Supporting Information

Water-adaptive and Repeatable Self-healing Polymers Bearing Bulky Urea Bond

J. I. Park[a], A. Choe[b], M. P. Kim,[b] H. Ko[b], T. H. Lee[c], S. M. Noh[c], J. C. Kim*[c] and I. W. Cheong*[a]*

[a]Department of Applied Chemistry, Kyungpook National University, Buk-gu, Daehak-ro 80, Daegu 41566, Republic of Korea
[b]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea
[c]Research Center for Green Fine Chemicals, Korea Research Institute of Chemical Technology, Ulsan, 44412, Republic of Korea

Table S1. Percent recoveries in relation to toughness, strain, and stress of the control (PH-HDI) and self-healing polymers (PtB-HDI, PtB-IPDI) obtained from the stress-strain curves shown in **Fig. 4**

Sample ID	Percent recovery ratio [%R][a)								
	PH-HDI			PtB-HDI			PtB-IPDI		
	Toughness[b)]	Strain	Stress	Toughness	Strain	Stress	Toughness	Strain	Stress
Virgin	100	100	100	100	100	100	100	100	100
1 day	7.1	13.1	34.3	45.0	54.7	54.8	26.8	33.8	54.1
2 days	5.3	11.5	27.4	73.7	67.8	79.2	43.1	71.4	52.6
3 days	5.3	14.8	19.3	75.6	68.9	89.5	46.7	65.7	62.1
4 days	2.8	6.9	33.4	97.1	89.1	94.9	71.8	87.3	75.4

[a)] The percent recoveries (%Rs) were calculated based on the physical properties of the virgin sample. [b)] Energy per unit volume absorbed during deformation until destroyed, as calculated from the area of the corresponding stress-strain curve.

Single-scratch testing of self-healing polymers using a razor blade

A microstage equipped with a width (or depth)-controllable razor blade was used to make scratches of the same width (or depth) on polymer-film specimens. Due to the different viscoelastic properties of the polymer films, width vs. blade load was first studied and calibrated. The optical, topographical, and corresponding height profiles observed by AFM are shown in **Fig. S1a–c**, respectively. In this work, scratches of approximately 2 μm wide were made on PH-HDI, PtB-HDI, and PtB-IPDI, with 0.08, 0.48, and 0.24 N load forces, respectively.

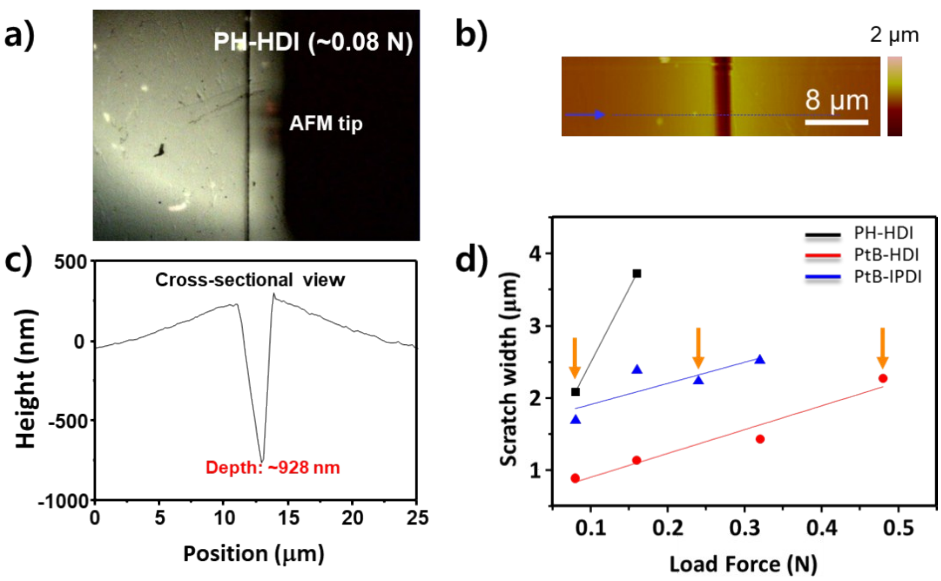

Fig. S1. a) A typical AFM image of a singly scratched PH-HDI polymer sample. b) The corresponding AFM topograph of the sample shown in a). c) The height profile obtained from the polymer surface shown in b). d) Calibration plots of scratch width (μm) against blade load force (N) in order to obtain scratches of similar width for each polymer surface. The yellow arrows in d) indicate the target scratch width (~2 μm).

Transparency of self-healing polymers and control polymer

Prepolymer and crosslinker solutions were prepared separately and then mixed together for crosslinking as mentioned in the main text (experimental section). Before curing, mixture was poured onto a slide glass. The reaction was maintained at room temperature (RT) under ambient conditions for 2 h and 60 ^{o}C oven for 1 day. Film thickness was ca. 30 μm. A bare slide glass was used as background.

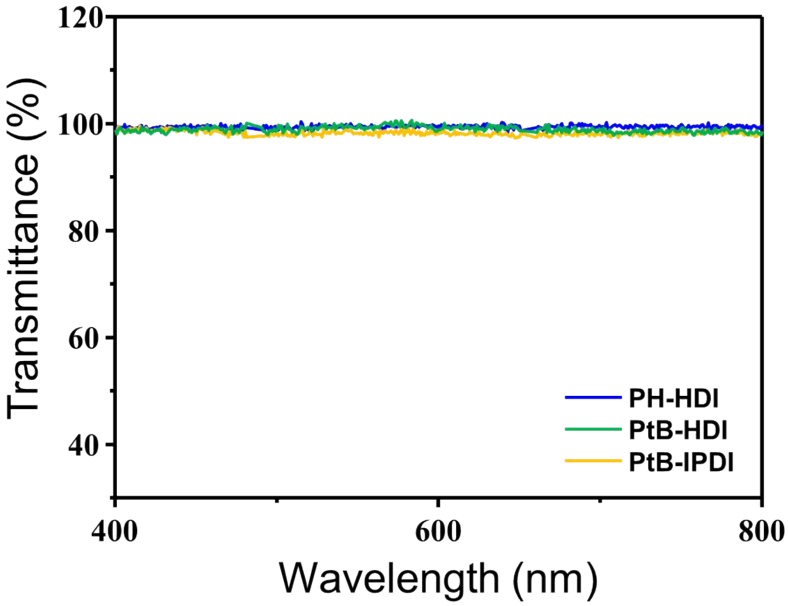

Fig. S2. Transmittance of self-healing and control polymers. All the polymers show ca. 99% of transmittance in the range of 400-700 nm wavelength.

Repetitive self-healing behavior under water

To evaluate the repetitive self-healing performance, the experimental setup shown in **Fig. S3** was used. Identical single scratches were made at the same location multiple times (eight times in this work). After scratching, a water droplet was placed onto the scratched region for 1 h, after which the remaining water was gently removed with a paper tissue. No AFM width data were obtained since the specimen could not be moved; optical images were taken instead.

Fig. S3. Photograph of the experimental set up for the repetitive scratch testing of the self-healing polymers under water. The yellow dashed circle highlights the water droplet at the region where the single-scratch is made.

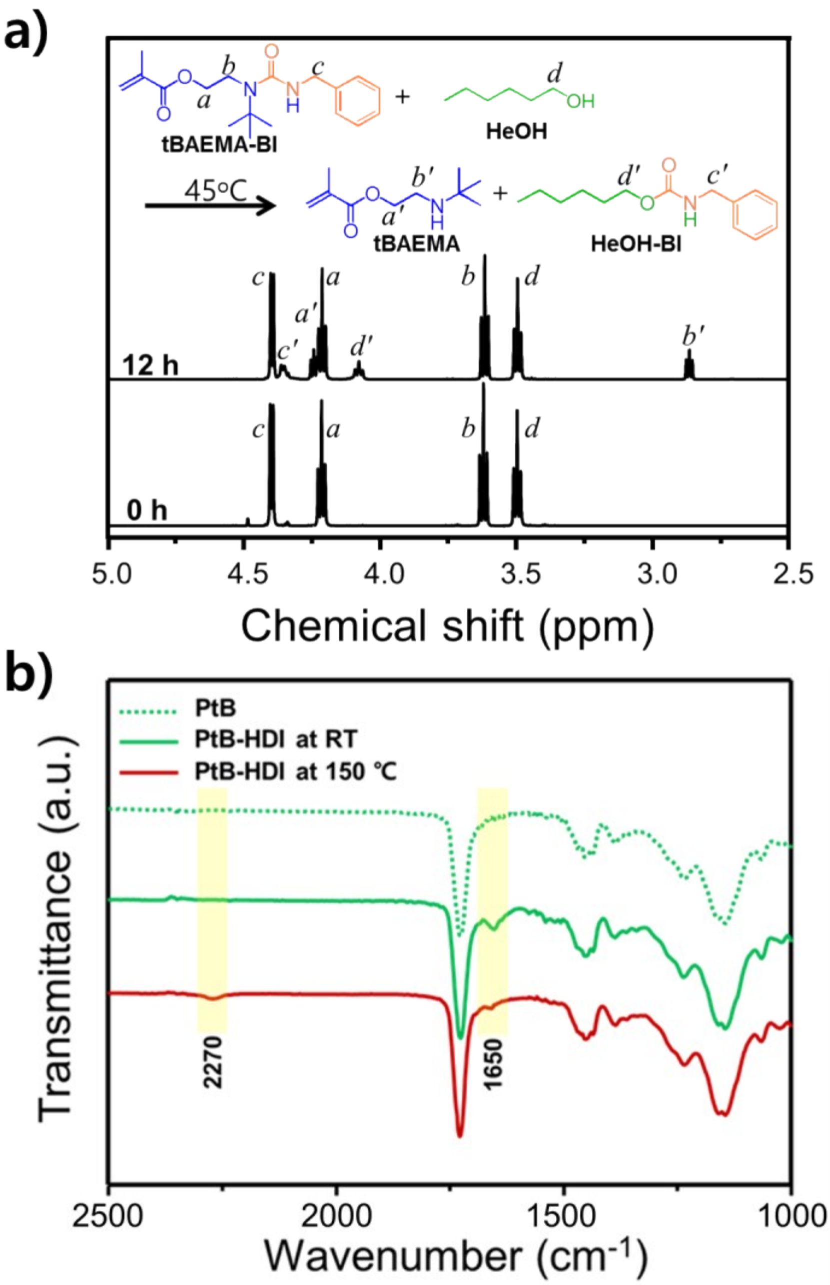

Fig. S4. a) ^{1}H-NMR spectra of the solution mixture of tBAEMA-BI and HeOH at immediately and aged at 45 °C for 12 h. b) FT-IR spectra of PtB-HDI self-healing polymer before and heating to 150 °C (PtB prepolymer was also shown for comparison).

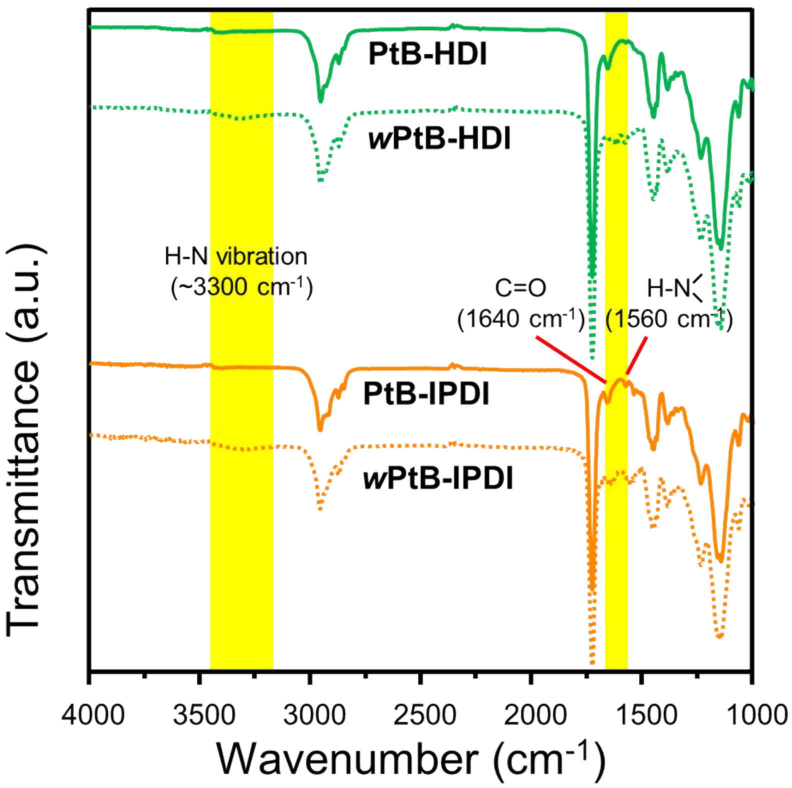

Fig. S5. FT-IR spectra of pristine (PtB-HDI, PtB-IPDI) and annealed (*w*PtB-HDI, *w*PtB-IPDI) self-healing polymers after aging in water at 60 °C for three weeks.