Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of Polymeric Topological Isomers based on Sequential Ugi-4CR and Thiol-yne Click Reactions with Sequence-Controlled Amino-Functionalized Polymers

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Experimental section

Synthesis of Monomers. The preparation of Ugi-DPE, l-[4-[N,N-Bis(trimethylsilyl)amino]phenyl]-l-phenylethylene, used as the copolymerization monomer was reported in the previous work.[1]

In Situ ^{1}H NMR Kinetics Studies of the Copolymerization of St/Ugi-DPE. The in situ ^{1}H NMR kinetics studies of the St/Ugi-DPE copolymerization in a 4/1 feed ratio was provided as an example for illustration. Ugi-DPE (0.08 g, 0.24 mmol) was dissolved in benzene-d_6 (1.8 ml) and initiated by Sec-BuLi (0.35 mol/L, 0.07 mL) under glovebox conditions. After 30 min, St (0.1 g, 0.96 mmol) was added to the reaction mixture and stirred well quickly. Next, the polymeric solution was transferred to a sealed NMR tube for in situ ^{1}H NMR. The first spectrum was used for confirming the specific amounts of all components. To monitor the reaction by in situ ^{1}H

NMR, all spectra were recorded at 400 MHz with four scans and a time interval between each measurement of 1 min. The experimentation did not terminated until the peaks of vinyl almost disappeared.

Synthesis of sequence-controlled in-chain amino-functionalized base polymers. In previous researches[2-9], the sequence-defined polymers could be synthesized by the copolymerization of St and DPE derivatives due to the unique feature of DPE derivatives. Furthermore, the sequence and number of DPE units in copolymerization were controlled by the feed ratio. In this work, two sequence-controlled polymers with similar number of Ugi-DPE units but with different sequence patterns were synthesized. According to different feed molar ratios of St/Ugi-DPE, the copolymers were named U4 (St/Ugi-DPE=4/1) and U10 (St/Ugi-DPE=10/1), respectively. The experimental process of U4 was described below. The living anionic polymerization experiment was carried out in a glovebox under high purity argon atmosphere. First, Ugi-DPE (0.733 g, 2.16 mmol) was dissolved in benzene and added in a sealed bottle. Sec-BuLi (0.35 mol/L, 0.48 mL) was then injected to initiate Ugi-DPE. After 30 min, St (0.9 g, 8.65 mmol) was injected quickly into the wine red reaction mixture. Subsequently, the color of polymeric solution showed orange red, which meant that the active species turned from Ugi-DPE to St. The polymerization was accomplished in 10 wt% benzene at 25°C for 24 h. The experimental process of U10 was the same as U4 except in different feed ratio. The productions were terminated with degassed isopropanol, precipitated with excess methanol and subsequently dissolved in THF, which was repeated twice until the residual Ugi-DPE was completely removed. The amino- functionalized base polymers (N4/N10) could be de synthesized by the deprotection of U4/U10. Deprotection of U4/U10 was effected by dissolving the polymers in dry THF solution of TBAF and stirring at 25 °C for 12 h under argon. The molar ratio of TBAF and amino groups in polymer chains was 2/1. Then the polymers were precipitated with excess methanol. The polymers were then dried under vacuum at room temperature.

Measurements

Size exclusion chromatographic (SEC) analyses of U4/U10 and N4/N10 were performed on a Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 mL/min in THF at 30 °C after calibration by polystyrene standard polymers.

Size exclusion chromatographic (SEC) analyses of exam-grafted polymers and corresponding alkynyl functionalized backbones and thiol terminated branches were performed on a Viscotek TDA-305 GPC (Viscotek Corp., Houston, TX) equipped with tetra-detectors [refractive index (RI), UV, viscosity(VISC), and two-angle laser light scattering (7° and 90°, laser wavelength, λ = 670 nm)] and two separation columns (Malvern, T6000 M×2), PS sample (Viscotek Corp. Mw = 104.071 kg/mol, Mn = 100.967 kg/mol) was used to calibrate the instrument. THF was used as the mobile phase at a flow rate of 1.0 mL/min and the column temperature of 35 °C. The samples were dissolved in THF with the concentrations of less than 2.0 mg/mL, depending on the precise concentration injected to characterize the composition of polymers precisely.

^{1}H-NMR spectra were recorded on a Bruker Avance II 400M NMR spectrometer at ambient temperature using $CDCl_3$ (tetramethylsilane, TMS) as the solvent.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF

MS) analysis was carried out on a Waters MALDI micro MX mass spectrometer. 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malonitrile (DCTB) and sodium trifluoro-acetate were used as dopants for PS-SH-2400, while silver acetate were used as dopants for PS-SH-4800.

The small-angle X-ray scattering (SAXS) experiments were carried out with the Bruker Microcalix. The incident beam had a wavelength of λ=0.154 nm. The evaluated q range was 0.08~3 nm^{-1}.

Necessary corrections were made include absorption correction and deducting background of toluene solvent. Quartz capillary with diameter of 1mm were used as sample containers. The samples were prepared in toluene with polymer concentrations at 0.2 wt%.

Additional data

Table S1. Characteristic of the copolymers of St/Ugi-DPE

Run	$[M_S]_0/[M_D]_0$	N_S/N_D[a]	M_n (kg/mol)[b]	M_w/M_n[b]
U4	4.0	4.2	7.5	1.14
U10	10.0	9.6	18.4	1.10

a) The ratio of St/Ugi-DPE in chain (N_S/N_D) was calculated by ^{1}H NMR. b) Determined by SEC on a Waters HPLC component system

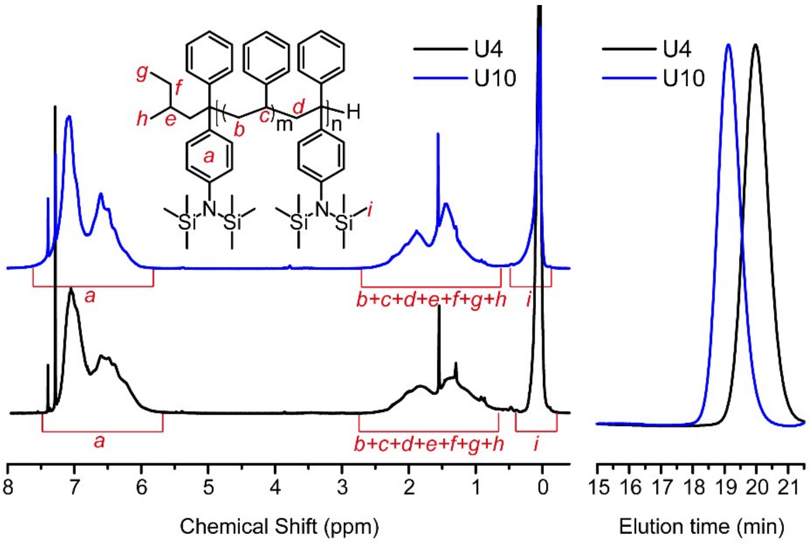


Figure S1. ^{1}H NMR spectra and SEC curves of the copolymers of St/Ugi-DPE

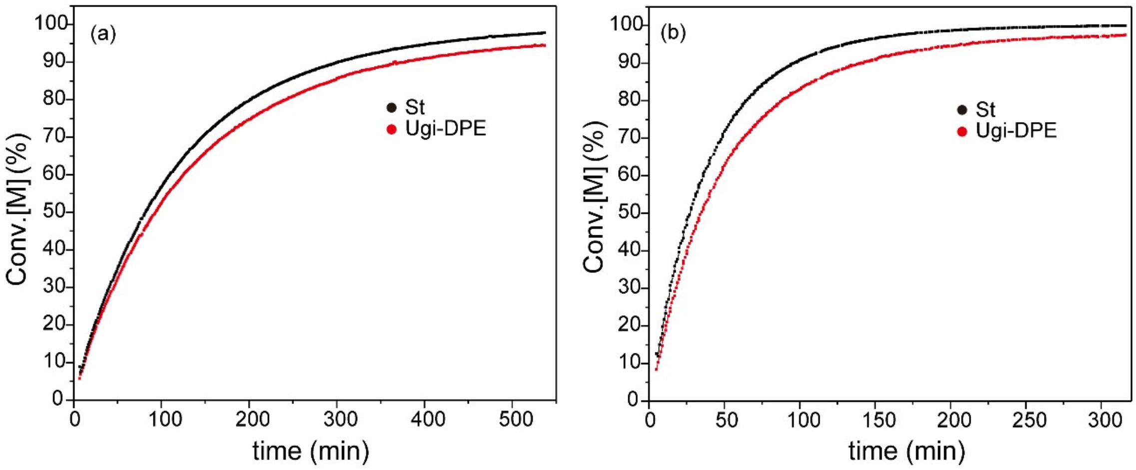


Figure S2. Conversion curves of the copolymerization of St and Ugi-DPE: (a) $[St]_0/[Ugi\text{-}DPE]_0=4:1$, (b) $[St]_0/[Ugi\text{-}DPE]_0=10:1$

$$S^- + D \xrightarrow{k_{SD}} D^-$$

$$S^- + S \xrightarrow{k_{SS}} S^-$$

$$D^- + S \xrightarrow{k_{DS}} S^-$$

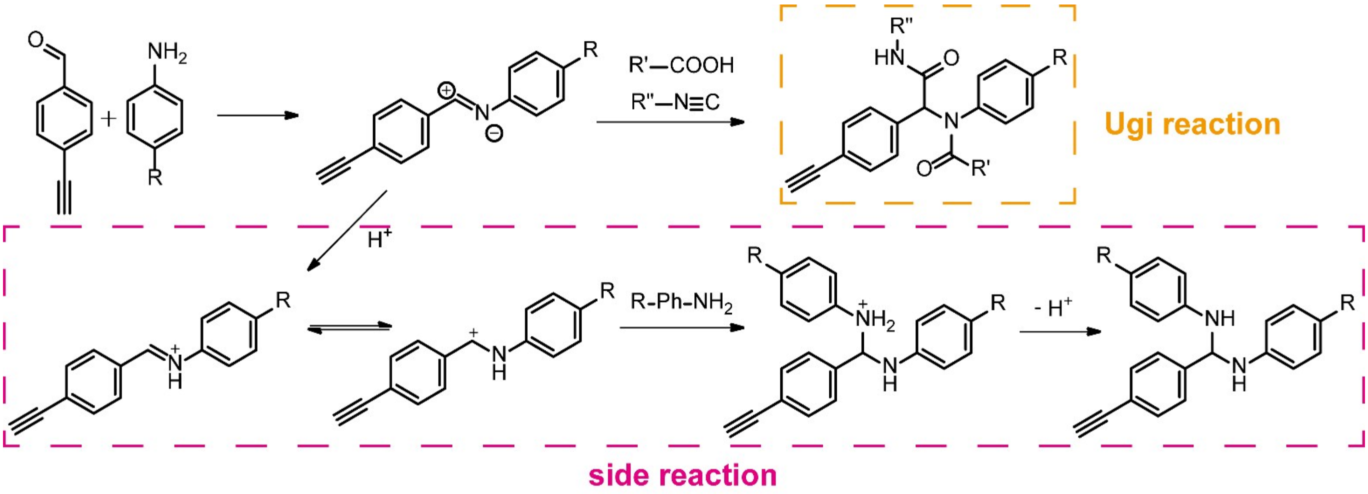
$$-\frac{d[DPE]}{dt} = k_{SD}[St^-]^{\frac{1}{2}}[DPE] = K_{DPE}[DPE]$$

$$-\frac{d[St]}{dt} = \{k_{SS}[St^-]^{\frac{1}{2}} + k_{DS}[DPE^-]^{\frac{1}{2}}\}[St] = K_{St}[St]$$

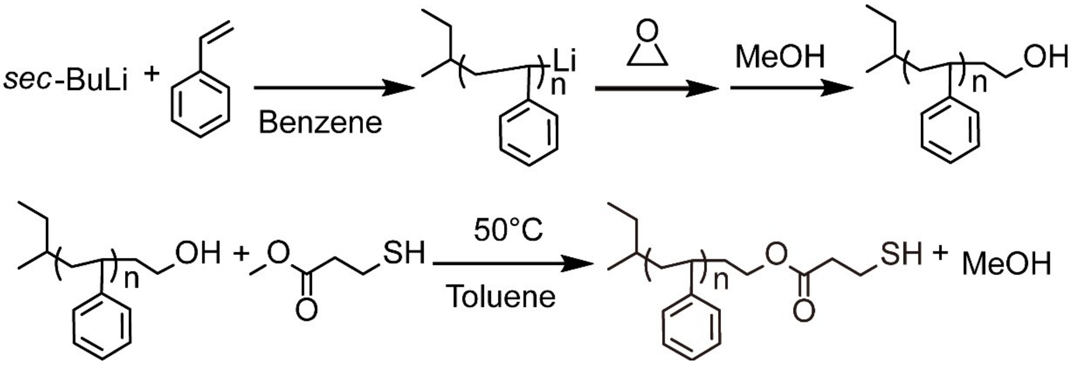
$$\ln\frac{[DPE]_0}{[DPE]} = k_{SD}[St^-]^{\frac{1}{2}}t = K_{DPE}t$$

$$\ln\frac{[St]_0}{[St]} = \{k_{SS}[St^-]^{\frac{1}{2}} + k_{DS}[DPE^-]^{\frac{1}{2}}\}t = K_{St}t$$

Scheme S1. Chain propagation elementary reaction and kinetic equations of copolymerization of St and Ugi-DPE



Scheme S2. Potential side reaction mechanism.



Scheme S3. Synthetic route for thiol-terminated polystyrene.

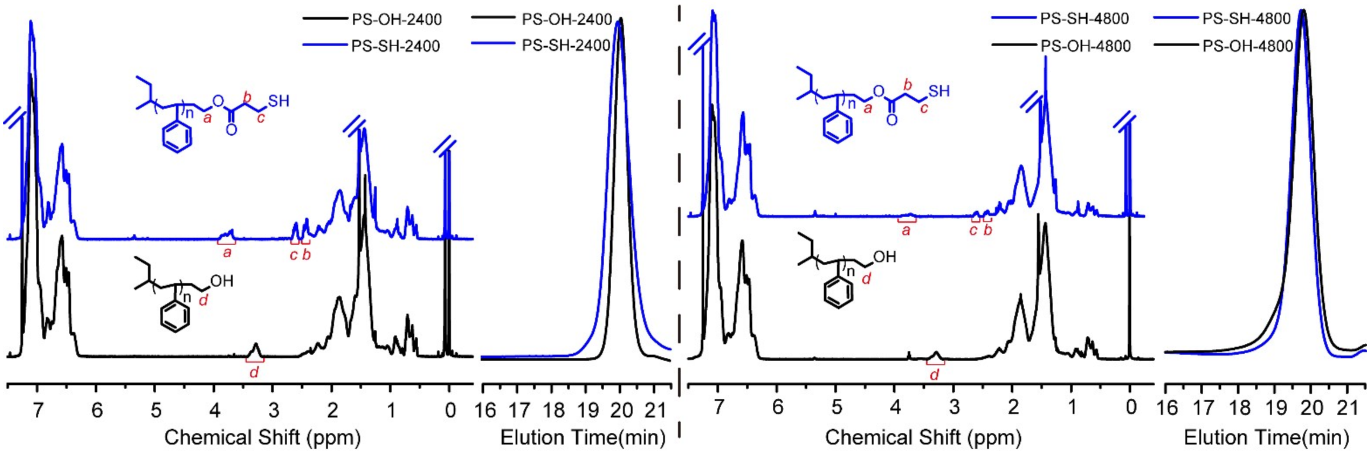


Figure S3. ^{1}H NMR spectra and SEC curves of the hydroxyl-terminated polystyrenes and corresponding thiol-terminated polystyrenes

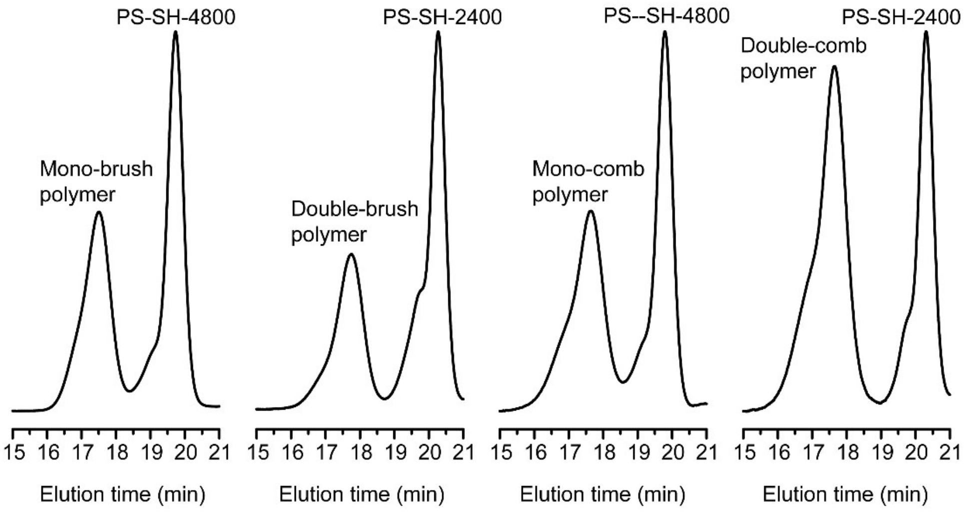


Figure S4. SEC curves of gafted polymers before fraction

Table S2. Architectural parameters of the sequence-controlled backbones

Run	M_n^{a} (kg/mol)	M_w/M_n^{a}	R_h^{a} (nm)	T_g^{b} (°C)
Mono-brush backbone	23.8	1.08	3.18	154
Double-brush backbone	18.6	1.45	3.45	165
Mono-comb backbone	26.1	1.18	3.76	138
Double-comb backbone	32.7	1.37	4.17	135

a) Determined by SEC with tetra-detectors. b) T_g was characterized by DSC.

Table S3. dn/dc of the polymeric components for well-defined grafted polymers

Run	dn/dc
N4	0.2042
Mono-brush backbone	0.1697
Double-brush backbone	0.1663
Mono-brush polymer	0.1885
Double-brush polymer	0.1730
N10	0.2350
Mono-comb backbone	0.2052
Double-comb backbone	0.1786
Mono-comb polymer	0.2487
Double-comb polymer	0.2105
PS-SH-2400	0.1712
PS-SH-4800	0.1680

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