Supporting information for:

A Robust Cross-linking Strategy for Block Copolymer Worms Prepared via Polymerization-Induced Self-Assembly

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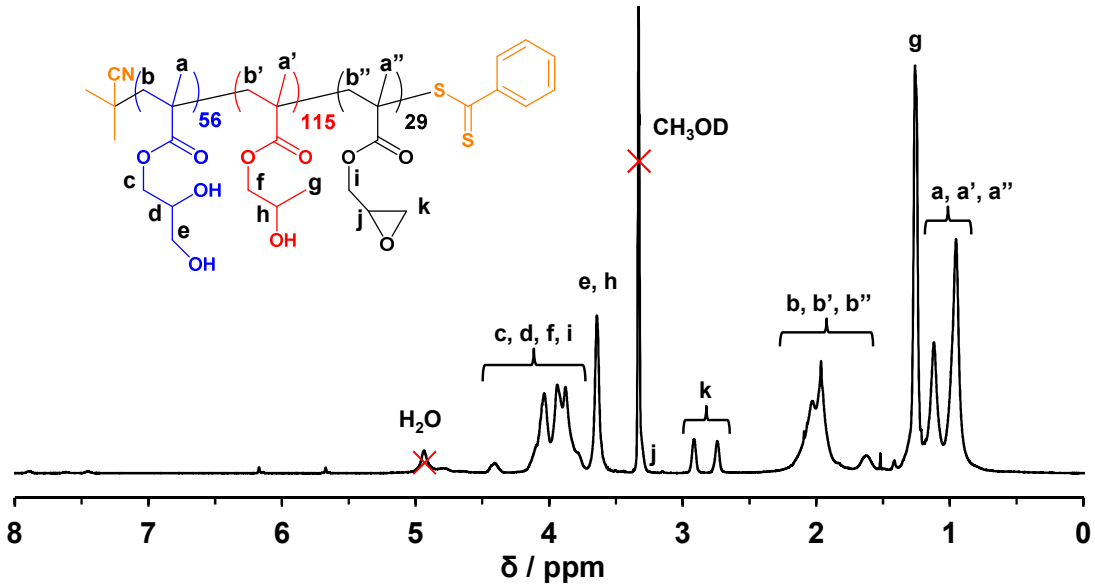

Figure S1. Assigned ^{1}H NMR spectra (CD_3OD) recorded for a $PGMA_{56}$-P($HPMA_{115}$-*stat*-$GlyMA_{29}$) diblock copolymer after reaching 98 % conversion after 105 min at 50°C. Comparing the integrated **k** protons with **g** protons indicated that 98% epoxide groups survived these polymerization conditions.

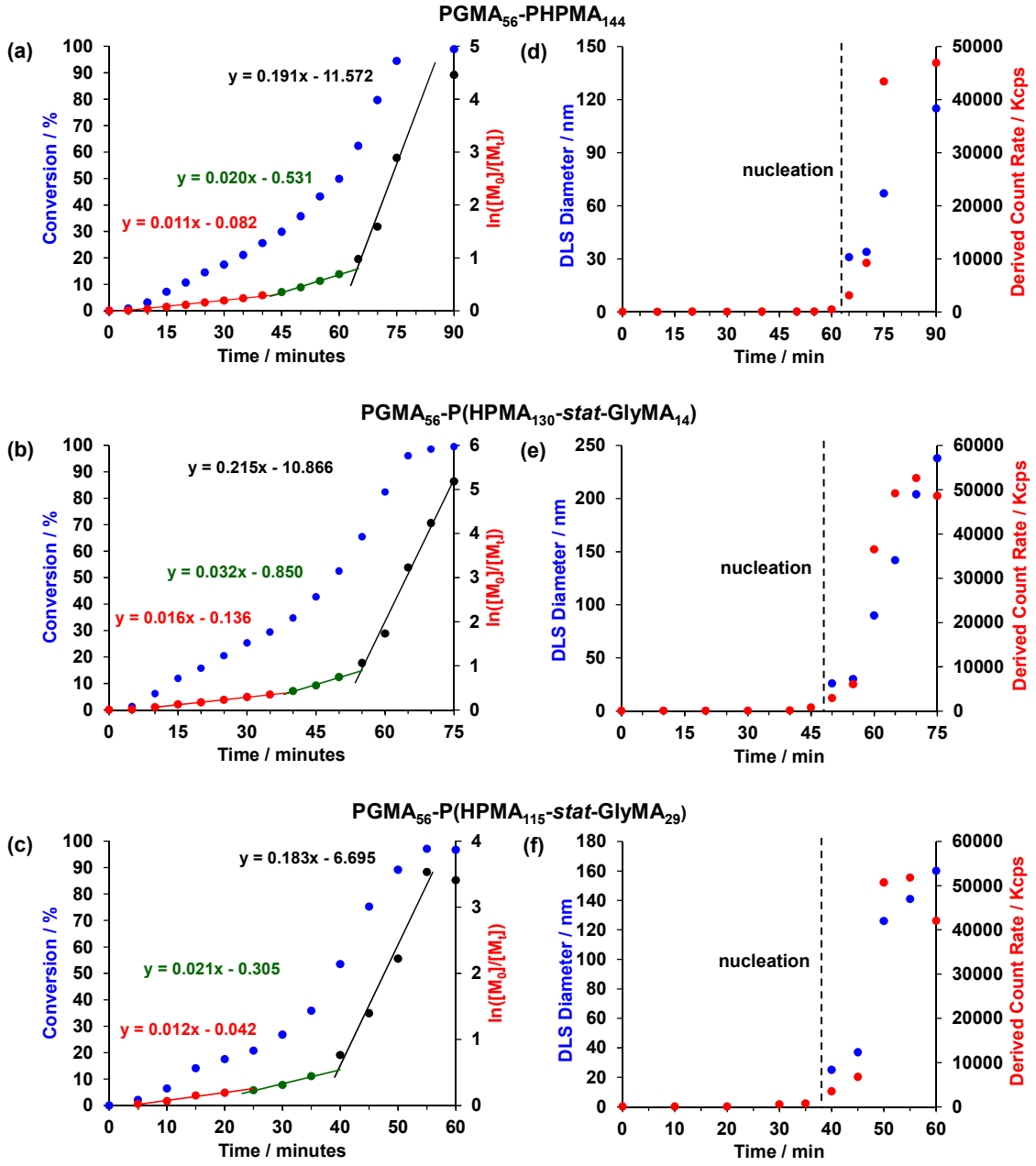

Figure S2. Conversion (calculated by ^{1}H NMR) and semi-logarithmic plots versus time for the chain extension of a $PGMA_{56}$ macro-CTA with varying amounts of HPMA and GlyMA at 70 °C and at 15 % w/w solids for (a) $PGMA_{56}$-$PHPMA_{144}$; (b) $PGMA_{56}$-P($HPMA_{130}$-*stat*-$GlyMA_{14}$) and (c) $PGMA_{56}$-P($HPMA_{115}$-*stat*-$GlyMA_{29}$). The DLS diameters and derived count rate versus time for the same diblock copolymers are shown in (d), (e) and (f) respectively. The onset of micellar nucleation (see dashed lines) was arbitrarily judged to be when the derived count rate exceeded 2500 Kcps. This time point is in good agreement with the ten-fold rate enhancement indicated by the semi-logarithmic plots. DLS diameters (blue data) are only shown after micellar nucleation.

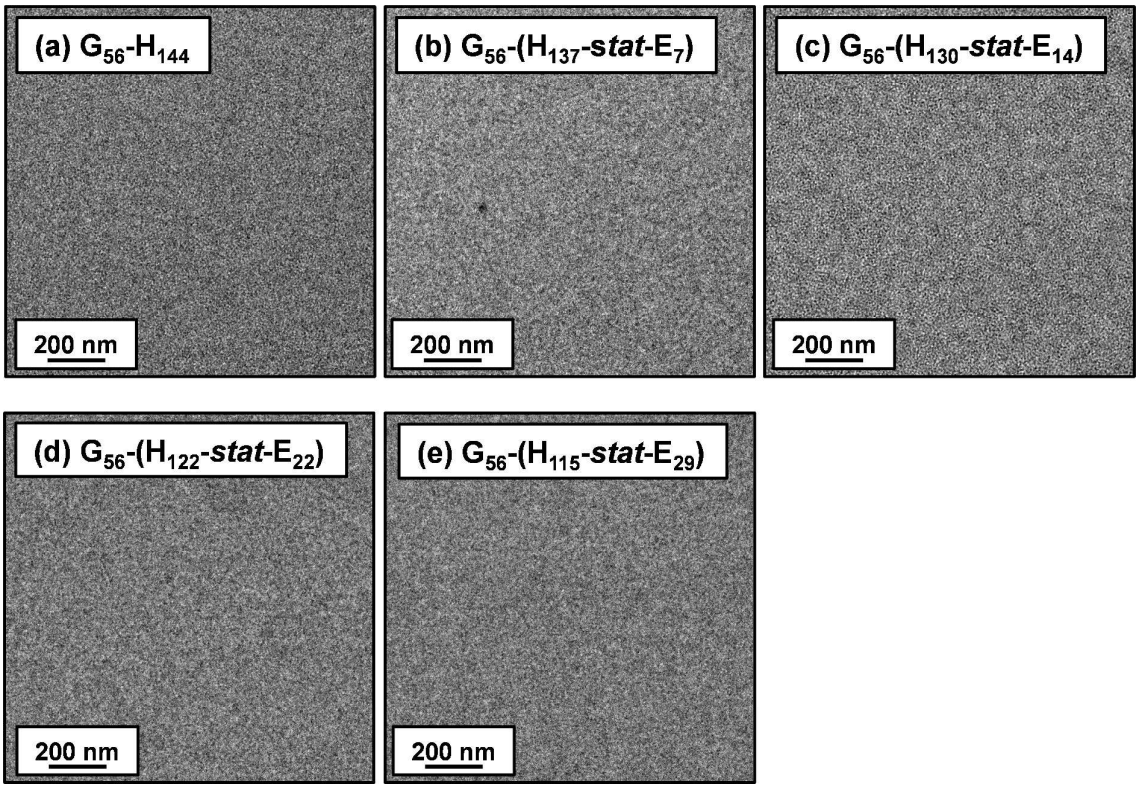

Figure S3. Representative TEM images obtained for $PGMA_{56}$-P($HPMA_y$-*stat*-$GlyMA_z$) diblock copolymers after dilution to 0.1 % w/w in methanol prior to cross-linking (where y + z = 144; these copolymers are denoted as G_{56}-(H_y-*stat*-E_z) for brevity). These featureless images confirm molecular dissolution of the copolymer chains under these conditions.

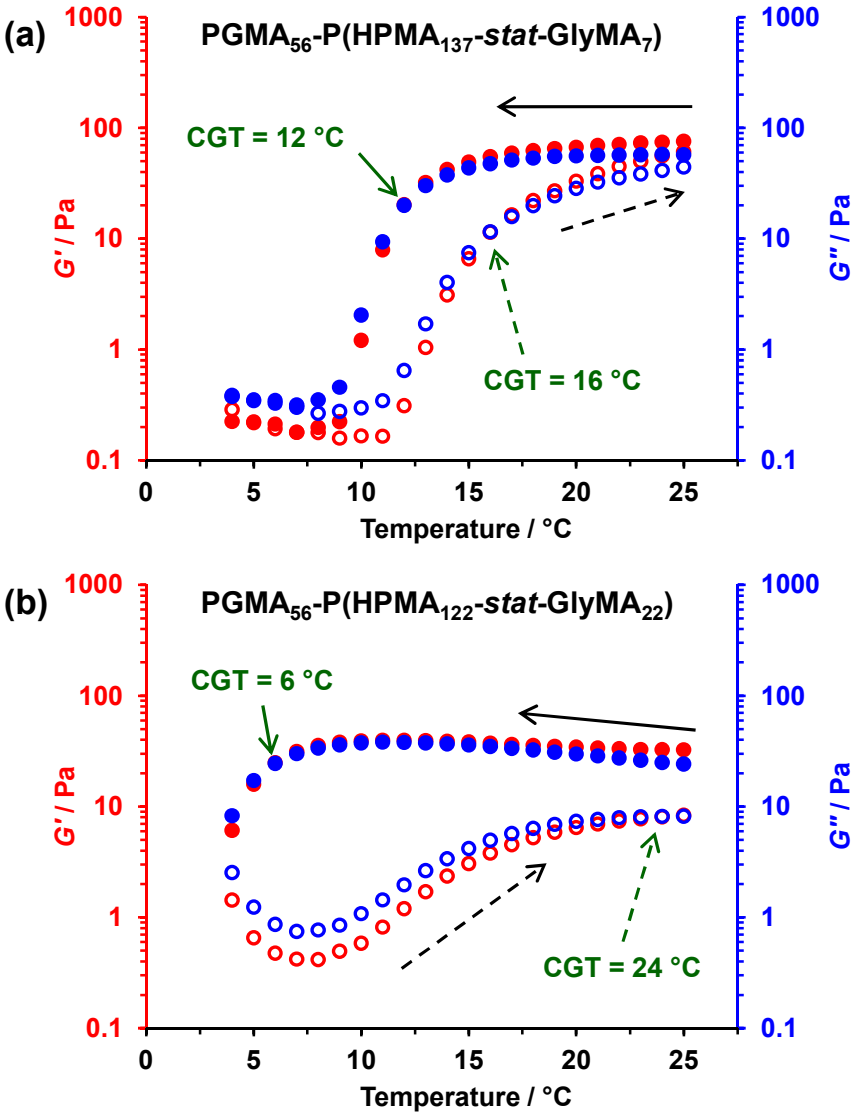

Figure S4. Variation of the storage modulus (*G'*, red circles) and the loss modulus (*G"*, blue circles) as a function of temperature (closed circles denote the 25 °C to 5 °C temperature sweep and open circles denote the 5 °C to 25 °C temperature sweep) for a 7.5 % w/w aqueous dispersion of (a) $PGMA_{56}$-P($HPMA_{137}$-*stat*-$GlyMA_7$) and (b) $PGMA_{56}$-P($HPMA_{122}$-*stat*-$GlyMA_{22}$) prior to cross-linking. Conditions: an angular frequency of 1.0 rad s^{-1} at an applied strain of 1.0 % and a temperature ramp of 0.5 °C min^{-1}.

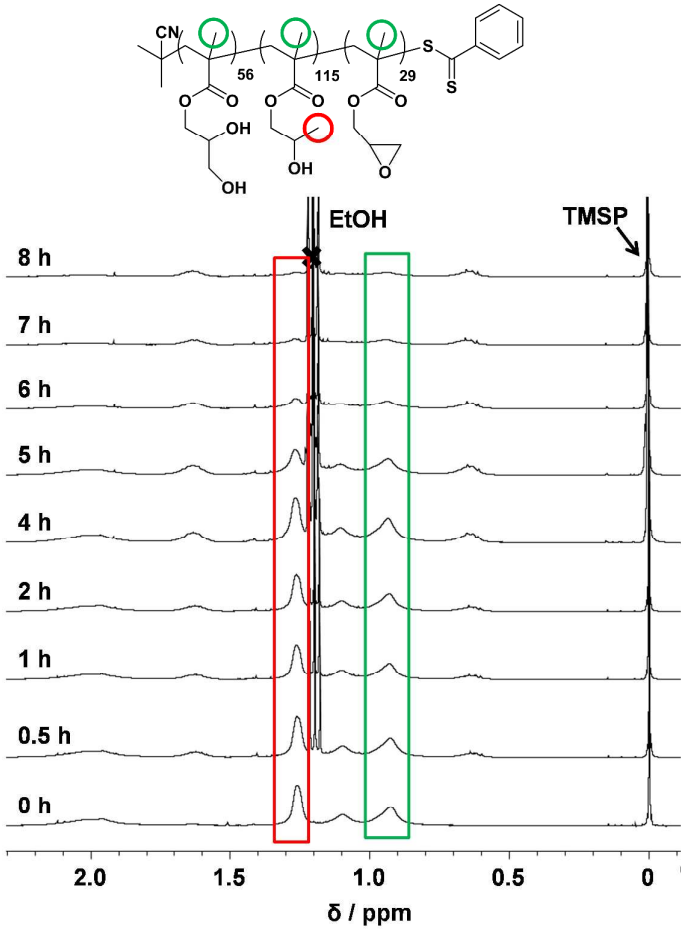

Figure S5. (a) ^{1}H NMR spectra obtained at various time points for the kinetics of the cross-linking of $PGMA_{56}$-P($HPMA_{115}$-*stat*-$GlyMA_{29}$) as indicated by the attenuation of the pendent methyl groups in the HPMA residues (see red box at 1.2 ppm) or the attenuation in the methyl groups assigned to the copolymer backbone (see green box at 0.9 ppm) normalized to TMSP.

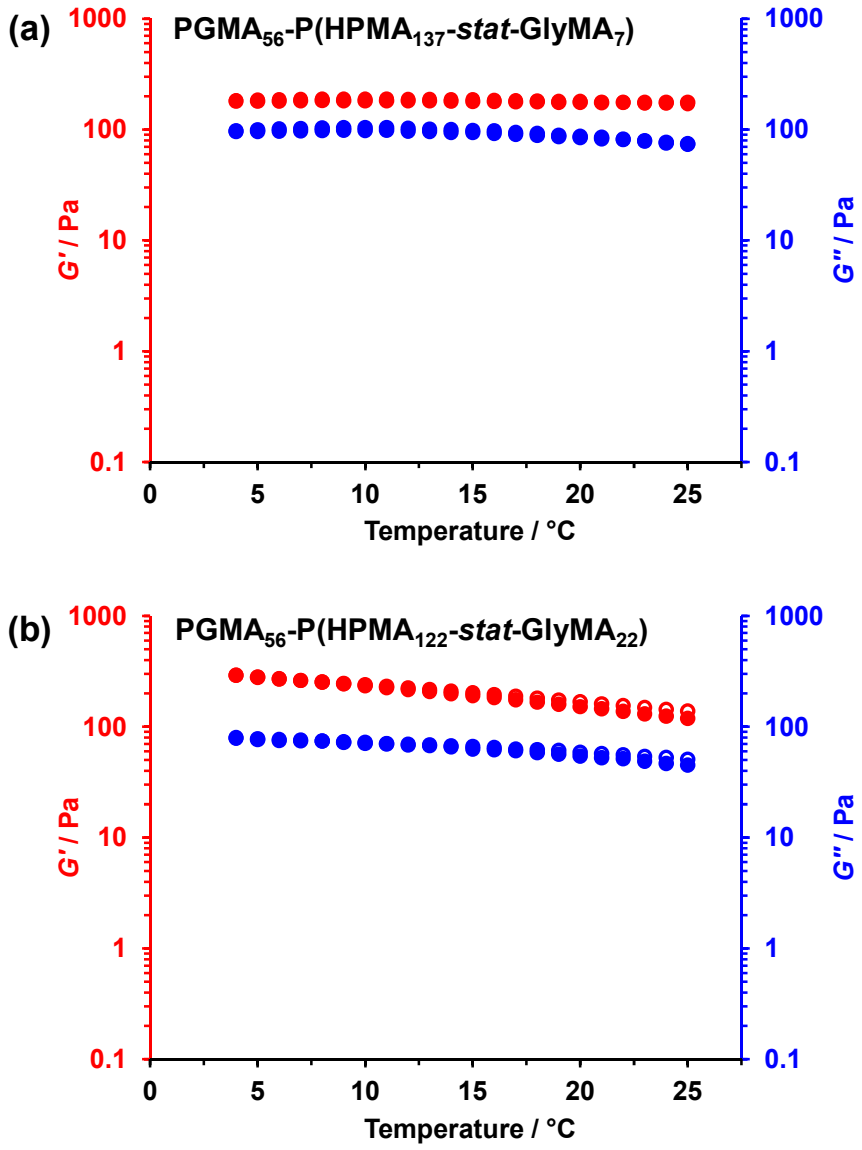

Figure S6. Variation of the storage modulus (*G'*, red circles) and the loss modulus (*G"*, blue circles) as a function of temperature (closed circles denote the 25 °C to 5 °C temperature sweep and open circles denote the 5 °C to 25 °C temperature sweep) for a 7.5 % w/w aqueous dispersion of (a) $PGMA_{56}$-P($HPMA_{137}$-*stat*-$GlyMA_7$) and (b) $PGMA_{56}$-P($HPMA_{122}$-*stat*-$GlyMA_{22}$) after cross-linking. Conditions: an angular frequency of 1.0 rad s^{-1} at an applied strain of 1.0 % and a temperature ramp of 0.5 °C min^{-1}.

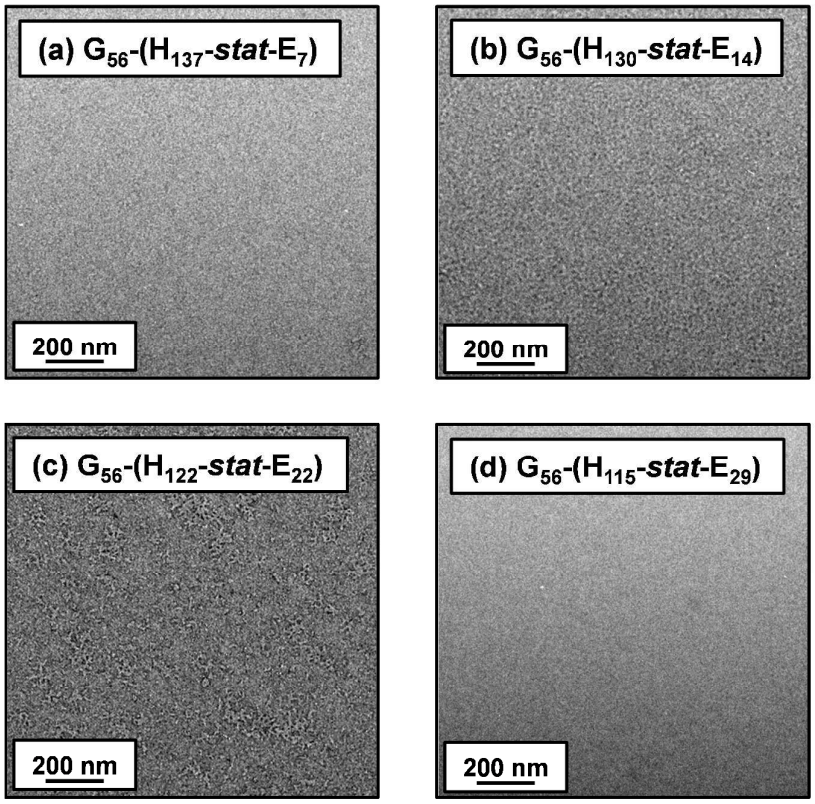

Figure S7. Representative TEM images obtained for $PGMA_{56}$-P($HPMA_y$-*stat*-$GlyMA_z$) diblock copolymers after dilution to 0.1 % w/w copolymer in a 1.0 % w/w aqueous SDS solution (1:10 copolymer/SDS mass ratio) prior to cross-linking (where y + z = 144; these copolymers are denoted as G_{56}-(H_y-*stat*-E_z) for brevity). These featureless images confirm molecular dissolution of the copolymer chains under these conditions.