

Supporting Information

**Ring-opening-isomerization anionic polymerization via Brook
rearrangement**

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Experimental section

1. Materials

Solvents for anionic polymerization were distilled over sodium-benzophenone under vacuum and dried by distillation over lithium aluminium hydride (LAH) just before use. HMPA was distilled over CaH_2 and stored in N_2 . Benzyl lithium was synthesized as reported¹. 2-(2-phenyl-2-trimethylsilylethyl)oxirane (**1a**) was synthesized from racemic epichlorohydrin by the procedure in the literature². 2-(2-phenylethyl)oxirane (**1b**) was synthesized as reported³. Other chemicals are used as received.

2. Anionic polymerization of monomer **1a**

Polymerization of monomer **1a** to obtain polymer **2a** was conducted by usual anionic polymerization technique. General procedure is as follows: monomer **1a** (0.50 g, 2.27 mmol) was freeze-dried in a glass vessel and THF (2.5 mL) was added by vacuum distillation. To the solution were added polymerization initiator (0.45 mmol) and the additive (0.57 mmol) at -78°C under nitrogen. After the reaction vessel was vacuum sealed, the reaction was carried out at a predefined temperature and time. The polymerization was terminated by an addition of methanol and the solution was concentrated in vacuo. The obtained polymer **2a** as a crude product was used for GPC and NMR measurements.

3. Hydrolysis of the polymer 2a

The obtained polymer **2a** (0.30 g) was dissolved in THF (10 mL). Into the solution was added dilute hydrochloric acid (5%, 1 mL) and the solution was allowed for stirring for 4 hours at 25 °C. The reaction solution was poured into excess amount of dilute hydrochloric acid (5 %) for precipitation of the polymer. The solvent was removed by decantation and the obtained precipitate was dried in vacuo. Subsequently, the polymer was purified by reprecipitation using THF and hexane. The obtained polymer was collected by filtration, and dried by freeze-drying from benzene (Yield: 0.2271g, 67%). The obtained polymer **3a** was used for characterizations by NMR, GPC and MALDI-TOF-MS measurements.

4. Measurements

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AVANCE 500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C), where chemical shifts (δ in ppm) were determined with respect to chloroform as an internal standard. ²⁹Si-NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (80 MHz) and the spectra were obtained by using the DEPT pulse sequence. Gel permeation chromatography (GPC) was recorded on Tosoh HLC8320 equipped with a refractive index (RI) detector by using chloroform as an eluent at a flow rate of 1.0 mL/min with Tosoh G5000HHR-G3000HHR columns at 40°C. Narrowed polystyrenes were used as a calibration standard. MALDI-

TOF-MS spectra were taken on a Bruker Autoflex Speed mass spectrometer. The operation was performed by a reflectron positive ion mode. Sample for MALDI-TOF-MS measurement was prepared as follows: the polymer solution was prepared in THF with the concentration of 1 g/L. As a matrix solution, 1,8-dihydroxy-9(10H)-anthracenone (dithranol) and sodium trifluoroacetate were mixed and dissolved in THF (10 and 1 g/L, respectively). Subsequently, the polymer solution (50 μ L) was mixed with 50 L of the matrix solution. A portion of the mixed solution (1 μ L) was deposited onto a sample target plate and allowed to dry in air at room temperature.

References

1. L. Chen, B. W. Rawe, K. Adachi, D. P. Gates, *Chem. Eur. J.*, 2018, **24**, 18012-18019
2. A. B. Smith III, R. Tong, *Org. Lett.*, 2010, **12**, 1260-1263
3. P. Kumar, M. Pandey, P. Gupta, S. V. Naidu, D. D. Dhavale, *Eur. J. Org. Chem.*, 2010, **36**, 6993-

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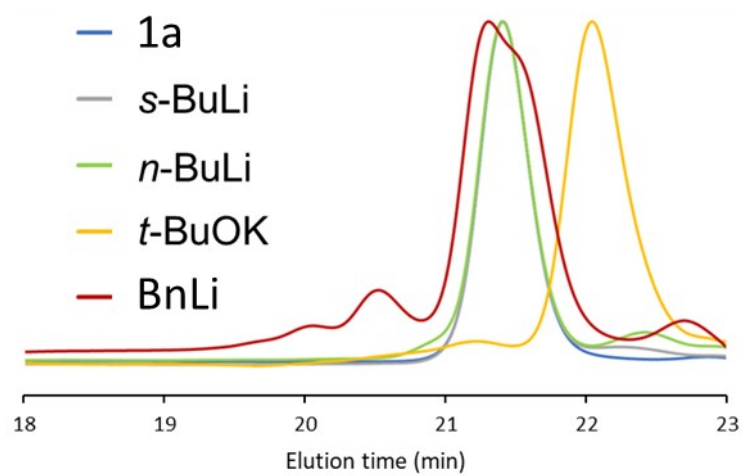


Figure S1. GPC curves of monomer **1a** and Run 1-4 (RI)

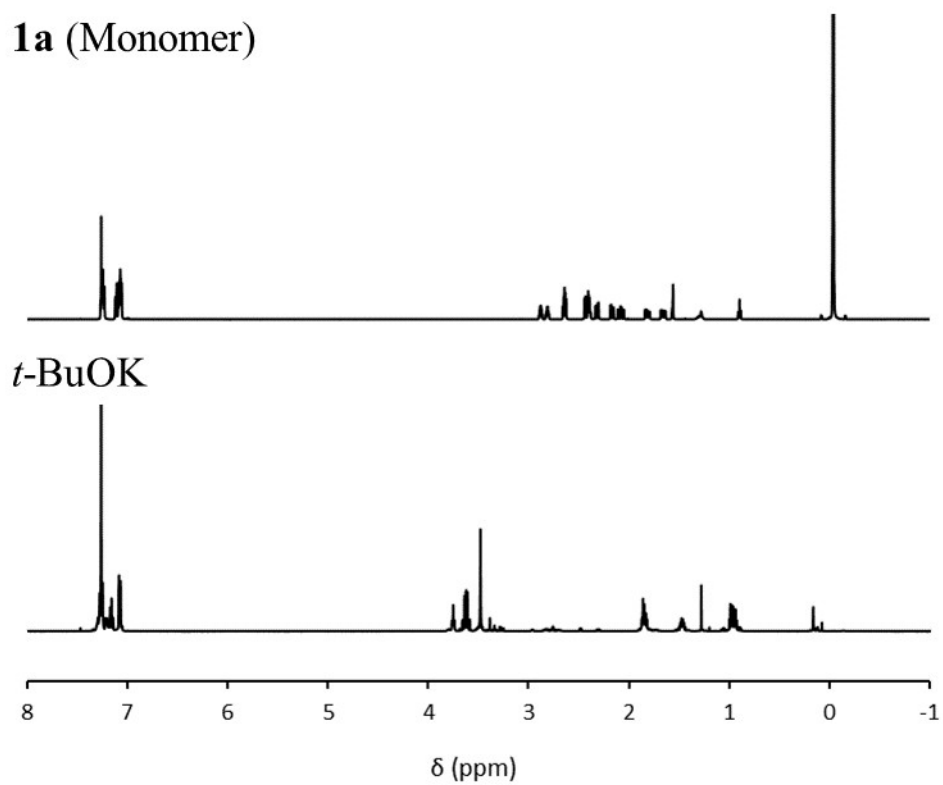
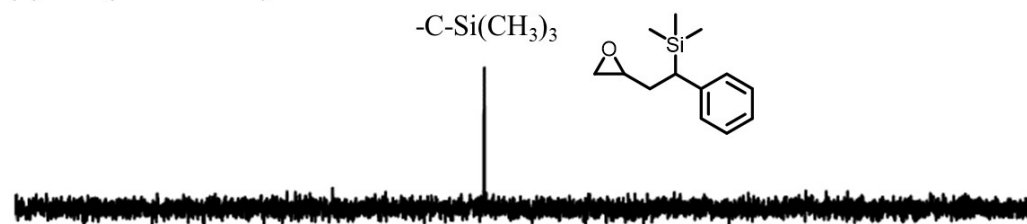


Figure S2. ¹H-NMR spectra of monomer **1a** and the product Run 3 using *t*-BuOK.

(a) **1a** (Monomer)



(b) **2a** (Polymer before hydrolysis)

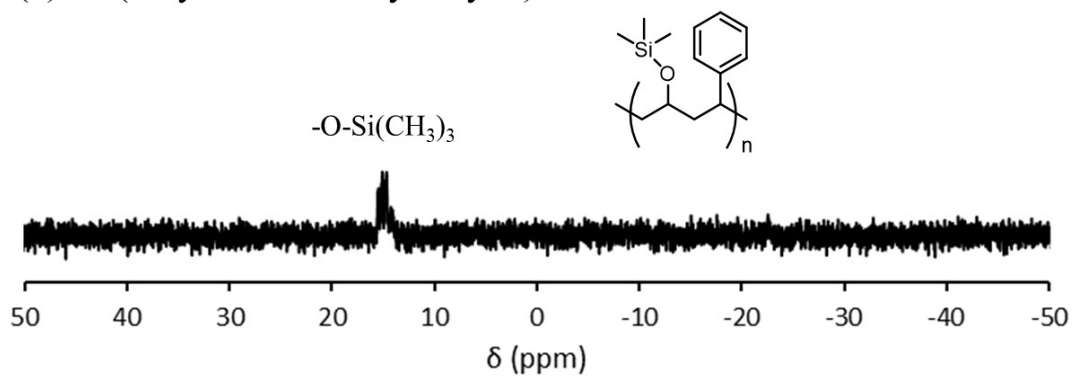


Figure S3. ^{29}Si -NMR spectra of (a) monomer **1a**, (b) obtained polymer **2a**.

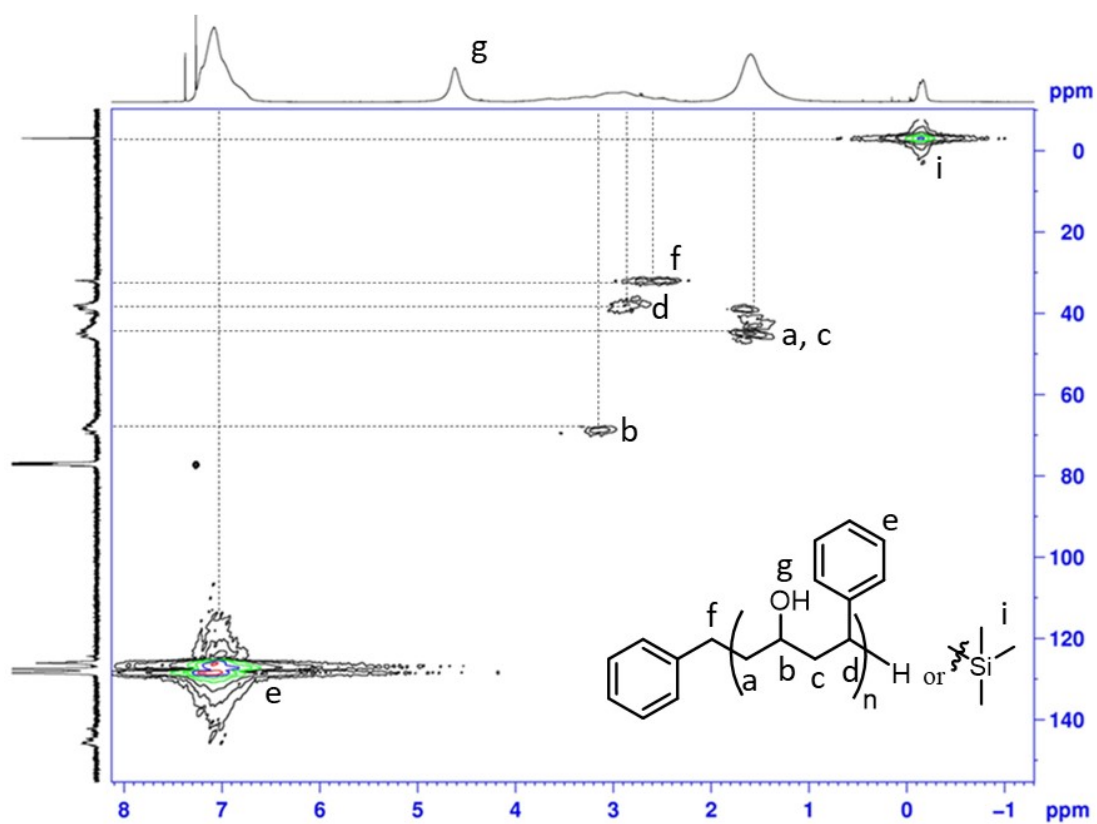


Figure S4. HMOC NMR spectrum of the obtained polymer after hydrolysis **3a**.

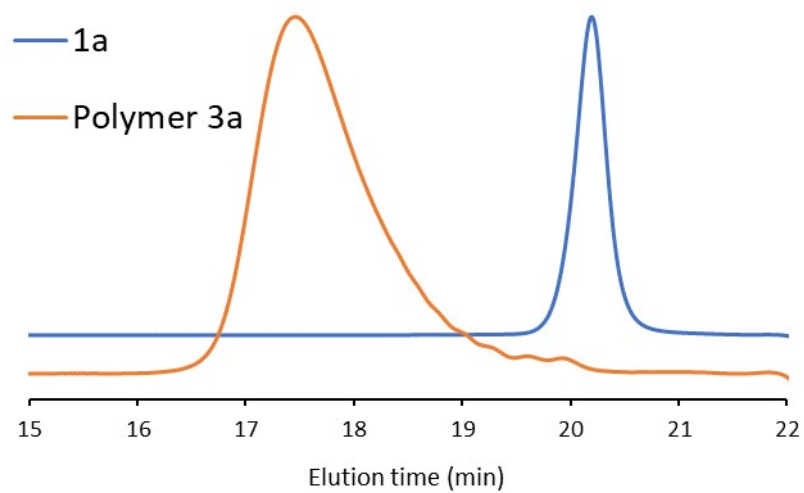


Figure S5. GPC curves of monomer **1a** and polymer **3a** after hydrolysis in THF (RI).