Sequence Regulation in Living Anionic Terpolymerization of Styrene and Two Categories of 1,1-Diphenylethylene (DPE) Derivatives

Lincan Yang+, Heyu Shen+, Li Han, Hongwei Ma*, Chao Li, Lan Lei, Songbo Zhang, Pibo Liu, Yang Li*

Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

+ co-first authors

*E-mail: mahw@dlut.edu.cn, liyang@dlut.edu.cn

Table S1 Results of the block terpolymers of DPE-yne/DPE-ene/St with two-step feeding

Entry [a]	$[D_{yne}]_0$/ [b] $[D_{ene}]_0/[St]_0$	Mn/ [c] $kg \, mol^{-1}$	PDI [c]	N_{D-yne}/ [d] N_{D-ene}/N_{St}	N_{D-yne} [e]	N_{D-ene} [e]	N_{St} [e]
P(D$_{yne}$/St)	1/0/1	3.3	1.20	1.0/-/1.07	8.5	-	9.1
P(D$_{yne}$/St-b-D$_{ene}$/St)	1/1/2.5	7.4	1.61	1.23/1.0/3.12	10.0	8.1	25.3

a) Terpolymerizations of DPE-yne/DPE-ene/St *via* a strategy that first DPE-yne was fed and followed DPE-ene was fed. b) Monomer feed ratio. c) Determined by SEC. d) Average numbers ratio of each monomer in chain, calculated from the ^{1}H NMR spectra of the corresponding polymer. e) Average numbers of each monomer units in the final polymer chain (eqn S1-3).

Eqn S1-3 are used for the calculation of average numbers of each monomer units in the DPE-yne/DPE-ene/St terpolymers.

$$\frac{2N_{Dene}}{9N_{Dyne} + 9N_{Dene} + 5N_{St}} = \frac{Area(b)}{Area(a) - \frac{1}{2}Area(b)} \quad (1)$$

$$\frac{9N_{DYne}}{2N_{Dene}} = \frac{Area(d)}{Area(b)} \quad (2)$$

$$MW_{St} \times N_{St} + MW_{Dyne} \times N_{Dyne} + MW_{Dene} \times N_{Dene} = \bar{M}_n \quad (3)$$

Eqn S4-6 are used for the calculation of average numbers of each monomer units in the DPE-(SiH/OMe)/DPE-NSi$_2$/St terpolymers.

$$\frac{3N_{DSiH/OMe}}{8N_{DSiH/OMe} + 9N_{DNSi2} + 5N_{St}} = \frac{Area(c)}{Area(a)} \quad (4)$$

$$\frac{3N_{DSiH/OMe}}{18N_{DNSi2}} = \frac{Area(c)}{Area(e)} \tag{5}$$

$$MW_{St} \times N_{St} + MW_{DSiH/OMe} \times N_{DSiH/OMe} + MW_{DNSi2} \times N_{DNSi2} = \bar{M}_n \tag{6}$$
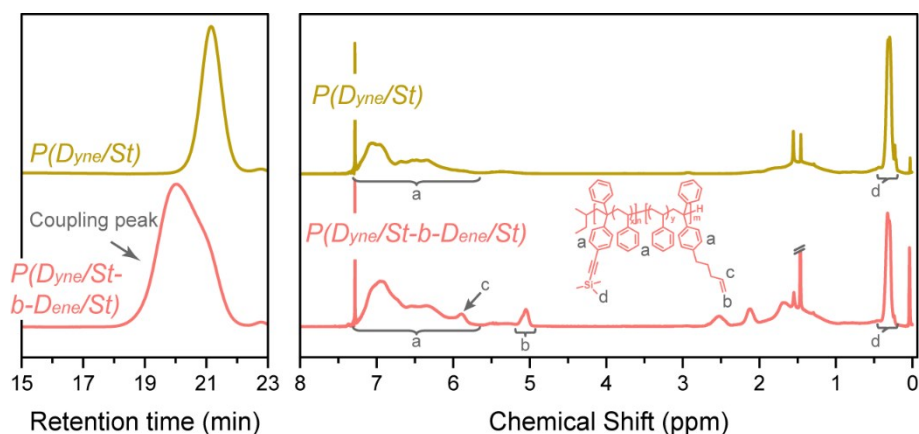

Figure S1 SEC curves and ^{1}H NMR spectra (in CDCl$_3$) of DPE-yne/DPE-ene/St block terpolymers that were synthesized based on a strategy that first DPE-yne was fed and followed DPE-ene was fed.
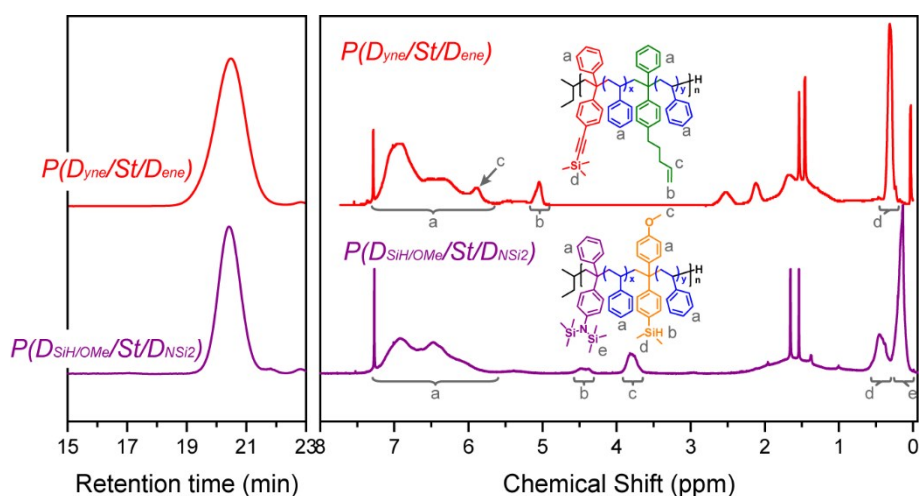

Figure S2 SEC curves and ^{1}H NMR spectra (in CDCl$_3$) of *in situ* ^{1}H NMR monitoring of DPE-yne/DPE-ene/St and DPE-(SiH/OMe)/DPE-NSi$_2$/St terpolymerizations *via* one-pot feeding method.
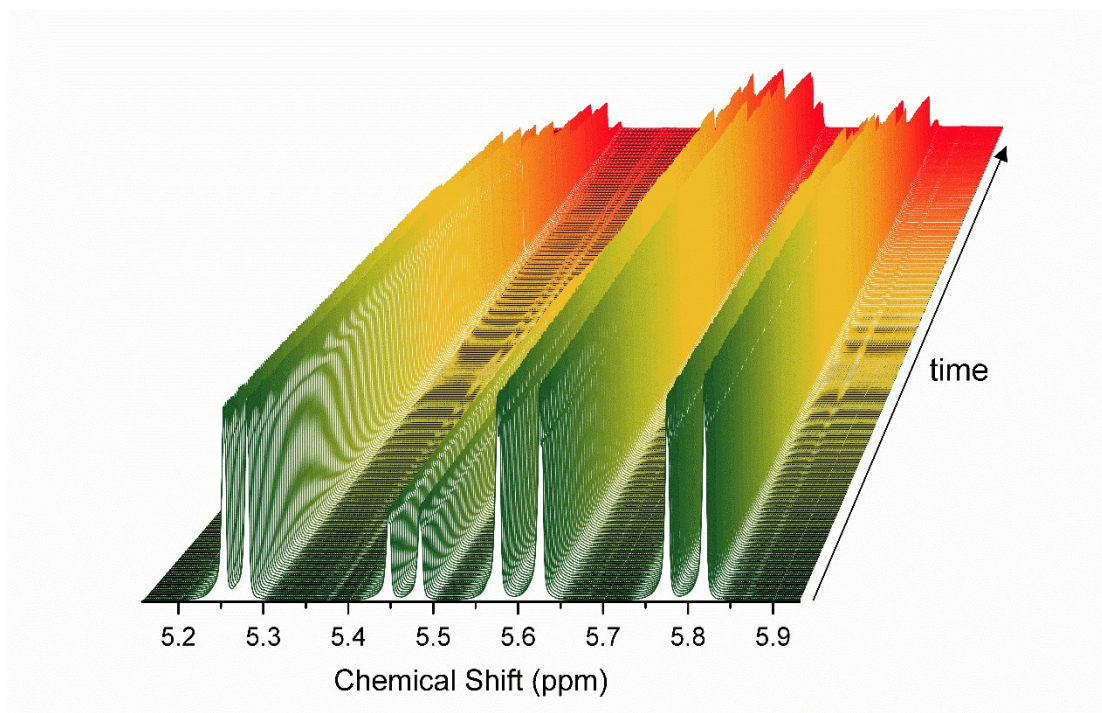
Figure S3 Stacked overlay of all the *in situ* ^{1}H NMR spectra of DPE-yne/DPE-ene/St terpolymerization *via* one-pot feeding method.
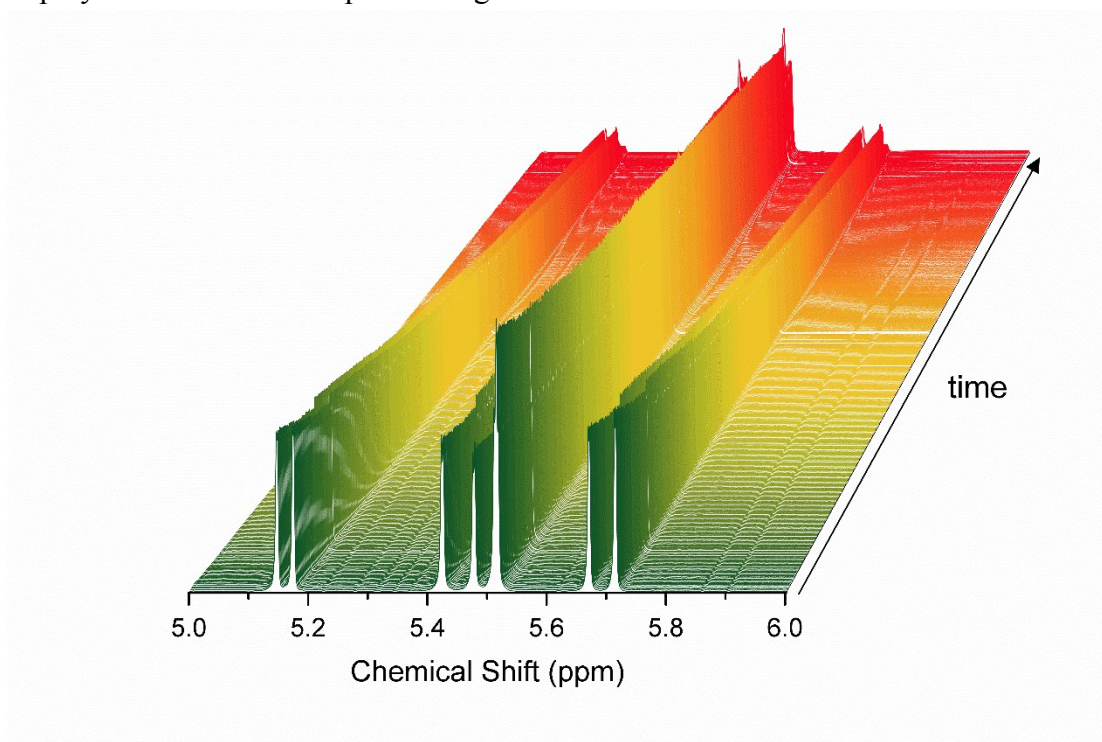

Figure S4 Stacked overlay of all the *in situ* ^{1}H NMR spectra of DPE-(SiH/OMe)/DPE-NSi$_2$/St terpolymerization *via* one-pot feeding method.