Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

Polymeric temperature sensor with a broad sensing regime

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Materials and Instrumentation

All chemicals and solvents were commercially available and use as received unless otherwise stated. Ethyl α-bromoisobutyrate (EBiB, 98%), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) were obtained from Sigma Aldrich. Pre-cut copper wire (Sigma-Aldrich, 99.9%) was pretreated with diluted sulphuric acid and milliQ water to remove oxidized copper. After drying under a nitrogen flow, the copper wire was stored under nitrogen atmosphere. 2-Methoxyethyl acrylate (MEA, 98%) and 2-hydroxyethyl acrylate (HEA) were purchased from Sigma-Aldrich and purified by passing over a neutralized aluminium oxide column to remove the inhibitor. Copper(II) bromide (CuBr2, 99%) was purchased from Fluka and used as received.

^1H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using deuterated chloroform or dimethyl sulfoxide (DMSO-d6) as solvent. Chemical shifts (d) are given in ppm relative to TMS.

Size-exclusion chromatography (SEC) characterization was performed on a Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a

1260 automatic liquid sampler (ALS), a thermostatted column compartment (TCC) at 50°C equipped with two PLgel 5 μm mixed D columns and a similar guard column (Agilent) in series, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). The used eluent was DMA containing 50mM of LiCl at a flow rate of 0.6 ml/min. The spectra were analysed using the Agilent Chemstation software with the GPC add on. Molar mass and PDI values were calculated against Varian PS standards.

Gas chromatography was performed on a 7890A from Agilent Technologies with an Agilent J&W Advanced Capillary GC column (30 m, 0.320 mm, and 0.25 μm). Injections were performed with an Agilent Technologies 7693 auto sampler. Detection was done with a FID detector. Injector and detector temperatures were kept constant at 250 and 280 ^{o}C, respectively. The column was initially set at 50 ^{o}C, followed by two heating stages: from 50 ^{o}C to 100 ^{o}C with a rate of 20 ^{o}C /min and from 100 ^{o}C to 300 ^{o}C with a rate of 40 ^{o}C /min, and then held at this temperature for 0.5 minutes. Conversion was determined based on the integration of monomer peaks using DMSO or DMF as internal standard.

UV-Vis spectra were collected on a Cary 300 Bio UV-Visible spectrophotometer with wavelength range from 700 to 250 nm and Peltier temperature control.

Dynamic light scattering (DLS) was performed on a Zetasizer Nano-ZS apparatus (Malvern Instruments Ltd) using disposable cuvettes. The excitation light source was a He−Ne laser at 633 nm, and the intensity of the scattered light was measured at 173°. This method measures the rate of the intensity fluctuation and the size of the particles is determined through the Stokes−Einstein equation

$$d(H)= kT/(3\pi\eta D)$$

where d(H) is the mean hydrodynamic diameter, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the dispersing medium, and D is the apparent diffusion coefficient. Before starting the measurements, samples were incubated at specific temperature for at least 300s to reach equilibrium. All samples were filtered through Millipore membranes with pore sizes of 0.2 μm prior to measurement.

Synthesis and characterization

Synthesis of (2-{N-ethyl-N-[4-(4-nitrophenylazo)phenyl]amino}ethyl acrylate) (DR1-A).

To a solution of disperse red 1 (DR1, 1 equivalent.) in anhydrous DCM, triethylamine (2 equivalents) were added followed by dropwise addition of acryloyl chloride (2 equivalents) at 0 °C. The resulting mixture was stirred and allowed to warm to room temperature overnight. Subsequently, the reaction solution was washed with water. After evaporation of the DCM, the crude product DR1-A was purified by silica gel chromatography eluting with n-hexane/diethyl ether (25:75). The ^{1}H NMR was collected with CDCl$_3$ as solvent, which confirms the success of the synthesis of this already known and commercially available compound.

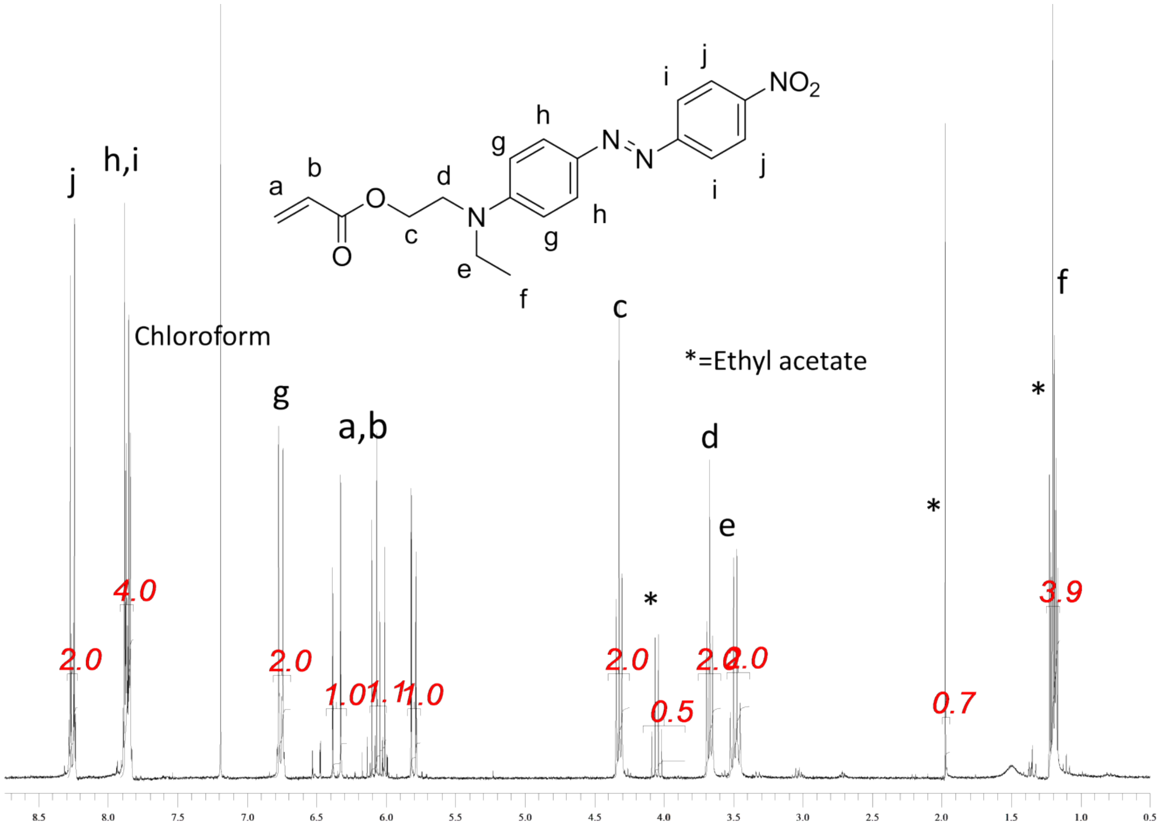

Figure S1 ^{1}H NMR spectrum for Disperse Red 1-Acrylate.

Cu(0)-mediated synthesis of gradient copolymer

HEA (or mTEGA), DR1-A, EBiB, Me_6TREN and $CuBr_2$ were first dissolved in DMSO in a schlenk vial. After degassing the solution three times by freeze-vacuum-thaw cycles, the polymerization was initiated by adding copper wire in the solution under nitrogen atmosphere. After 15 min of reaction, the continuous addition of MEA dissolved in DMF to the reaction mixture was started (syringe pump). The addition of MEA finished in 60 min, after which the polymerization was allowed to proceed for another 20 min. The copolymerization was stopped by immersing the schlenk vial into liquid nitrogen. After addition of DCM to the frozen solution, the mixture was incubated at room temperature to allowed melting of the frozen solution. A neutralized aluminum oxide column eluting with DCM was used to remove the copper salts. The resulting polymers were isolated by precipitation in n-hexane/diethyl ether (75/25) for three times followed by drying under reduced pressure at room temperature. The conversion of HEA (or mTEGA) and MEA were followed in time by gas chromatography (GC) with DMSO and DMF as internal standards, respectively.

The synthesis of the HEA-MEA statistical copolymer was performed using Cu(0)-mediated copolymerization in a similar procedure as the synthesis of the gradient copolymers.

Supporting figures

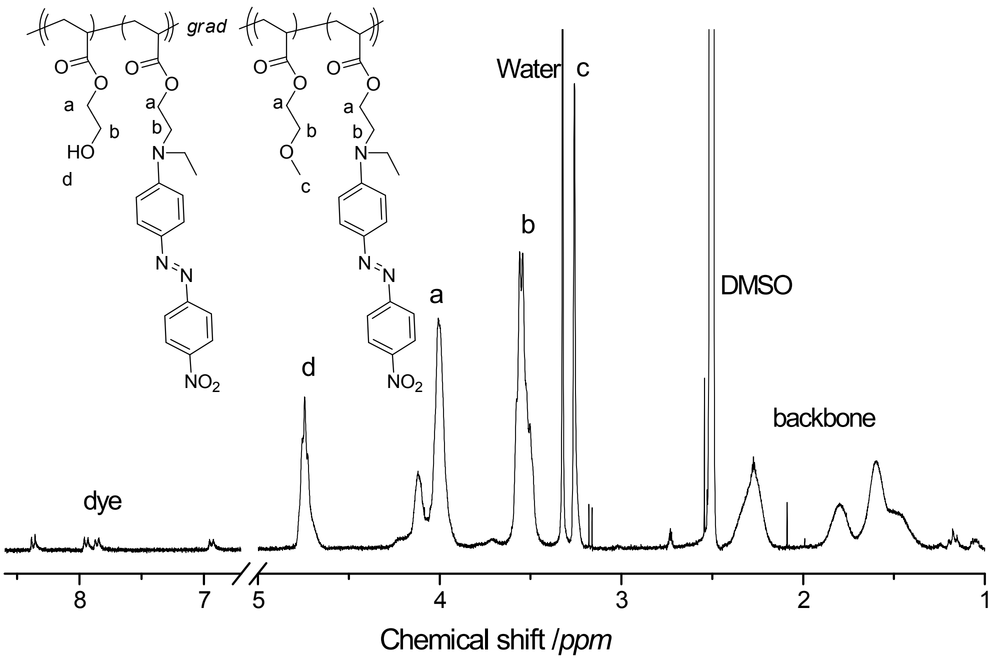

Figure S2 ^{1}H NMR spectrum for HEA$_{45}$-*grad*-MEA$_{23}$-DR1-A

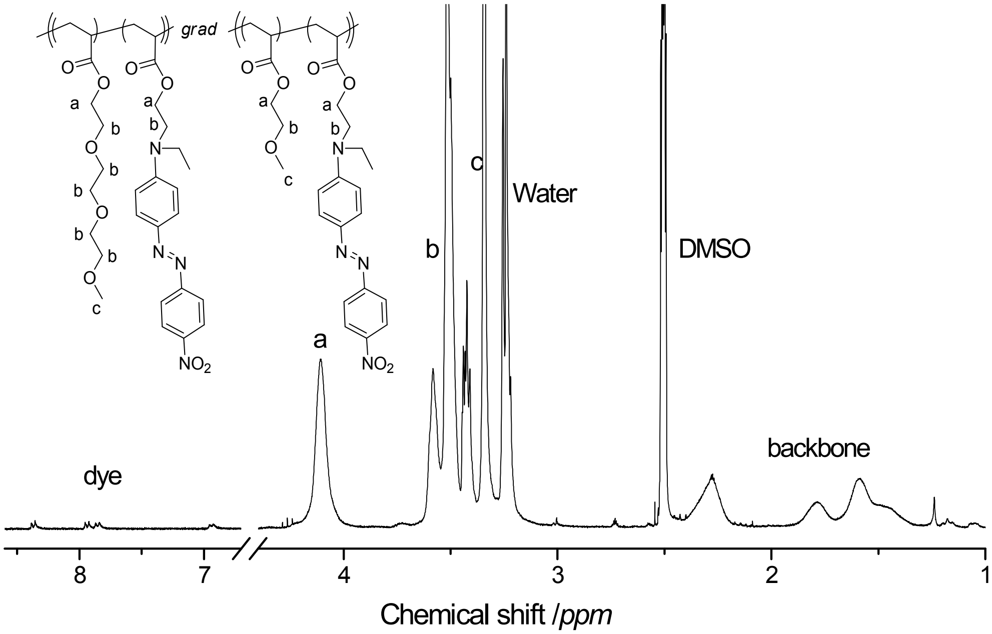

Figure S3 ^{1}H NMR spectrum for mTEGA$_{38}$-*grad*-MEA$_{13}$-DR1-A

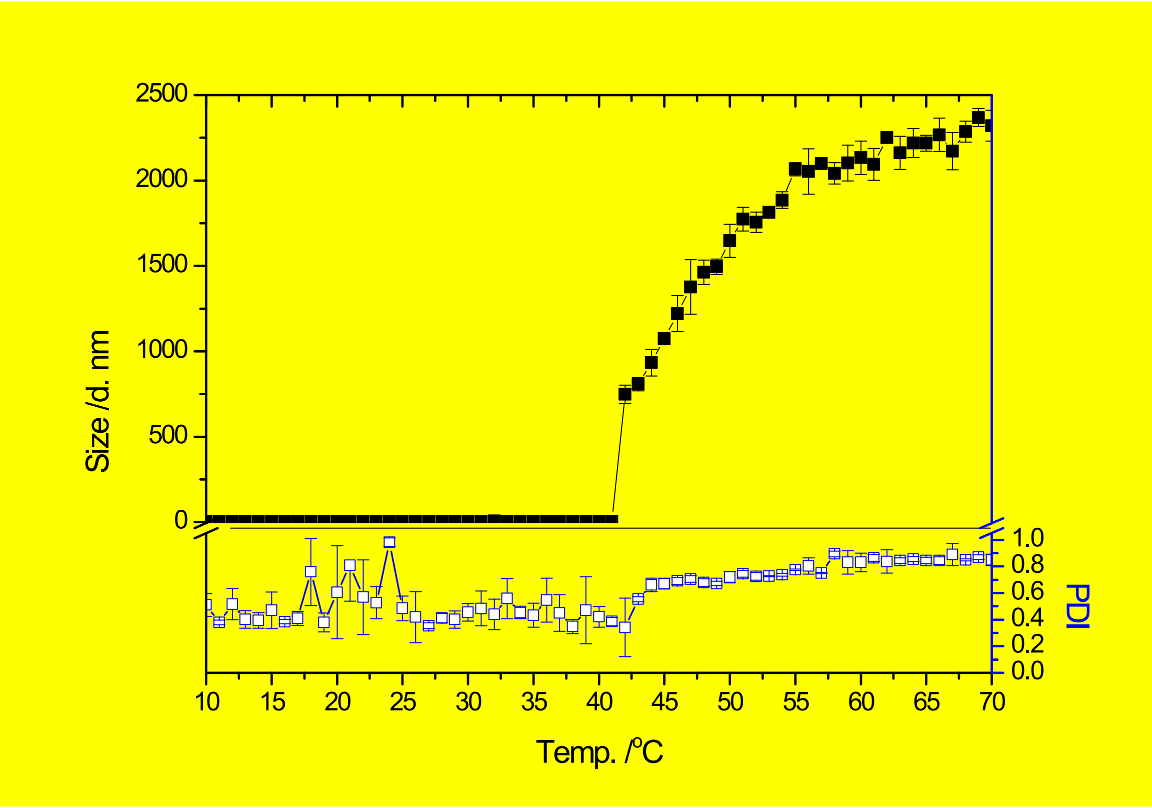

Figure S4 Size and PDI versus temperature for HEA$_{45}$-*grad*-MEA$_{23}$-DR1-A solution at 0.2 mg/ml in MilliQ water, measured by dynamic light scattering (DLS)

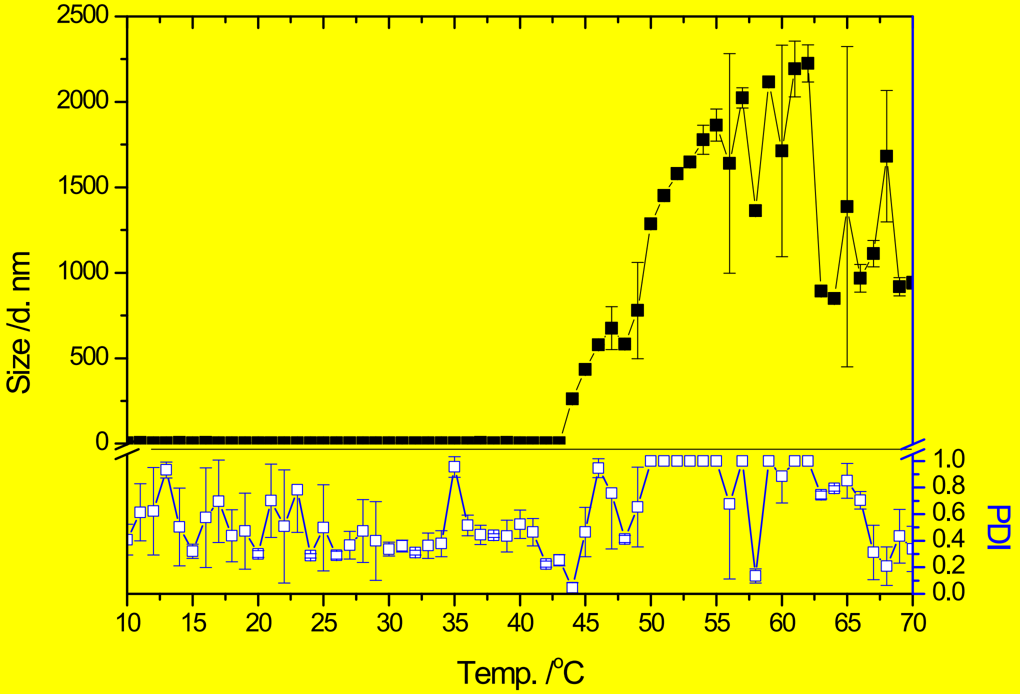

Figure S5 Size and PDI versus temperature for mTEGA$_{38}$-*grad*-MEA$_{13}$-DR1-A solution at 0.2 mg/ml in MilliQ water, measured by DLS