Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A Water-Soluble Polymer for Selective Colorimetric Sensing of Cysteine and Homocysteine withTemperature Tunable Sensitivity

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Experimental Section

Materials

Dimethyl acrylamide was purified by passage through a column filled with basic alumina in order to remove inhibitors. N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid (HEPES), nitrobenzaldehyde, 4-dimethylaminopyridine (DMAP), tin oxide (SnO_2), sodium nitrite, N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (CTA), cysteine, homocysteine, glutathione, alanine, methionine, valine, phenylalanine, and glycine were purchased from Aldrich at the highest available purity and were used as received without further purification. 4-Aminobenzaldehyde was synthesized according to a previous literature procedure.[1]

Instrumentation

^1H NMR spectra of the monomer and polymer were collected in $CDCl_3$ and D_2O on a Bruker Avance 300 MHz NMR spectrometer. The apparent molecular weight and molecular weight distributions were measured by GPC (Agilent Technologies 1200 series) using a polystyrene standard, with DMF as the eluent at 30 °C and a flow rate of 1.00 mL/min. UV−Vis spectra were recorded using an Optizen 3220 UV−Vis spectrophotometer equipped with a digital temperature controller. A 650 nm wavelength was used to determine LCST. The temperature range was from 51 to 70 °C with a heating and cooling rate of 1 °C/min. DLS measurements were carried out using a Zetasizer (Nano ZS90, Malvern, UK) with Zetasizer software 7.03.

Synthesis of 2-(methyl(phenyl)amino)ethyl acrylate (1)

A solution of acrylic acid (1.14g, 15.8 mmol), 4-(dimethylamino)pyridine (DMAP), 0.16 g, 1.3 mmol), and 2-(N-methylanilino)ethanol (2.0 g, 13.2 mmol) in DCM (25 mL) was cooled to 0 °C and treated with 1-ethyl-3-((dimethylamino)propyl)carbodiimide hydrochloride (EDC.HCL) (3.0 g, 15.8 mmol). The reaction mixture was stirred at 0 °C for 30 min and then at 25 °C (RT) for 12 h. The solution was concentrated to dryness in vacuo, and the residue

was taken up in ethyl acetate and water. The organic layer was separated, washed with saturated NH_4Cl solution and water, and dried with $MgSO_4$. The crude product was further purified by column chromatography to obtain a colorless liquid. Yield = 2.5 g (92%). ^{1}H-NMR ($CDCl_3$, 300 MHz, δ in ppm): 7.26- 6.77 (5H, m, Ar-H), 6.37-5.83 (3H, m, vinyl-H), 4.37 (2H, t, O-CH_2-), 3.67 (2H, t, N-CH_2), 3.02 (3H, s, N-CH_3).

Synthesis of (E)-2-((4-((4-formylphenyl)diazenyl)phenyl)(methyl)amino)ethyl acrylate M1: Compound 1 and 4-aminobenzaldehyde were subjected to diazotization according to a previously reported procedure.[2] Yield = 1.9 g (89%). ^{1}H-NMR ($CDCl_3$, 300 MHz, δ in ppm): 10.0 (1H, s, CHO), 7.93- 6.83 (8H, m, Ar-H), 6.42-5.83 (3H, m, vinyl-H), 4.41 (2H, t, O-CH_2-), 3.79 (2H, t, N-CH_2), 3.15 (3H, s, N-CH_3).

Synthesis of polymer (P1): M1 (0.37g, 0.54 mmol), dimethylacrylamide (1g, 10.08 mmol), CTA (0.02g, 0.053 mmol), and AIBN (0.21 mg, 0.001mmol) were added to a Schlenk flask with 8 mL of dry DMF. The reaction mixture was purged for 30 minutes to remove the oxygen and then heated for 12 hr at 80 ºC. Yield = 0.7 g. The reaction mixture was concentrated and then precipitated in diethyl ether. The obtained polymer was further purified by re-precipitation. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ in ppm): 10.0 (1H, s, CHO), 7.92- 6.83 (8H, m, Ar-H), 4.22 (2H, t, O-CH_2-), 3.75 (2H, t, N-CH_2), 3.14-0.84 (12H, s, N-$(CH_3)_2$ and aliphatic H). GPC: Mn = 13000, Mw = 14400 and PDI = 1.1.

Sensing studies: The P1 solution was prepared (according to 5% incorporation of M1 along the polymer chain) in a 5.0×10^{-4} M concentration of aldehyde moieties. The molar absorption coefficient of P1 was calculated to be 2.7×10^4 mol^{-1} L cm^{-1}. The sensing studies were carried out by adding 250 μL of cysteine at different concentrations (0.1 ~ 1.0 mM, 2.5 x 10^{-8} ~ 2.5 x 10^{-7} mol of cysteine) into 0.5 mL of P1 + 0.5 mL of buffer (2.5 x10^{-7} mol of aldehyde moieties) solution. The drastic spectral change of P1 was observed up to the addition of 1 mM of cysteine, above which no change was observed.

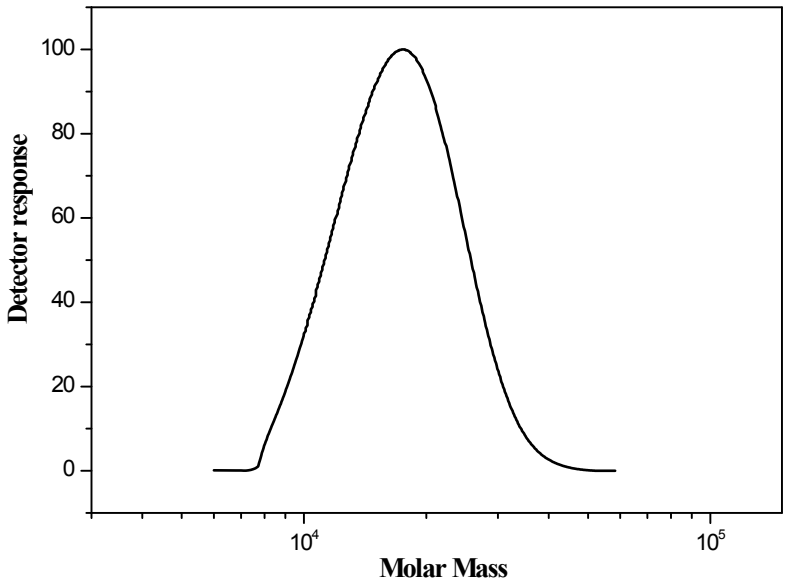

Figure S1. *The GPC chromatogram of Poly-Azo-CHO* ***(P1)****.*

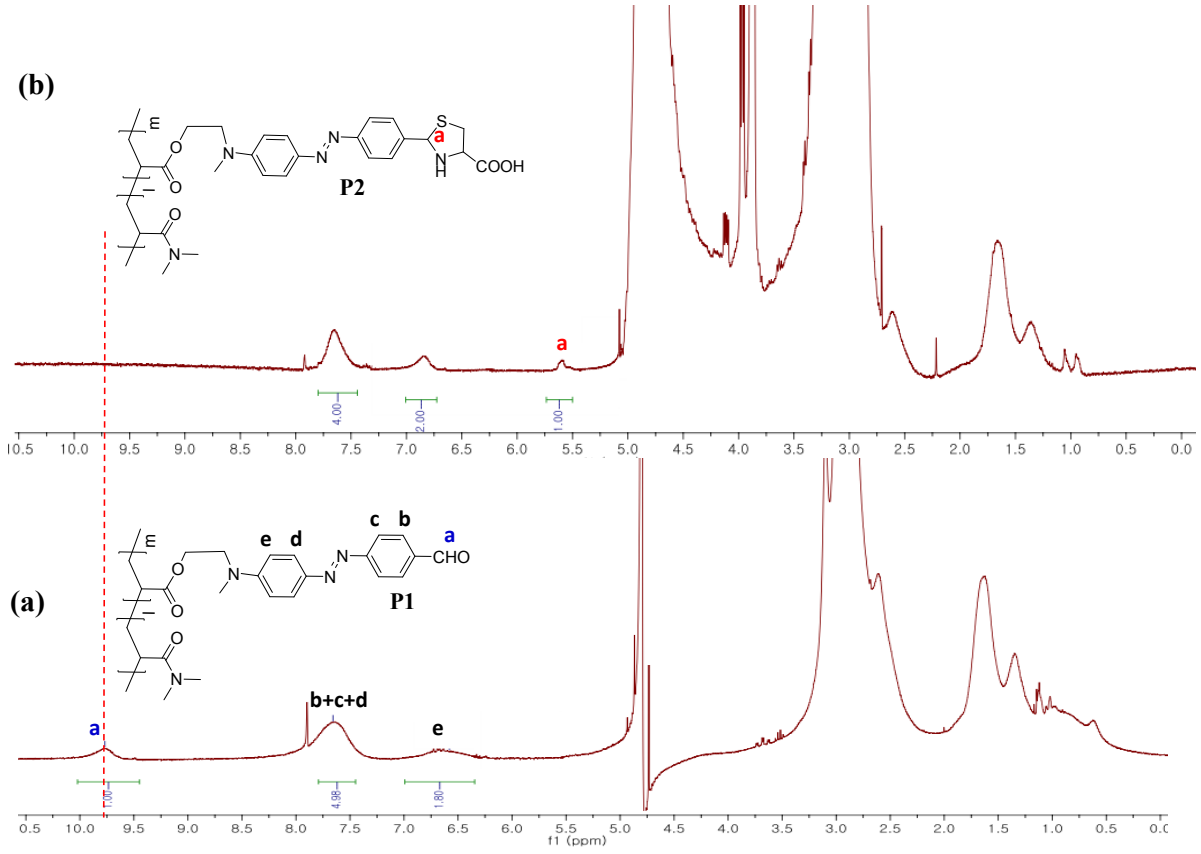

Figure S2. *^{1}H-NMR spectra (a) the polymer (P1) and (b) P1 with cysteine (P2) at 25 ºC in D_2O.*

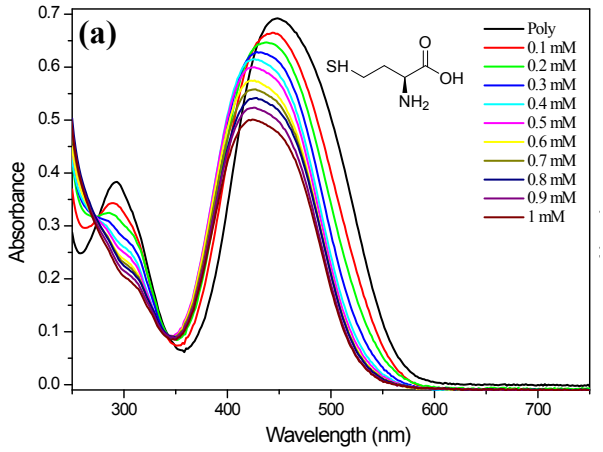

Figure S3: *UV-Vis absorption spectra of P1 (2.5 × 10^{-4} M) with various concentrations of (a) homocysteine.*

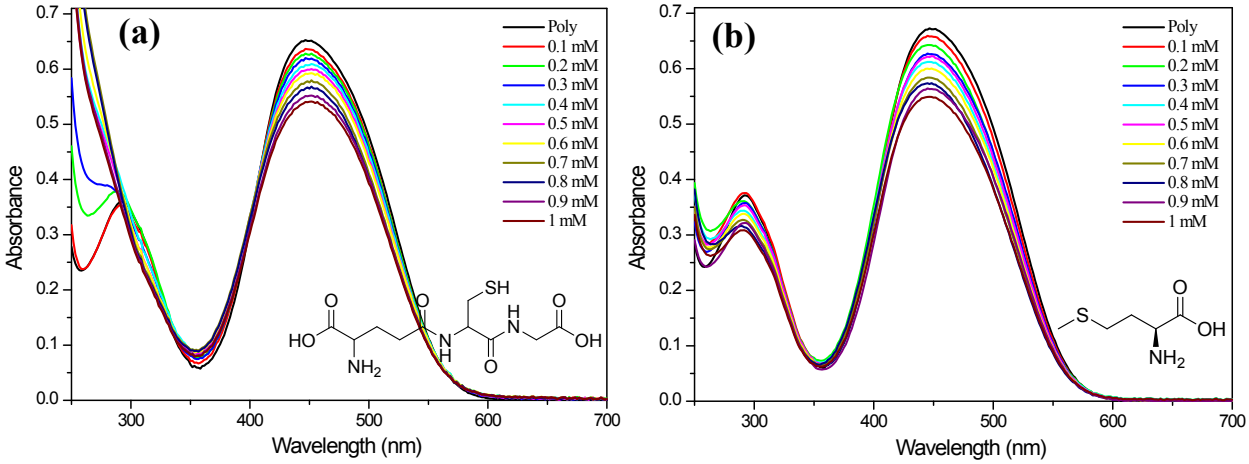

Figure S4: *UV-Vis absorption spectra of (2.5 × 10^{-4} M) with various concentrations of (a) glutathione and (b) methionine.*

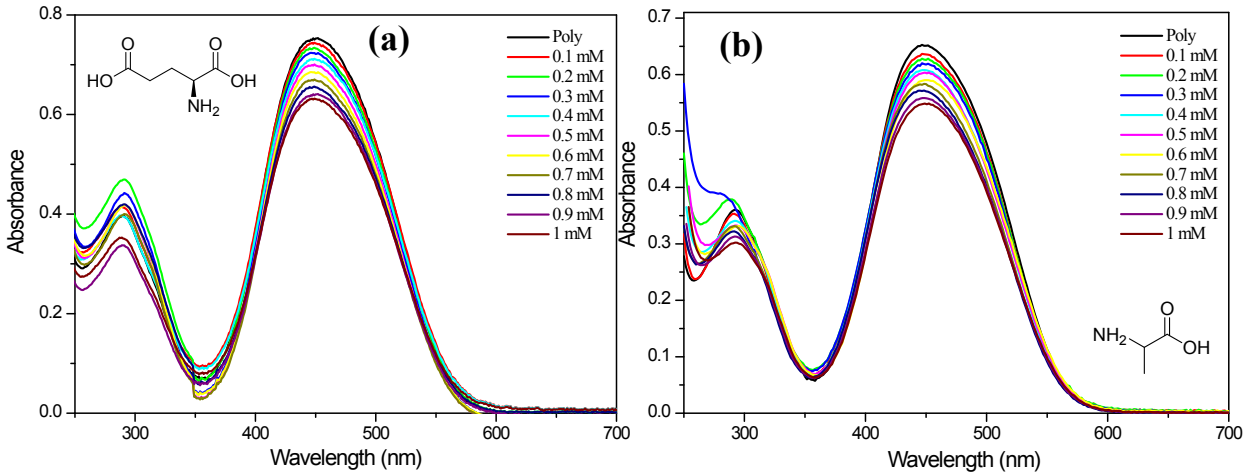

Figure S5: *UV-Vis absorption spectra of (2.5 × 10^{-4} M) with various concentrations of (a) glutamic acid and (b) alanine.*

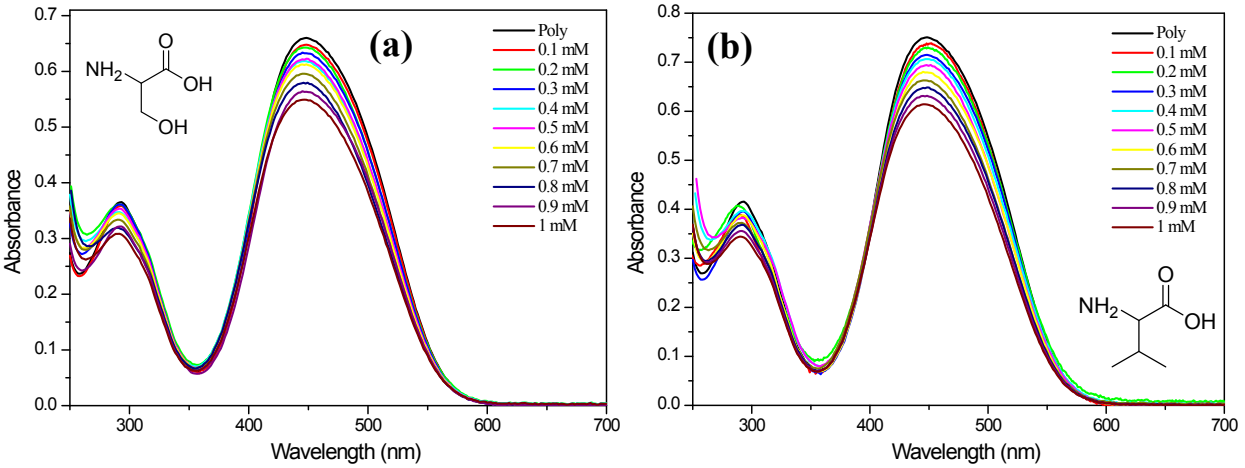

Figure S6: *UV-Vis absorption spectra of (2.5 × 10^{-4} M) with various concentrations of (a) serine and (b) valine.*

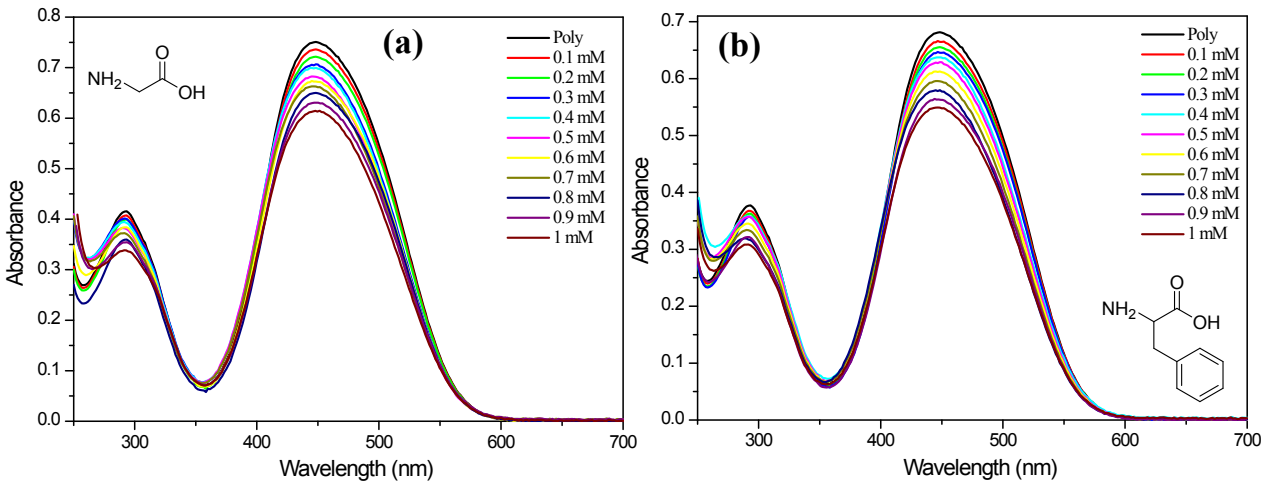

Figure S7: *UV-Vis absorption spectra of (2.5 × 10^{-4} M) with various concentrations of (a) glycine and (b) phenylalanine.*

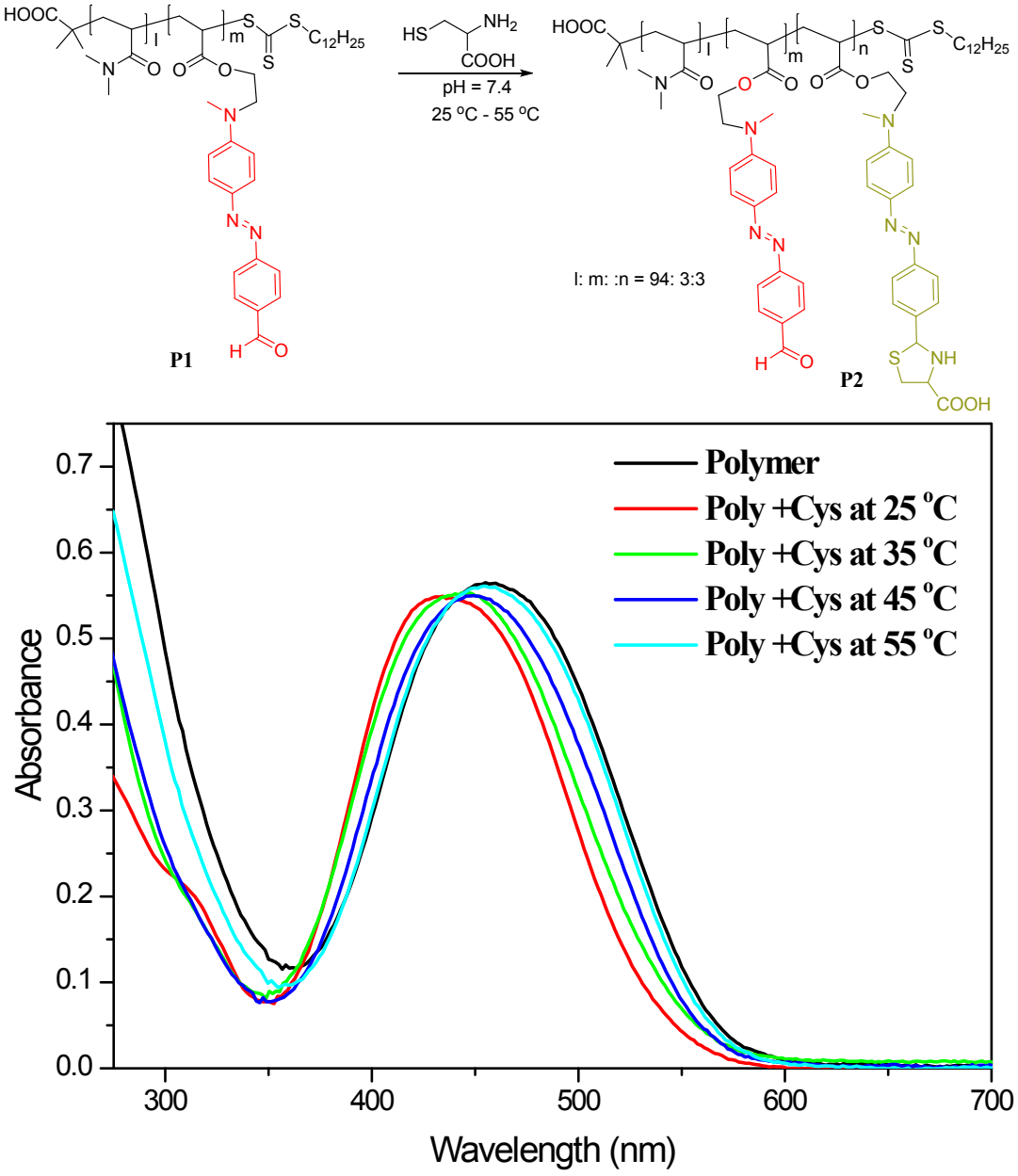

Figure S8: *Temperature dependent sensing studies: absorption spectra of P1 with* 0.6 mM *of cysteine at various temperature*s.

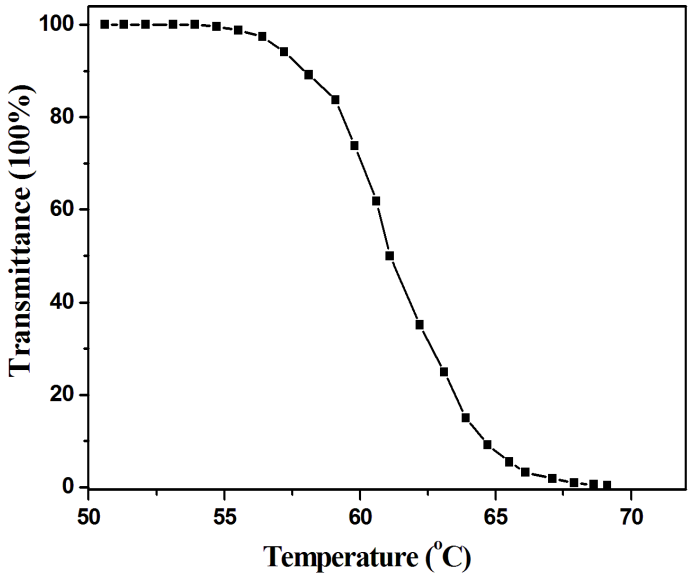

Figure S9: *The plot of percent transmission vs temperature of polymer P1.*

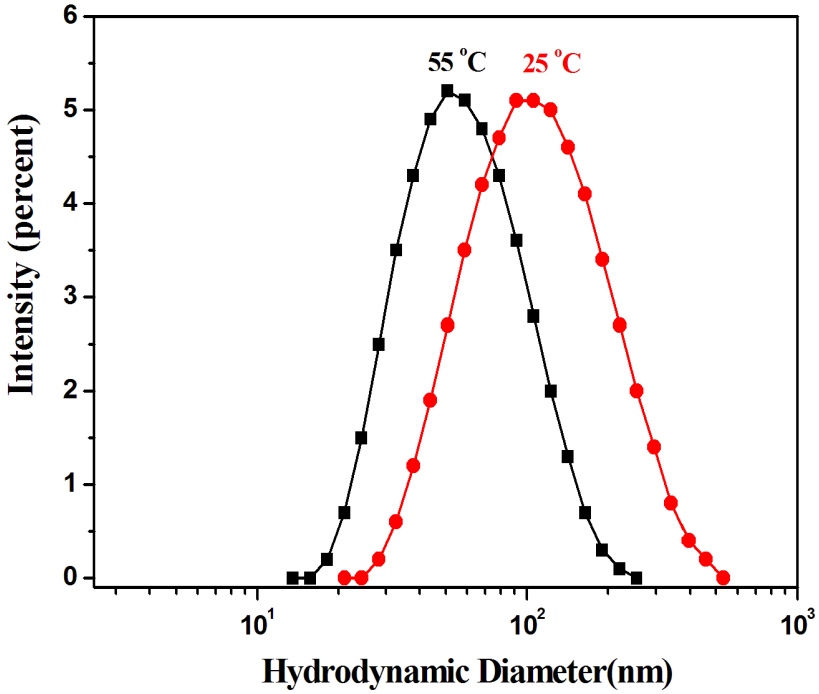

Figure S10: *DLS plot of P1 at 25 and 55 ºC.*

1. H. G. Beard, H. H. J. Hodgson, *J. Chem. Soc*. **1944**, 4-5

2. A. K. Singh, J. Das, N. Majumdar, *J. Am. Chem. Soc.* **1996,** 118, 6185-6191.