ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Thermoresponsive Shape-Memory Hydrogel Actuators Made by Phototriggered Click Chemistry

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Synthesis of BA-diazide

BA-diazide was synthesized by following reported procedure with slight modification.[1] Bisphenol A diglycidylether (BPA) (10 g, 0.03 mol) was dissolved in 100 mL methanol with rapid stirring. Then ammonium chloride (4.71 g, 0.09 mol) and sodium azide (5.72 g, 0.09 mol) were dissolved in a separate 120 mL of methanol. These two separate solutions were mixed together and refluxed for overnight. The reaction mixture was cooled and concentrated using a rotary evaporator. The product was extracted into diethyl ether (3100 mL) from water mixture followed by brine solution and the organic phase was passed through the Na_2SO_4. The solvent was evaporated to get a viscous yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.16 (m, 4H), 6.82 (m, 4H), 4.09 (m, 2H), 4.01 (m, 4H), 3.52 (m, 4H), 2.80 (br s, 2H), 1.65 (s, 6H).

Synthesis of tri-alkyne derivative of glycerol ethoxylate

Sodium hydride (60% dispersed in mineral oil) (1 g, 0.025 mol) was dispersed in dry THF in an oven dried 500 mL round bottom flask. In a separate vessel glycerol ethoxylate (5 g, 0.005 mol) was dissolved in 50 ML THF. Then this solution added dropwise to suspension of sodium hydride solution slowly in presence of N_2 atmosphere. After 1h of stirring propargyl bromide solution 80 wt% in toluene (3.71 g, 0.025 mol) was added dropwise to the reaction mixture and stirred it for 12h. The reaction mixture was filtered, and the solvent was evaporated to dryness in rotaevaporator. The product was further purified through precipitation in cold diethyl ether 6 times.

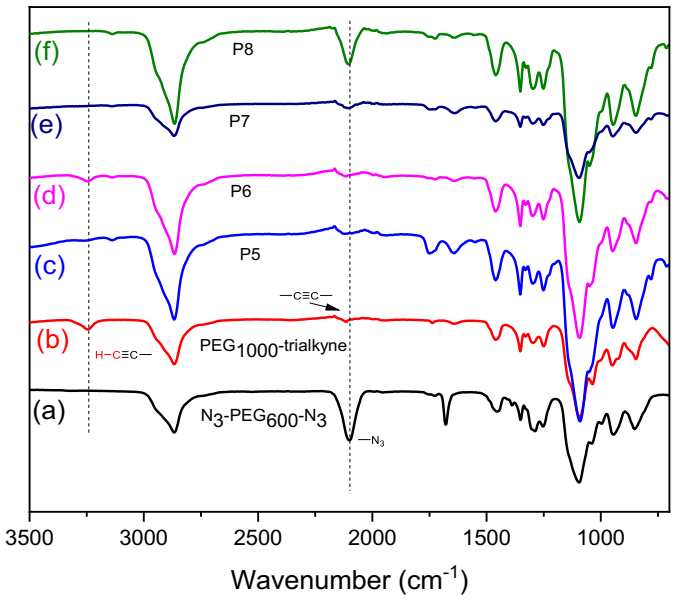

Figure S1. FTIR spectra of a) PEG_{600}-diazide b) 1a c) P5, d) P6 e) P7 and f) P8.

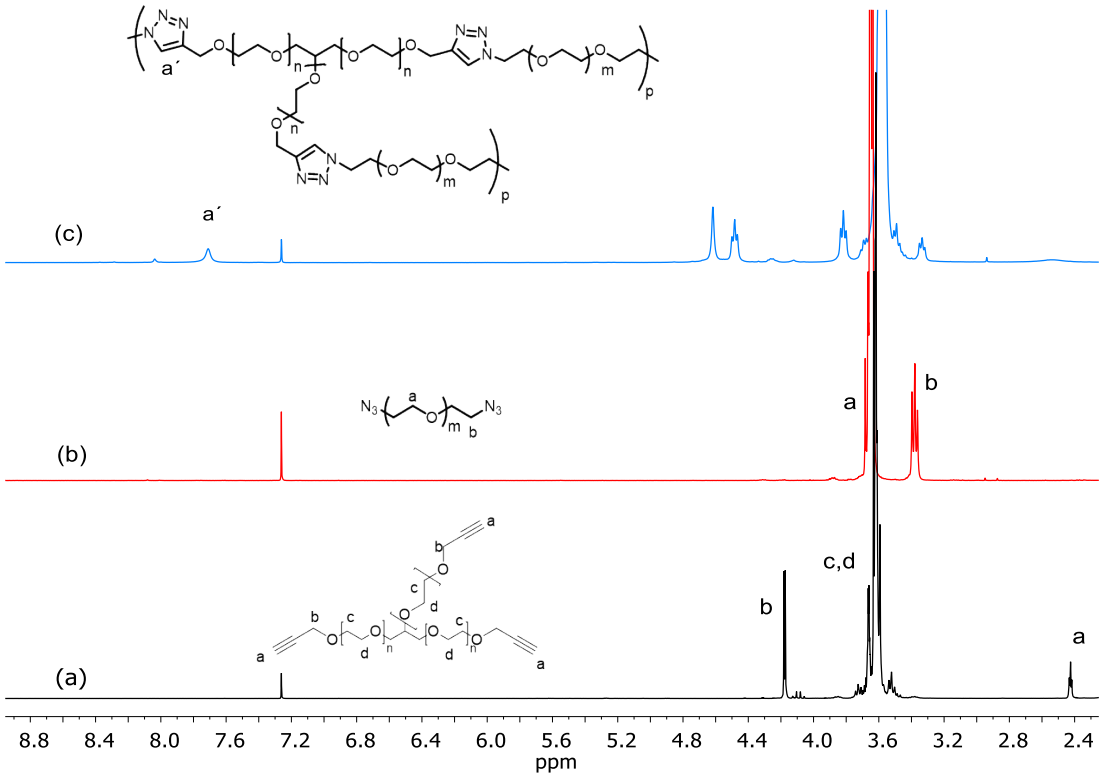

Figure S2. ^{1}H NMR spectra of a) trialkyne derivative of glycerol ethoxylate b) PEG-dizide c) HB polymer P6 in $CDCl_3$.

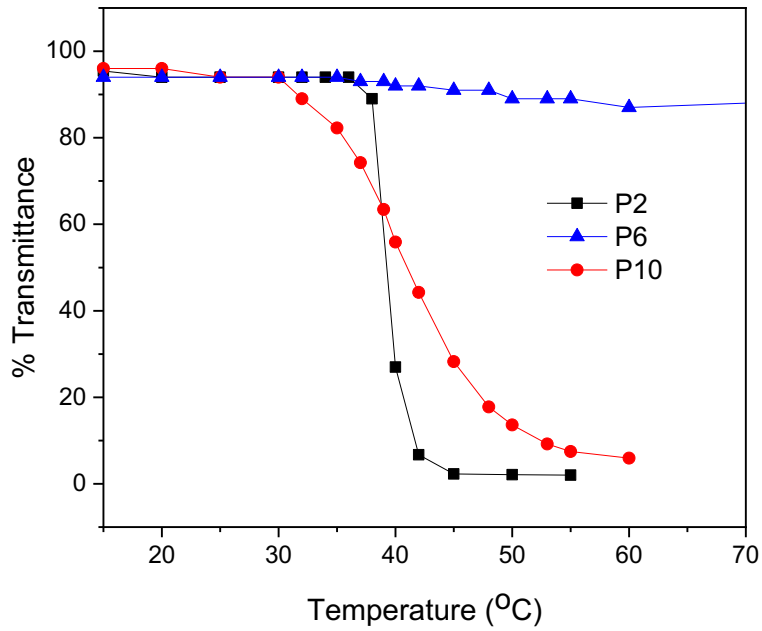

Figure S3. Variation of % T with temperature for the aqueous solutions (2.0 mg/mL) of P2, P6 and P10 polymers.

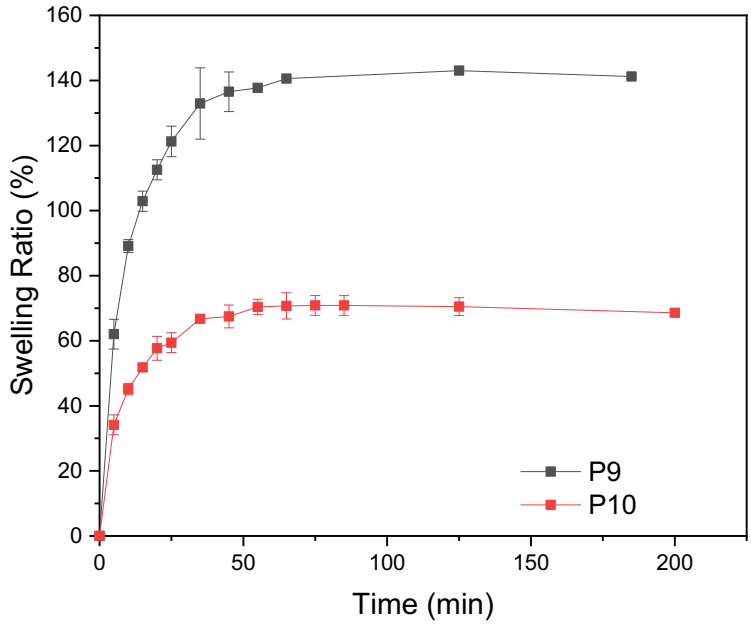

Figure S4. Comparison of equilibrium swelling ratios for a) P9 and P11 at 22 °C as a function of time.

Table S1. Summary of TGA measurements.

Polymer	**T_{inici} (ºC)**	**T_5 (ºC)**	**T_{50} (ºC)**	**T_{max} (ºC)**	**Residue (%)**
P1	190.9	279.0	375.2	371.6/403.5*/533.8	1.2
P2	119.9	242.1	367.2	345.8*/370.4/381.3/518.9	4.9
P3	212.2	301.9	377.0	342.6*/371.6/531.4	1.5
P4	184.0	245.8	377.2	253.8/349.4/397.4/528.1	2.6
P5	143.3	253.6	368.1	370.2/393.4*	8.1
P6	50.0	121.7	365.1	370.0/527.7	1.2
P7	145.4	228.2	358.2	233.6*/282.4*/362.3/392.2*/471.3	3.9
P8	130.8	182.6	328.7	218.3/253.0/343.4/512.0	0.0
P9	166.7	241.5	368.2	215.9*/344.2/368.0/381.7/391.4/560.4	3.2
P11	177.6	278.3	385.3	341.7/383.3/400.7/556.4	3.2

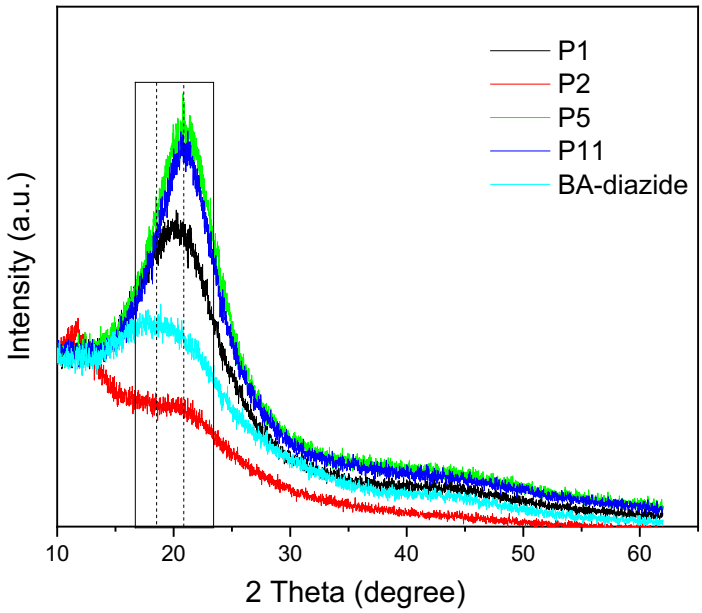

Figure S5. WAXS patterns of various polymer.

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[1] X. Sheng, T. C. Mauldin, and M. R. Kessler, *J. Polym. Sci. Part A: Polym. Chem.*, **2010**, *48*, 4093-4102.