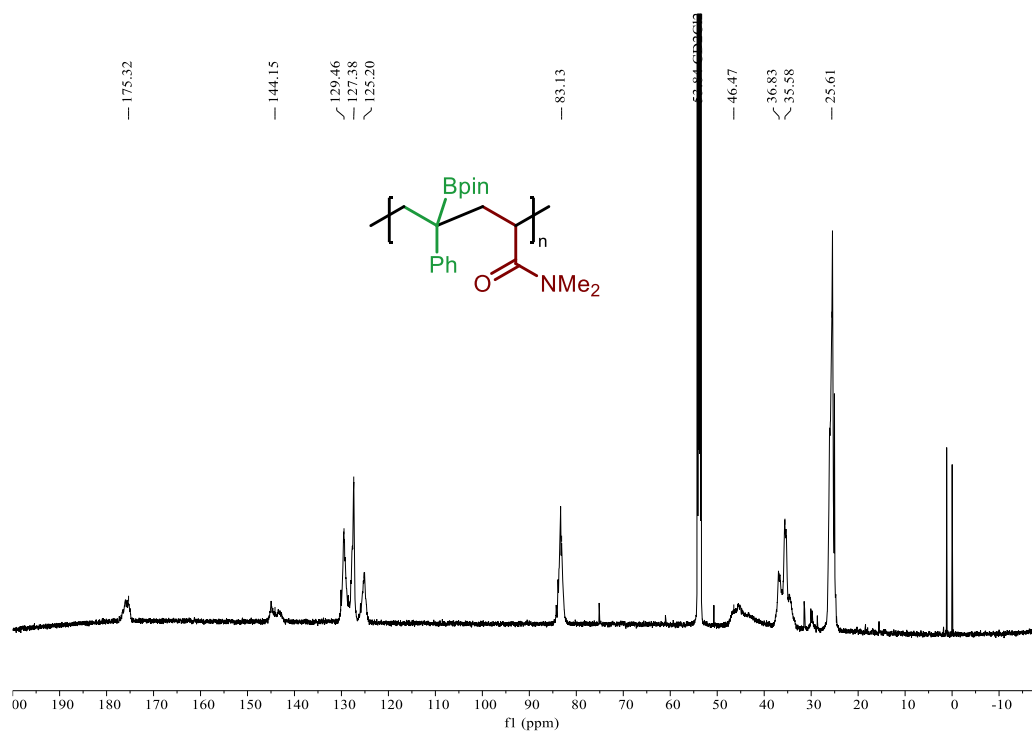


Figure S5. ^{13}C NMR spectra (151 MHz) of poly(StBpin-*alt*-DMAA)

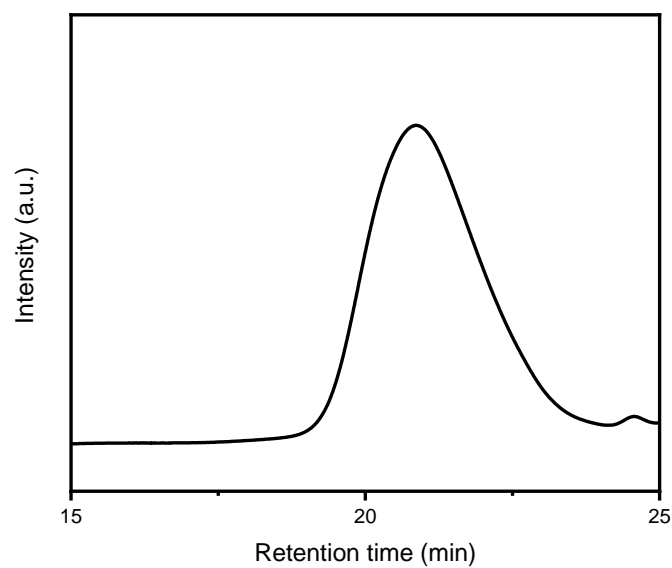


Figure S6. Size exclusion chromatograms of poly(StBpin-*alt*-DMAA)
SEC condition : eluent = THF

poly(**StBpin-*alt*-AN**): yield: 75%, $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.22 (br, 5H), 2.46 – 1.36 (m, 5H), 1.37 – 0.92 (m, 12H). $^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2) δ 142.35, 141.78, 128.80, 128.05, 126.85, 122.99, 84.75, 84.61, 43.34, 40.48, 36.69, 34.71, 25.37, 25.13.

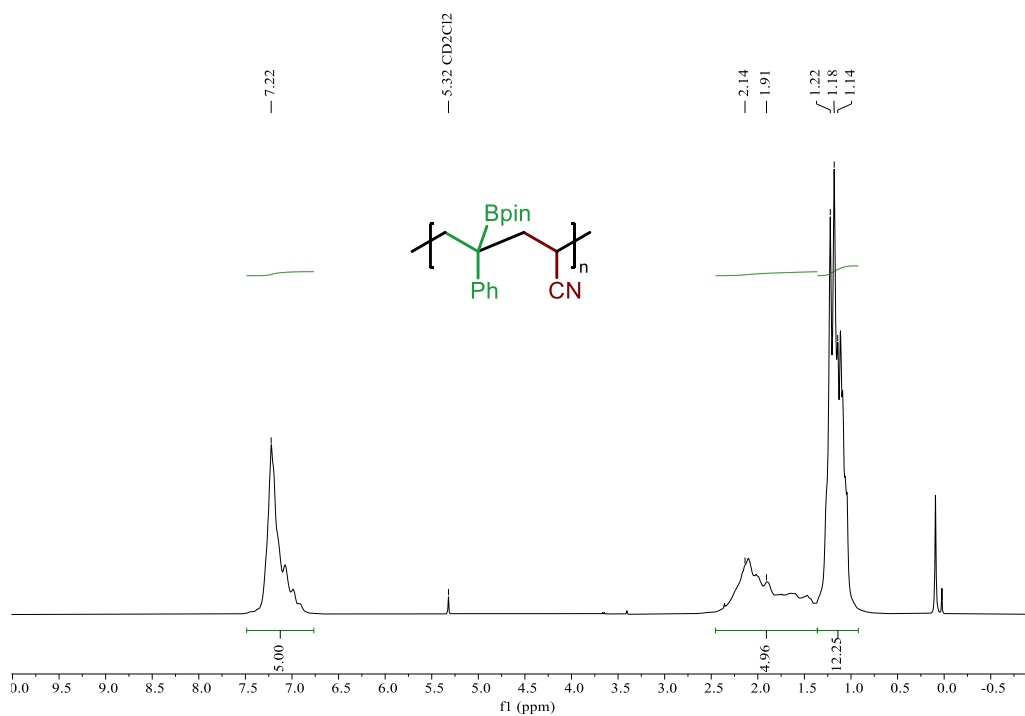


Figure S7. $^1\text{H NMR}$ spectra (400 MHz) of poly(**StBpin-*alt*-AN**)

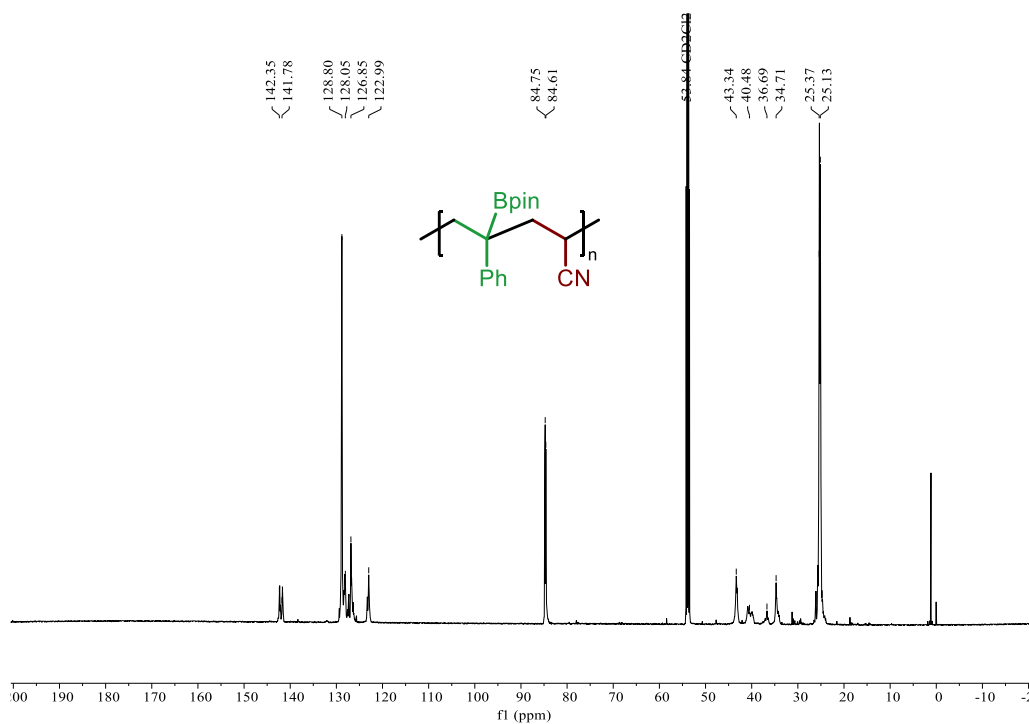


Figure S8. $^{13}\text{C NMR}$ spectra (151 MHz) of poly(**StBpin-*alt*-AN**)

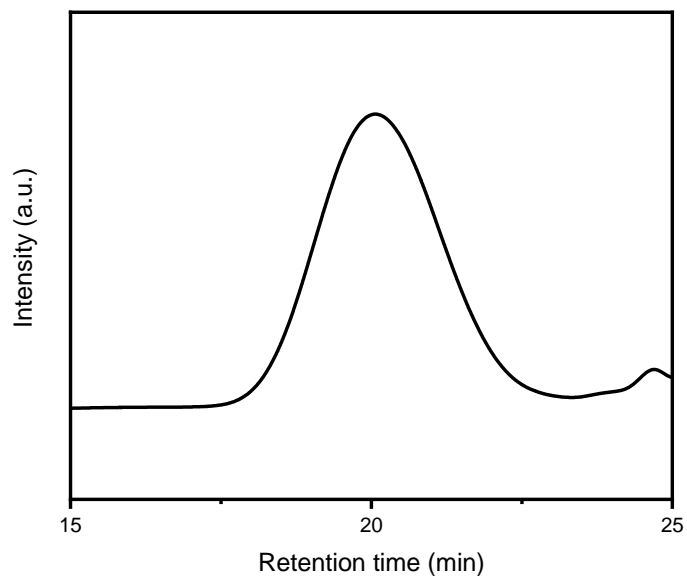


Figure S9. Size exclusion chromatograms of poly(**StBpin-alt-AN**)
SEC condition : eluent = THF

poly(**StBpin-alt-EMI**): yield: 63%, ^1H NMR (400 MHz, CD_2Cl_2): δ 7.08 (br, 5H), 3.93 – 0.39 (m, 21H).; ^{13}C NMR (151 MHz, CD_2Cl_2) δ 179.16, 143.16, 128.00, 84.16, 83.51, 40.55, 36.73, 34.16, 25.67, 13.27.

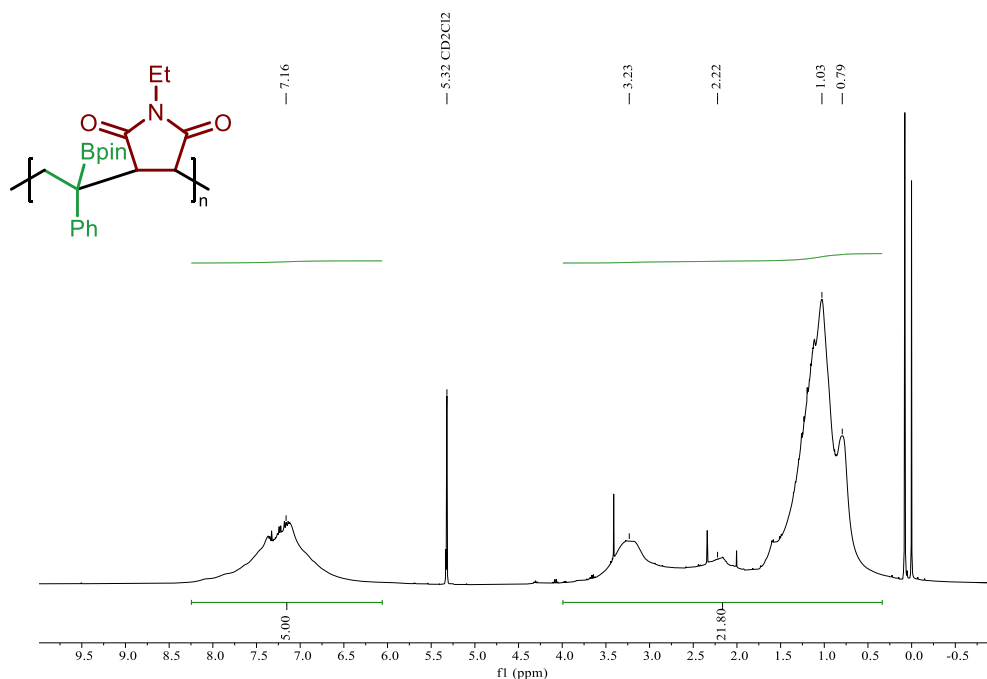


Figure S10. ^1H NMR spectra (400 MHz) of poly(**StBpin-alt-EMI**)

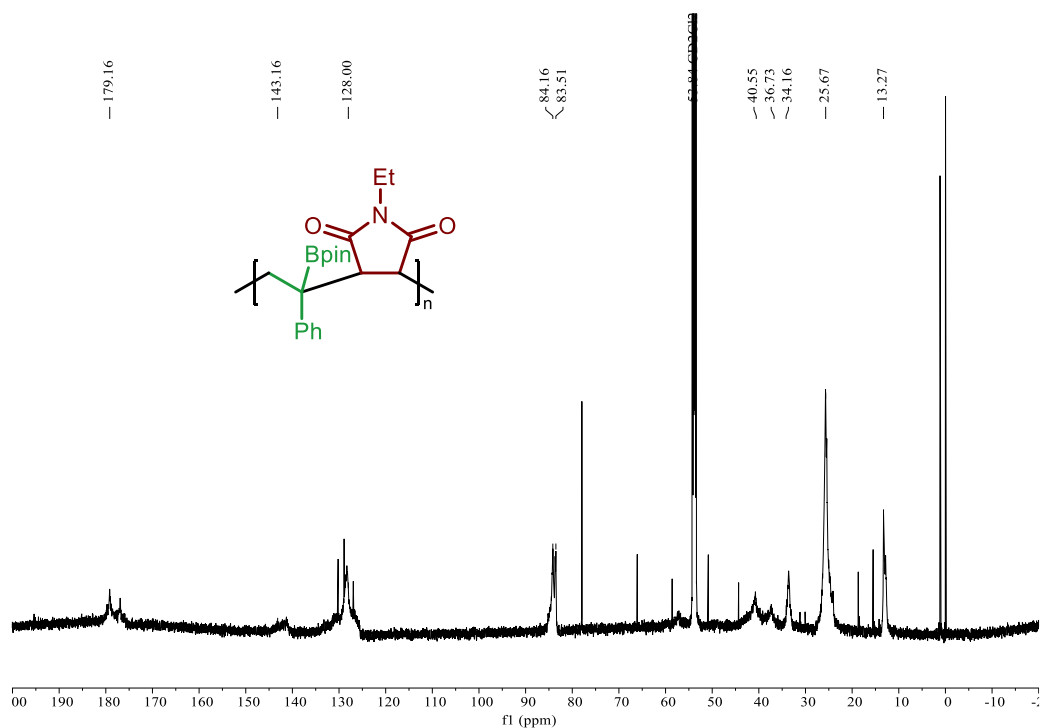


Figure S11. ^{13}C NMR spectra (151 MHz) of poly(StBpin-*alt*-EMI)

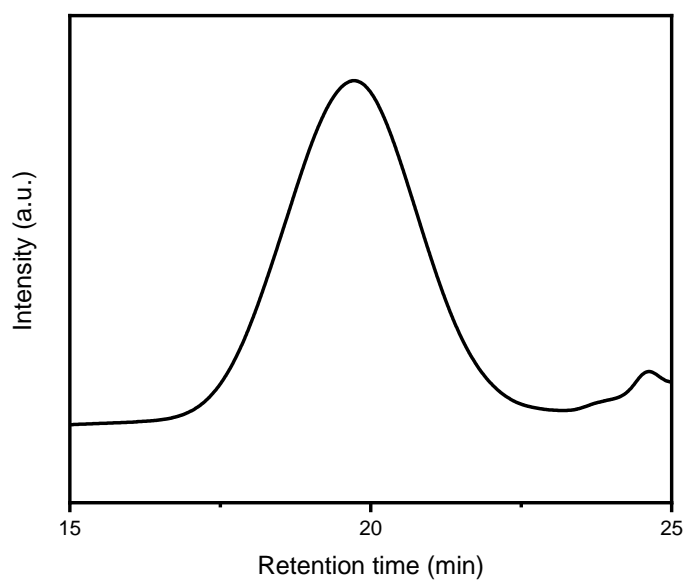


Figure S12. Size exclusion chromatograms of poly(StBpin-*alt*-EMI)
SEC condition : eluent = THF

poly(St-co-*n*BA): yield: 88%, $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.40 – 6.45 (m, 5H), 4.21 – 3.33 (m, 2H), 2.60 – 0.51 (m, 13H).

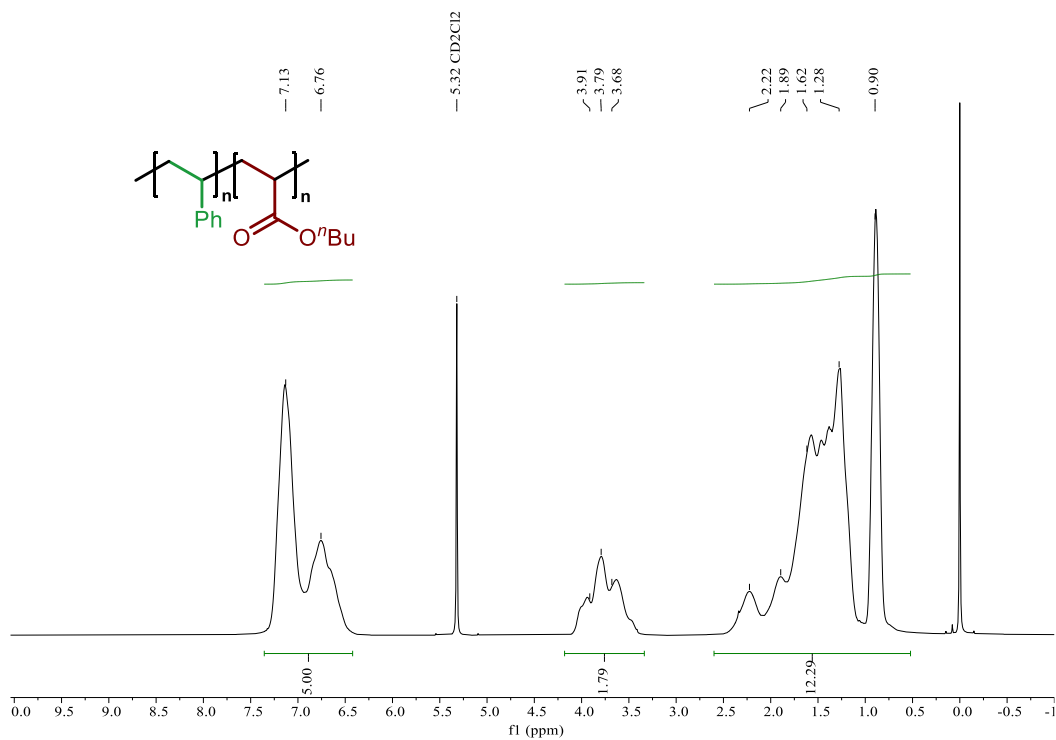


Figure S13. $^1\text{H NMR}$ spectra (400 MHz) of poly(St-co-*n*BA)

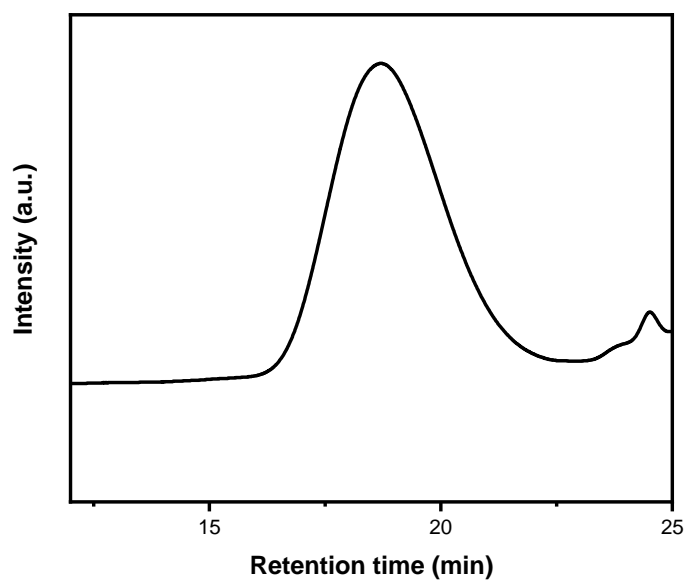


Figure S14. Size exclusion chromatograms of poly(St-co-*n*BA)
SEC condition : eluent = THF

poly(**St-co-DMAA**): yield: 98%, $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.49 – 6.33 (m, 5H), 3.27 – 0.84 (m, 12H).

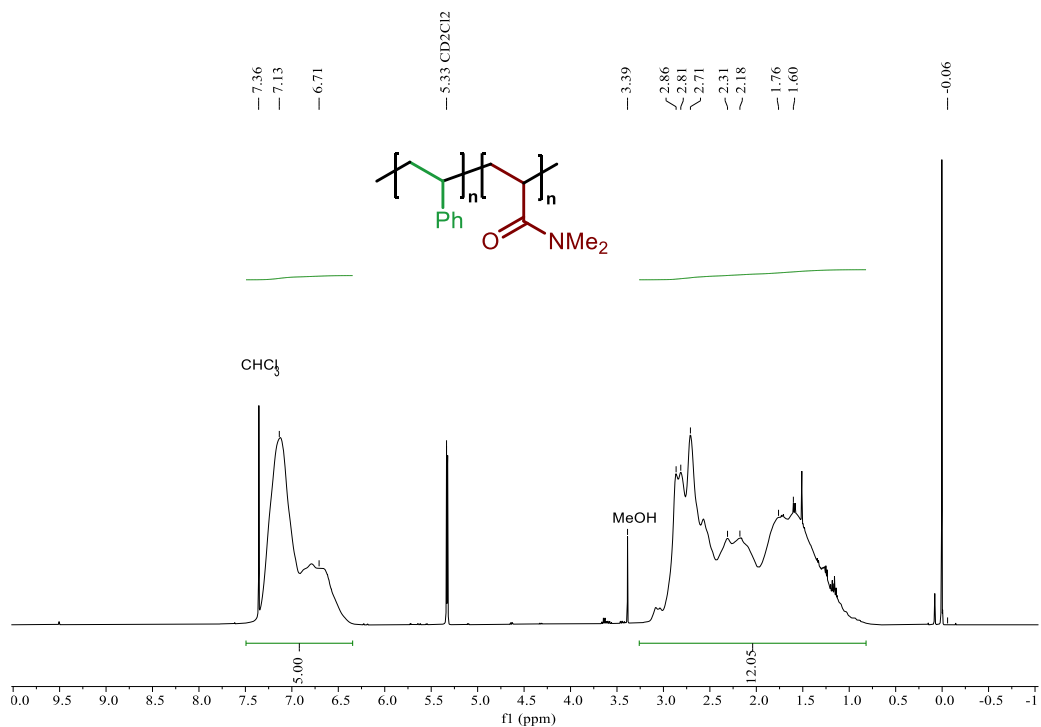


Figure S15. $^1\text{H NMR}$ spectra (400 MHz) of poly(**St-co-DMAA**)

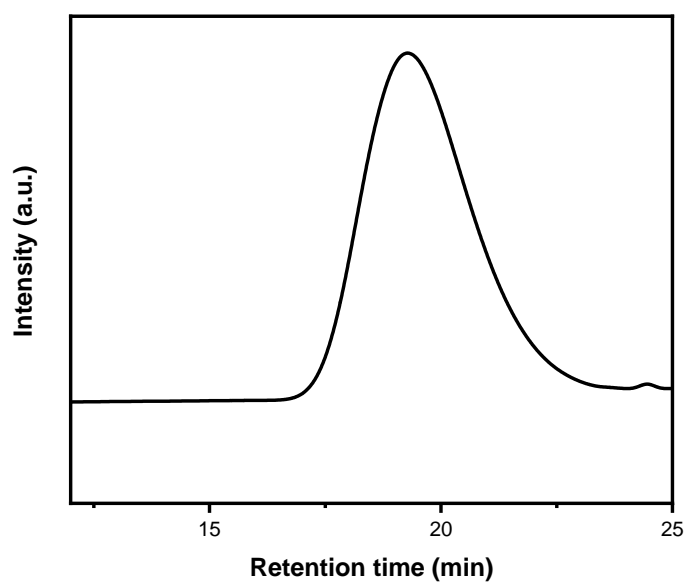


Figure S16. Size exclusion chromatograms of poly(**St-co-DMAA**)
SEC condition : eluent = THF

poly(*St-co-AN*): yield: 99%, $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.48 – 6.47 (m, 5H), 3.07 – 1.06 (m, 6H).

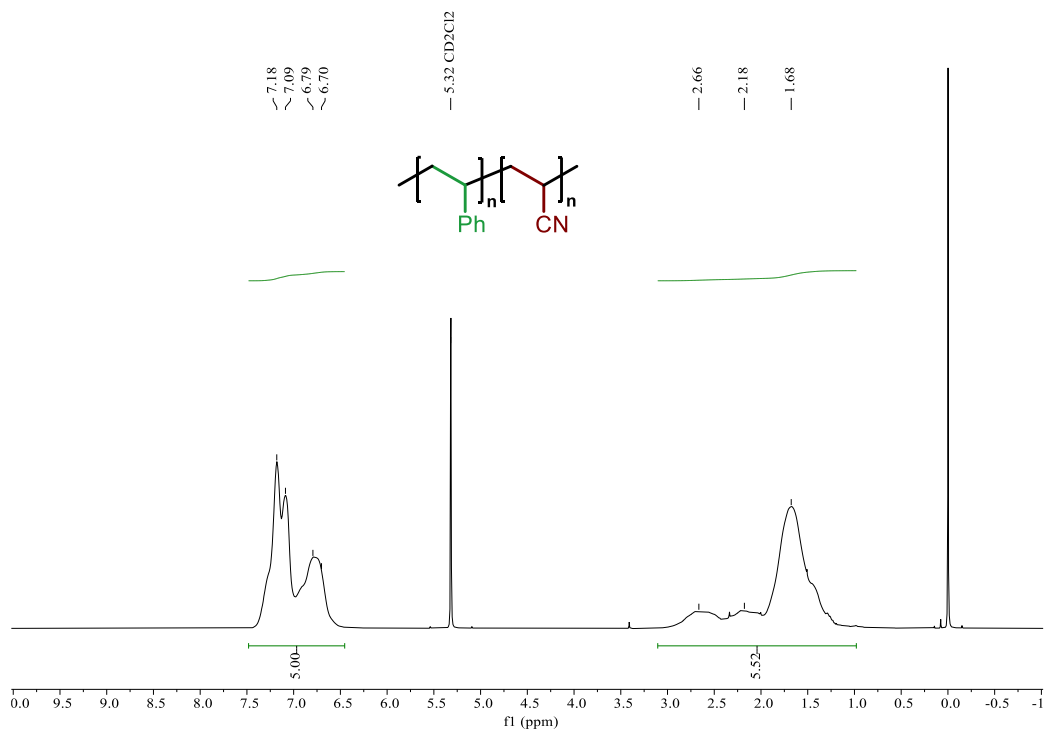


Figure S17. $^1\text{H NMR}$ spectra (400 MHz) of poly(*St-co-AN*)

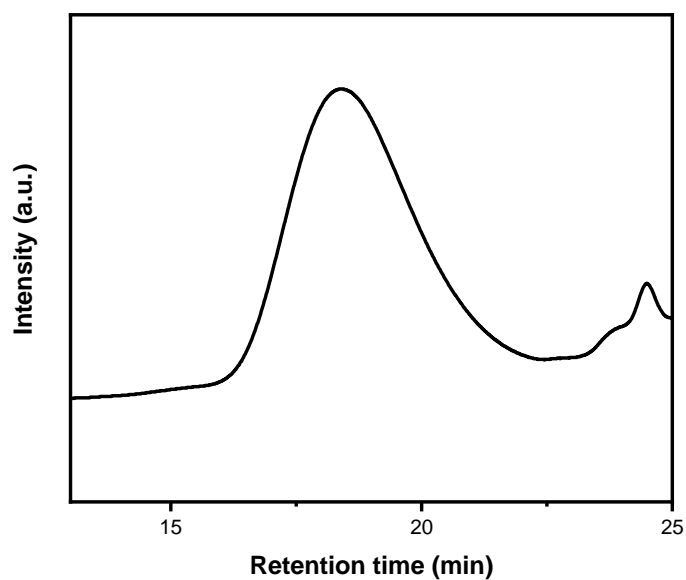


Figure S18. Size exclusion chromatograms of poly(*St-co-AN*)
SEC condition : eluent = THF

poly(**St-co-EMI**): yield: 99%, $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.70 – 5.91 (m, 5H), 3.87 – 1.32 (m, 7H), 0.95 (br, 3H).

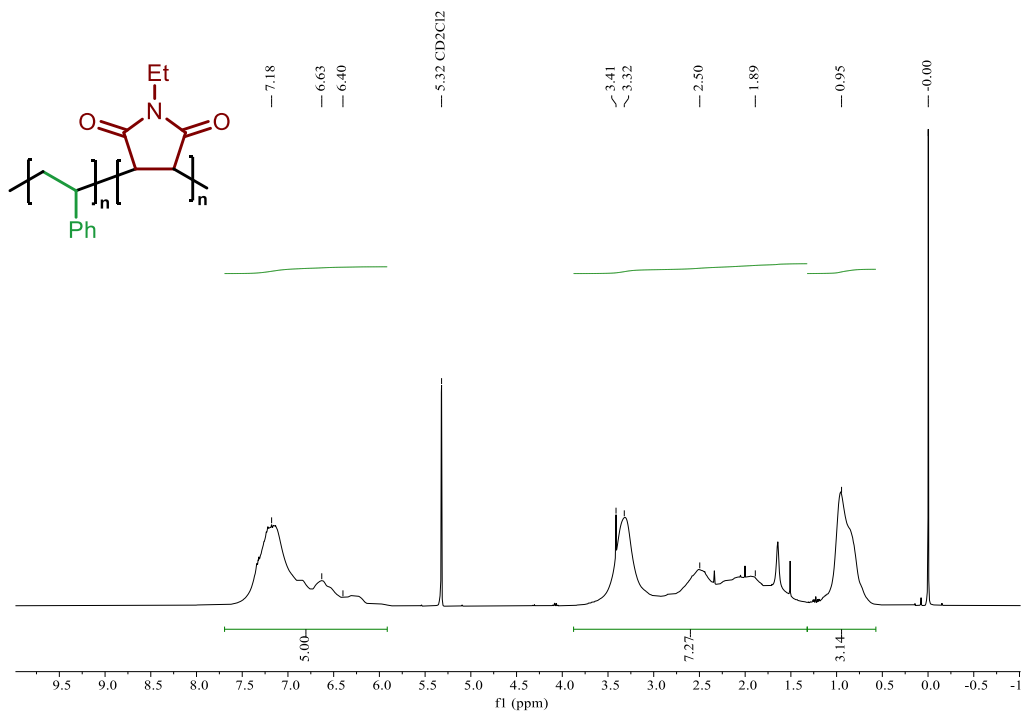


Figure S19. $^1\text{H NMR}$ (400 MHz) spectra of poly(**St-co-EMI**)

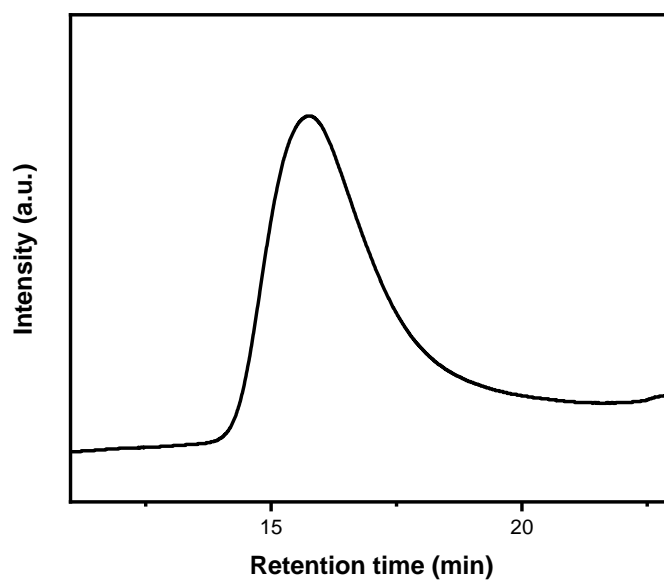
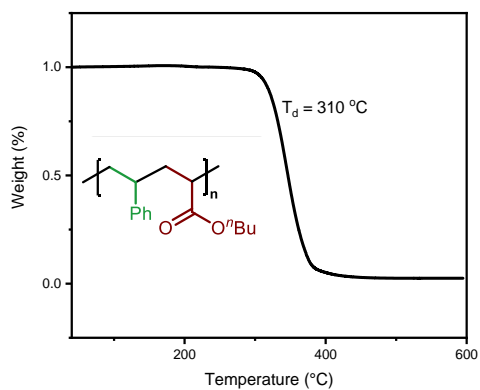


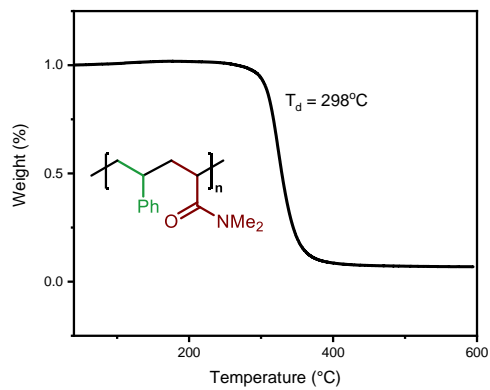
Figure S20. Size exclusion chromatograms of poly(**St-co-EMI**)
SEC condition : eluent = THF

4) TGA data of the copolymers

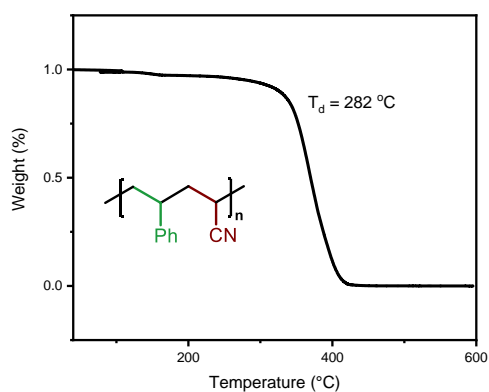
a) poly(StBpin-*alt*-ⁿBA)



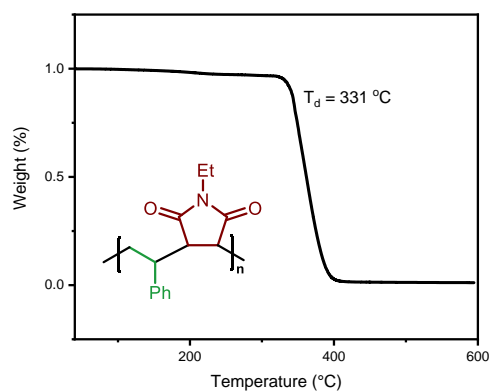
b) poly(StBpin-*alt*-DMAA)



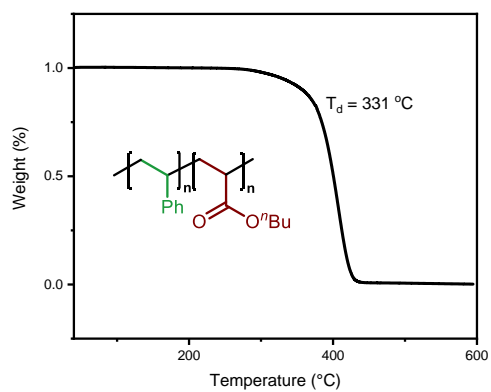
c) poly(StBpin-*alt*-AN)



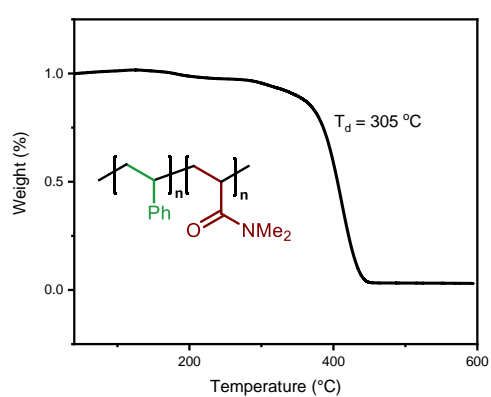
d) poly(StBpin-*alt*-EMI)



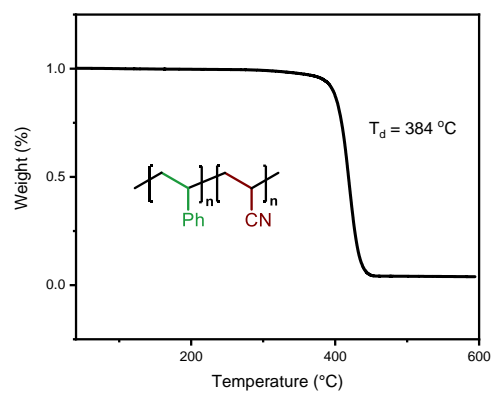
e) poly(St-*co*-ⁿBA)



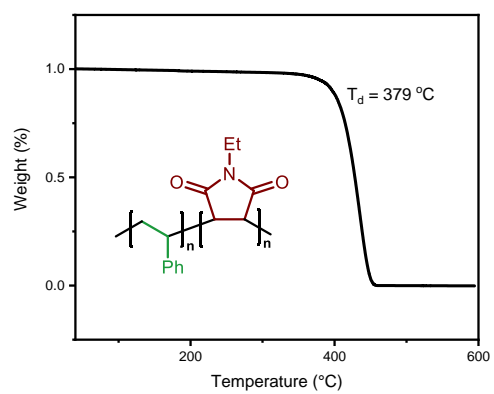
f) poly(St-*co*-DMAA)



g) poly(St-co-AN)



h) poly(St-co-EMI)



5) References

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