## **Electronic Supplementary Information**

## Enhanced Thermomechanical Property of Self-healing Polymer via Self-

## assembly of Reversibly Crosslinkable Block Copolymer

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**Scheme S1**. (a) Chemical structures of PtB and PH matrix polymers, (b) synthesis of PtB-CPDT of macro-RAFT agent, and (c) synthesis of PtB-*b*-P4VP block copolymer.



**Figure S1.** Photographic images for solvent solubilities of PtB and P4VP homopolymers in MEK, CHCl<sub>3</sub> or DMF. The vertical white line seen on the vial in the photo is LED backlight. P4VP is not soluble in MEK and CHCl<sub>3</sub>, so the solutions under a LED light are opaque.



Figure S2. Representative GISAXS patterns of (a) HSP0, (b) HSP33, (c) HSP50 and (d) HSP100 thin film samples meaured using syncrotron ligh source of  $\lambda = 1.223$  nm. (e) 1-D in-plain profiles extracted along  $q_z = 0.16$  nm<sup>-1</sup> from the GISAXS pattern of Figure S2(a-d).



**Figure S3.** Transmittance of thin coatings of HSP0~100 and PH0 on glass plate measured at 600 nm wavelength.



**Figure S4.** Load–displacement curves for of PH0 and HSP0~100 as recorded in nano-indentation measurements.



**Figure S5.** OM images (left), AFM images (middle), and corresponding height profiles (right) of single-scratch self-healing tests for HSP0 at 25, 55, and 75 °C.



**Figure S6.** OM images (left), AFM images (middle), and corresponding height profiles (right) of single-scratch self-healing tests for HSP33 at 25, 55, and 75 °C.



**Figure S7.** OM images (left), AFM images (middle), and corresponding height profiles (right) of single-scratch self-healing tests for HSP50 at 25, 55, and 75 °C.



**Figure S8.** OM images (left), AFM images (middle), and corresponding height profiles (right) of single-scratch self-healing tests for HSP100 at 25, 55, and 75 °C.



**Figure S9.** OM images (left), AFM images (middle), and corresponding height profiles (right) of single-scratch self-healing tests for PH0 at 25, 55, and 75 °C.



**Figure S10.** Self-healing efficiency (%SHE) values of HSP0~100 and PH0 obtained from the width changes in single-scratch self-healing tests at 25, 55, and 75 °C.



Figure S11. Stress-strain curves for uncut (in black) and self-healed specimens (in red) of (a) HSP0,(b) HSP33, (c) HSP50, (d) HSP100, and (e) PH0 after crosscut and rebonding.