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Supporting information for

PHEMA hydrogel films crosslinked with dynamic disulfide bonds:

synthesis, swelling-induced mechanical instability and self-healing

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**Fig. S1.** The experimental setup for crosslinking PHEMA films using  $H_2O_2$  vapor. Temperature was controlled at 60°C using a circulator.



Fig. S2. GPC curves of the P(HEMA-ATEMA) copolymers.



**Fig. S3.** A PHEMA film dissolves in DMF. The film was fabricated using linear PHEMA polymer without pendant thiol groups. It was treated with  $H_2O_2$  vapor in the same way with P(HEMA-MEMA) film. The result suggests the film can not be crosslinked by  $H_2O_2$  without thiol groups. The film was dyed with methylene blue to make it visible.



**Fig. S4.** (A) Raman spectra (–S-S- region) s of a P(HEMA-MEMA)-10.0 film before and after treated with  $H_2O_2$  vapor. (B, C) Analysis of the Raman spectra data before (B) and after  $H_2O_2$  treatment (C) using Lorentzian profiles. Black lines: the observed spectra; green lines: individual Lorentzian profiles; red lines: fitted Lorentzian profiles. The peak centered at 525 cm<sup>-1</sup> was assigned to the -S-S- bond. The peak center at 600 cm<sup>-1</sup> was used as reference. After  $H_2O_2$  treatment, the amount of

-S-S- in the film increases by a factor of 1.69. (Ref: M. Gosselin, C. J. Kapustij, U. D. Venkateswaran, V. R. Leverenz and F. J. Giblin, Raman spectroscopic evidence for nuclear disulfide in isolated lenses of hyperbaric oxygen-treated guinea pigs. Experimental Eye Research, 2007, 84, 493-499.)

## Legends for Supplementary Movies S1-2:

## Supplementary Movie S1 :

Evolution of surface morphology of a PHEMA film crosslinked with disulfide bonds. The film was prepared from P(HEMA-MEMA)-5.0. The thickness of the original dry film was 360  $\mu$ m. The solvent was 30% ethanol/water mixture. The whole process lasted for ~9 h. The instability patterns generated on the gel surface continued to change and finally vanished.

## Supplementary Movie S2:

Evolution of surface morphology of a PHEMA film crosslinked with regular covalent bonds. The film was synthesized according to Ref.[14] using EGDMA as crosslinker. The thickness of the original dry film was 880  $\mu$ m. The solvent was 30% ethanol/water mixture. The whole process lasted for ~12 h. The instability patterns generated on the gel surface stopped changing in ~ 4 h.