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Supporting Information

A Facile Dynamic Crosslinked Healable Poly(oxime-urethane) Elastomer with High Elastic Recovery and Recyclability

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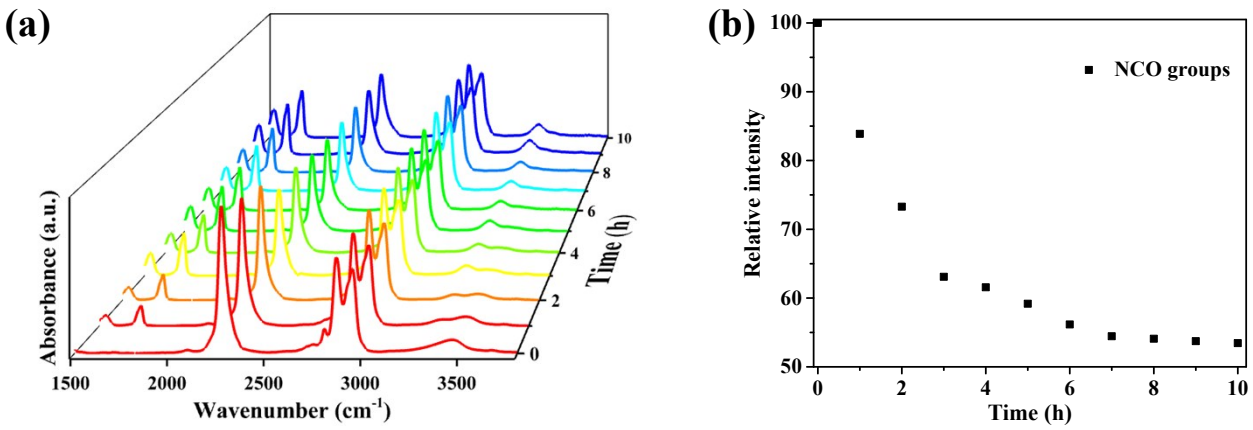

Figure S1. (a) FTIR spectra of the mixture of PTMEG and IPDI with a mole ratio of 1:2 after reacted at 80 °C for various time. (b) The relative intensity of NCO groups (peak around 2264 cm^{-1}).

After pre-polymerized at 80 °C for 10 h, almost 50% of the NCO groups have been consumed and nearly no hydroxyl groups (peak around 3465 cm^{-1}) were detected. Several new peaks around 3330 cm^{-1}, 1720 cm^{-1}, 1703 cm^{-1} and 1531 cm^{-1} which are respectively belonged to ν(NH), ν(C=O, free urethane carbonyl), ν(C=O, hydrogen-bonded urethane carbonyl) and amine Ⅱ (δ(N-H) + ν(C-N)) appeared. A good precursor of PTMEG-IPDI has been formed.

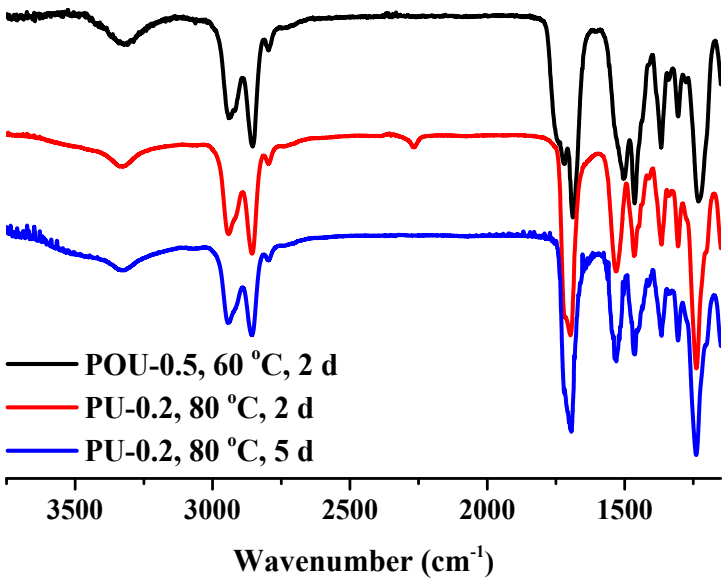

Figure S2. FTIR spectra of POU-0.5 and PU-0.2 after reacted under different conditions.

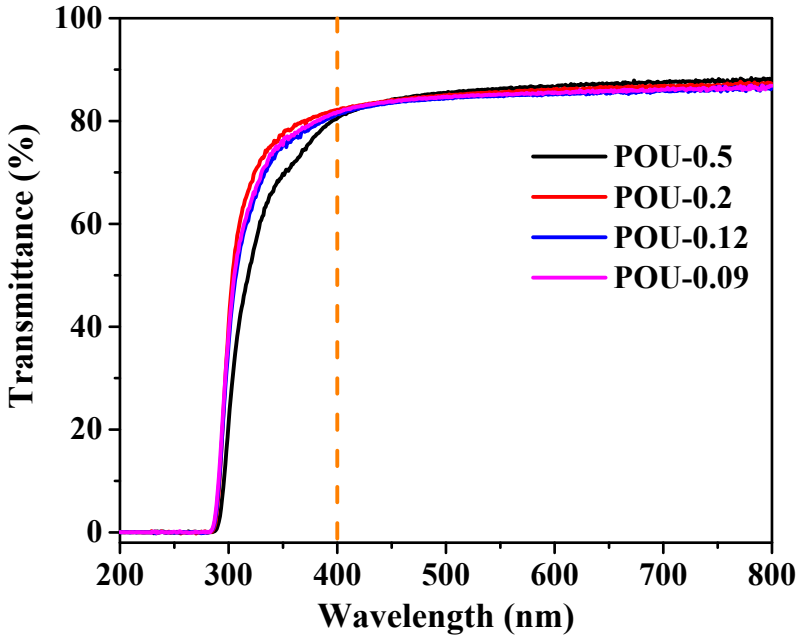

Figure S3. Transmission spectra for POU films with a thickness of ~0.5 mm.

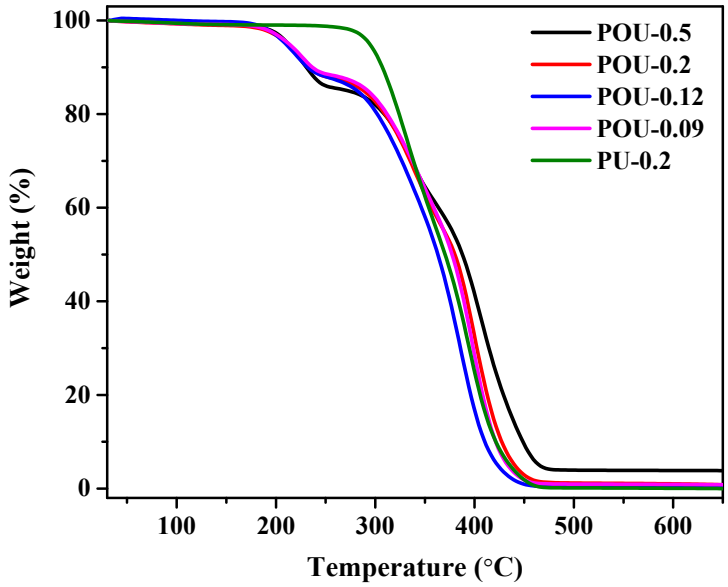

Figure S4. TGA traces of POUs and the control sample PU-0.2 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

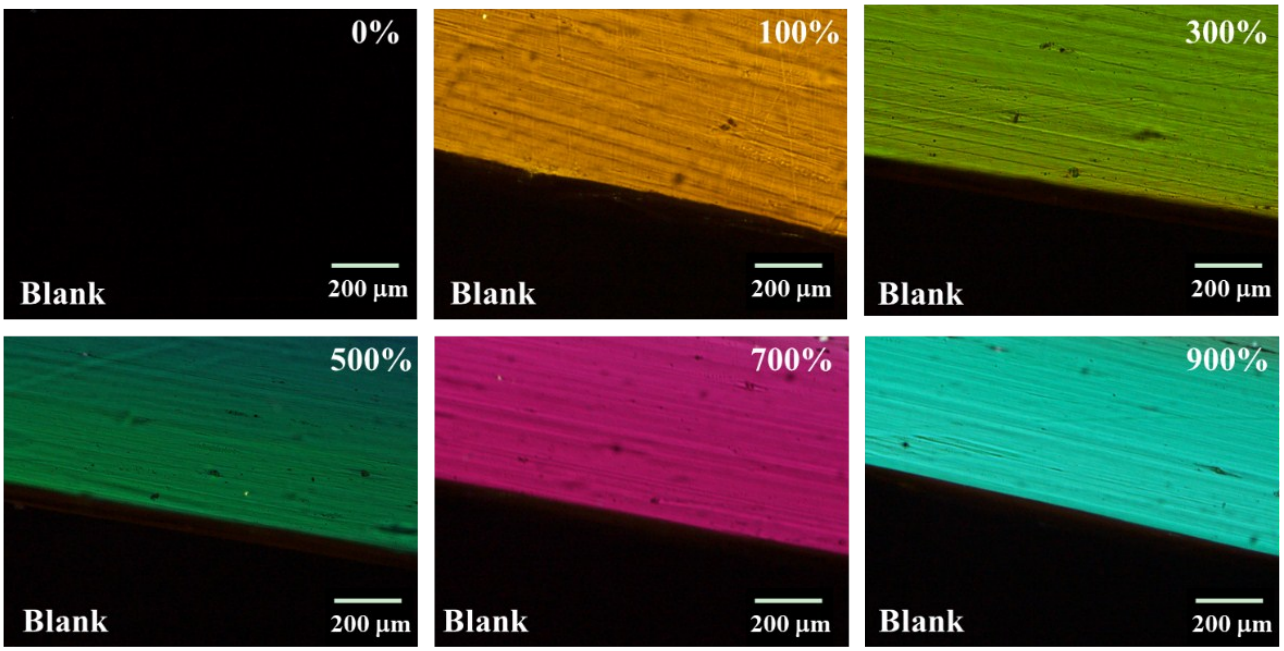

Figure S5. Polarized optical microscopy images of POU-0.2 under various stretch ratios (0%, 100%, 300%, 500%, 700% and 900%) at room temperature. Top right regions are the POU-0.2 samples and bottom left regions are blank.

Figure S5 shows the polarized optical microscopy (POM) images of POU-0.2 under various stretch ratio (0%, 100%, 300%, 500%, 700% and 900%). The POM image is dark before stretched, the material exhibits isotropic properties. After stretched, the materials exhibit anisotropic properties due to strain induced polymer chains orientation and possible crystallization. In addition, interference colors of materials change with the elongation ratio as the anisotropic degree and thickness of the materials are altered.

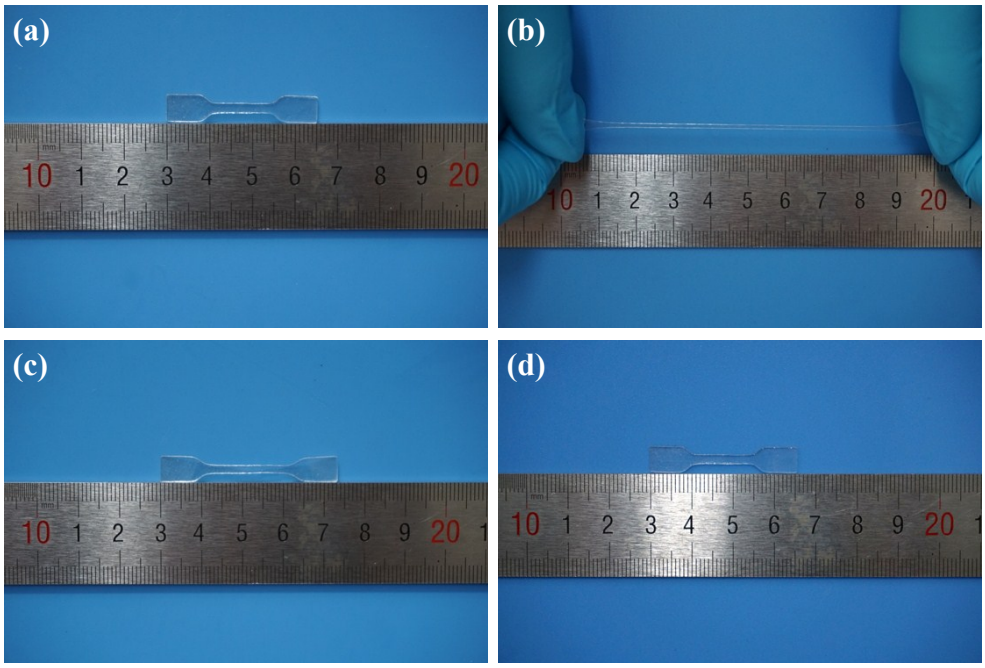

Figure S6. Shape recovery property of POU-0.2: (a) original shape, (b) stretched to ~500%, (c) release the stress, (d) after stored at RT for 12 h.

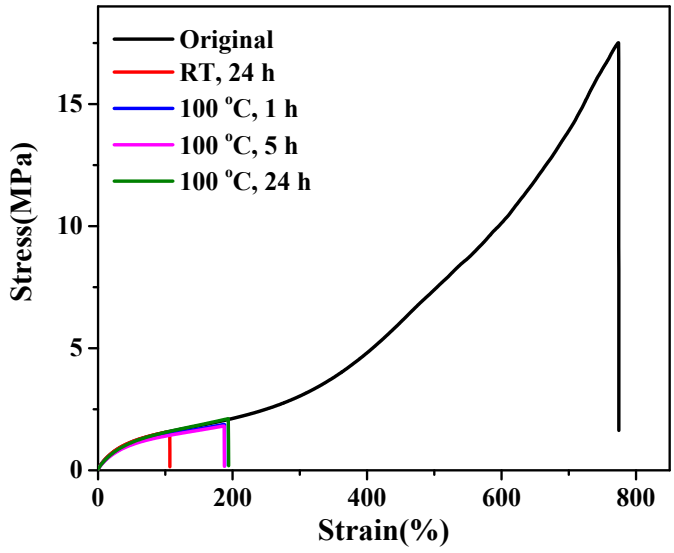

Figure S7. Stress-strain curves of the original and healed PU-0.2.

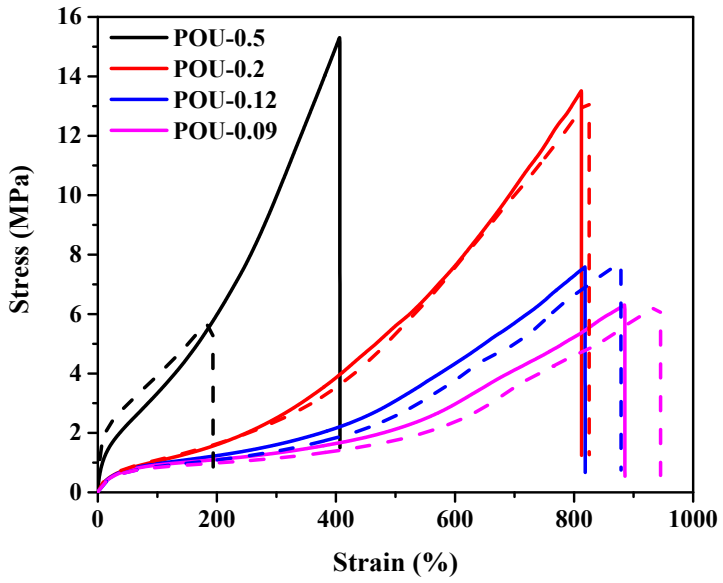

Figure S8. Stress-strain curves of the original (solid line) and healed (dash line) POUs. Healing conditions: POU-0.5 (110 °C, 5 h), POU-0.2 (100 °C, 2 h), POU-0.12 (100 °C, 10 min), POU-0.09 (100 °C, 10 min).

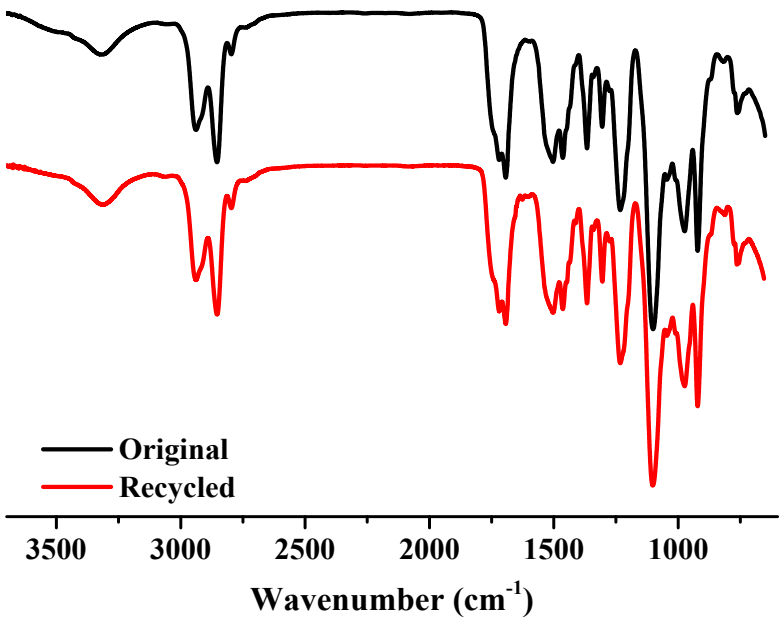

Figure S9. ATR-FTIR spectra of original and recycled POU-0.2.

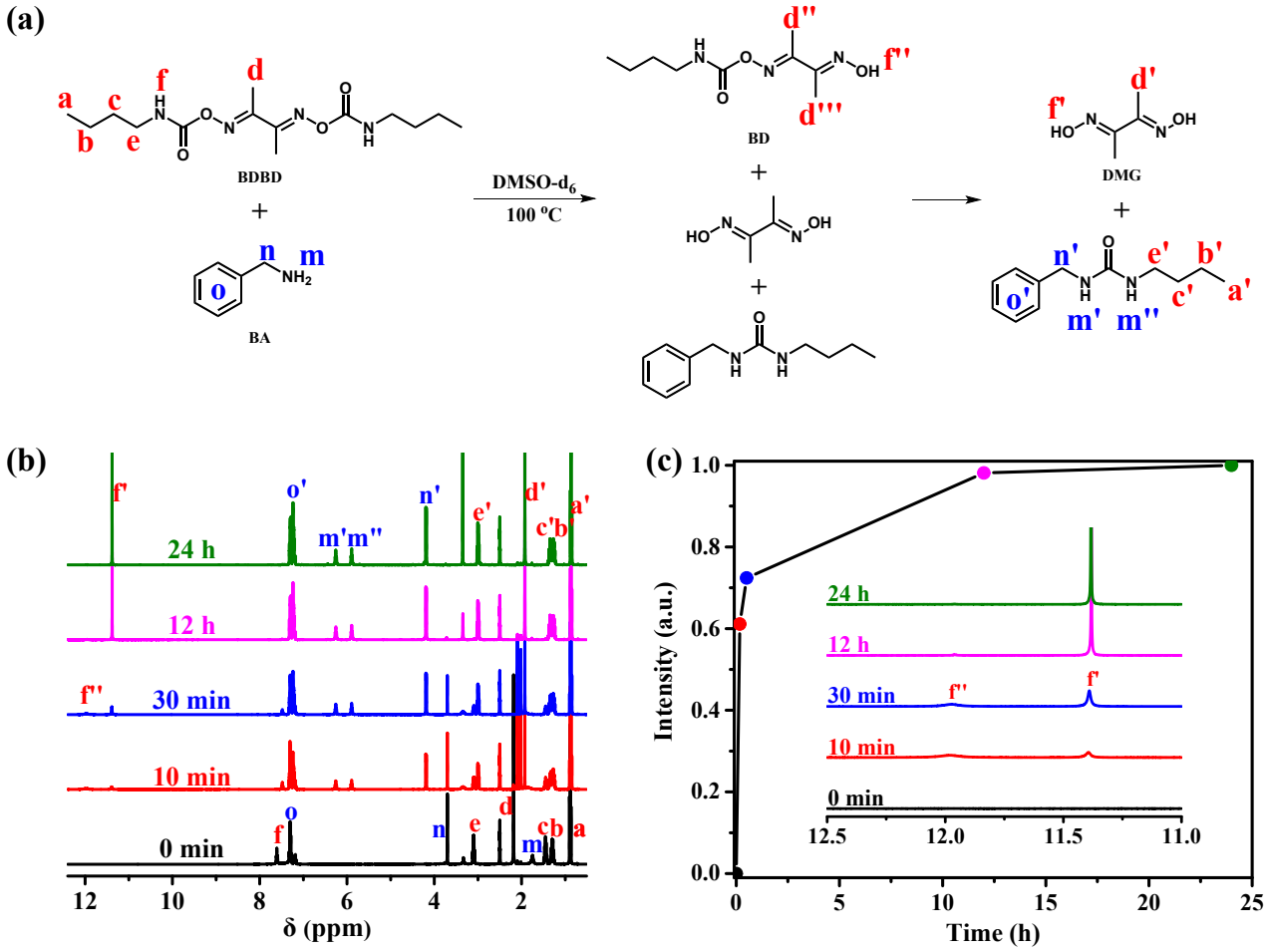

Figure S10. (a) Reaction of the small model molecule 2,3-butane-2,3-dione *O*,*O*-dibutylcarbamoyl dioxime (BDBD) and benzylamine (BA) in DMSO-d_6 with 1:2 molar ratio under 100 °C for various time. (b) ^{1}H NMR spectra of the mixture after reacted for different time. (c) Relative intensity of oxime groups that generated from the reverse reaction of oxime-carbamates, and the insert diagram is the amplification of the ^{1}H NMR spectra.

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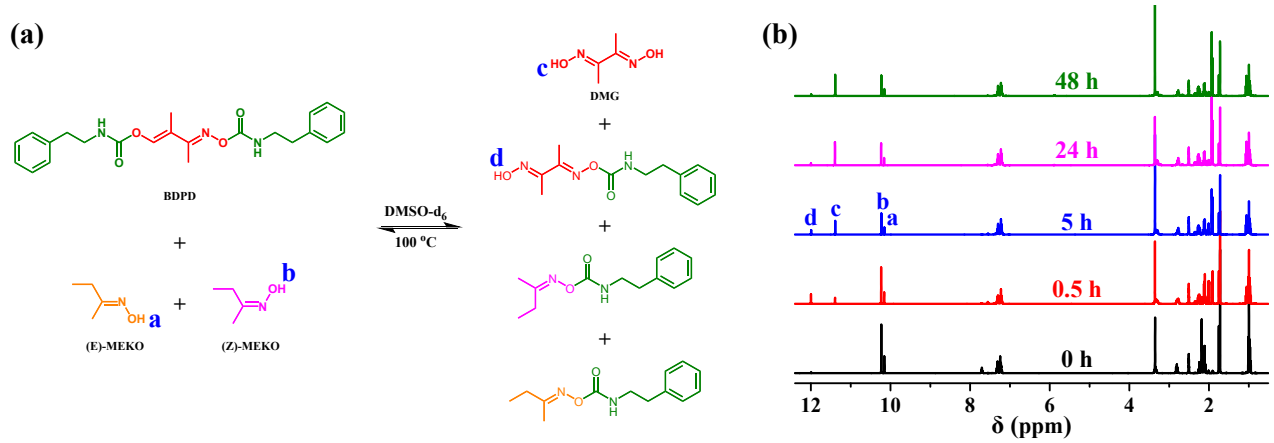

Figure S11. (a) Reaction of the small model molecule 2,3-butane-2,3-dione *O*,*O*-diphenethylcarbamoyl dioxime (BDPD) and 2-butanone oxime (MEKO) in DMSO-d_6 with 1:2 molar ratio under 100 °C for various time. (b) ^{1}H NMR spectra of the mixture after reacted for different time.

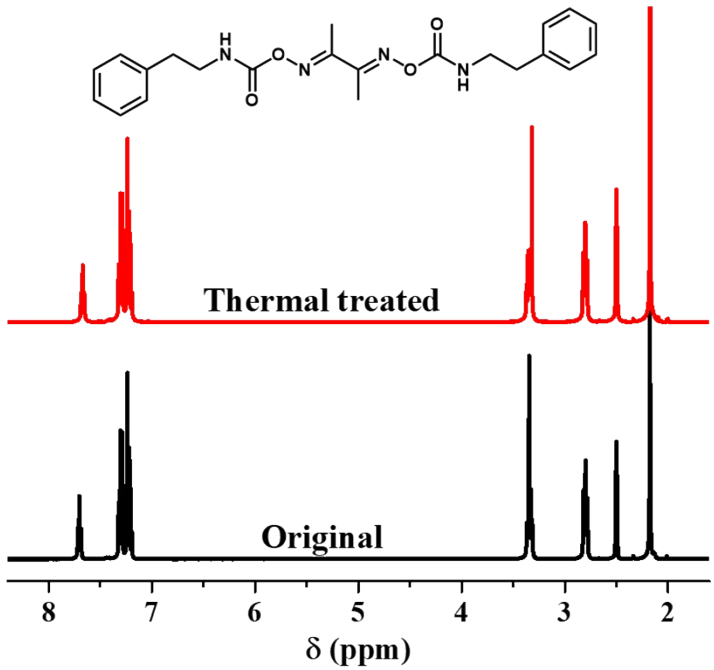

Figure S12. ^{1}H NMR spectra of 2,3-butane-2,3-dione *O*,*O*-diphenethylcarbamoyl dioxime (BDPD) before and after thermal treated under 130 °C for 24 h

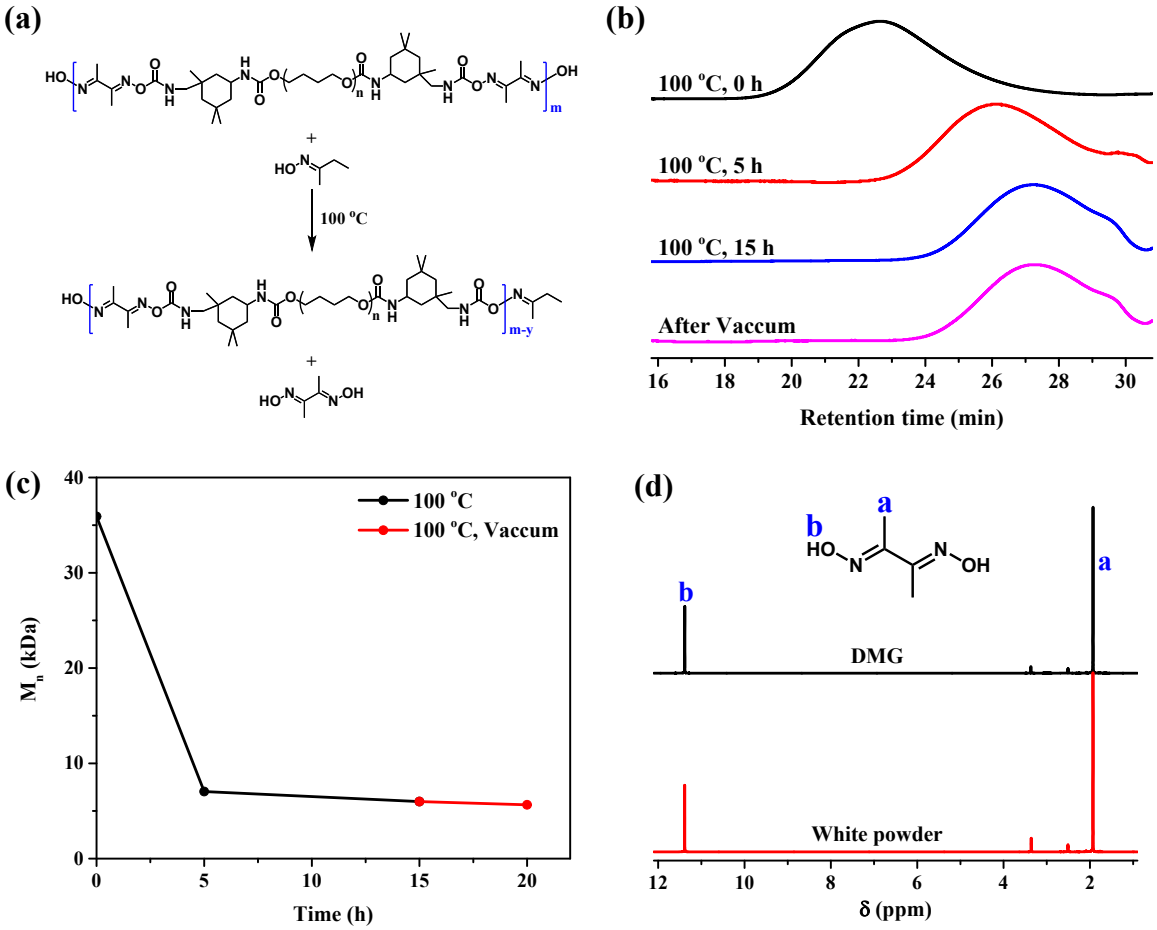

Figure S13. (a) Reaction of linear POU and 2-butanone oxime (MEKO) (~2 equiv to oxime-carbamate bonds in the linear POU) at 100 °C. (b) GPC traces and (c) molecular weight of the mixture after heated at 100 °C for various time and vacuum distilled at 100 °C for 5 h. (d) The ^{1}H NMR spectra comparison of the white powder with DMG's.

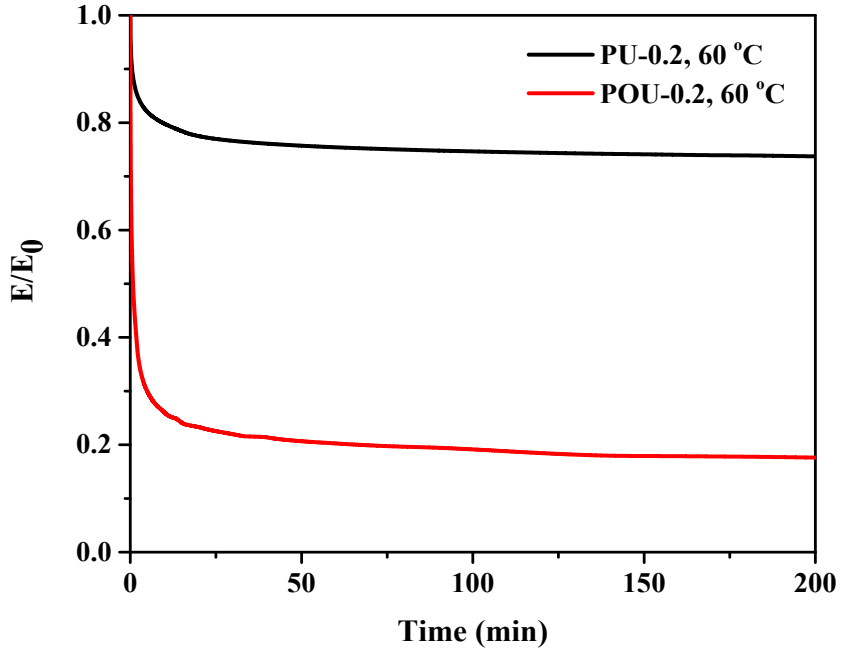

Figure S14. Normalized stress relaxation curves of PU-0.2 and POU-0.2 at 60 °C.

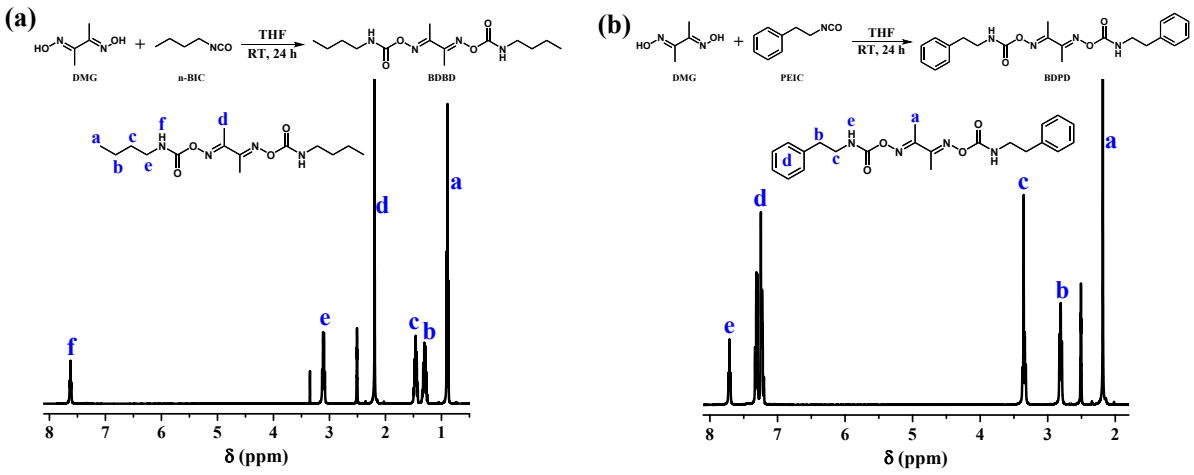

Figure S15. Synthetic routs and ^{1}H NMR spectra of (a) 2,3-butane-2,3-dione *O*,*O*-dibutylcarbamoyl dioxime (BDBD) and 2,3-butane-2,3-dione *O*,*O*-diphenethylcarbamoyl dioxime (BDPD) .