Electronic Supplementary Information

for

Investigation on Eight-arm Tapered Star Copolymers Prepared from Anionic Copolymerization and Coupling Reaction

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Table S1 The feeding amounts for preparing all polymers in this work.

Entry	Sample	Feed ratio (n_{St}:n_{Ip})	*sec*-BuLi (mmol)	St (mmol)	Ip (mmol)	OVPOSS (mmol)
P1-P7	P(I-*co*-S)	1:1	0.91	30	30	-
P8	PI-*b*-PS	1:1	0.08	30	30	-
P9	P(I-*co*-S)$_2$	1:1	0.09	20×2	20×2	-
P10	P(I-*co*-S)$_2$	2:1	0.07	20×2	10×2	-
P11	P(I-*co*-S)$_2$	1:2	0.07	10×2	20×2	-
P12	8[P(I-*co*-S)$_1$]-POSS	1:2	0.36	30	60	0.05
P13	8[P(I-*co*-S)$_2$]-POSS	1:2	0.24	10×2	20×2	0.03
P14	8[P(I-*co*-S)$_3$]-POSS	1:2	0.36	10×3	20×3	0.05

In a glovebox filled with argon atmosphere, the anionic copolymerization of St and Ip was conducted in cyclohexane using *sec*-BuLi as the initiator. The sampling was used to get tapered linear copolymers at different reaction time for 10 min, 20 min, 30 min, 50 min, 90 min, 180 min, and 540 min, respectively, and the sample numbers were set as P1-P7.

Firstly, ^{1}H NMR and GPC analyses were used to characterize the chemical structure and molecular weights of the tapered copolymer P(I-*co*-S) at different reaction time. The ^{1}H NMR spectra are shown in Fig. S1, GPC curves are shown in Fig. S2, and the data are summarized in Table S2. The attribution of the proton peak on the benzene ring is found from 7.21~6.24 ppm, and the double bond in the PI segment are found at 5.18~4.80 and 4.80~4.43 ppm, which indicates that the copolymerization of styrene and isoprene has successfully occurred. As the reaction time increased from P1 to P7, the proton peak area of PS segment was also increased, which can be preliminarily speculated to meet the characteristics of tapered copolymer, that is, Ip reacts first and then St starts to react.

The molecular weights of the tapered copolymers were calculated according to the ^{1}H NMR spectra. Taking P1 as an example, set the integral area of the proton peaks on the two

methyl groups of sec-BuLi as 6 (A_a = 6), the benzene ring of the St repeating unit has 5 protons, and the corresponding integral area of proton peaks is A_{i+j+k}. The relative molecular weight $\bar{M}_{n,\,NMR\text{-}PS}$ and $\bar{M}_{n,\,NMR\text{-}PI}$ can be calculated by equations (1) and (2), where 104.15 and 68.12 are the molecular weight of St and Ip monomer. The mass fraction of PS block (w_{PS}) in the copolymer can be calculated by equation (3), and the volume fraction of PS (f_{PS}) can be calculated by equation (4), where 0.91 g cm^{-3} is the density of PI and 1.05 g cm^{-3} is the density of PS. All the molecular weights, mass fractions and volume fractions of PS segments in polymers in this paper are calculated according to the above methods.

$$\bar{M}_{n,\,NMR\text{-}PS} = \frac{A_{i+j+k}}{5} \times 104.15 \tag{1}$$

$$\bar{M}_{n,\,NMR\text{-}PI} = (A_c + \frac{A_e}{2}) \times 68.12 \tag{2}$$

$$w_{PS} = \frac{\bar{M}_{n,\,NMR\text{-}PS}}{\bar{M}_{n,\,NMR\text{-}PS} + \bar{M}_{n,\,NMR\text{-}PI}} \tag{3}$$

$$f_{PS} = \frac{\bar{M}_{n,\,NMR\text{-}PS}/1.05}{\bar{M}_{n,\,NMR\text{-}PS}/1.05 + \bar{M}_{n,\,NMR\text{-}PI}/0.91} \tag{4}$$

Meanwhile, the GPC elution curves (Fig. S2) of copolymers are symmetrical with low dispersity ($Đ$ = 1.06 ~1.10). With the passage of reaction time, the curves clearly shift to the direction of higher molecular weight, indicating the successful occurrence of living copolymerization. At the beginning of the reaction, the molecular weight increased rapidly. The number-average molecular weight ($\bar{M}_{n,\,GPC}$) were 1.45 kg mol^{-1}, 2.02 kg mol^{-1}, 2.93 kg mol^{-1}, and 4.28 kg mol^{-1} when the reaction proceeded at 10 mins, 20 mins, 30 mins, and 50 mins. After 50 min of reaction, the increase was slow, and the difference was small compared with 90 min of reaction ($\bar{M}_{n,\,GPC}$ = 5.98 kg mol^{-1}). The molecular weights slowly increased to 6.37 kg mol^{-1} and 6.42 kg mol^{-1} after 180 and 540 mins of reaction. Moreover, the dispersity increased a little with the increase of reaction time.

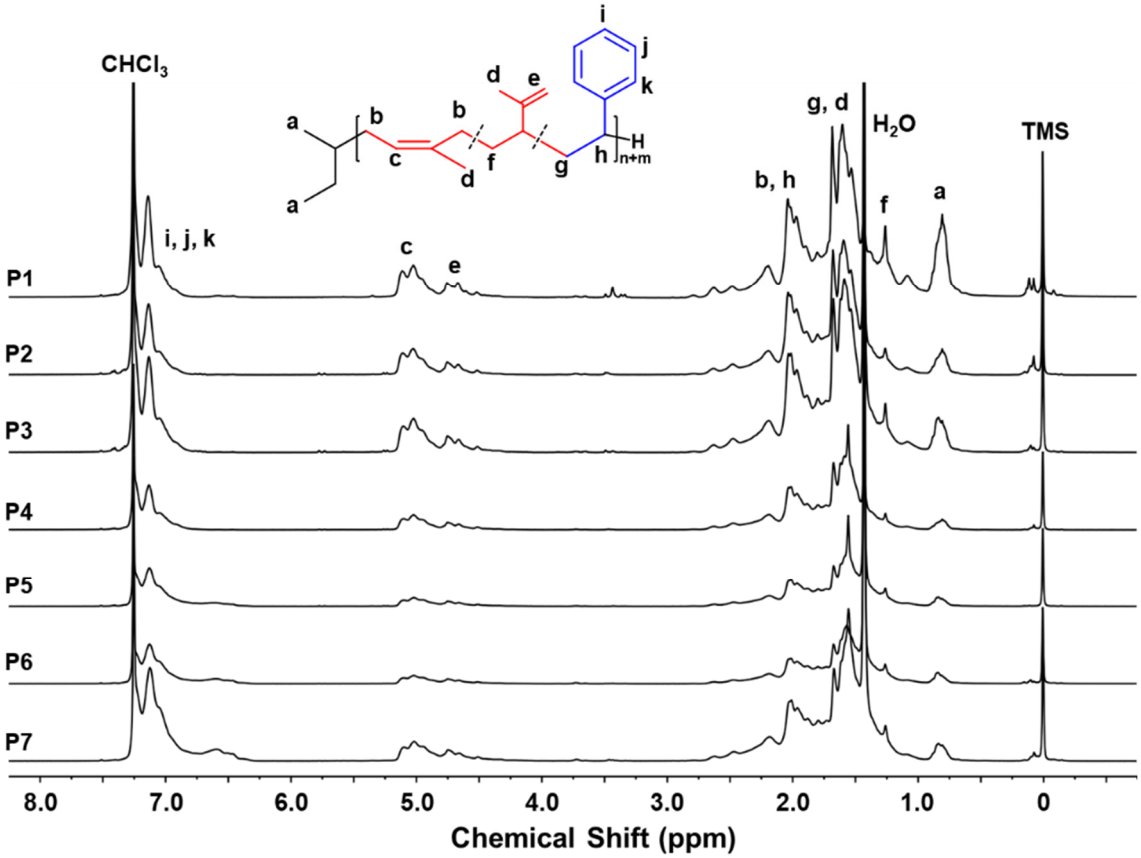

Fig. S1 ^{1}H NMR spectra of P(I-*co*-S) synthesized at different reaction time.

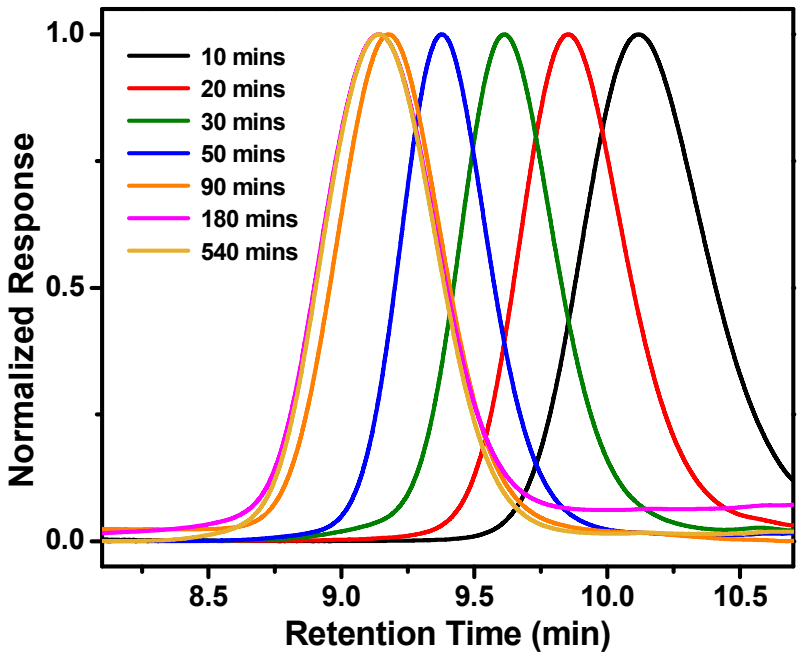

Fig. S2 GPC traces of P(I-*co*-S) synthesized at different reaction time.

Table S2 Molecular weight and composition of P(I-*co*-S) synthesized at different reaction time.

Entry	Reaction time (min)	$\bar{M}_{n,\,GPC}$ (kg mol^{-1})[a]	$Đ$[a]	$\bar{M}_{n,\,NMR}$ (kg mol^{-1})[b]	f_{PS}[b]	w_{PS}[b]
P1	10	1.45	1.06	1.16	0.35	0.38
P2	20	2.02	1.05	1.91	0.36	0.39
P3	30	2.93	1.06	3.13	0.33	0.37
P4	50	4.28	1.09	5.13	0.38	0.41
P5	90	5.98	1.09	5.38	0.52	0.55
P6	180	6.37	1.09	5.46	0.57	0.60
P7	540	6.42	1.10	6.37	0.54	0.58

[a] Determined by GPC with THF as the eluent and PS as the standards.

[b] Calculated from ^{1}H NMR spectra.

In addition, MALDI-TOF MS analysis was used to characterize the chain structure of tapered copolymers with different reaction time. The mass spectrum of P(I-*co*-S) after 10 mins of reaction is shown in Fig. S3, the other spectra for the rest of reaction time are shown in Figs. S4-S8. The full spectrum of the copolymer is shown on the left region. The peak shape is a normal distribution, and there is only one set of distribution. The partially enlarged spectrum is shown on the right part. The AC peak interval is 68.06, which is the molecular weight of one Ip repeating unit. The AD peak interval is 104.06, which is the molecular weight of one St repeating unit. It can be found that m/z value is x styrene (104.06 g mol^{-1}) + y isoprene (68.06 g mol^{-1}) + counter ion Ag (106.91 g mol^{-1}) + terminal hydrogen (1.01 g mol^{-1}) + the sum of *sec*-BuLi end groups (57.07 g mol^{-1}). For example, when x=10 and y=4, its theoretical molecular weight can be calculated by $M_{Calcd.}$ = 10 × 68.06 + 4 × 104.06 + 106.91 + 57.08 + 1.01 = 1261.86, which is very close to the value found in mass spectrum (*m/z* = 1262.03 Da) and means that there are 10 Ip units and 4 St units in this chain. Using the same method, the ratios of the number of repeating units in PI

segment and PS segments for peaks A, B, C and D are determined to be 10:4, 9:5, 11:4, and 10:5, respectively. The results indicated that the number of PI repeating units of copolymer is more than PS segment after 10 mins of reaction when the feed ratio of monomers is 1:1. The data from MALDI-TOF mass spectra of P(I-*co*-S) copolymer with different reaction time are summarized in Fig. S9, in which the abscissa is the number of total degree of polymerization (DP_{Ip+St}), the left ordinate is the DP number of Ip unit (DP_{Ip}), and the right ordinate is the DP number of St unit (DP_{St}). It can be observed that when DP_{Ip+St} is small, DP_{Ip} is significantly larger than DP_{St}. As DP_{Ip+St} increases, that is, the reaction time increases, DP_{Ip} grows slowly and DP_{St} seems to increase a lot. For example, when DP_{Ip+St} is above 50, DP_{St} increases sharply from 18 to 37, but DP_{Ip} slowly increases from 34 to 39. This indicated that St participated in the reaction in a large amount at this time, and Ip had been exhausted and no longer involved in the copolymerization. It meets the characteristics of a tapered copolymer, that is, Ip polymerized faster than St in the copolymerization.

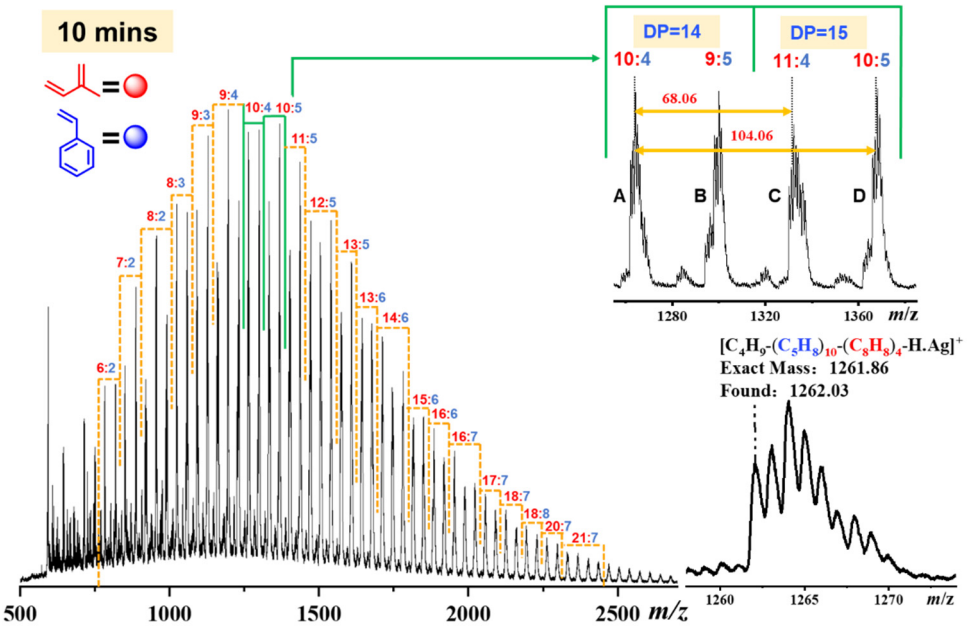

Fig. S3 MALDI-TOF mass spectrum of P(I-*co*-S) after 10 mins of reaction.

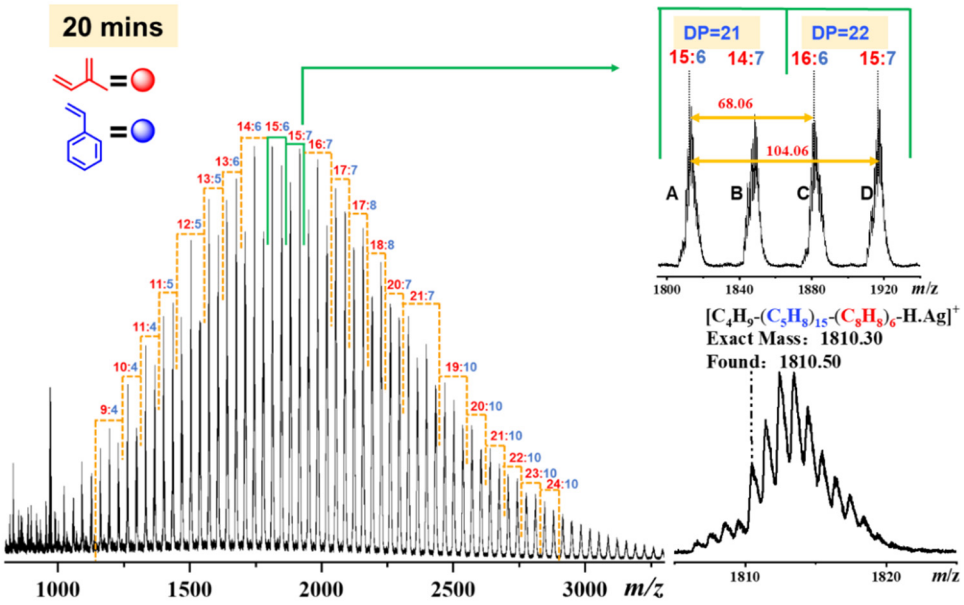

Fig. S4 MALDI-TOF mass spectrum of P(I-*co*-S) after 20 mins of reaction.

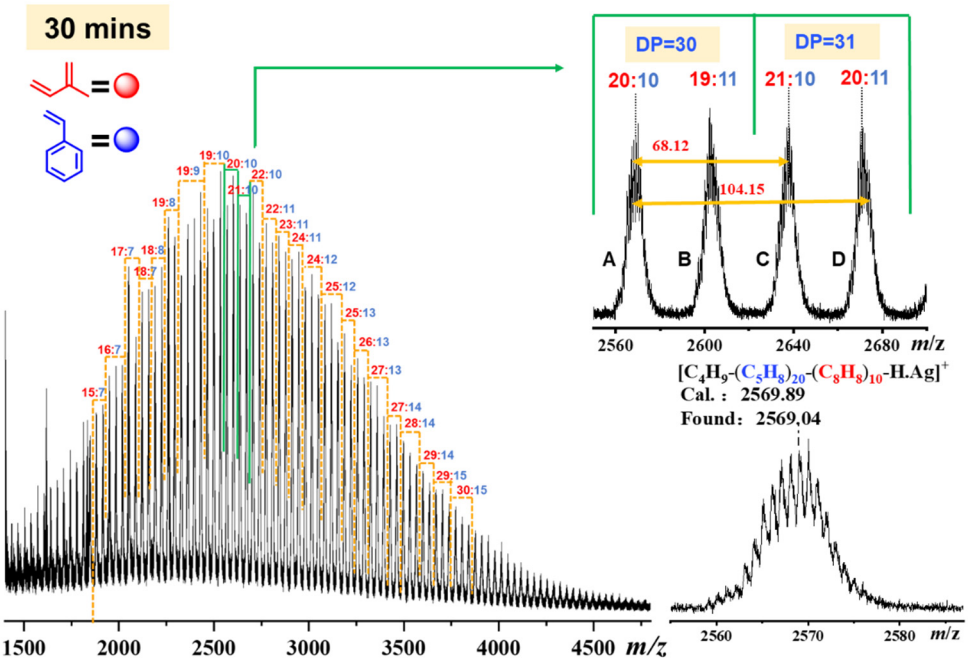

Fig. S5 MALDI-TOF mass spectrum of P(I-*co*-S) after 30 mins of reaction.

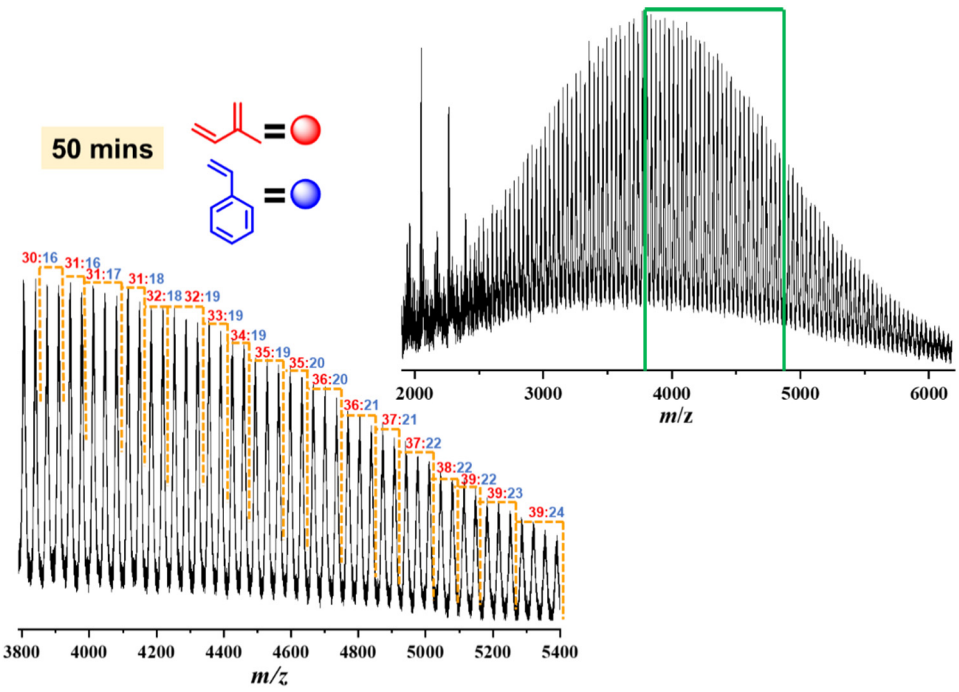

Fig. S6 MALDI-TOF mass spectrum of P(I-*co*-S) after 50 mins of reaction.

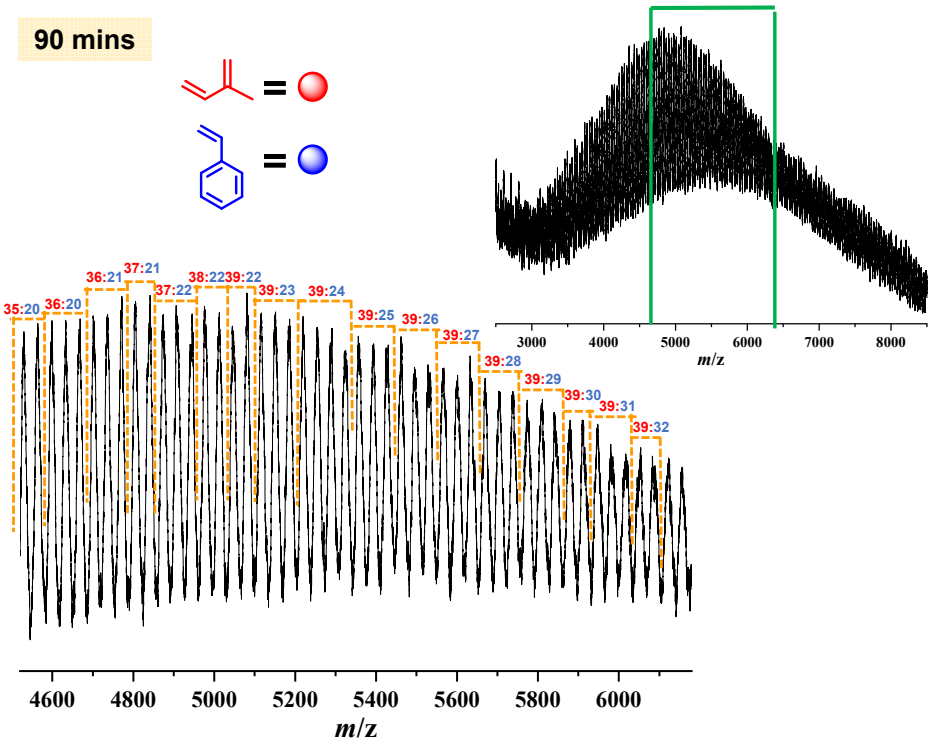

Fig. S7 MALDI-TOF mass spectrum of P(I-*co*-S) after 90 mins of reaction.

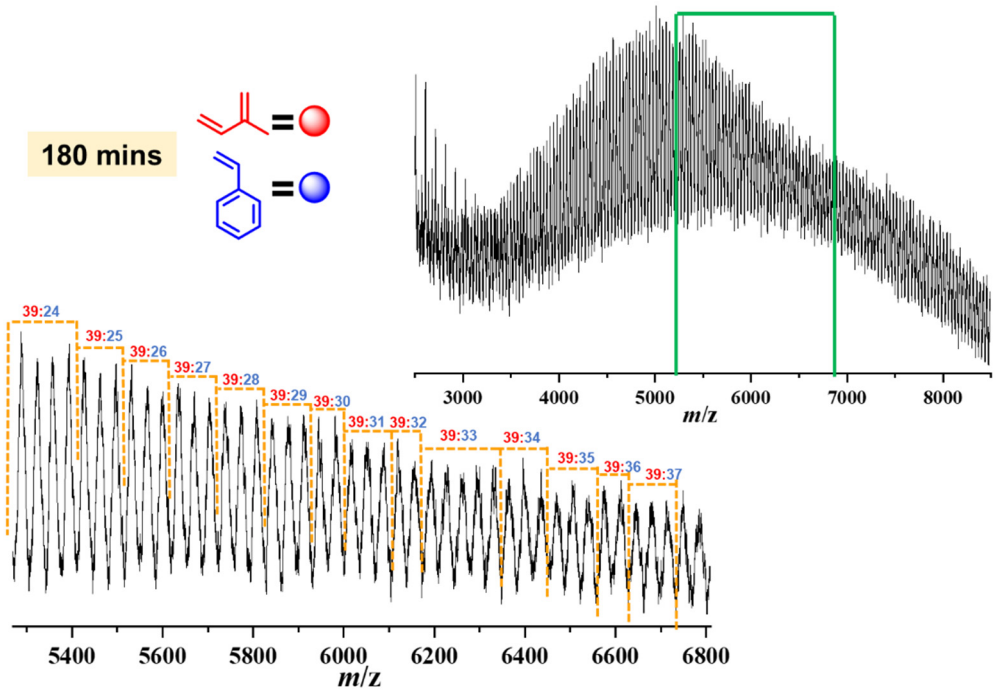

Fig. S8 MALDI-TOF mass spectrum of P(I-*co*-S) after 180 mins of reaction.

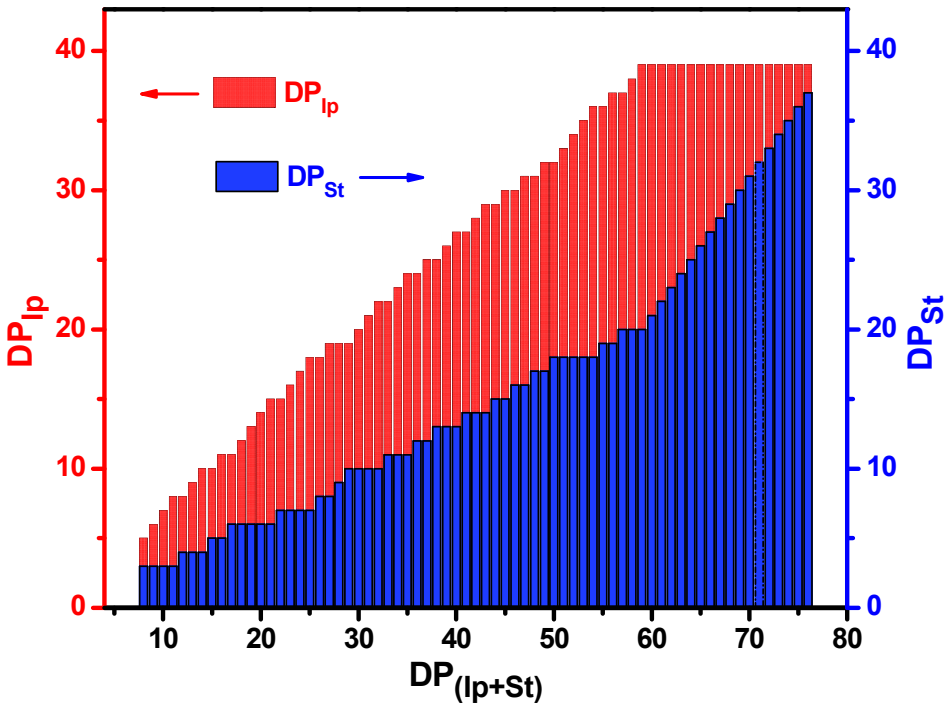

Fig. S9 The DP values of different repeating units in the tapered copolymer.

On the other hand, the real-time ^{1}H NMR monitoring method was used to track the anionic copolymerization of Ip and St. The superimposed ^{1}H NMR spectra including the zoomed-in region are shown in the Fig. S10. Among them, δ 6.53~6.39 ppm is the characteristic peak of tertiary hydrocarbon proton in Ip monomer, and the signal at δ 5.75~5.55 ppm is the proton of vinyl group in St monomer. It can be seen that as the reaction time increases, the peak area of tertiary hydrocarbon proton in Ip decreases significantly, while the peak area of vinyl proton in St is almost unchanged. This indicated that Ip monomer reacted faster during the copolymerization and it was completely consumed when the reaction time was about 3 h, while St was still involving the reaction, which satisfied with the characteristics of tapered copolymerization.

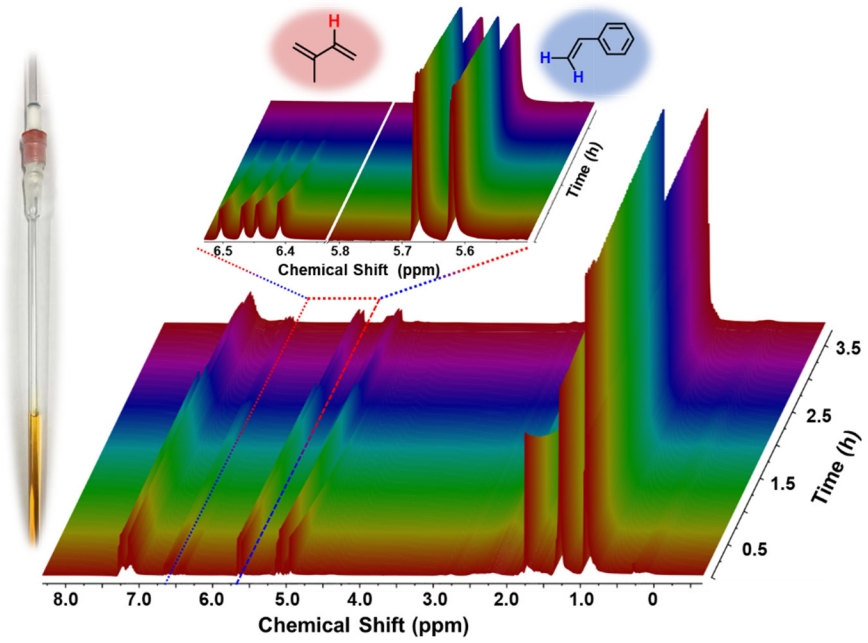

Fig. S10 Stacked ^{1}H NMR spectra (benzene-d_6) including the zoomed-in region as a function of time of the real-time ^{1}H NMR kinetics characterization of the statistical copolymerization of Ip and St.

At the same time, the characteristic peak area of Ip monomer is set as A_I, the characteristic peak area of St monomer is set as A_S, and the consumption degree of monomers can be calculated from equations (5)-(10). The relationship of conversion rate *versus* reaction time is shown in Fig. S11A, it can be found that when the reaction time is close to 200 mins, the conversion rate curve of Ip tends to be flat and the conversion rate

of Ip reaches around 90%. However, at this time, the conversion rate of St is about 53% and does not increase thereafter. The kinetic curves of the two monomers in the copolymerization process, ln[1/(1-Conv.M)] *vs.* reaction time, are shown in Fig. S11B. The apparent rate constants of two monomers are k_{Ip} = 0.01035 min^{-1} and k_{St} = 0.00355 min^{-1}, which is obtained by kinetic curve fitting. It further demonstrates that under this condition without additive, compared with St, Ip exhibits higher activity in anionic copolymerization in nonpolar solvent and the tapered copolymers can be produced.

$$\Delta n_{\mathrm{S}} = n_{0,\mathrm{S}} \times \left(1 - \frac{A_{\mathrm{S}}}{A_{0,\mathrm{S}}}\right) \tag{5}$$

$$\Delta n_{\mathrm{I}} = n_{0,\mathrm{I}} \times \left(1 - \frac{A_{\mathrm{I}}}{A_{0,\mathrm{I}}}\right) \tag{6}$$

$$\Delta Conv.\mathrm{S} = \frac{\Delta n_{\mathrm{S}}}{n_{0,\mathrm{S}}} \tag{7}$$

$$\Delta Conv.\mathrm{I} = \frac{\Delta n_{\mathrm{I}}}{n_{0,\mathrm{I}}} \tag{8}$$

$$k_{\mathrm{S}}t = \frac{1}{1 - Conv.\mathrm{S}} \tag{9}$$

$$k_{\mathrm{I}}t = \frac{1}{1 - Conv.\mathrm{I}} \tag{10}$$

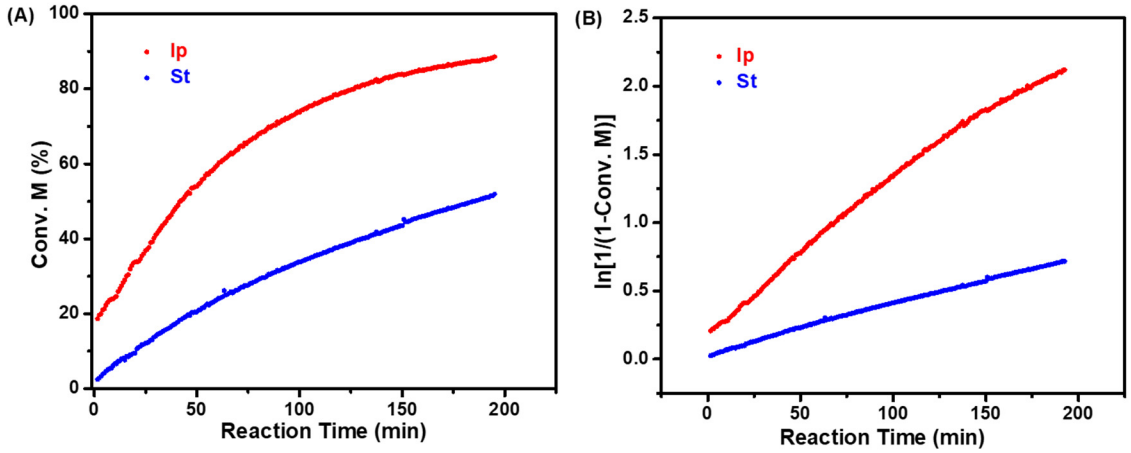

Fig. S11 (A) The curves of conversion rates *versus* reaction time of P(I-*co*-S); (B) the kinetic curves of the copolymerization of Ip and St.

Generally, the calculation methods of reactivity ratio mainly include Mayo-Lewis (M-L) method, Fineman-Ross (F-R) method, Kelen-Tüdös (K-T) method, and Yezrielev-Brokhina-Roskin (YBR) method.[1] Herein, based on the results of real-time ^{1}H NMR kinetic study, the reactivity ratios of monomers were calculated from equations (11)-(15) by the F-R method, and the result is shown in Fig. S12. The reactivity ratios of Ip (r_{Ip}) and St (r_{St}) were calculated to be 9.04 and 0.08, respectively. It can be found that the reactivity ratio of Ip monomer is significantly higher than that of St monomer, that is, Ip tends to be homopolymerized to generate longer PI segments. After Ip is exhausted, St begins to participate in the reaction, which satisfies the characteristics of a tapered copolymer.

$$n_S = n_{0,S} \times \frac{A_S}{A_{0,S}} \tag{11}$$

$$n_I = n_{0,I} \times \frac{A_I}{A_{0,I}} \tag{12}$$

$$\text{Set } f_I = \frac{n_I}{n_S + n_I},\ F_I = \frac{dn_I}{dn_S + dn_I} \tag{13}$$

$$G = H \times r_I - r_S \tag{14}$$

$$\frac{f_I \times (2F_I - 1)}{(1 - f_I) \times F_I} = \frac{f_I^2 \times (1 - F_I)}{(1 - f_I)^2 \times F_I} \times r_I - r_S \tag{15}$$

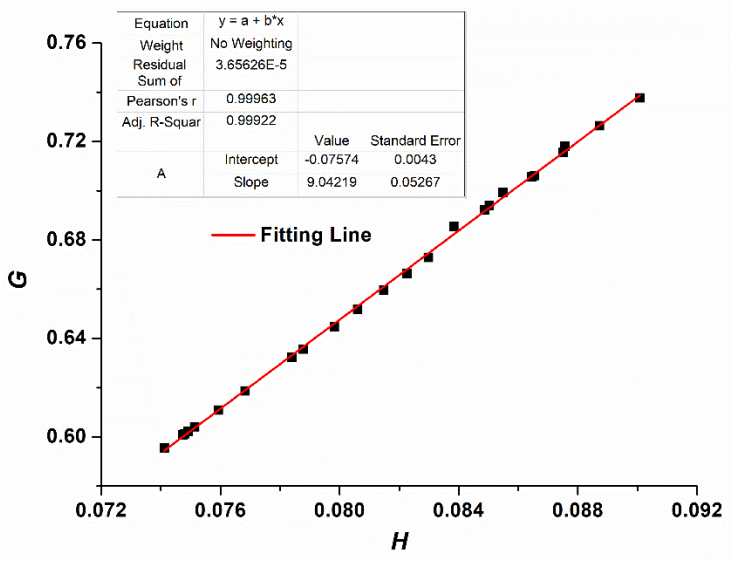

Fig. S12 Evaluation of reactivity ratios using the Fineman-Ross method.

Table S3 Evaluation of reactivity ratios using the Fineman-Ross method.

	A_I	A_S	M_I	M_S	$[M_I]$	$[M_S]$	f_I	F_I	G	H
1	70.49	194.92	0.79	0.94	0.17	0.02	0.46	0.89	0.738	0.090
2	69.40	194.54	0.78	0.94	0.18	0.02	0.45	0.89	0.726	0.089
3	68.58	194.26	0.77	0.94	0.19	0.02	0.45	0.89	0.718	0.088
4	67.42	193.82	0.76	0.93	0.20	0.03	0.45	0.88	0.706	0.086
5	68.35	194.16	0.77	0.94	0.19	0.02	0.45	0.89	0.715	0.088
6	67.46	193.83	0.76	0.93	0.20	0.03	0.45	0.88	0.706	0.087
7	66.79	193.60	0.75	0.93	0.21	0.03	0.45	0.88	0.699	0.085
8	66.28	193.39	0.75	0.93	0.21	0.03	0.44	0.88	0.694	0.085
9	66.10	193.32	0.74	0.93	0.22	0.03	0.44	0.88	0.692	0.085
10	65.44	193.08	0.74	0.93	0.22	0.03	0.44	0.88	0.685	0.084
11	64.28	192.59	0.72	0.93	0.24	0.03	0.44	0.88	0.673	0.083
12	63.00	192.06	85.36	199.31	0.71	0.93	0.25	0.03	0.660	0.081
13	62.25	191.74	85.36	199.31	0.70	0.92	0.26	0.04	0.652	0.081
14	61.58	191.45	85.36	199.31	0.69	0.92	0.27	0.04	0.645	0.080
15	60.71	191.07	85.36	199.31	0.68	0.92	0.28	0.04	0.636	0.079
16	60.39	190.93	85.36	199.31	0.68	0.92	0.28	0.04	0.632	0.078
17	59.07	190.33	85.36	199.31	0.66	0.92	0.30	0.04	0.619	0.077
18	58.32	189.98	85.36	199.31	0.66	0.92	0.30	0.04	0.611	0.076
19	57.67	189.67	85.36	199.31	0.65	0.91	0.31	0.05	0.604	0.075
20	57.49	189.58	85.36	199.31	0.65	0.91	0.31	0.05	0.602	0.075
21	57.39	189.54	85.36	199.31	0.65	0.91	0.31	0.05	0.601	0.075
22	57.35	189.52	85.36	199.31	0.64	0.91	0.32	0.05	0.601	0.075
23	56.83	189.27	85.36	199.31	0.64	0.91	0.32	0.05	0.595	0.074

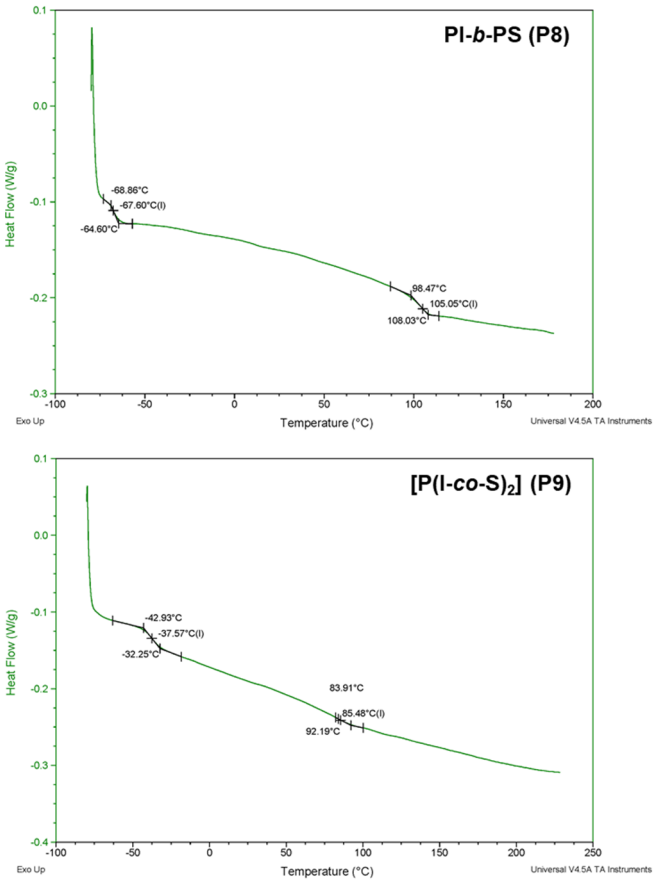

Fig. S13 Original DSC thermograms of P8 and P9 copolymers.

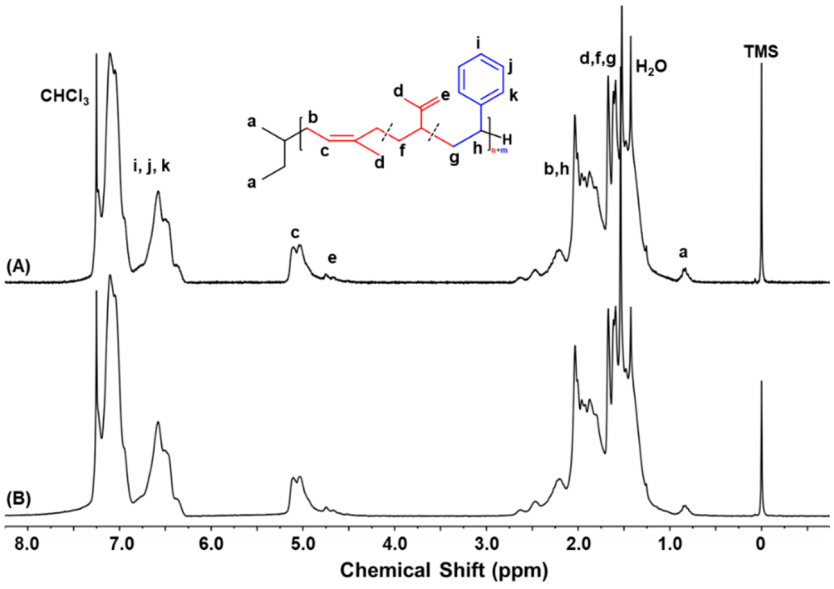

Fig. S14 ^{1}H NMR spectra of tapered linear copolymer and its precursor: (A) P10-i and (B) P10.

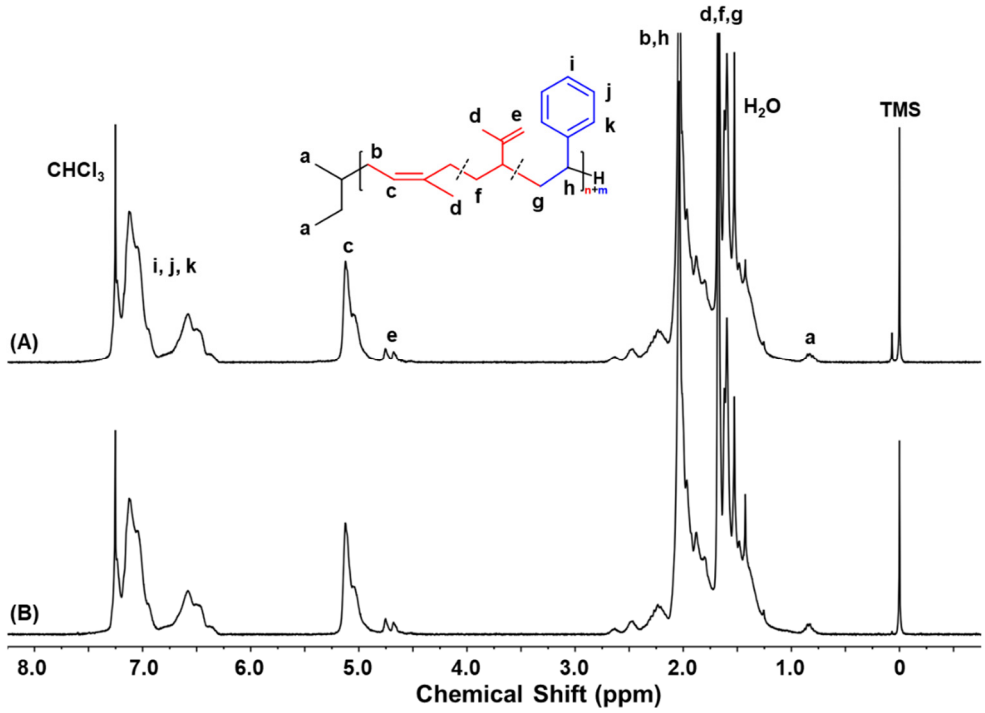

Fig. S15 ^{1}H NMR spectra of tapered linear copolymer and its precursor: (A) P11-i and (B) P11.

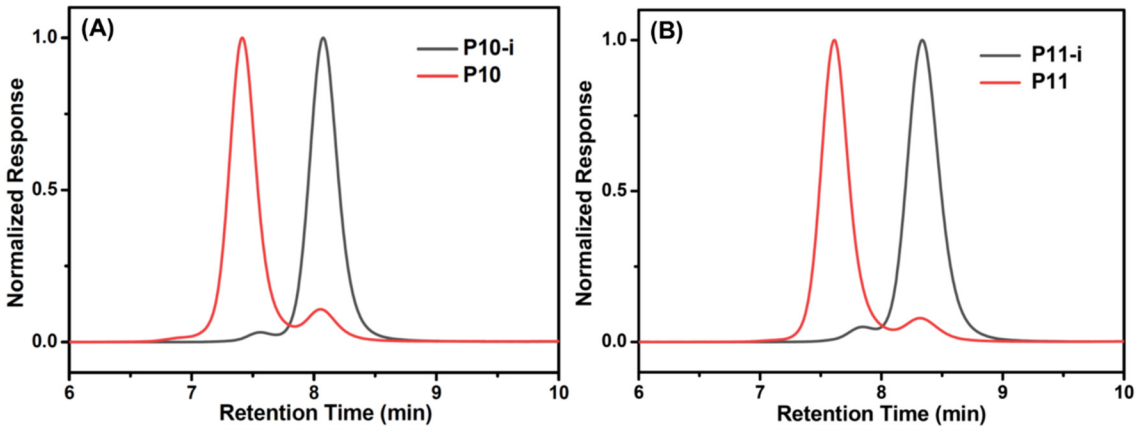

Fig. S16 GPC traces of tapered linear copolymers with different feed ratios and their precursors: (A) P10-i and P10; and (B) P11-i and P11.

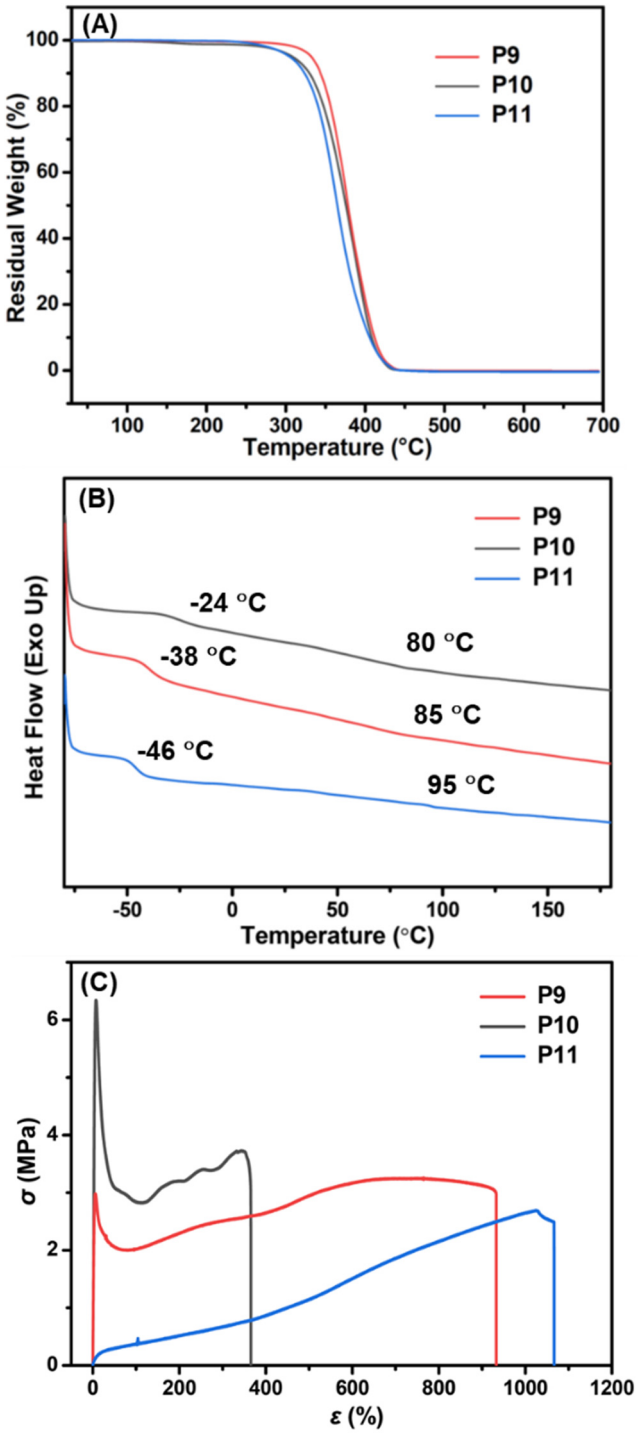

Fig. S17 (A) TGA thermograms, (B) DSC thermograms, and (C) representative stress-strain (σ-ε) curves of P9, P10, and P11 copolymers.

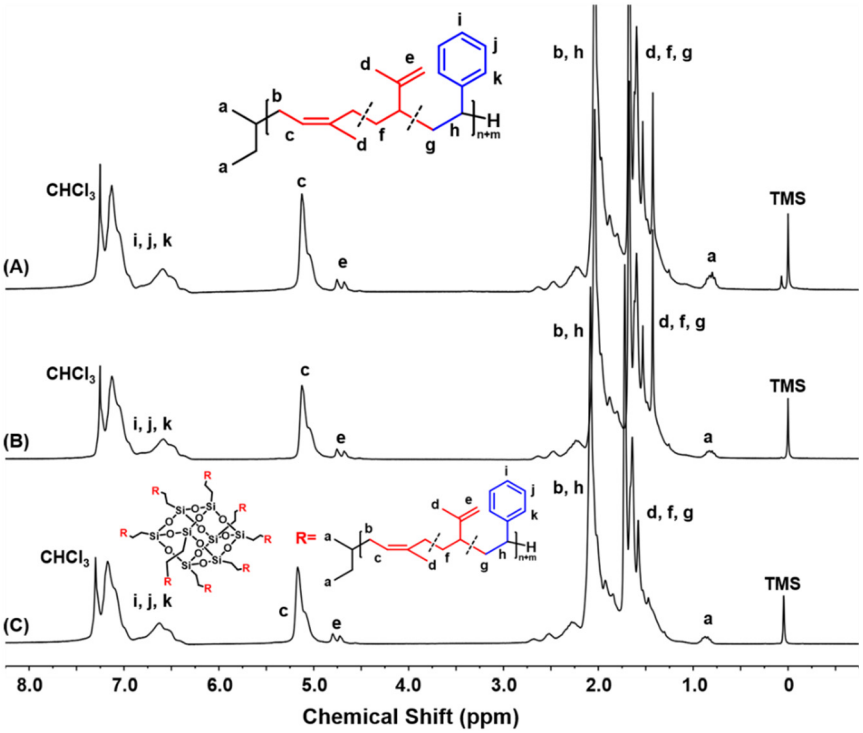

Fig. S18 ^{1}H NMR spectra of tapered star copolymer and its precursors: (A) P13-i, (B) P13-ii, and (C) P13.

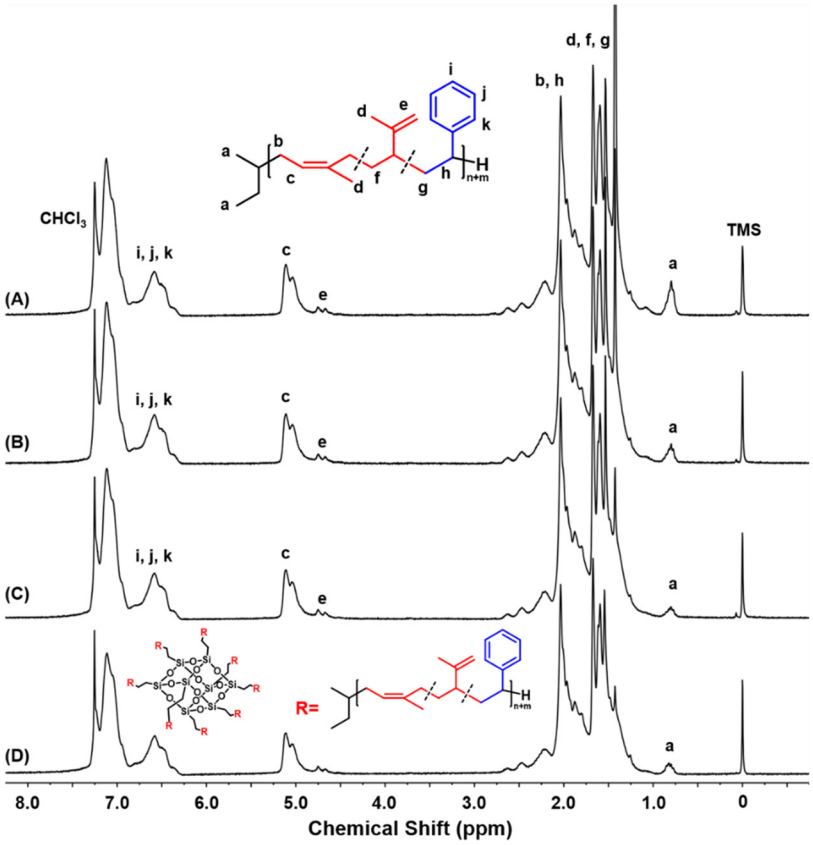

Fig. S19 ^{1}H NMR spectra of tapered star copolymer and its precursors: (A) P14-i, (B) P14-ii, (C) P14-iii, and (D) P14.

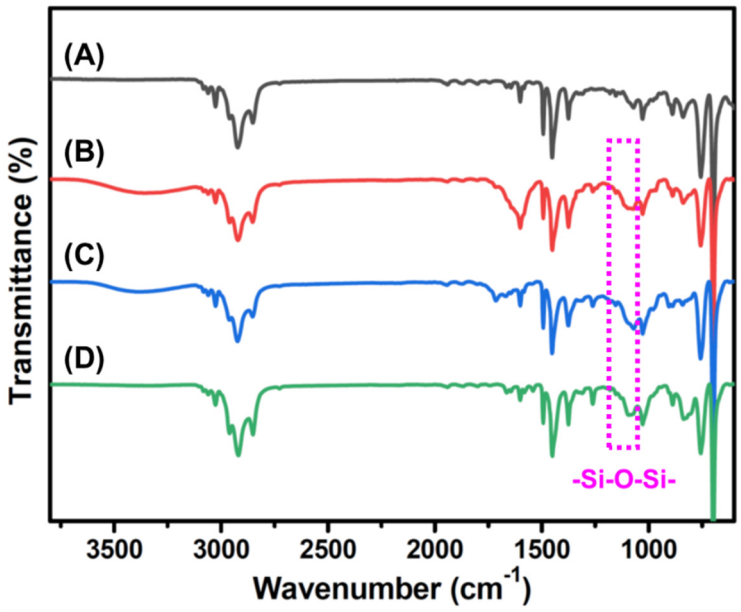

Fig. S20 FT-IR spectra of copolymers: (A) P12-i, (B) P12, (C) P13, and (D) P14.

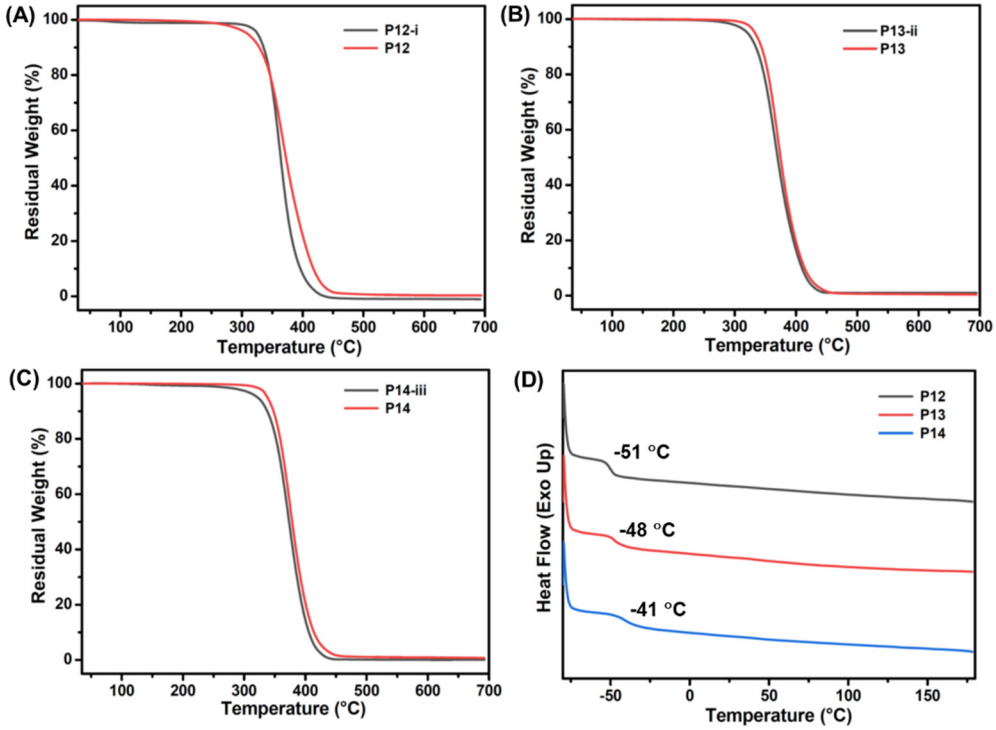

Fig. S21 TGA thermograms of tapered star copolymers and their precursors for (A) P12, (B) P13, and (C) P14. (D) DSC thermograms of tapered star copolymers.

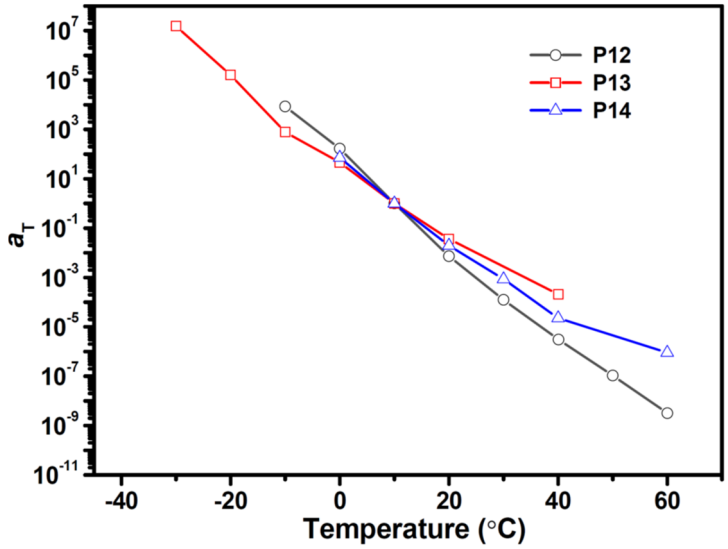

Fig. S22 The horizonal shifting factor (a_T) as a function of temperature for tapered star copolymers.

Reference

[1] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey and A. H. E. Müller, *Macromolecules*, 2019, **52**, 9299-9310.