Supplementary Information

Stimuli-Responsive Dendronized Polymeric Hydrogels through Schiff-Base Chemistry Showing Remarkable Topological Effects

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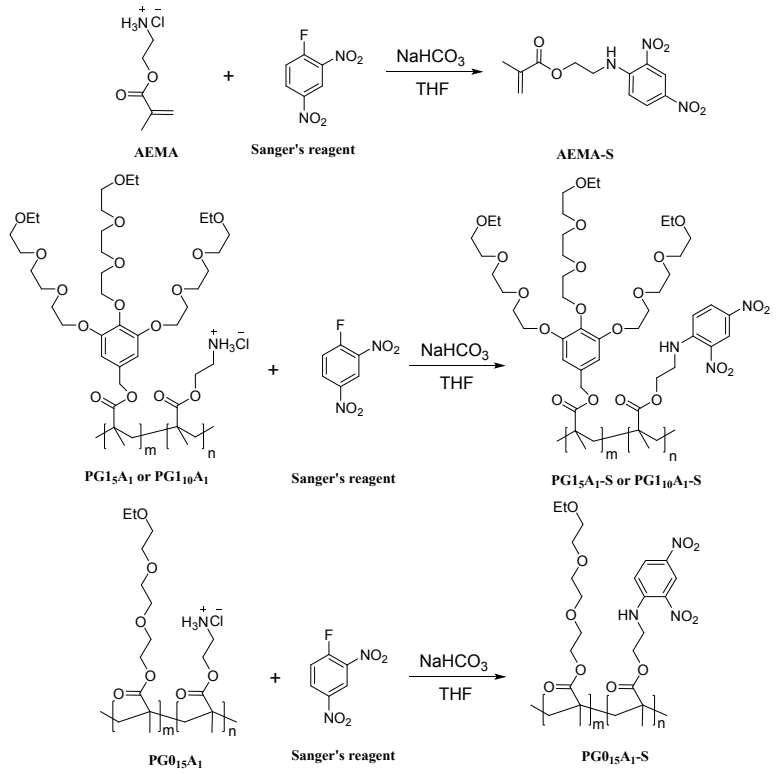

Scheme S1 Synthetic routes for Sanger's reagent modified monomers **AEMA-S** and its corresponding copolymers **PG1A-S** and **PG0A-S**.

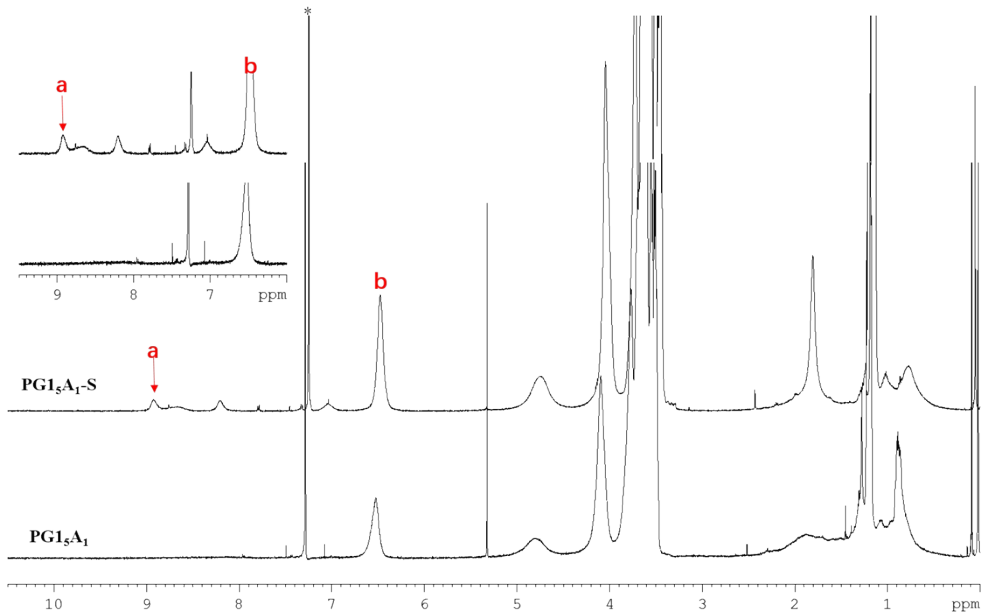

Fig. S1 ^{1}H NMR spectra of copolymers **$PG1_5A_1$** and **$PG1_5A_1$-S** in $CDCl_3$ at room temperature. The signals from $CDCl_3$ are marked as *.

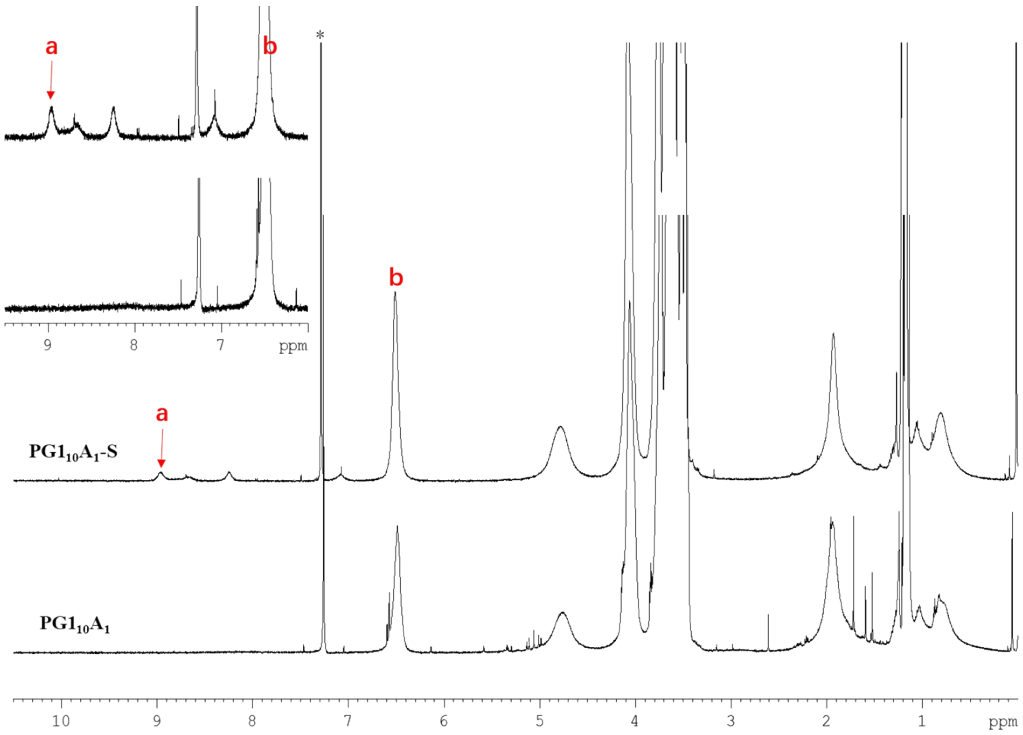

Fig. S2 ^{1}H NMR spectra of polymers **PG1$_{10}$A$_1$** and **PG1$_{10}$A$_1$-S** in $CDCl_3$ at room temperature. The signals from $CDCl_3$ are marked as *.

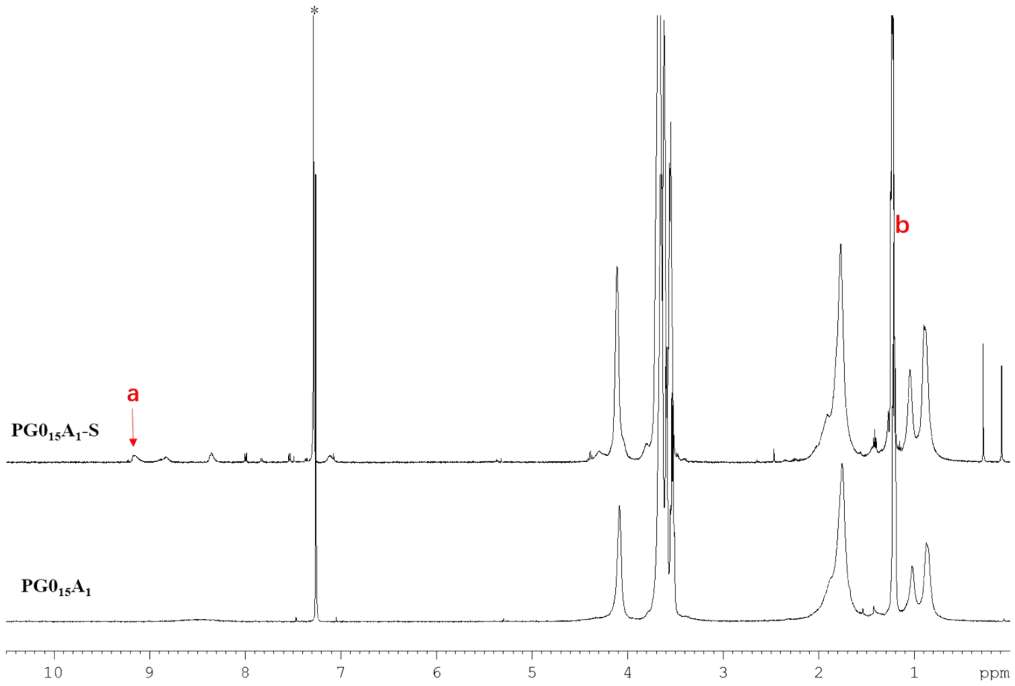

Fig. S3 ^{1}H NMR spectra of polymers **PG0$_{15}$A$_1$** and **PG0$_{15}$A$_1$-S** in $CDCl_3$ at room temperature. The signals from $CDCl_3$ are marked as *.

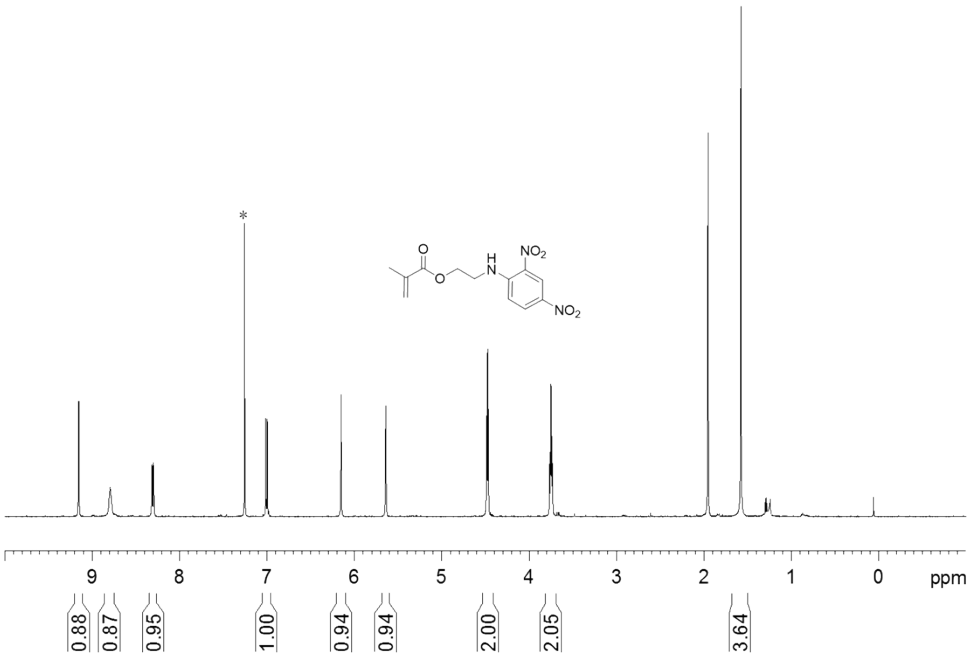

Fig. S4 ^{1}H NMR spectrum of the monomer **AEMA-S** in $CDCl_3$ at room temperature. The signals from $CDCl_3$ are marked as *.

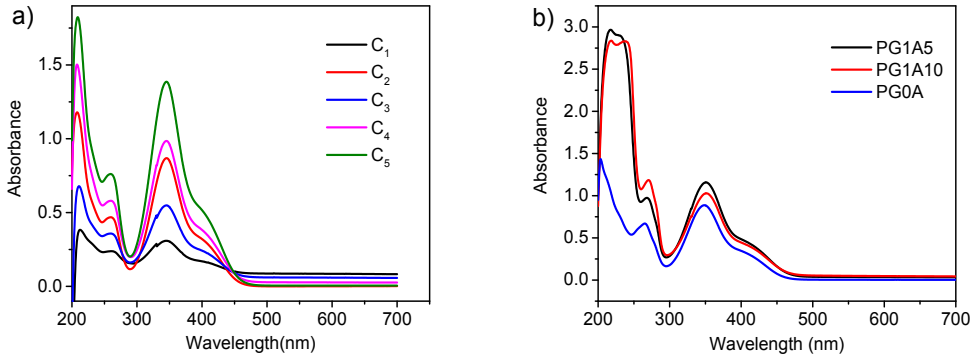

Fig. S5 a) UV/Vis spectra of **AEMA-S** aqueous solutions at different concentrations and b) **PG1$_5$A$_1$-S**, **PG1$_{10}$A$_1$-S** and **PG0$_{15}$A$_1$-S** aqueous solutions at different concentrations.

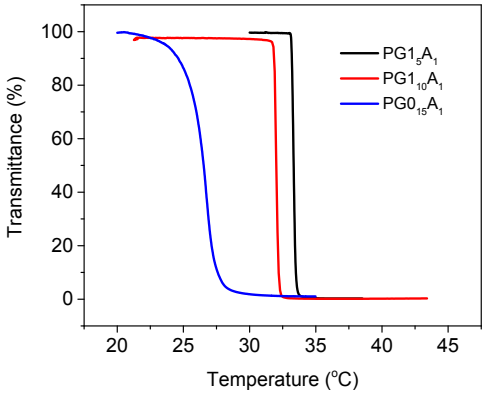

Fig. S6 Plots of transmittance versus temperature for copolymers **PG1$_5$A$_1$**, **PG1$_{10}$A$_1$** and **PG0$_{15}$A$_1$** in 0.25 wt % aqueous solutions. Heating and cooling rate = 10 °C/min.

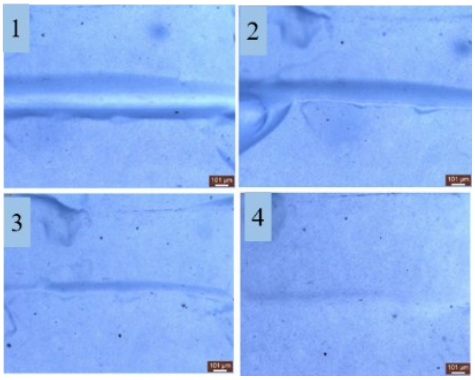

Fig. S7 Photographs of self-healing process of the hydrogel by optical microscope.

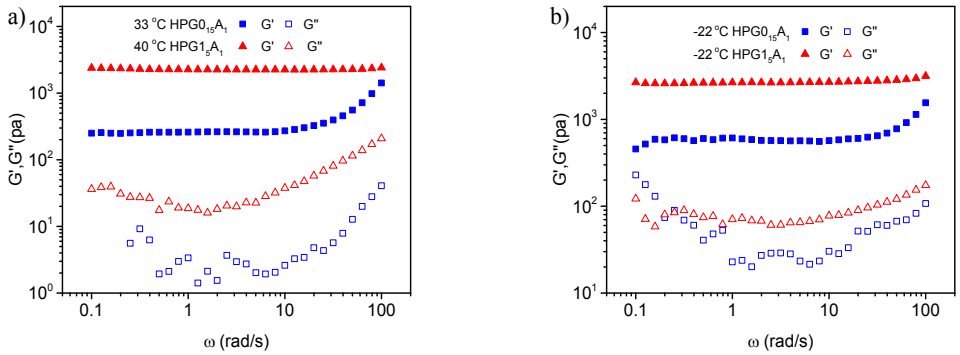

Fig. S8 Comparison of rheological properties of hydrogels **PG1$_5$A$_1$** and **PG0$_{15}$A$_1$** prepared at a) above polymer T_c and b) below polymer T_f.

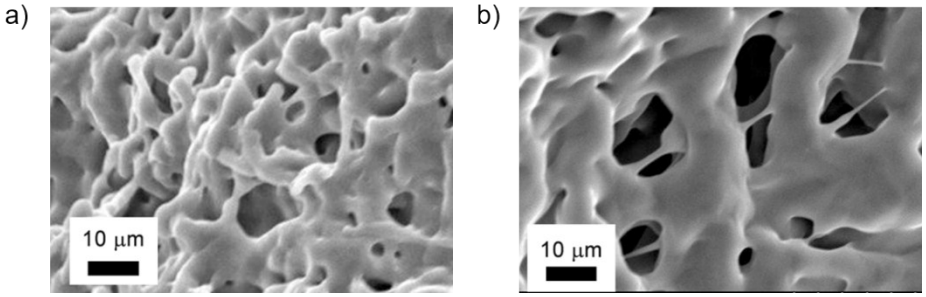

Fig. S9 SEM images of **PG0$_{15}$A$_1$** hydrogels prepared at a) 33 °C and b) -22 °C.

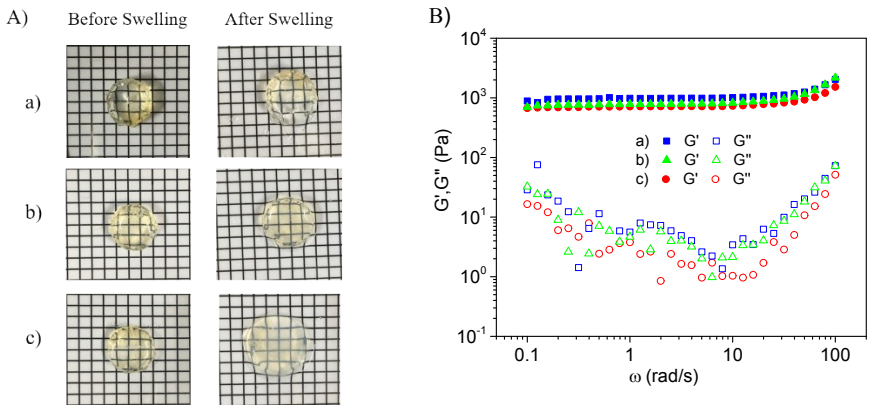

Fig. S10 Swelling behavior (A) and rheological properties (B) of three different hydrogels from **$PG1_5A_1$** prepared in different buffer solutions (25 °C, 10 wt%): a) $NaHCO_3$/NaOH，b) $KHCO_3$/KOH, c) NH_4Cl/NH_4OH.

Synthesis of Sanger's reagent modified compounds

General procedures. A solution of **AEMA** or **PGAs** in THF and H_2O was treated with $NaHCO_3$ and 1-fluoro-2, 4-dinitrobenzene and then stirred for 8 h at room temperature, diluted with ethyl acetate, and washed with saturated aqueous NH_4Cl solution. The aqueous phase was re-extracted once with ethyl acetate, and the combined organic phases were dried over $MgSO_4$ and concentrated. After that, the copolymer was dialyzed against deionized water and lyophilized.

AEMA-S: According to general procedure for reaction, from **AEMA** (22.17 mg, 0.13 mmol), THF (2 mL), $NaHCO_3$ (20.32 mg, 0.24 mmol) and 1-fluoro-2, 4-dinitrobenzene (79 mg, 0.43 mmol), stirred for 8 h at room temperature afforded AEMA-S (28.33 mg, 72%) as a yellow solid. ^{1}H NMR ($CDCl_3$, δ): 1.58 (s, 3H, CH_3), 3.75 (q, 2H, CH_2), 4.48 (t, 2H, CH_2), 5.64 (s, 1H, CH), 6.15 (s, 1H, CH), 7.00 (d, 1H, ArH), 8.29-8.32(m, 1H, ArH), 8.79 (s, 1H, NH), 9.15(d, 1H, ArH).

$PG1_5A_1$-S: According to general procedure for reaction, from **$PG1_5A_1$** (21.11 mg), THF (0.5 mL), $NaHCO_3$ (1.50 mg, 0.017 mmol) and 1-fluoro-2, 4-dinitrobenzene (10.00 mg, 0.06 mmol), stirred for 8 h at room temperature afforded $PG1_5A_1$-S as a yellow solid. ^{1}H NMR ($CDCl_3$, δ): 0.20-1.45 (m, CH+CH_2), 1.43-2.72 (m, CH_2), 2.80-4.38 (m, CH_2), 4.75 (s, CH_2), 6.48 (br, ArH), 7.05 (br, ArH), 8.21 (br, ArH), 8.67 (br, NH), 8.92 (br, ArH).

$PG1_{10}A_1$-S: According to general procedure for reaction, from **$PG1_{10}A_1$** (20.04 mg), THF (0.5 mL), $NaHCO_3$ (1.53 mg, 0.017 mmol) and 1-fluoro-2,4-dinitrobenzene (10.00 mg, 0.06 mmol), stirred for 8 h at room temperature afforded $PG1_{10}A_1$-S as a yellow solid. ^1H NMR ($CDCl_3$, δ): 0.22-1.52 (m, CH+CH_2), 1.55-2.73 (m, CH_2), 2.80-4.41 (m, CH_2), 4.89 (s, CH_2), 6.51(br, ArH)7.08 (br, ArH), 8.26 (br, ArH), 8.67 (br, NH), 8.98 (br, ArH).

$PG0_{15}A_1$-S: According to general procedure for reaction, from **$PG0_{15}A_1$** (20.11 mg), THF (0.5 mL), $NaHCO_3$ (1.62 mg, 0.019 mmol) and 1-fluoro-2,4-dinitrobenzene (10.00 mg, 0.06 mmol), stirred for 8 h at room temperature afforded $PG0_{15}A_1$-S as a yellow solid. ^1H NMR ($CDCl_3$, δ): 0.86-1.02 (m, CH+CH_2), 1.54-2.12 (m, CH_2), 3.40-3.86 (m, CH_2), 3.93-4.18 (m, CH_2), 7.08 (br, ArH), 8.34 (br, ArH), 8.79 (br, NH), 9.11 (br, ArH).