**Supplementary information**

# Trapping bond exchange phenomenon revealed for off-stoichiometry cross-linking of phase-separated vitrimer-like materials

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# 1. Synthesis protocol

Scheme S1. Synthesis of copolymers.
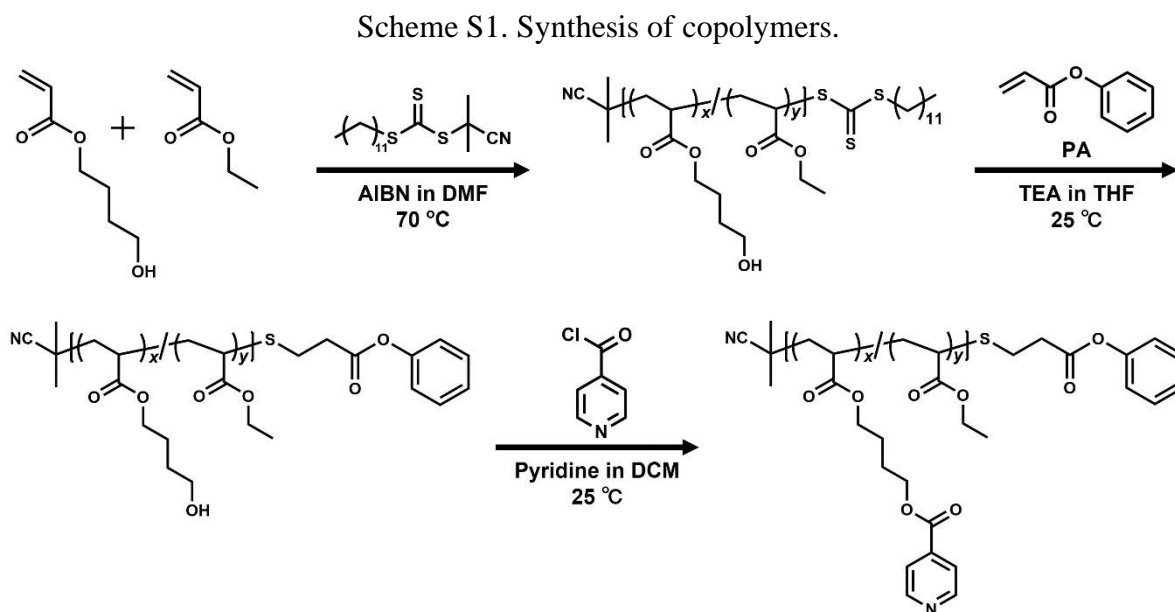


## RAFT copolymerization

Scheme S1 explains the synthesis scheme of random copolymers with pyridine side groups. First, random copolymers with OH groups were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization, using ethyl acrylate (EA) and 4-hydroxybutyl acrylate (4HBA). Note that the radical reactivity of acrylate monomers and 4HBA is nearly 1, and thus the OH side groups can be well distributed along the chain in such random copolymer systems[S1]. Two different copolymers were prepared with different ratios of acrylate monomers. One was made at EA : 4HBA = 7 : 1, and the other was made at EA : 4HBA = 14 : 1. In both cases, the mole ratio of monomers (EA + 4HBA) : CTA : AIBN was 190 : 1 : 0.1. EA, 4HBA, CTA, and AIBN were dissolved in DMF (super hydrated) in a 100 mL flask at the monomer concentration of 40 wt%, and the solution was degassed using Ar gas bubbling in an ice bath. For polymerization, the solutions were heated and stirred at 70 °C for 60 min. The polymerization was terminated by cooling the solution in an ice bath to inactivate radicals. The polymers were purified by repeated reprecipitations, using THF as the good solvent and water/methanol (7/1 by volume) as the poor solvent.

S1) Mun, G. A.; Nurkeeva, Z. S.; Beissegul, A. B.; Dubolazov, A. V.; Urkimbaeva, P. I.; Park, K.; Khutoryanskiy, V. V. Temperature-responsive water-soluble copolymers based on 2-hydroxyethyl acrylate and butyl acrylate. *Macromol. Chem. Phys*. 2007, 208 (9), 979-987.

**Modification of the RAFT residue**

The RAFT residue (trithiocarbonate group) in the chain end was replaced with a phenyl group by the one-shot aminolysis reaction and Michael addition reaction, which was to prevent dimerization at high temperatures. The polymer was dissolved in THF (the polymer concentration was 1.5 wt%), and other reagents, PA (10 eq. to the OH group), PhA (10 eq. to the OH group), and TEA (0.33 eq. to the OH group), were added. After stirring at 25 °C for 48 h, the solvent and reagents were removed by an evaporator. The polymer was finally purified by reprecipitation, using THF as the good solvent and hexane as the poor solvent.

**Attachment of Pyridine Side Groups**

The above polymer was dissolved in dichloromethane (DCM) and pyridine (catalyst, 5 eq. to the OH group) with an addition of INCH (5 eq. to the OH group), where the polymer concentration was 0.5 wt%. After the reaction at 25 °C for 48 h, the solution was washed by NaHCO$_3$ saturated aqueous solution. The solvent in the organic phase was then removed by an evaporator. The polymer was finally purified by reprecipitation, using THF as the good solvent and water as the poor solvent.

**2. SEC data**

Figure S1 summarizes the SEC curves for the random copolymers bearing OH groups (OH-precursor), the copolymers after cleavage of RAFT residue (End group modification), and the copolymer after reaction with INCH (Py-1k and Py-2k).
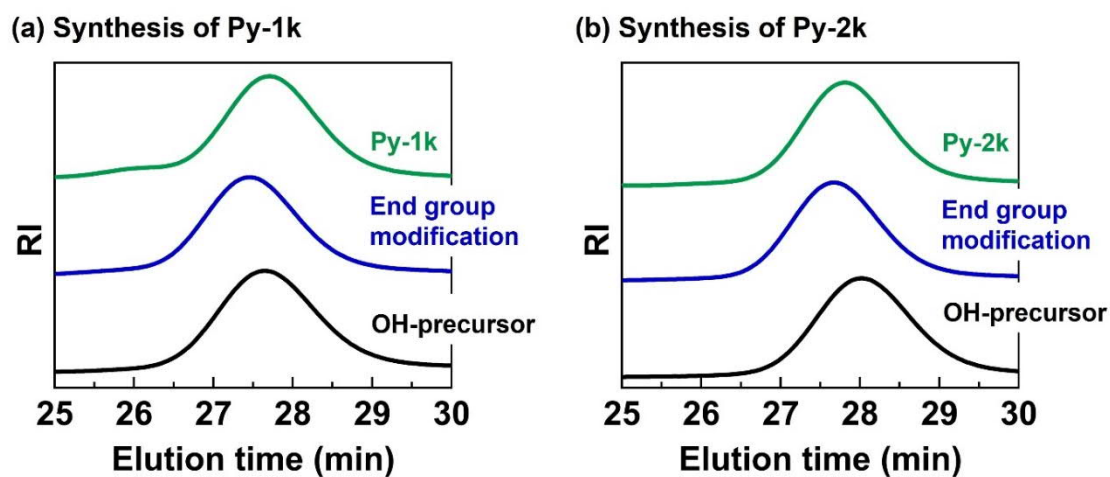


Figure S1. SEC curves for the random copolymers bearing OH groups (OH-precursor), the copolymers after cleavage of RAFT residue (End group modification), and the copolymer after reaction with INCH (Py-1k and Py-2k): (a) for synthesis of Py-1k and (b) for synthesis of Py-2k.

## 3. $^1$H-NMR spectra

Syntheses of random copolymers bearing OH groups (OH-precursor) and subsequent reaction with INCH (Py-1k and Py-2k) were confirmed by $^1$H-NMR in DMSO-$d$6. Figures S3-S4 represent the $^1$H-NMR spectra. In these Figures, the alphabet in the spectra corresponds to the protons with the same alphabet in the chemical structures shown in Figure S2. In the spectrum of OH-precursor, the integral ratio of signals b, f, g was used for the estimation of the unit mole ratio of EA and 4HBA unit bearing pyridine group.

The number average degree of polymerization was estimated as follows. The unit mole ratio of EA and 4HBA bearing pyridine group was estimated by $^1$H-NMR, and the unit mole ratio was nearly consistent with the feed mole ratio of EA : 4HBA (= 7 : 1 or 14 : 1) Therefore, using the number average molecular weight $M_n$, the following relationship can be obtained.

$$M_n = M_{Py} \times n_{Py} + M_{EA} \times n_{EA} \quad (S1)$$

$$n_{EA} : n_{Py} = 7 : 1 \text{ or } 14 : 1 \quad (S2)$$

, where the quantities with the subscript "Py" represent the information for the 4HBA unit bearing pyridine group. $M_{Py}$ and $M_{EA}$ indicate the formula mass of each monomeric unit (285.73 for $M_{Py}$ and 100.12 for $M_{EA}$), and $n_{Py}$ and $n_{EA}$ indicate the number average degree of polymerization for each monomeric unit. Finally, the simultaneous equation of S1 and S2 is solved to provide the values of $n_{Py}$ and $n_{EA}$.
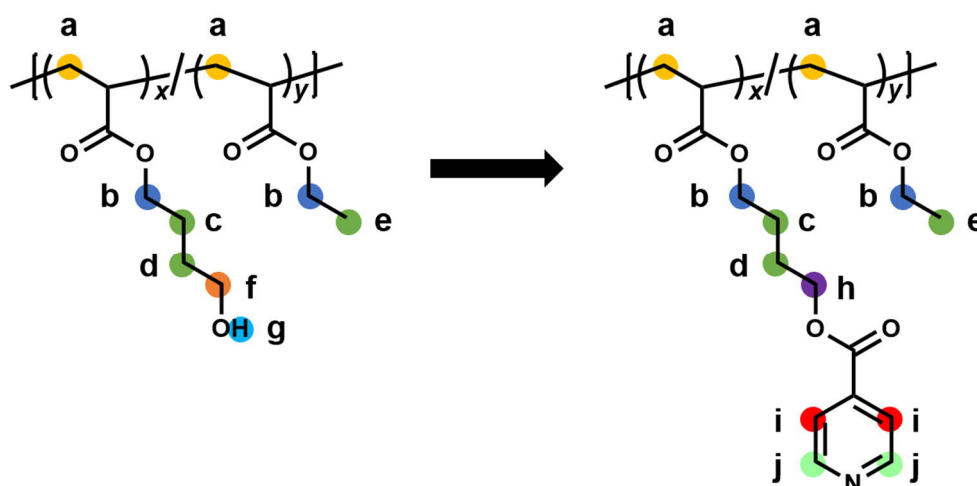


Figure S2. Assignment of signals for the $^1$H-NMR spectra. Alphabet in the spectra of Figure S3 and S4 corresponds to the protons with the same alphabet in the chemical structures.
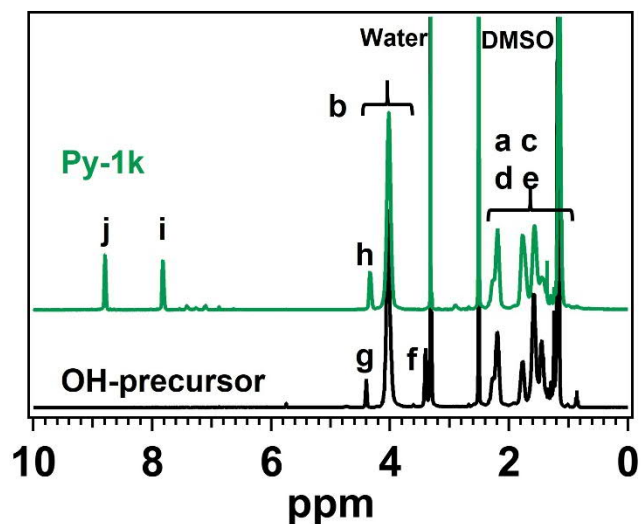
Figure S3. $^1$H-NMR spectra in DMSO-$d_6$ for the synthesis of Py-1k (random copolymers bearing OH groups (OH-precursor) and subsequent reaction with INCH (Py-1k)).
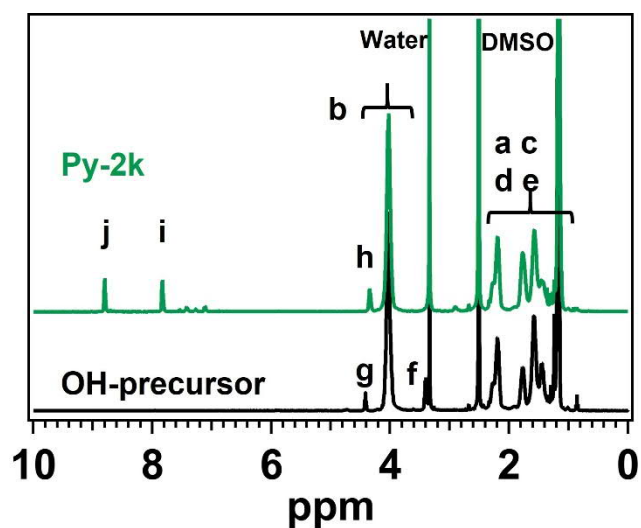


Figure S4. $^1$H-NMR spectra in DMSO-$d_6$ for the synthesis of Py-2k (random copolymers bearing OH groups (OH-precursor) and subsequent reaction with INCH (Py-2k)).

## 4. UV-vis spectra

Figure S5 summarizes the UV-vis spectra for the random copolymers bearing OH groups (OH-precursor), the copolymers after cleavage of RAFT residue (End group modification).

**(a) For Py-1k**

**(b) For Py-2k**
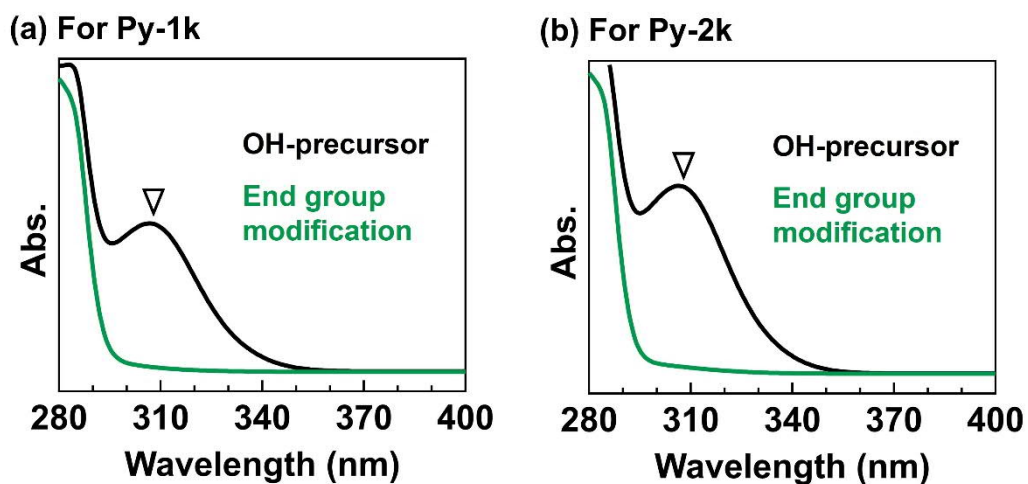
OH-precursor
End group modification
Abs.
Wavelength (nm)

Figure S5. UV-vis spectra for the random copolymers bearing OH groups (OH-precursor), the copolymers after cleavage of RAFT residue (End group modification): (a) for Py-1k and Py-2k.

## 5. FT-IR spectra

Figure S6 represents the FT-IR spectra for the precursor copolymers and the cross-linked samples, where a specific wavenumber region for the free pyridine and quaternized pyridine is focused.
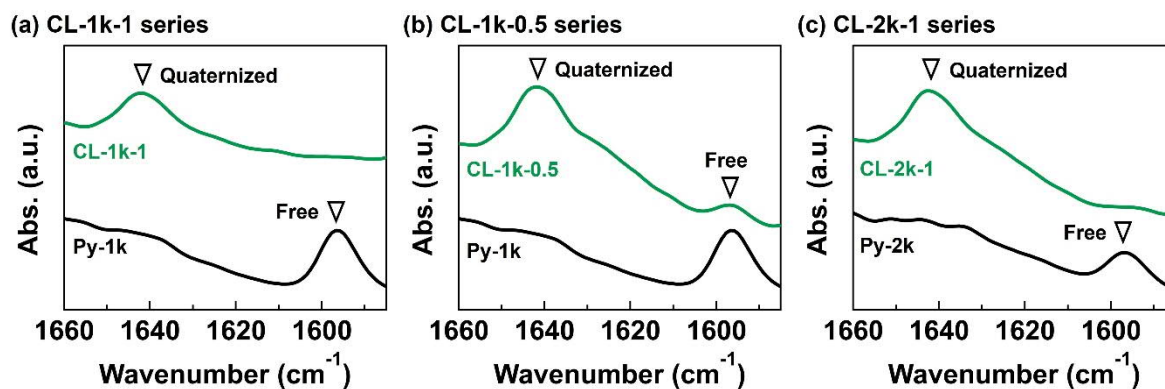


Figure S6. FT-IR spectra for the precursor polymers and cross-linked samples: (a) for CL-1k-1 series, (b) for CL-1k-0.5 series, and (c) for CL-2k-1 series.
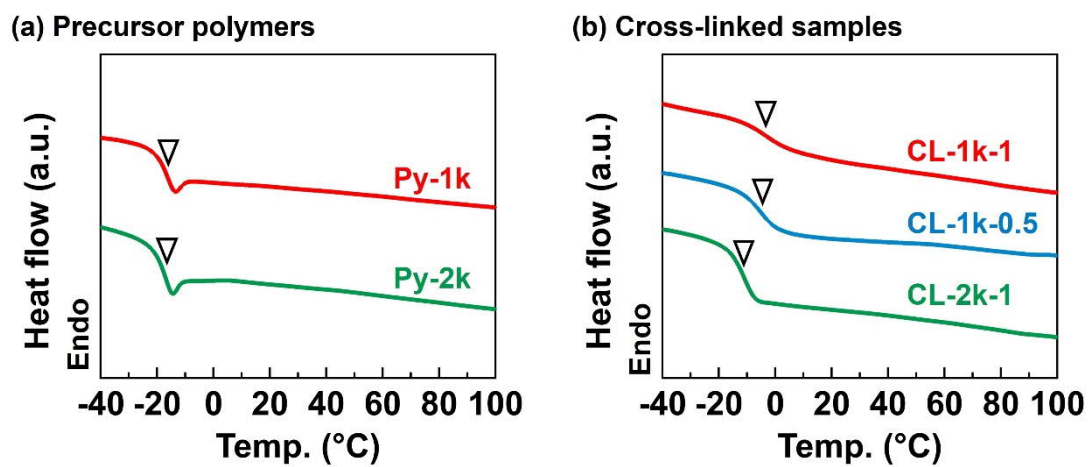
## 6. DSC thermograms

**(a) Precursor polymers**

**(b) Cross-linked samples**

Figure S7. DSC thermograms for (a) precursor copolymers and (b) cross-linked samples. The arrows represent the $T_g$ position.
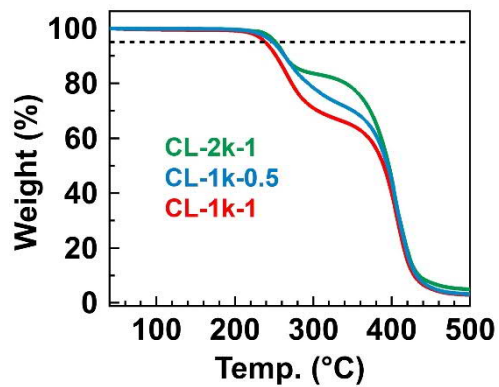
## 7. TGA thermograms



Figure S8. TGA thermograms for the cross-linked samples. The dotted line indicates 5% weight loss.

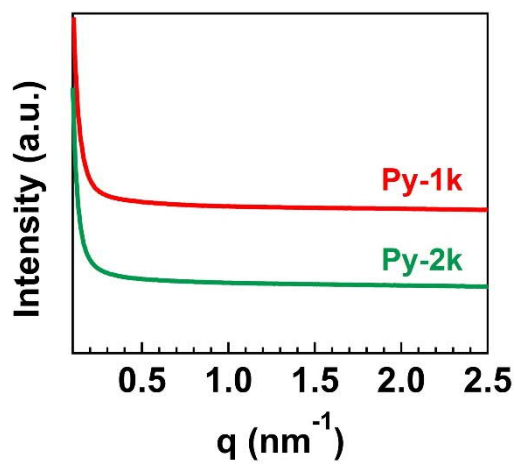## 8. SAXS data for the precursor polymers



Figure S9. SAXS spectra for the precursor copolymers, Py-1k and Py-2k.

## 9. Fitting parameters for the stress-relaxation spectra

Table S1. The fitting parameters and $<\tau>$

| Sample | $\tau$ (s)[a] 130ºC/140ºC/150ºC/160ºC | $\beta$(-)[b] 130ºC/140ºC/150ºC/160ºC | $<\tau>$ (-)[c] 130ºC/140ºC/150ºC/160ºC |
|---|---|---|---|
| CL-1k-1 | 4068/1652/821/346 | 0.69/0.71/0.75/0.76 | 5194/2072/975/406 |
| CL-1k-0.5 | 6731/2894/1241/484 | 0.72/0.75/0.76/0.77 | 8319/3463/1466/563 |
| CL-2k-1 | 3229/1418/706/242 | 0.72/0.81/0.81/0.83 | 3970/1595/793/268 |

[a]Specific relaxation time. [b]Degree of the distribution of $\tau$. [c]first-order average relaxation time. See the explanation in the main text.

**10. SAXS data at 170 °C and 180 °C for CL-1k-0.5**

SAXS data were taken at 170 °C and 180 °C for CL-1k-0.5 after the thermal treatment at 160 °C for 30 min. The shoulder-like peak at $q \sim 0.3$ nm$^{-1}$ was stable at these high temperatures.
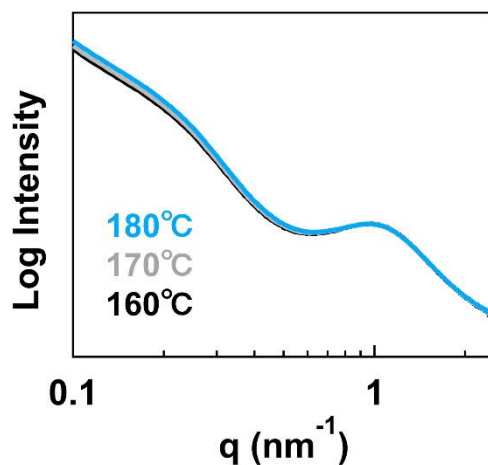


Figure S10. SAXS spectra for CL-1k-0.5 at 170 °C and 180 °C, where the data taken after the thermal treatment at 160 °C for 30 min was also shown for comparison.

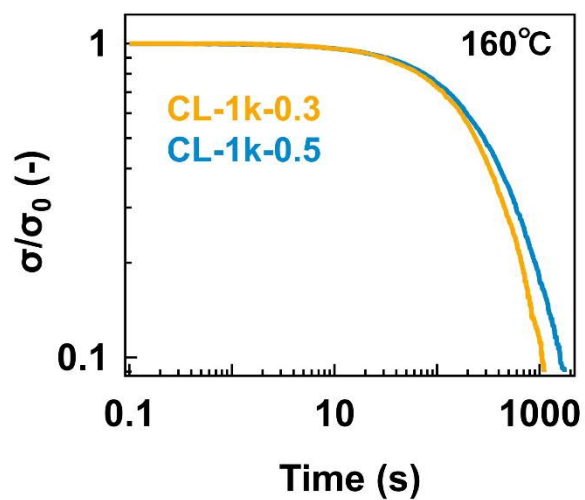## 11. Comparison of stress-relaxation between CL-1k-0.3 and CL-1k-0.5

Figure S11. Stress-relaxation spectra at 160 °C for CL-1k-0.3 and CL-1k-0.5.
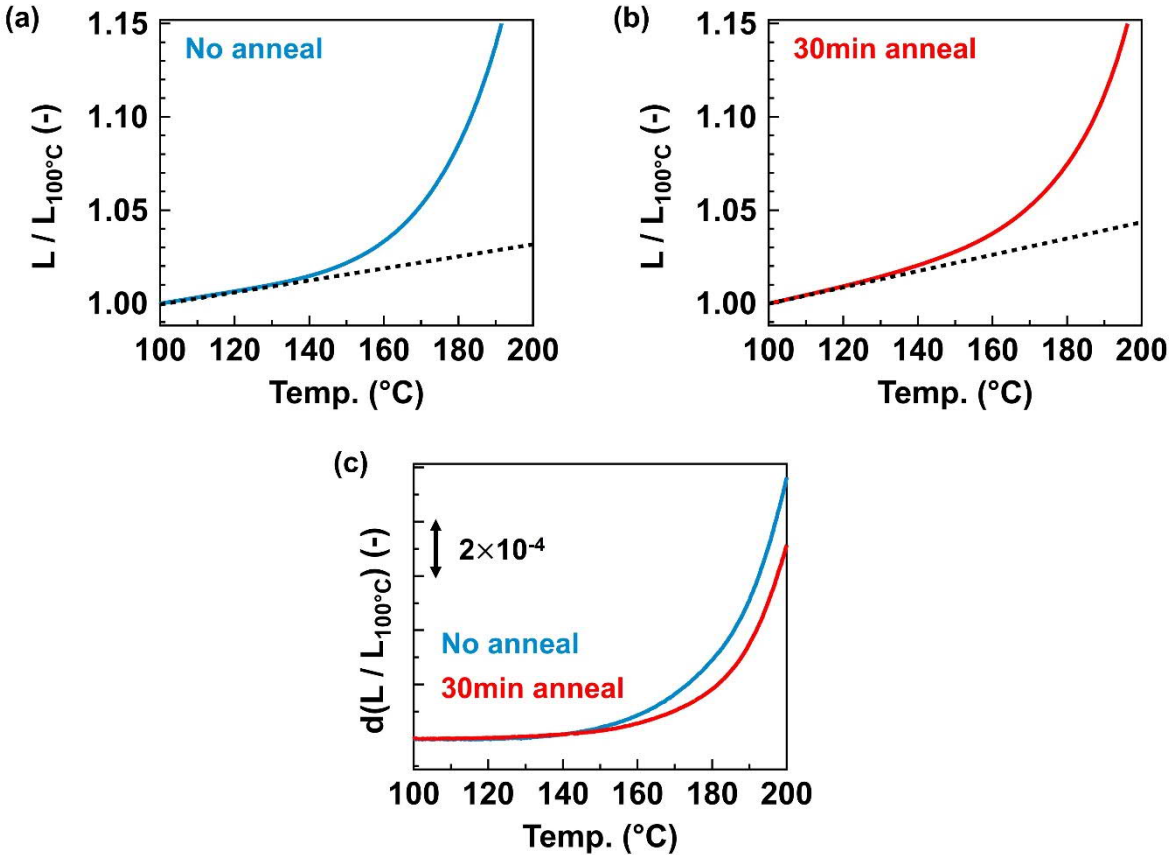
## 12. Creep data for CL-1k-0.5 after annealing

Figure S12. Temperature-ramp creep data for CL-1k-0.5, where (a) the fresh sample with no annealing and (b) the sample after 30 min annealing at 160 °C are compared. The Y-axis represents the sample length ($L$) normalized by the length at 100 °C ($L_{100°C}$). The dotted line indicates the approximation straight line extrapolated from low temperature. (c) The comparison of length increase manners (i.e., $d(L/L_{100°C})$) for the samples in (a) and (b).