Supplementary Information

Efficient linking of two epoxides using potassium thioacetate in water and its use in polymerization

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Contents

1. General

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (400 MHz) or Bruker Avance III HD 600 MHz spectrometer. All chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for ^{1}H in CDCl$_3$) or 3-(trimethylsilyl)-1-propanesulfonic Acid Sodium Salt (0 ppm for ^{1}H in D$_2$O) as an internal standard. Molecular weight was determined using TOSOH HLC-8320. Tensile test was performed using Shimadzu EZ-SX. Viscosity was measured using A&D SV-1A.
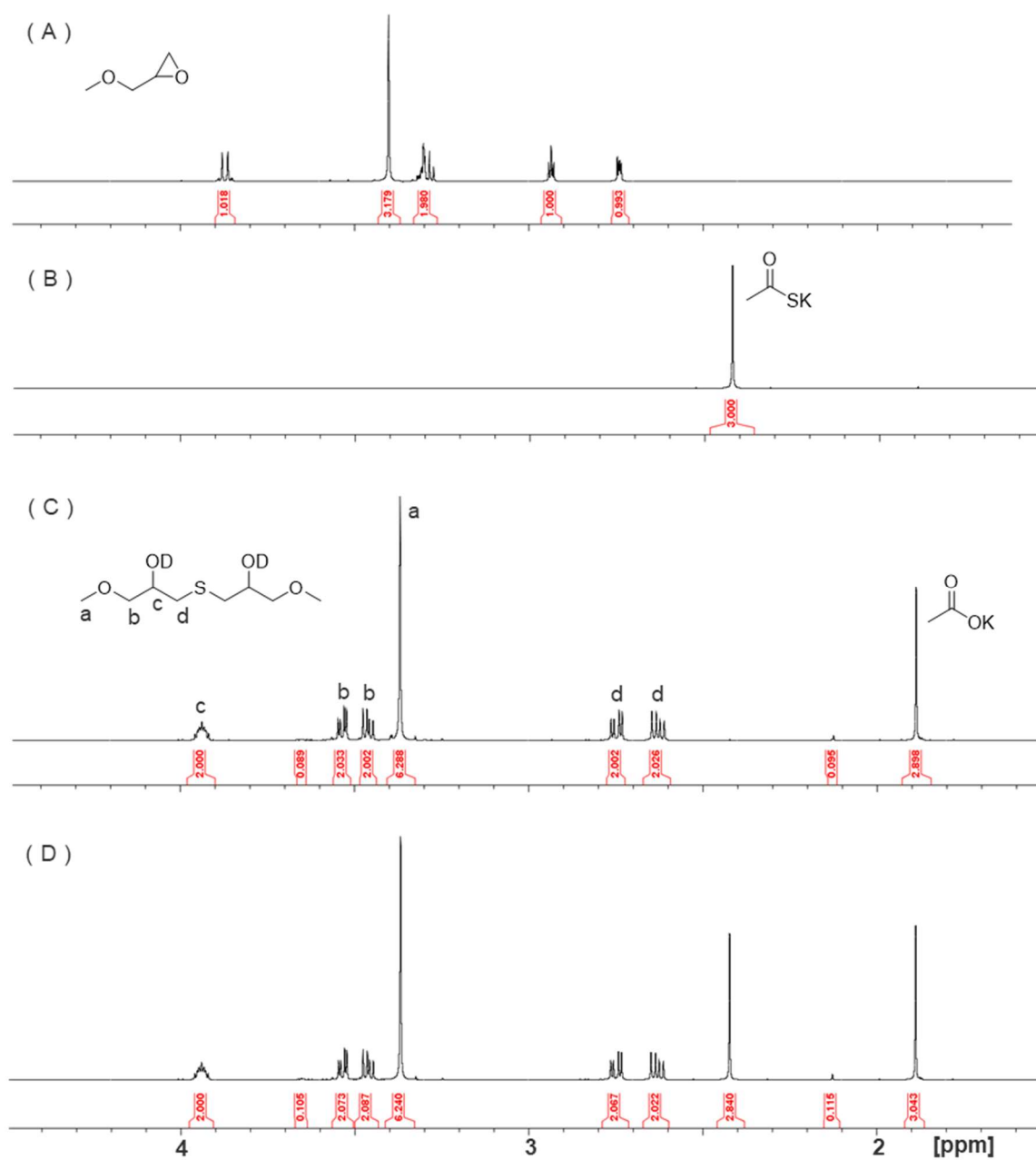
2. Model reaction of (*S*)-GME with AcSK or DTT

Fig. S1 ^{1}H NMR spectra (in D$_2$O at 298 K) of (A) (*S*)-GME, (B) AcSK, and (C, D) mixtures of (*S*)-GME and AcSK measured 4 hours after the reaction started: [AcSK]/[(*S*)-GME] = (C) 0.5 and (D) 1.0.

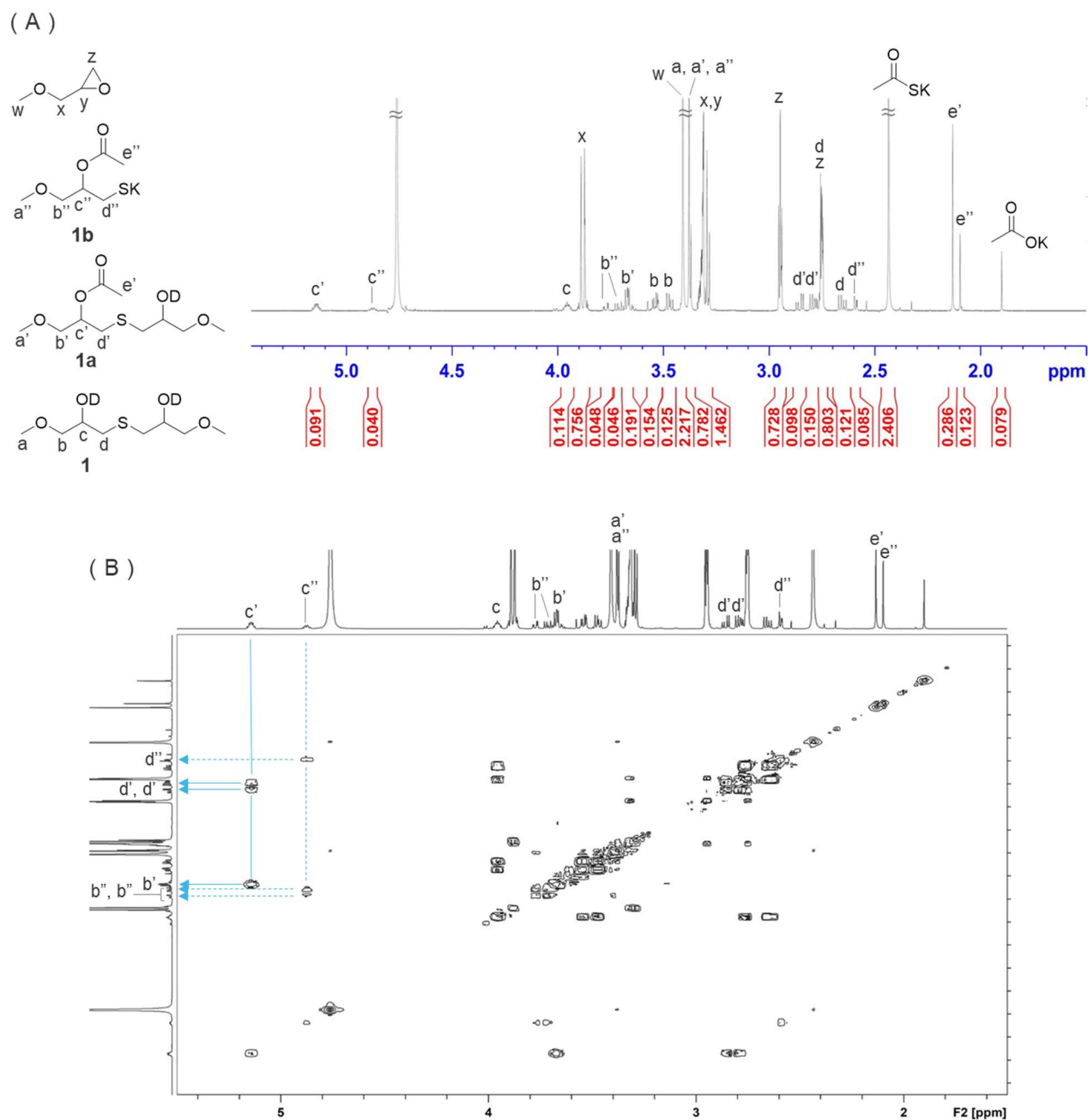**Fig. S2** (A) ^{1}H NMR spectrum and (B) ^{1}H-^{1}H COSY spectrum of a mixture of (*S*)-GME and AcSK: [AcSK]/[(*S*)-GME] = 1.0, [(*S*)-GME] = 0.1 M, [AcSK] = 0.1 M, D$_2$O, 298 K. Note that mono-functionalized **1b** is a minor species although excess amount of AcSK was used. (A) Measurement was started at 249 sec after mixing and conducted for 1 min. (B) Measurement was started at 273 sec after mixing and conducted for 38 min.
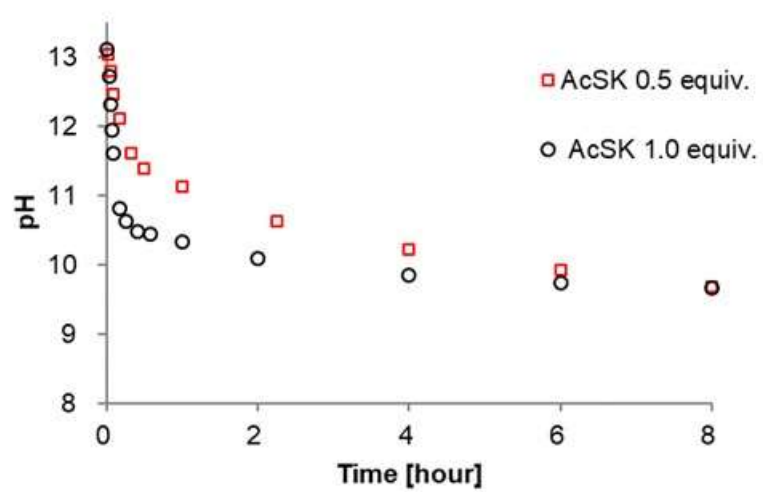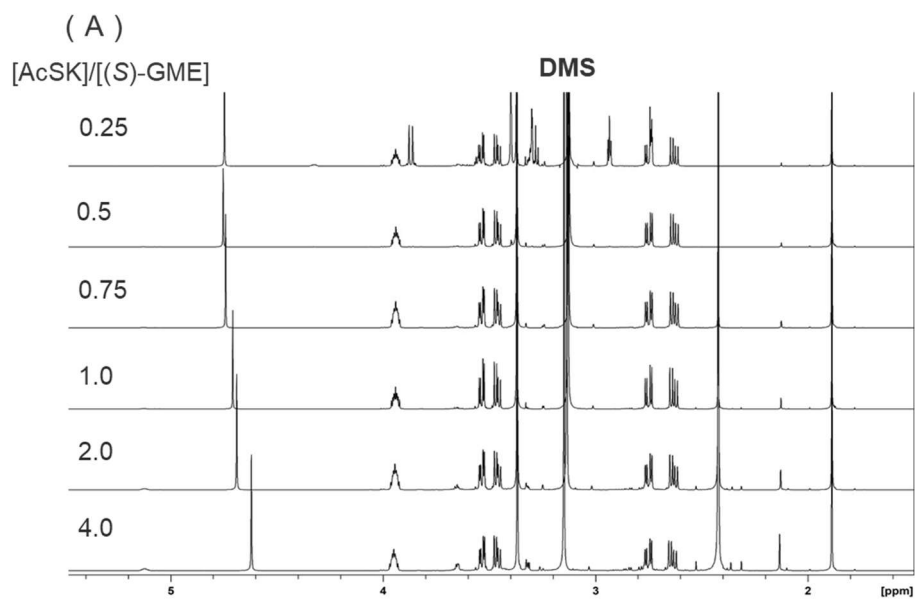
Fig. S3 Time-dependent changes in pH of a mixture of (*S*)-GME and AcSK observed upon mixing these reagents: [(*S*)-GME] = 1.0 M, [AcSK] = 0.5 or 1.0 M, H_2O, 298 K.

(A)

[AcSK]/[(S)-GME]

DMS

0.25

0.5

0.75

1.0

2.0

4.0

5   4   3   2   [ppm]

(B)

[AcSK]/[(S)-GME]	Yield (%)	
	1	1a
0.25	90	1
0.50	96	3
0.75	96	4
1.0	94	5
2.0	84	10
4.0	69	18

Fig. S4 (A) ^{1}H NMR spectra of mixtures of (S)-GME and AcSK measured 4 hours after the reaction started. DMS (dimethyl sulfone, an internal standard for quantitative evaluation of reaction yield) was added just before NMR measurement: [(S)-GME] = 1.0 M, [AcSK]/[(S)-GME] = 0.25 to 4.0, [DMS]/[(S)-GME] = 1.0, D$_2$O, 298 K. (B) Reaction yields of **1** and **1a** estimated based on the NMR signal.
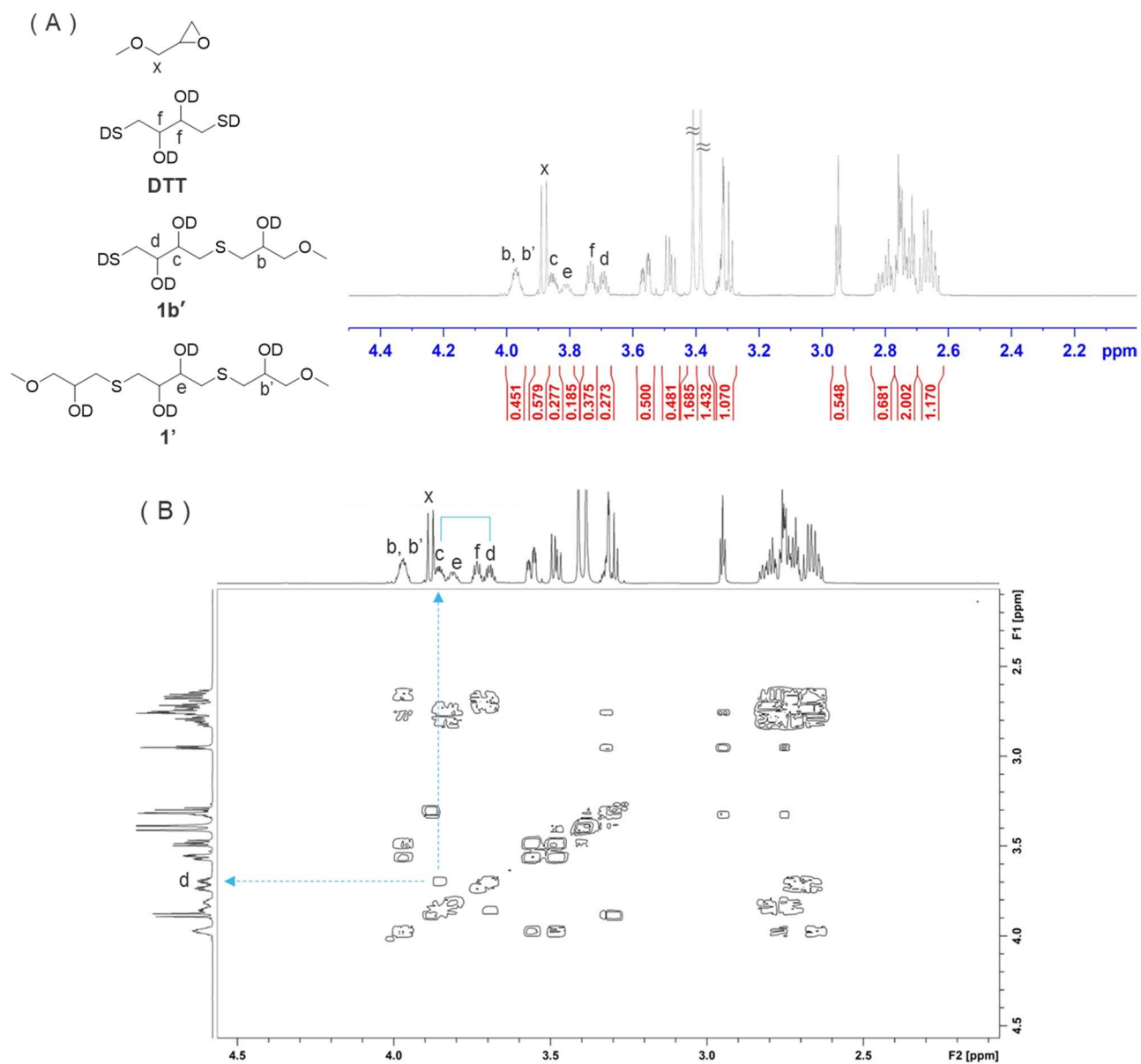
Fig. S5 (A) ^{1}H NMR spectrum and (B) ^{1}H-^{1}H COSY spectrum of a mixture of (*S*)-GME and DTT: [DTT]/[(*S*)-GME] = 0.5, [(*S*)-GME] = 0.1 M, [DTT] = 0.05 M, D_2O, 298 K. (A) Measurement was started at 4 hours after mixing and conducted for 1 min. (B) Measurement was started at 4 hours after mixing and conducted for 1 hour.

3. Evaluation of the reaction rate constants

For the consecutive reaction shown in Fig. 1B, we evaluated the rate constants for the first (k_1) and second (k_2) reaction using following equation (1) referring to previously reported method.[S1-S3]

$$\tau = \int_1^{1/\beta} \frac{dw}{(\frac{2}{S} - 2)w + \frac{1}{\kappa - 1}(2\kappa - 1 - w^{1-\kappa})} \qquad (1)$$

Variables τ, β, κ and S in equation (1) were defined as following (2) – (5);

$$\tau = k_1[AcSK]_0 t \qquad (2)$$

$$\beta = \frac{[AcSK]}{[AcSK]_0} \qquad (3)$$

$$\kappa = \frac{k_1}{k_2} \qquad (4)$$

$$S = 2\frac{[AcSK]_0}{[(S) - GME]_0} \qquad (5)$$

t is reaction time.

The right side of equation (1) was numerically calculated using computation program Microsoft basic language. To calculate this, we obtained the relationship between β and t (Fig. S6B) from ^{1}H NMR analysis exemplified in Fig. S6A using equation (3-1).

$$\beta = \frac{[AcSK]}{[AcSK]_0} = \frac{[AcSK]}{[AcSK] + [\mathbf{AcOK}] + [\mathbf{1a}] + [\mathbf{1b}]} \qquad (3-1)$$

Using the resultant data, the values of τ against t were calculated by assuming a certain value of κ. According to the equation (2), the relationship of τ and t should be liner-proportional, where the values of the corresponding correlation coefficients (R^2) against values of κ were obtained from the fitting of the liner equations using the least square method (Fig. S6C).

As showed in Fig. S6D, the plotting values of R^2 for values of κ gave the maximum of $R^2 = 0.9981$ at $\kappa = 31$, indicating that the rate constants for the first (k_1) reaction was 31 times larger than that for second one.

Using equation (2), the slope of the relationship between τ and t in Fig. S6C corresponds to k_1 [AcSK]$_0$. With [AcSK]$_0$ = 0.075 M, k_1 was determined to be 0.37 M^{-1} min^{-1}. Subsequently, because of k_2/k_1 = 31, k_2 was estimated to be 12 M^{-1} min^{-1}.
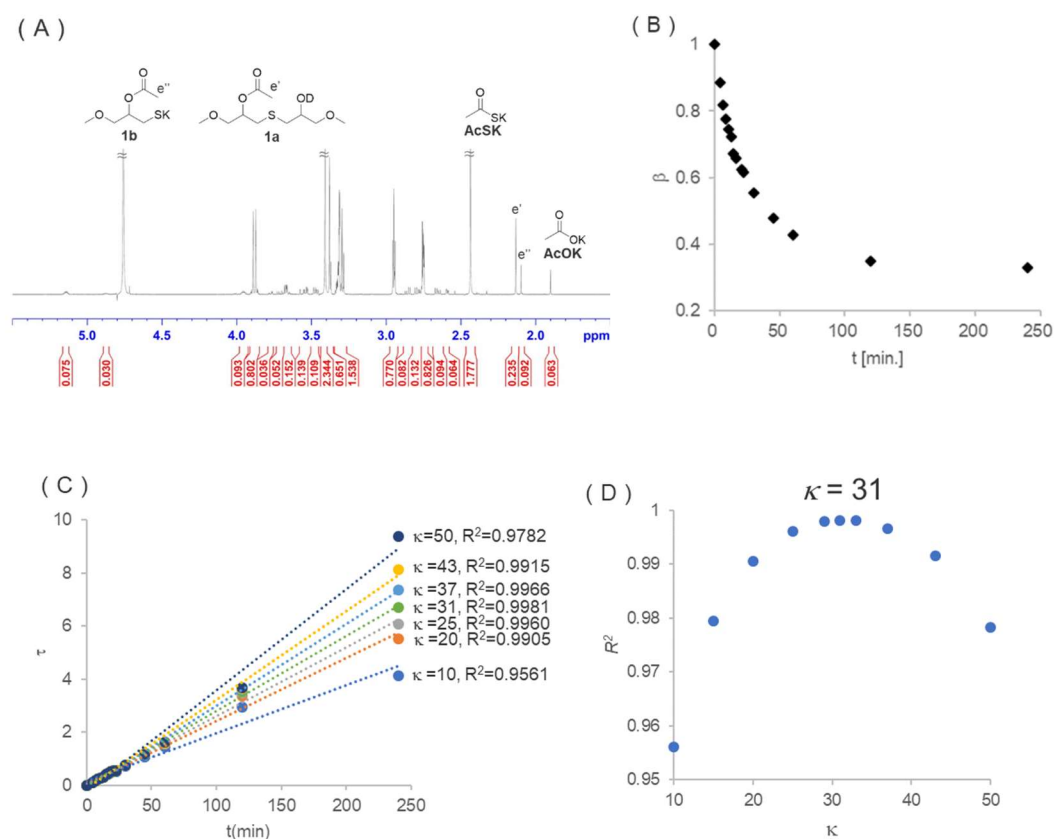

Fig. S6 (A) ^{1}H-NMR spectrum of a mixture of (*S*)-GME and AcSK measured 274 sec after mixing: [AcSK]/[(*S*)-GME] = 0.75, [(*S*)-GME] = 0.1 M, D$_2$O, 298 K. (B) Relationship between β and t determined by ^{1}H NMR analysis. (C) Relationship between τ and t for various κ. (D) Relationship between κ (k_2/k_1) and correlation coefficient R^2.

4. Polymerization of EX-830

To an aqueous solution of EX-830 (1.0 M with respect to the epoxy group; 1.0 mL), an aqueous solution of AcSK (0.3–0.8 M; 1.0 mL) was added. The reaction mixture was stirred at room temperature for 1 hour, and water was evaporated. Chloroform (c.a., 5 mL) was added, and the organic phase was dried over magnesium sulfate. Insoluble materials were filtered off, and solvent was evaporated to dryness. The same procedure was conducted using DTT in place of AcSK for comparison. The obtained viscous materials were characterized by ^{1}H NMR (400 MHz, CDCl$_3$, Fig. S7) and size exclusion chromatography using polystyrene standard (Fig. 3 and Fig. S8).
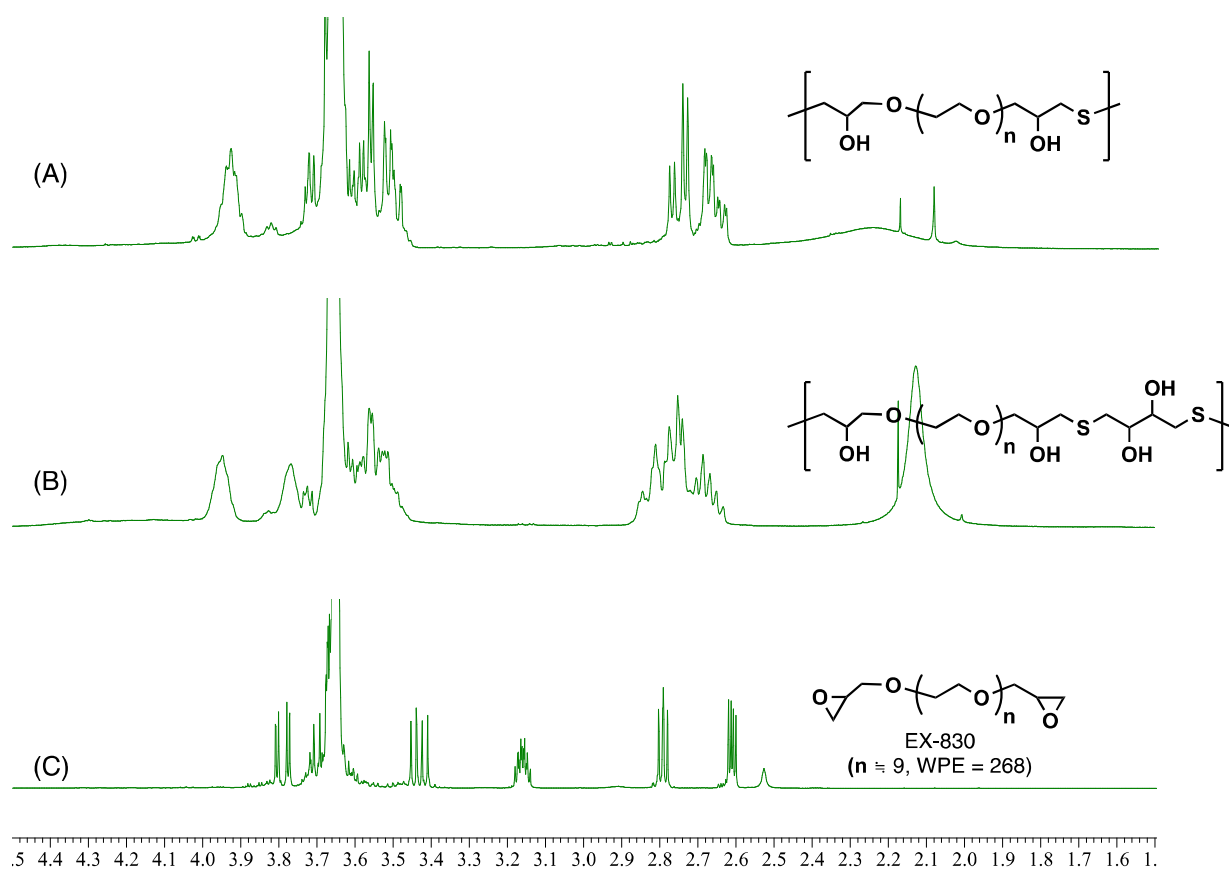

Fig. S7 ^{1}H NMR spectra of (A) a polymer obtained from EX-830 and AcSK, (B) a polymer obtained from EX-830 and DTT, and (C) EX-830 (400 MHz, CDCl$_3$).
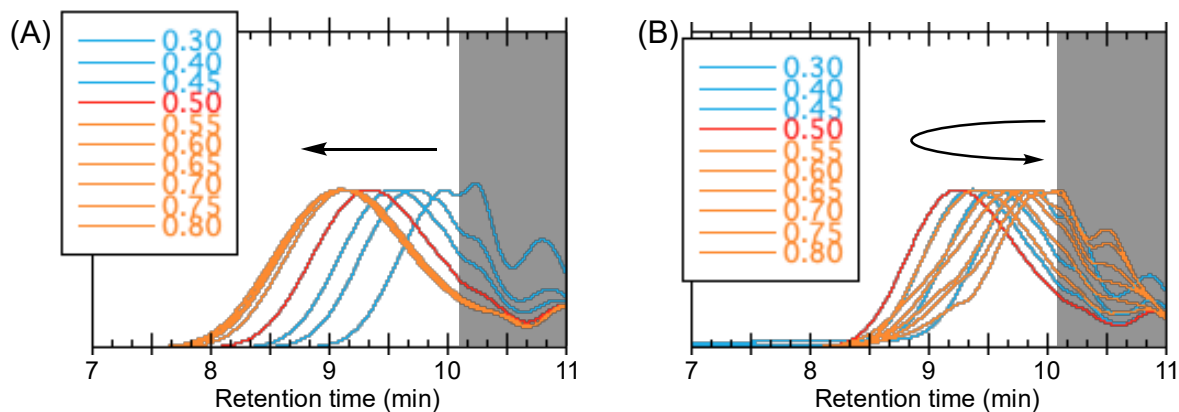
Fig. S8 Size exclusion chromatography of mixtures obtained after polymerization of EX-830 using (A) AcSK and (B) DTT as described above. Note that molecular weights (Fig. 3) were determined based on the larger peaks, excluding the minor species which were attributed to cyclic products (highlighted in gray). The numbers indicate the ratio of AcSK to epoxide groups: i.e., [AcSK]/[epoxide in EX-830].

5. Gelation test

Typical procedure was conducted as follows. EX-830 (1.6 g; 6.0 mmol with respect to epoxy group) and EX-521 (1.1 g; 6.0 mmol with respect to epoxy group) were dissolved in 1.6 g of water (solution A; total 4.3 g; 12 mmol with respect to epoxy group). AcSK (5.7 g; 50 mmol) was dissolved in 44.3 g of water (solution B; 1 mmol/g). To solution A, the given amounts of solution B were added in a glass vial (5.4–9.6 g; 5.4–9.6 mmol), and the mixture was left at room temperature. Gelation was confirmed by the inverted test tube method. The same procedure was conducted using DTT (4.8, 6.0, or 7.2 mmol) in place of AcSK for comparison. To monitor the gelation kinetics using viscometer (Fig. S9), the similar procedure was applied but samples were diluted four times to slow the reaction. Changes in the viscosity were monitored two minutes after the solutions A and B were mixed.
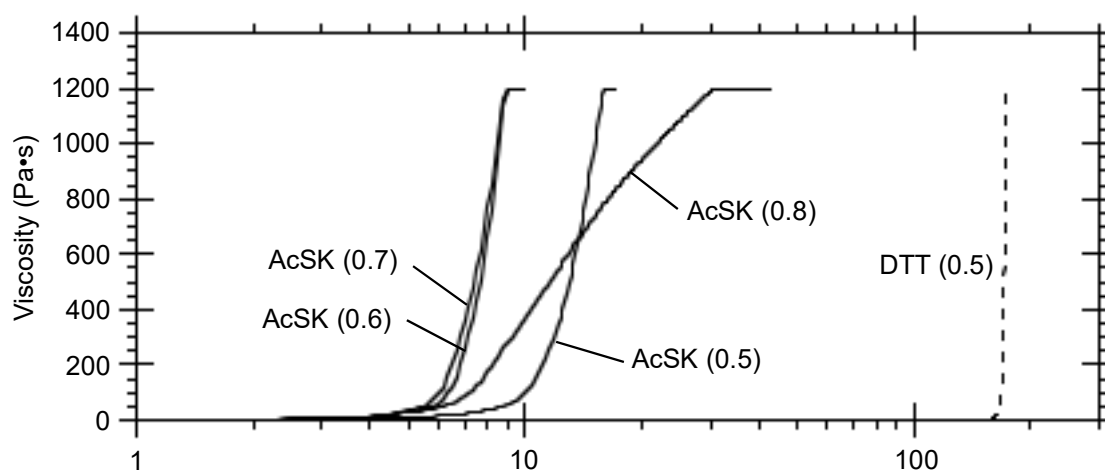

Fig. S9 Changes in viscosity of aqueous solutions of EX-830 and EX-521 upon addition of AcSK or DTT. The numbers in parenthesis indicate the molar ratio of AcSK or DTT to the total epoxy groups in EX-830 and EX-521.

6. Film preparation

A mixture of EX-830, EX-521, and AcSK in water prepared according to the procedure described above (see, gelation test) was spread in a Petri dish (diameter = 9 cm) before gelation. The mixture was left under ambient condition, water was gradually evaporated, and polymeric film was obtained. After 12 days, weight loss of the film had unchanged, at which point, water content in the film was estimated to be 3-5%. The same procedure using DTT in place of AcSK provided a film for comparison.

Film was cut using JIS K6251-7 cutter. Five pieces were measured for each film, and rupture stress and rupture strain were obtained as average values of three pieces, after excluding the highest and lowest values among the five prepared pieces.
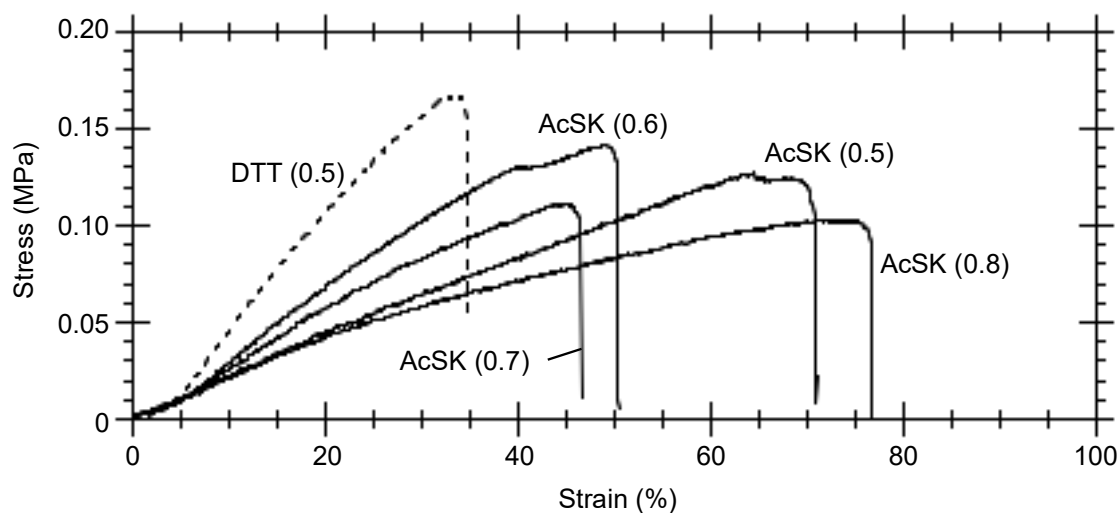

Fig. S10 Strain-stress curves of polymers obtained from EX-830, EX-521, and AcSK or DTT. The numbers in parenthesis indicate the molar ratio of AcSK or DTT to the total epoxy groups in EX-830 and EX-521.

7. Supplementary references

S1) N. Kihara, S. Komatsu, T. Takata and T. Endo, *Macromolecules*, 1999, **32**, 4776−4783.

S2) E. Goto, S. Ando, M. Ueda and T. Higashihara, *ACS Macro Lett.*, 2015, **4**, 1004-1007.

S3) P. Sun, J. Chen, J. Liu and K. Zhang, *Macromolecules*, 2017, **50**, 1463-1472.