Redox Responsive Behavior of Thiol/Disulfide-Functionalized Star Polymers Synthesized via Atom Transfer Radical Polymerization

Jun Kamada, ^{1,2} Kaloian Koynov, ³ Cathrin Corten, ⁴ Azhar Juhari, ³ Jeong Ae Yoon, ² Marek W. Urban, ⁴

Anna C. Balazs⁵ and Krzysztof Matyjaszewski²,*

 $^{\rm 1}$ Material Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265,

Japan

² Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania
15213, USA

³ Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

⁴ School of Polymers and High Performance Materials, Shelby F. Thames Polymer Science Research Center, The University of Southern Mississippi, 118 College Drive, Hattiesburg, Mississippi 39406, USA

⁵ Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, USA

*Corresponding author: Tel +1-412-268-3209; e-mail km3b@andrew.cmu.edu

X-ray Scattering. Wide-angle and small-angle X-ray scattering (WAXS and SAXS) measurements were performed using an 18 kW rotating anode X-ray source (Rigaku, RA-Micro 7) with a pinhole collimation and a two-dimensional detector (Bruker, Highstar) with 1024×1024 pixels. A double graphite monochromator for the Cu K α radiation ($\lambda = 0.154$ nm) was used and the beam diameter was about 0.8 mm. The recorded 2-D scattered intensity distributions were integrated over the azimuthal angle and are presented as a function of the scattering wave vector ($q = (4\pi/\lambda)\sin(2\theta/2)$, where 2θ is the scattering angle).

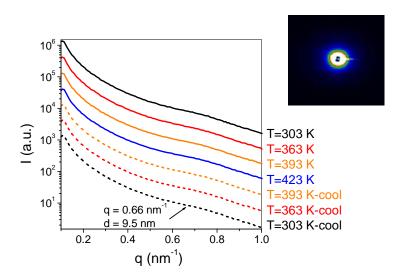


Figure S1. SAXS spectra of SS cross-linked star (SS3) at various temperature.

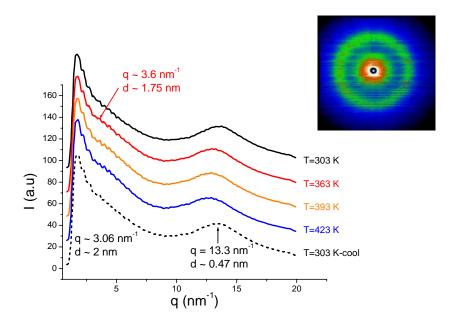


Figure S2. WAXS spectra of SS cross-linked star (SS3) at various temperature.

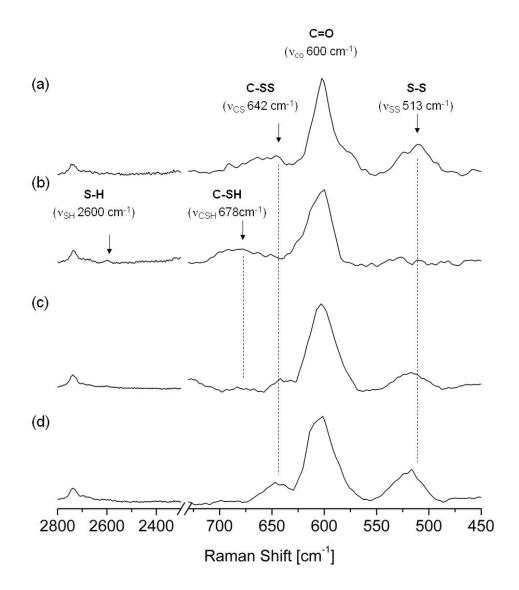


Figure S3. Raman spectra of SH/SS-star polymers; (a)SS-star (SS3), (b)Degraded star (*r*-SS3), (c) Re-linked star (conversion: 50%) and (d) Re-linked star (*r*,*o*-SS3; conversion 86%). Reduction condition: In 0.5 M solution of *n*-Bu₃P in THF at room temperature for 12 h. Oxidation condition: In 5 mM solution of FeCl₃ in CHCl₃/THF (80:20 v/v) at room temperature for 12 h (c) or 24 h (d).