Supporting Information

Synthesis of sequence-controlled in-chain alkynyl/tertiary amino dual-functionalized terpolymer via living anionic polymerization

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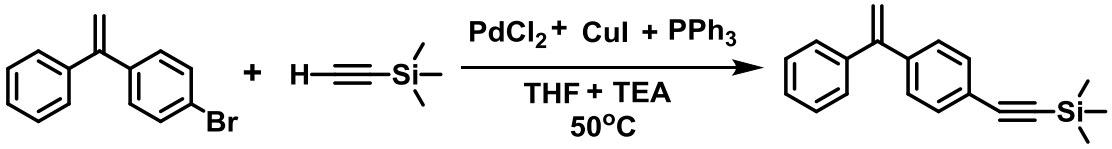
Synthesis of trimethyl((4-(1-phenylvinyl)phenyl)ethynyl)silane (DPE-yne)

The experimental operations of the precursor of DPE-yne, 1-bromo-4-(1-phenylvinyl)benzene (DPE-Br), have been reported in other studies via Wittig reaction1. Then the synthetic route for DPE-yne is shown in Scheme S1. Trans-dichlorobis(triphenyl-phosphine)Palladium(II) (2.1 g, 3 mmol) and CuI (0.726 g, 4 mmol) were placed to a three necked round bottom flask in the glovebox followed by adding triphenylphosphine (1.57 g, 6 mmol) and DPE-Br (25.8 g, 100 mmol) under the argon atmosphere. All stuff was dissolved using freshly dried THF (300 mL) and TEA (300 mL). Then trimethylsilylacetylene (21.2 mL, 162 mmol) was dropwise added to the flask at 50 ^{o}C. After dropping, stir the solution for 24 h at 50 ^{o}C for completion. The product was isolated via column chromatography (eluent: n-hexane) to give 24.4 g of DPE-yne as a colorless transparent oil with a yield of 88.4%. Further purification involved stirring and degassing over n-BuLi, keeping the typical red wine color of DPE-yne anion for at least 2h and proceeding high vacuum distillation to get pure monomer. ^{1}H NMR (400 MHz, $CDCl_3$, δ):7.24-7.43 (m, 9H, Ar-H), 5.46-5.47 (d, 2H, C=CH2, J = 3.8Hz), 0.25 (s, 9H, -Si(CH3)3).



Scheme S1 the synthetic route for DPE-yne

Synthesis of the copolymers of styrene and DPE-yne

The copolymerization of styrene (St) and DPE-yne in benzene was performed using *sec*-BuLi as the initiator under glovebox conditions. Herein, the detailed description of the polymerization implemented in $[DPE\text{-}yne]_0/[St]_0 = 1:4$ is provided as an example: benzene (10 w/v%) and DPE-yne (0.133 g, 0.48 mmol) were added to a 20-mL sealed vial, and then *sec*-BuLi (0.364 mL, 0.1 mmol) was injected to initiate DPE-yne. The typical red wine color of DPE-yne anion appeared immediately following the injection. To achieve sufficient initiation, the solution was stirred for 20 min. Next, St (0.20 g, 1.92 mmol) was added to the bottle rapidly, and the solution was stirred for 72 h at room temperature. Then, the copolymerization was terminated with isopropanol. The product was precipitated with sufficient methanol and subsequently dissolved in an appropriate amount of THF; this process was repeated twice to ensure that the residual monomers were completely removed.

Synthesis of chain-end-functionalized polystyrenes end-capped with DPE-yne and DPE-NMe_2

Poly(styryl)lithium (0.6 g, 5.8 mmol, M_n = 2000 Da) was prepared under glovebox conditions using *sec*-BuLi (0.84 mL, 0.3 mmol) as the initiator in benzene (10 w/v%) at room temperature. Then, the poly(styryl)lithium was divided into three equal parts. The portions were end-capped with DPE-yne (0.014 g, 0.05 mmol), DPE-yne (0.042 g, 0.15 mmol) or a mixture of DPE-yne (0.014 g, 0.05 mmol) and DPE-NMe_2 (0.023 g, 0.1 mmol). After 6 h, each of the three polymerization systems was terminated with

isopropanol. Finally, all the samples were precipitated with sufficient methanol and subsequently dissolved in a suitable amount of THF; this process was repeated twice to ensure that the residual monomers were completely removed.

The determination of St reactivity ratio

The determination of St reactivity ratio utilized an integrated form of the composition equation:

$$C = 1 - \frac{M}{M_0} = 1 - [\frac{f_1}{f_1^0}]^{\alpha}[\frac{1-f_1}{1-f_1^0}]^{\beta}[\frac{f_1^0-\delta}{f_1-\delta}]^{\gamma}$$

Where 1-M/M_0 (C) is conversion, f_1 is the feed ratio of St at that value of conversion, $(f_1)_0$ is the initial feed ratio, $\alpha = r_2/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, $\delta = (1 - r_2)/(2 - r_1 - r_2)$, and $\gamma = (1 - r_1r_2)/[(1 - r_1)(1 - r_2)]$. According the experimental data points of timing-sample or in-situ ^{1}H NMR, we can get a series of corresponding 1-M/M_0 and f_1. Under a given r1 and r2, the difference between 1-M/M_0 and $1 - [\frac{f_1}{f_1^0}]^{\alpha}[\frac{1-f_1}{1-f_1^0}]^{\beta}[\frac{f_1^0-\delta}{f_1-\delta}]^{\gamma}$ can be calculated. Then the average sum of the squares of these differences ($S(r_1,r_2)$) about many experimental data points of f_1 and 1-M/M_0 can be calculated:

$$S(r_1, r_2) = \frac{1}{n}\sum_{i=1}^{n}\{1 - \left[\frac{f_{1,i}}{f_1^0}\right]^{\alpha}\left[\frac{1-f_{1,i}}{1-f_1^0}\right]^{\beta}\left[\frac{f_1^0-\delta}{f_{1,i}-\delta}\right]^{\gamma} - C_i\}^2$$

Where, $f_{1,i}$ and C_i are f_1 and C at the ith experimental data point, respectively. And according the special characteristic of DPE derivatives, r_2 is zero. So the $S(r_1,r_2)$ can be evaluated for a range of r_1 for a given data set using a computer application which has

a looping structure. When $S(r_1,r_2)$ is minimum value, the r_1 would close to theoretical value.

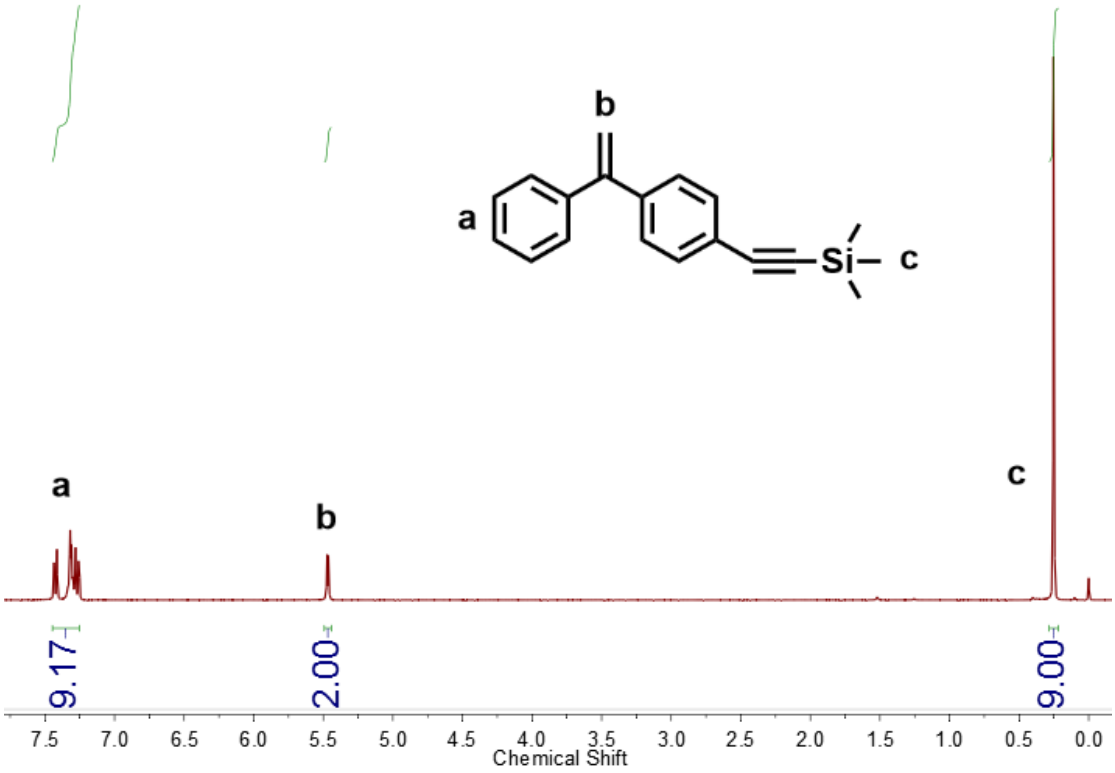


Figure S1. ^{1}H NMR spectrum (in $CDCl_3$) of DPE-yne

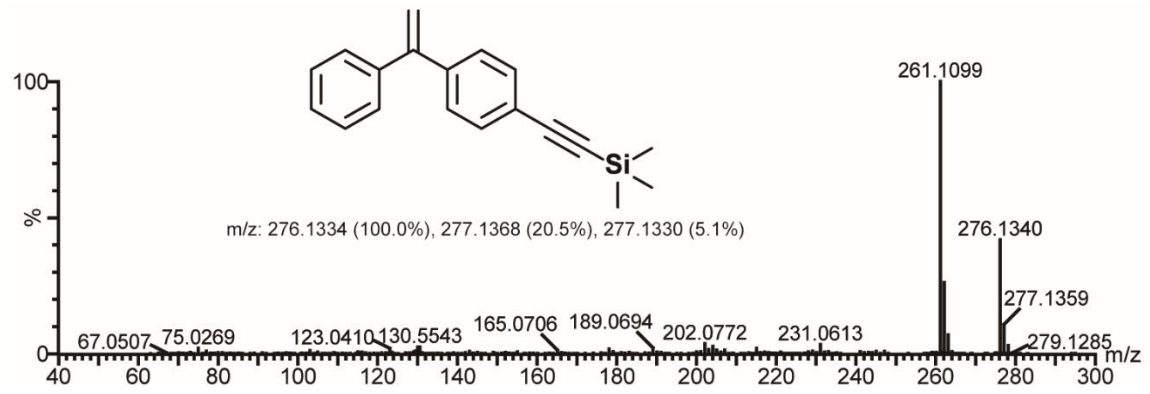


Figure S2. MS-EI spectrum of DPE-yne

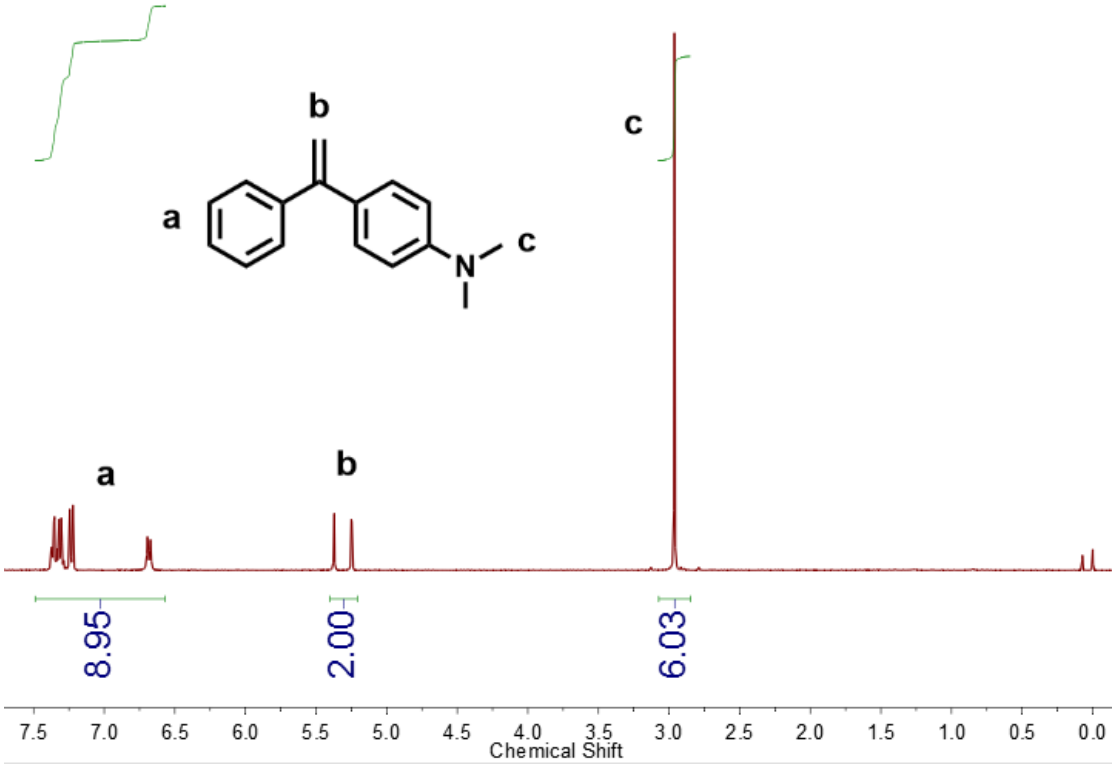


Figure S3. ^{1}H NMR spectrum (in $CDCl_3$) of 1-(4-dimethylaminophenyl)-1-phenylethylene (DPE-NMe_2)

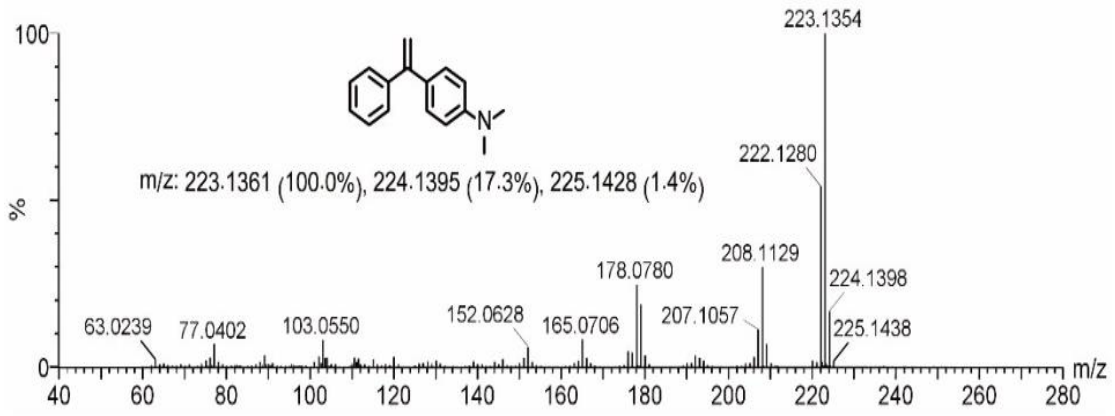


Figure S4. MS-EI spectrum of DPE-NMe_2

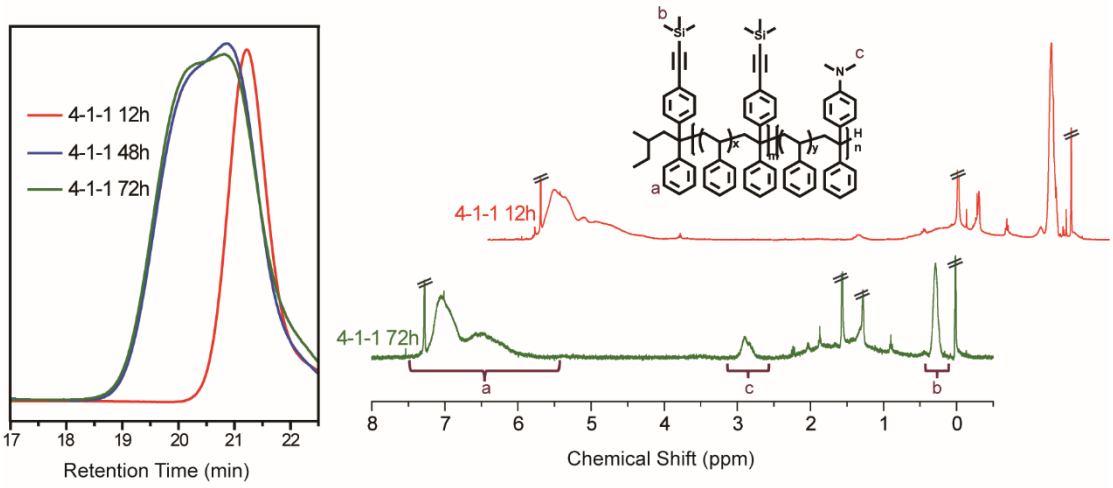


Figure S5. SEC curves and ^{1}H NMR spectra (in $CDCl_3$) of St/DPE-yne/DPE-NMe_2 terpolymerization in 4:1:1 feed ratio initiated by *sec*-BuLi at room temperature using living anionic polymerization

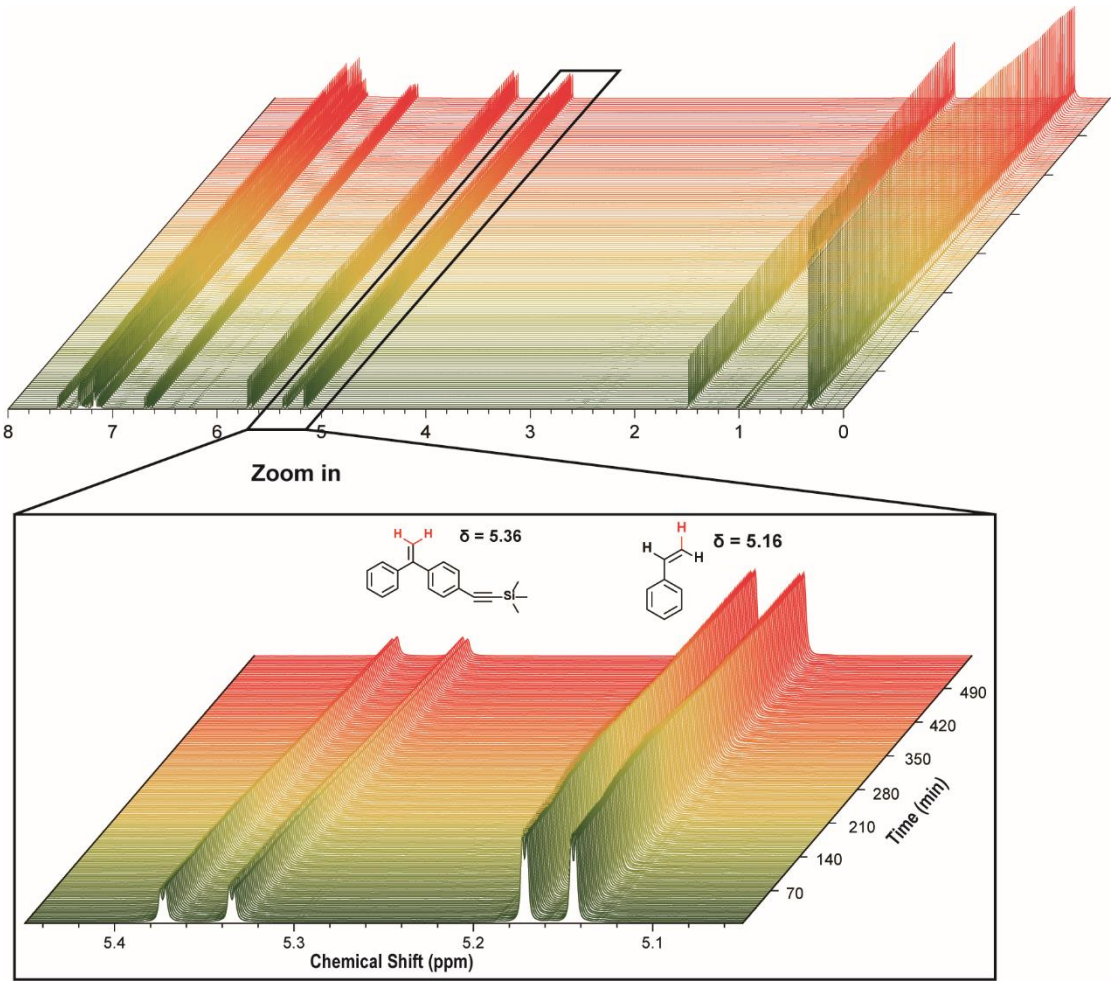


Figure S6. *in situ* ^{1}H NMR spectra stacked overlay and partial enlarged view of $[St]_0/[DPE\text{-}yne]_0$ = 4:1 copolymerization initiated by *sec*-BuLi in C_6D_6 at room temperature using living anionic polymerization

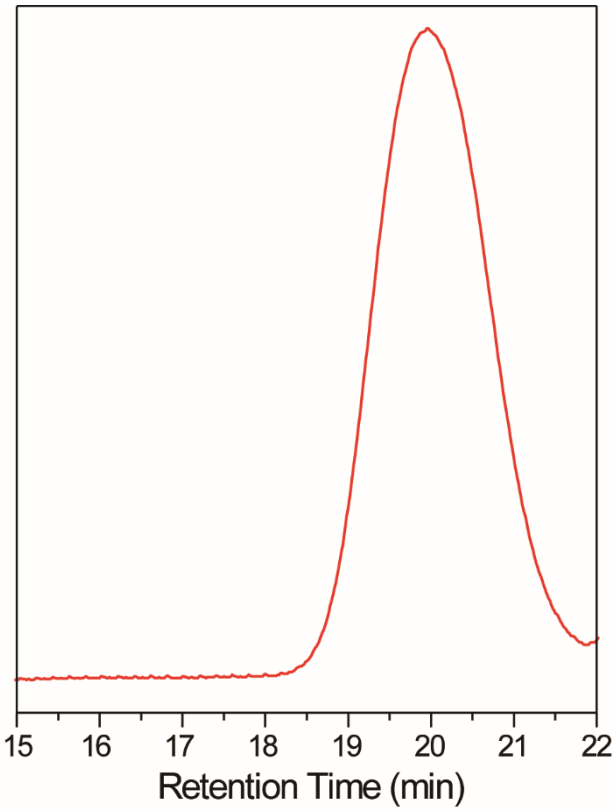


Figure S7. SEC curve of the terpolymer obtained from *in situ* ^{1}H NMR monitoring of $[St]_0/[DPE\text{-}yne]_0/[DPE\text{-}NMe_2]_0$ = 4:1:4 terpolymerization initiated by *sec*-BuLi in C_6D_6 at room temperature using living anionic polymerization. M_n= 5500 g/mol, PDI= 1.40.

Equations list:

$$\frac{9N_{DPE-yne}}{9N_{DPE-yne}+5N_{St}} = \frac{Area(j)}{Area(a)} \quad \text{S1}$$

$$E_{D-yne} = \frac{Area(j)/9}{Area(e+f)/6} \times 100\% \quad \text{S2}$$

$$E_{D-NMe2} = \frac{Area(l)/6}{Area(e+f)/6} \times 100\% \quad \text{S3}$$

$$\frac{9N_{AD}}{9N_{AD}+5N_{S}} = \frac{Area(c)}{Area(a)} \quad \text{S4}$$

$$\frac{9N_{AD}}{6N_{ND}} = \frac{Area(c)}{Area(b)} \quad \text{S5}$$

$$MW_{St} \times N_{St} + MW_{Dyne} \times N_{Dyne} + MW_{Dnme2} \times N_{Dnme2} = \overline{M_n} \quad \text{S6}$$

$$-\frac{d[DPE]}{dt} = k_{SD}[S^-]^{\frac{1}{2}}[DPE] = K_{DPE}[DPE] \quad \text{S7}$$

$$-\frac{d[St]}{dt} = (k_{DS}[D^-]^{\frac{1}{2}} + k_{SS}[S^-]^{\frac{1}{2}})[St] = K_{St}[St] \quad \text{S8}$$

$$\ln\frac{[M_{DPE}]_0}{[M_{DPE}]} = K_{DPE}t \quad \text{S9}$$

$$\ln\frac{[M_{St}]_0}{[M_{St}]} = K_{St}t \quad \text{S10}$$

$$S(r_1, r_2) = \frac{1}{n}\sum_{i=1}^{n}\{1 - \left[\frac{f_{1,i}}{f_1^0}\right]^{\alpha}\left[\frac{1-f_{1,i}}{1-f_1^0}\right]^{\beta}\left[\frac{f_1^0-\delta}{f_{1,i}-\delta}\right]^{\gamma} - C_i\}^2 \quad \text{S11}$$

$$-\frac{d[DPE_{yne}]}{dt} = k_{SDyne}[S^-]^{\frac{1}{2}}[DPE_{yne}] = K_{Dyne}[DPE_{yne}] \quad \text{S12}$$

$$-\frac{d[DPE_{NMe2}]}{dt} = k_{SDnme}[S^-]^{\frac{1}{2}}[DPE_{NMe2}] = K_{DNme2}[DPE_{NMe2}] \quad \text{S13}$$

$$-\frac{d[St]}{dt} = (k_{DyneS}[DPE_{yne}{}^-]^{\frac{1}{2}} + k_{DnmeS}[DPE_{NMe2}{}^-]^{\frac{1}{2}} + k_{SS}[St^-]^{\frac{1}{2}})[St] = K_{St}[St] \quad \text{S14}$$

$$\ln\frac{[M_{Dyne}]_0}{[M_{Dyne}]} = K_{Dyne}t \quad \text{S15}$$

$$\ln\frac{[M_{DNme2}]_0}{[M_{DNme2}]} = K_{DNme2}t \quad \text{S16}$$

$$\ln\frac{[M_{St}]_0}{[M_{St}]} = K_{St}t \quad \text{S17}$$

REFERENCES

(1) Hirao, A.; Haraguchi, N.; Sugiyama, K. Synthesis of Functionalized Polymers by Means of Anionic Living Polymerization. 1. Synthesis of Functionalized Polymers with α-Methylstyryl Groups by Anionic Reactions with Use of 1-{4-[3-(4-Isopropenylphenyl)propyl]phenyl}-1-phenylethylene. *Macromolecules* **1999**, 32, 48-54.