Supporting Information

Unlocking Features of locked-unlocked anionic polymerization

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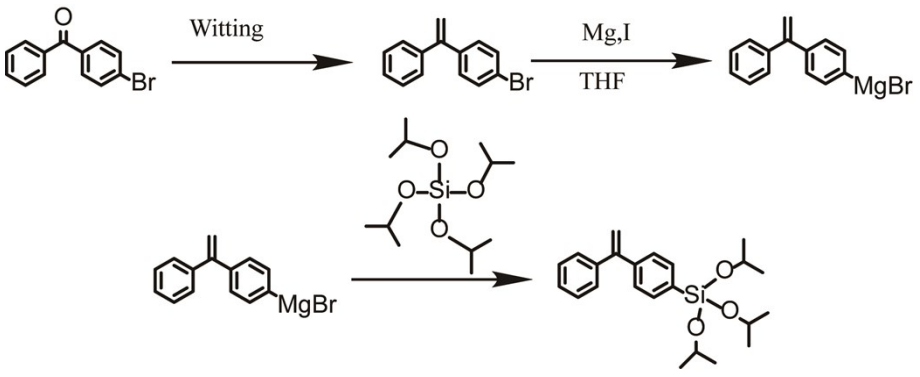
Contents

1. Synthesis of DPE-Si(O*i*Pr)$_3$



Scheme S1. The routes for synthesizing DPE-Si(O-*i*Pr)$_3$

2. The detail calculation of the unlocking efficiency

Table S1.The detail information for unlocking efficiency of the samples

Run	Theoretical Endcapping	Locked A(D_{SiO}-H)[b]		Unlocked A(D-H)[c]	Equiv of DPE/St[d]	Unlocking Efficiency[e]
1[a]	0.50	0.45	0.33	-	0/20	26.7%
2	1.00	0.91	0.26	0.16	6/5	71.4%
3	1.00	0.91	0.30	0.13	6/5	67.0%
4	0.50	0.45	0.20	0.22	10/9	55.5%
5	0.50	0.50	0.02	0.63	10/9	96.0%
6	1.00	0.90	0.19	0.62	6/5	78.9%
7	1.00	0.87	0.04	0.67	6/5	95.4%
8	1.00	0.82	0.04	0.67	6/5	95.1%
9	1.00	0.90	0.09	0.55	6/5	90.0%
10	0.5	0.39	0.02	0.73	6/5	94.8%

a) Run 1 was conducted for studying the kinetics influence and 8.0 eq of NaODP and 20 eq of St were fed during the unlocking process, so that there is no DPE end H in the chains; b) A(D_{SiO}-H) (marked as d in the spectra: 3.6-3.4 ppm); c) A(D-H) (marked as d`: 3.0-2.9 ppm); d) the equivalents of DPE/St were the feeding ratio in the unlocking process; e) The unlocking efficiency were calculated accounting to equation (S1).

The unlocking efficiency were calculated with the following equation:

$$Unlocking\ Efficiency = \frac{A_{D_{SiO}-H}(Locked) - A_{D_{SiO}-H}(Unlocked)}{A_{D_{SiO}-H}(Locked)}\ x\ 100\% \quad (1)$$

$A_{D_{SiO-H}(Locked)}$ and $A_{D_{SiO-H}(Unlocked)}$ represent the integral values in the region from *δ*=3.6-3.4 ppm in Locked Samples and Unlocked Samples respectively.

Eg.

As shown in Figure S1, the ^{1}H-NMR spectra of samples from Run 1 were displayed. During the four stages, the interval of End-H of DPE-Si(O*i*Pr)$_3$ were changed in different state such as 0.45 H of locked and 0.33 H of unlocked. Further more, it is the transformation from PSt-D_{SiO}-Li to PSt-Li lead to the integral changes in these spectra. Account for that, based on a standand of 6 H for *sec*-butyl group, the integral areas of D_{SiO}-H in different spectra could be compared.

For the data in equation (1), A_{DSiO-H}(locked)=0.45 H, A_{DSiO-H}(unlocked)=0.33 H

$$Unlocking\ Efficiency = \frac{0.45 - 0.33}{0.45} x\ 100\% = 26.7\%$$

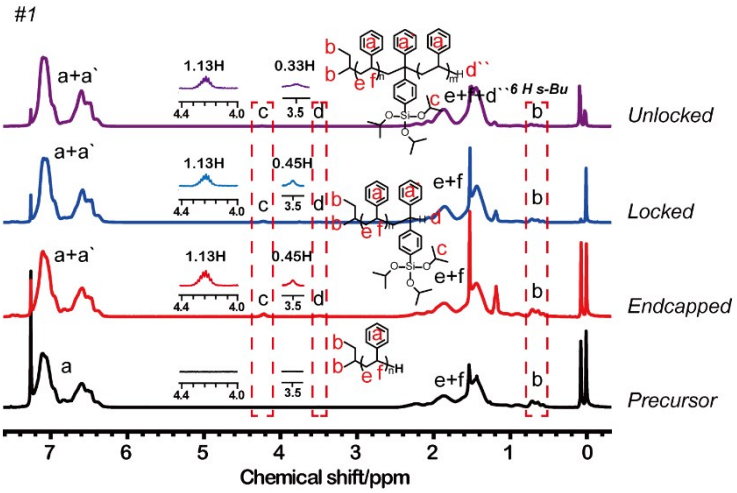


Figure S1. Full ^{1}H NMR spectra of samples of Run 1 in Table S1

3. Additional data of ^{1}H-NMR spectra and SEC curves

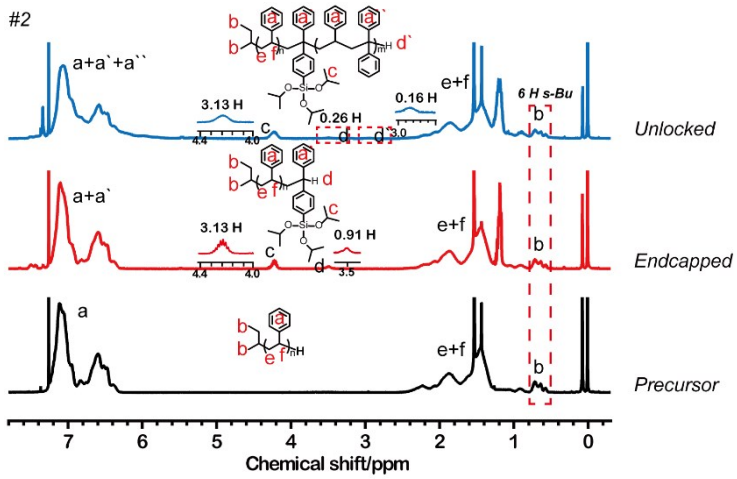


Figure S2. Full ^{1}H NMR spectra of samples of Run 2 in Table S1

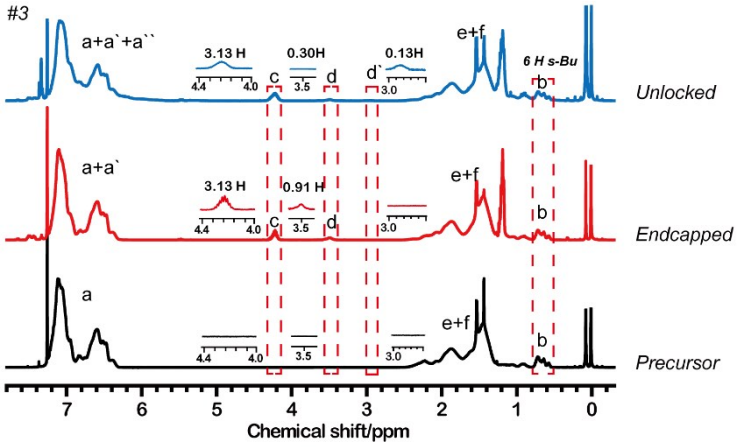


Figure S3. Full ^{1}H NMR spectra of samples of Run 3 in Table S1

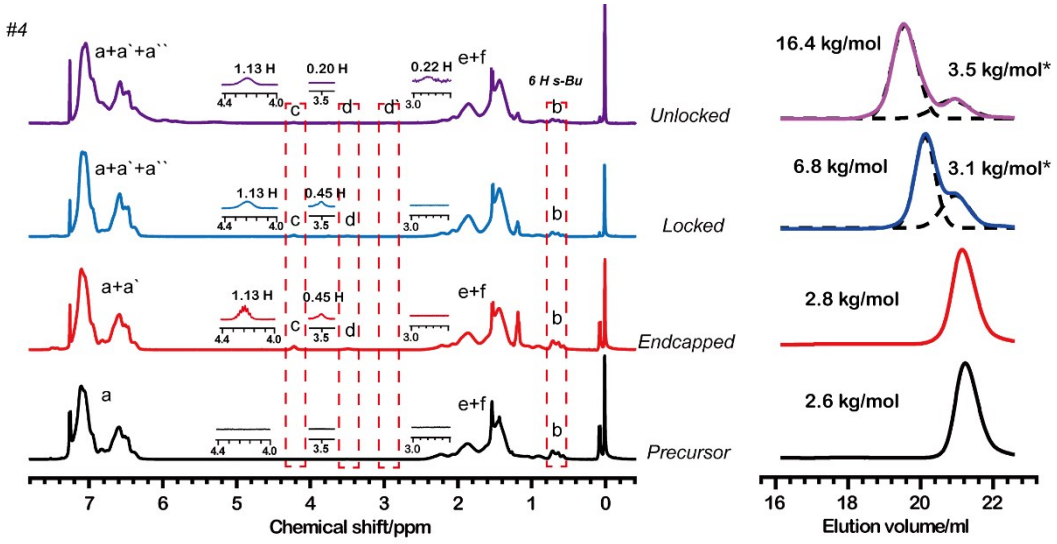


Figure S4. Full ^{1}H-NMR and SEC of samples of Run 4 in Table S1

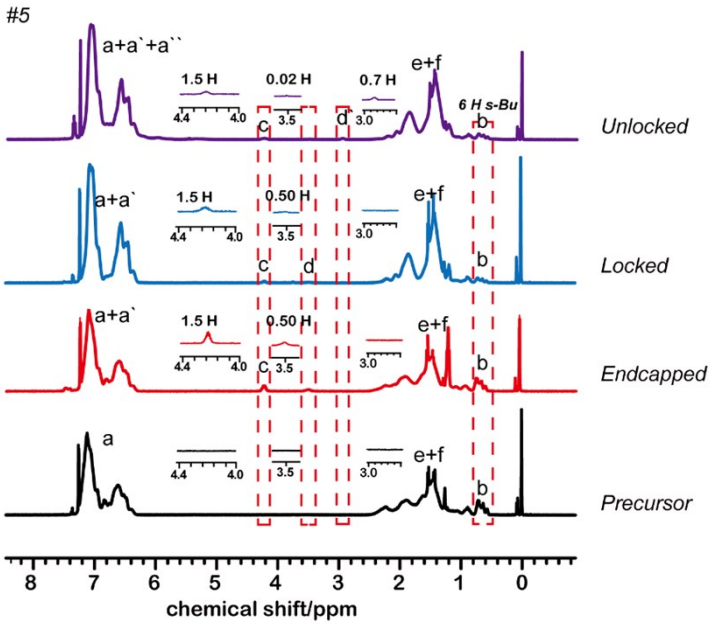


Figure S5. Full ^{1}H NMR spectra of samples of Run 5 in Table S1

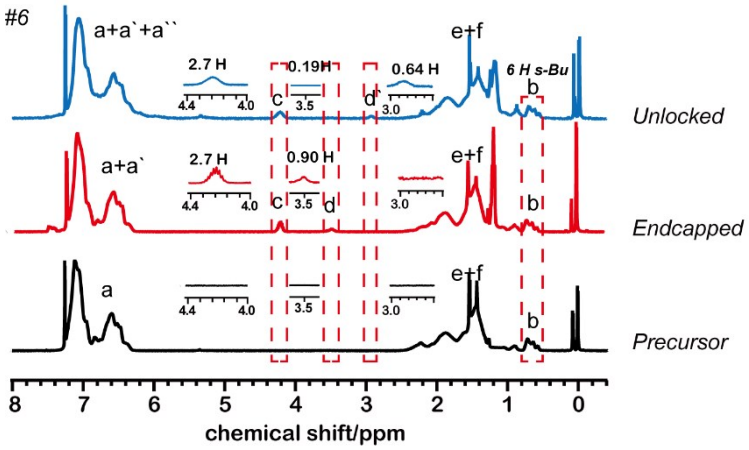


Figure S6. Full ^{1}H NMR spectra of samples of Run 6 in Table S1

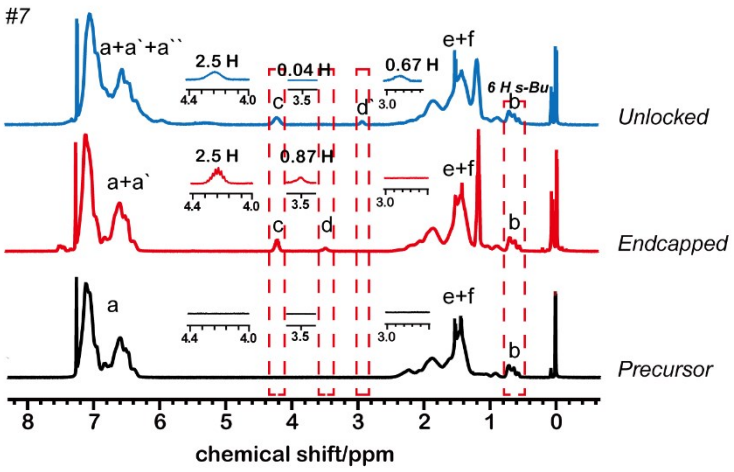


Figure S7. Full ^{1}H NMR spectra of samples of Run 7 in Table S1

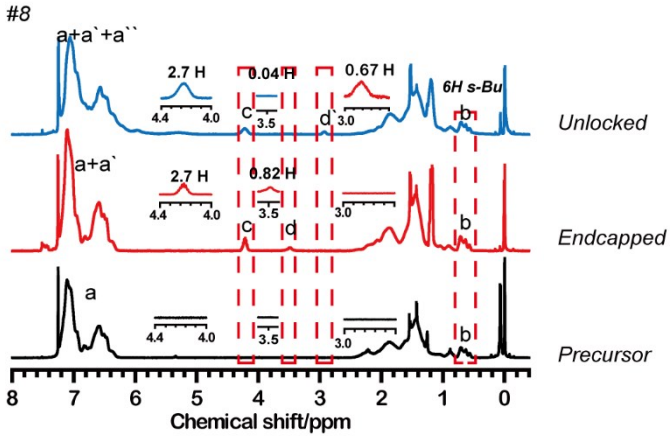


Figure S8. Full ^{1}H NMR spectra of samples of Run 8 in Table S1

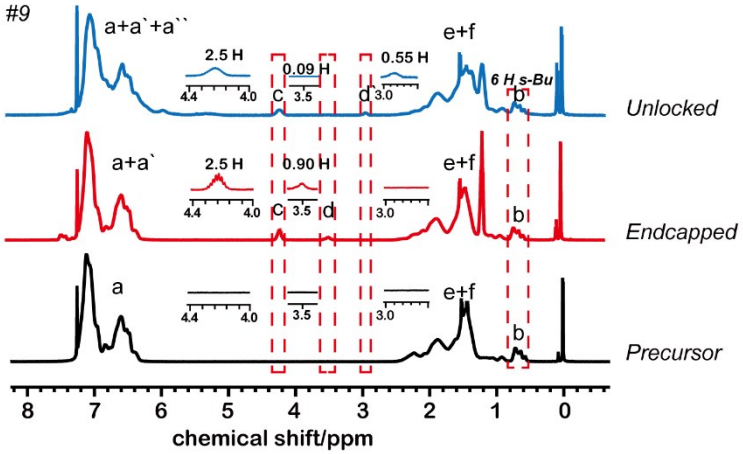


Figure S9. Full ^{1}H NMR spectra of samples of Run 9 in Table S1

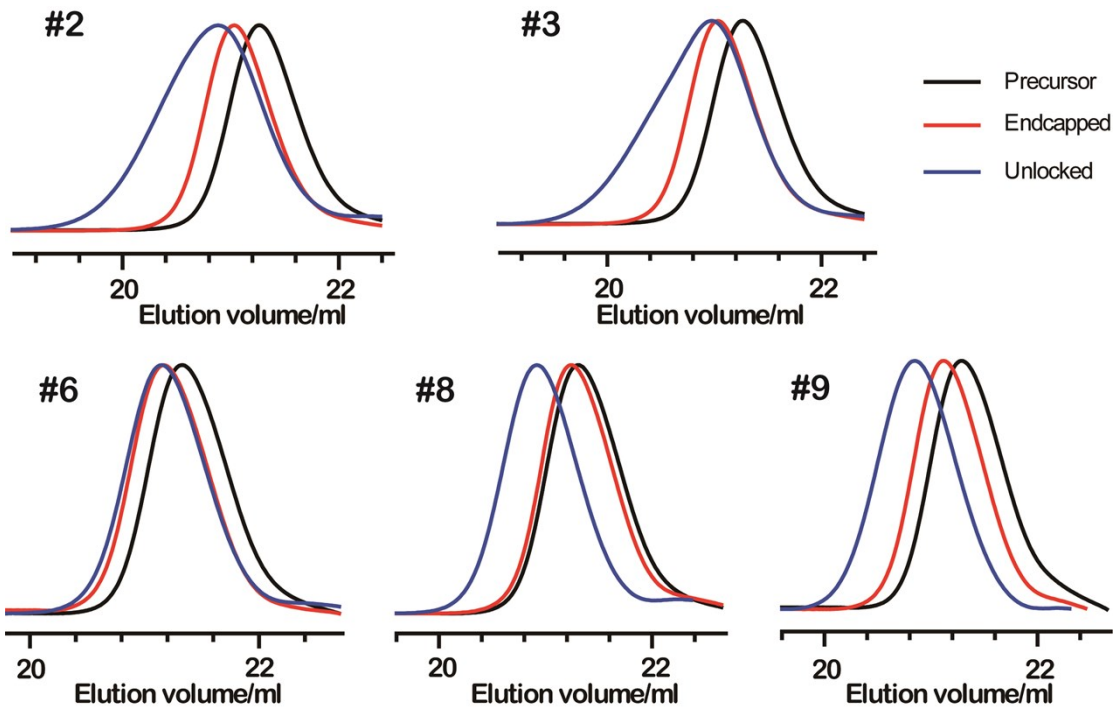


Figure S10. SEC spectrum of Run 2,3,6,8,9

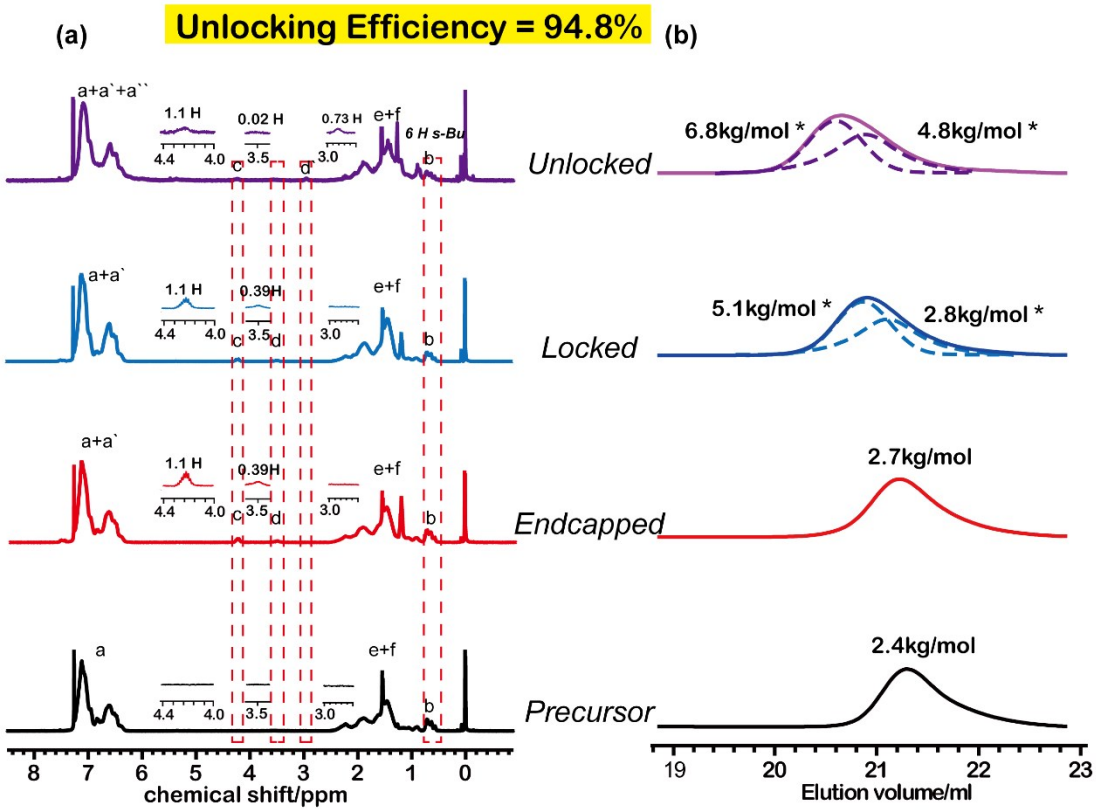


Figure S11. 1H NMR and SEC of half-locked species with lower molecular weight(RUN 10 in Table S1)

4. Additional MALDI-TOF-MS spectra

During studying the unlocking capacity of t-BuOK, due to the limitation of experimental instruments of MALDI-TOF-MS, the sample's MWs should be lower and with narrow PDI values for more precise analyzation. So we designed a new experiment with lower molecular weight than Run 4 discussed in main text for studying the unlocking process under half-locked species and the feeding ratio of t-BuOK was 2.0 eq in this experiment. The products in this process were also carefully characterized by ^{1}H-NMR and SEC as shown in Figure S11.

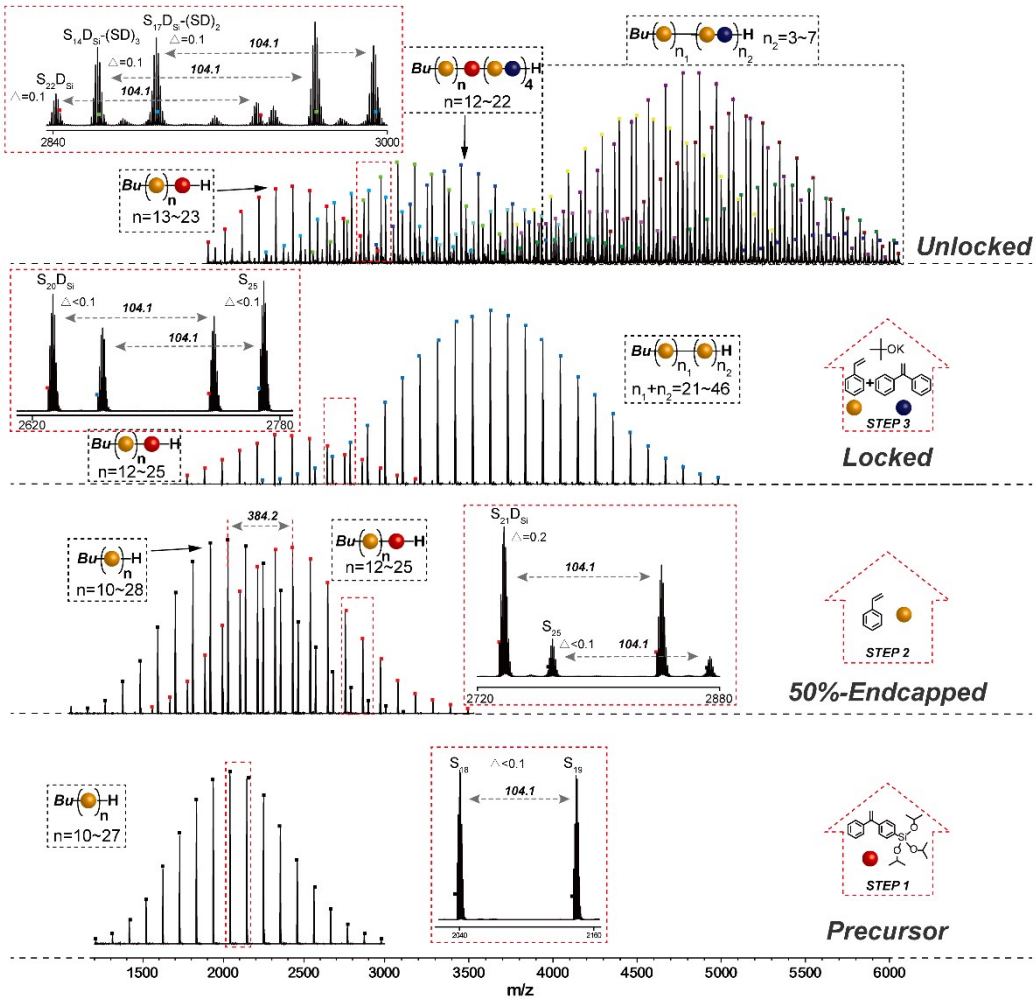


Figure S12. MALDI-TOF-MS of the partially DPE-Si(O*i*Pr)$_3$ end-capped PS (DPE-Si(OiPr)3/Li/t-BuOK=0.5/1.0/2.0

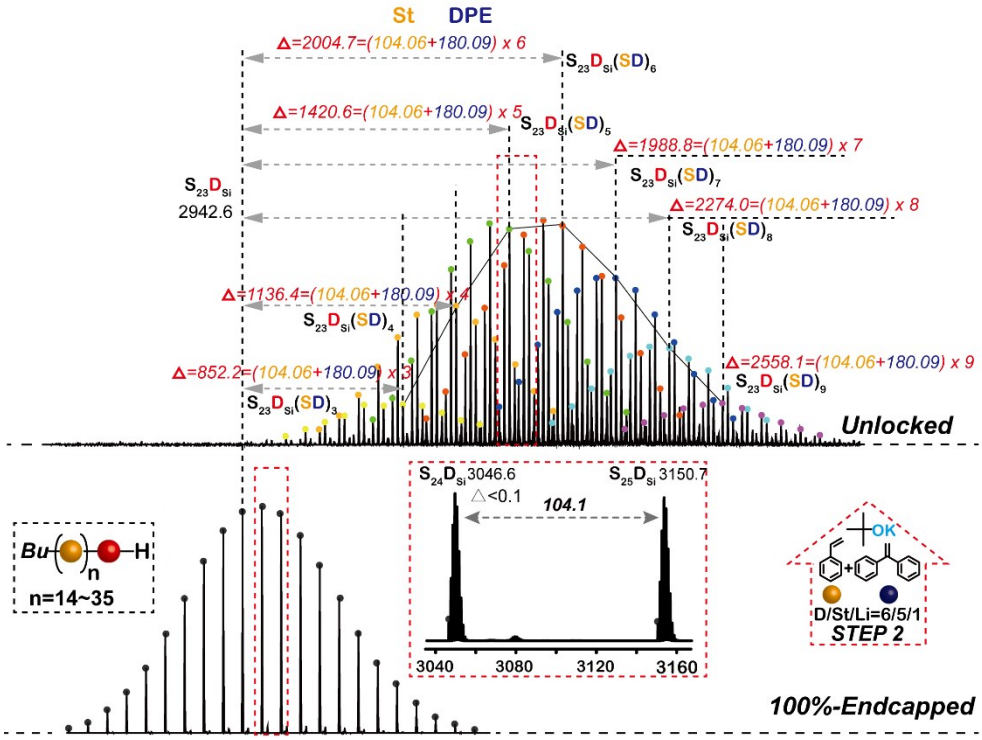


Figure S13 MALDI-TOF-MS of samples taken from Run 7 (eqv. (DPE-Si(O*i*Pr)$_3$/Li/t-BuOK)=1/1/2)

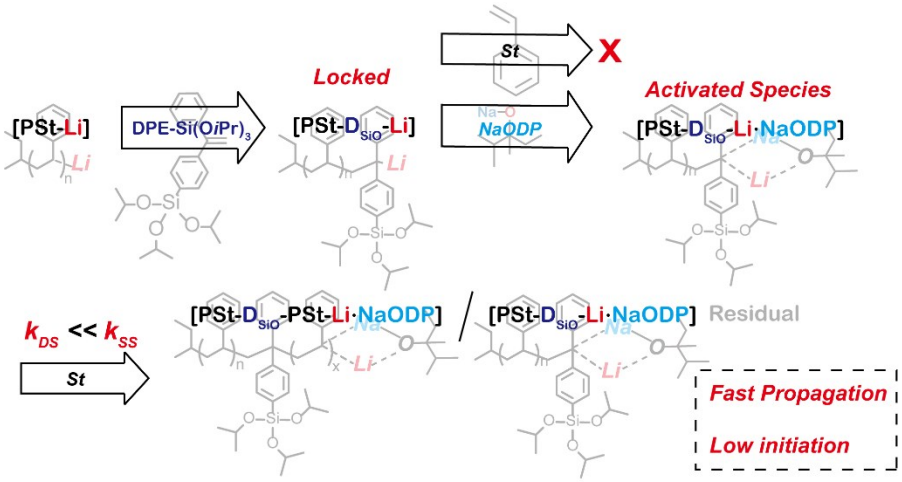
5. The detail data of DFT calculations of alkali metal alkoxides

Table S2. The propersities of bases utilized in the switchable polyerization

Alkalis		t-BuOLi	NaODP	t-BuOK
Radius of alkali metal /Å		1.54	1.91	2.34
Bond-properties of M-O [b]	Length/Å	1.634	2.003	2.270
	Dipole/Debye	6.2114	9.2792	9.8552
	Charge[c] Mt(δ^+)	0.602	0.697	0.938
	Charge[c] O(δ^-)	-0.626	-0.716	-1.110

a) the Radius was abtained from the pertinent literatures; b) the data for bond properties of M-O were calculated using M062x/6–311G(d,p) by Gaussian 09

6. Kinetic feature of propagation in locked-unlocked process



Scheme S2 Kinetic feature of the cross-over propagation in locked-unlocked anionic polymerization with St as re-starting monomer.