Supporting Information

Self-Assembly Bahavior of Thermoresponsive Oligo(ethylene glycol) Methacrylates Random Copolymer

Baoliang Peng[1,2], Nathan Grishkewich[1], Zhaoling Yao[1], Xia Han[2], Honglai Liu[2,*], and Kam C. Tam[1,*]

[1]Department of Chemical Engineering, Waterloo Institute for Nanotechnology

University of Waterloo, 200 University

Avenue West, Waterloo, Ontario, Canada N2L 3G1

[2]Department of Chemistry, East China University of Science and Technology, 130

Meilong Road, Shanghai 200237, P. R. China

Experimental Part

Materials

2-(2-Methoxyethoxy)ethyl methacrylate (M_n ~ 188, 95%), poly (ethylene glycol) methyl ether methacrylate (M_n ~ 2,080, 50 wt% in water) were purchased from Sigma-Aldrich and purified by passing them through a column filled with basic alumina prior to use. Methyl 2-bromopropionate (MBP), copper (I) chloride, 2, 2'-bipyridyl (Bipy) and ethanol were purchased from Sigma-Aldrich and used as received. Water used in all experiments was obtained from the Millipore-Q water purification system, which has a resistivity of $18.2 \mu\Omega$·cm.

Synthesis of P(MEO$_2$MA-*co*-PEGMA$_{2080}$) via ATRP

The copolymer was synthesized in ethanol via the ATRP process using MBP as the initiator and CuBr/Bipy as the catalyst. A typical procedure is described as follows: CuBr (35.9 mg, 0.25 mmol) and Bipy (78.1 mg, 0.5 mmol) were added to a 25 mL flask, and then the flask was sealed and purged with argon for 30 mins. Then, a degassed mixture of 2-(2-methoxyethoxy) ethyl methacrylate (2.3 g, 12.4 mmol), poly (ethylene glycol) methyl ether methacrylate (2080 g/mol) (0.26 g, 0.0625 mmol), methyl 2-bromopropionate (20.9 mg, 0.125 mmol) and ethanol (3.32 mL) was transferred using a double tipped needle into the flask charged with CuBr/Bipy equipped with a magnetic stirring bar under argon atmosphere. The mixture was heated at 60 °C for 3h, and the reaction was stopped by opening the flask after several hours. The reacted mixture was dialyzed against Millipore Water for 2 days, and the final product was collected after freeze drying. The GPC results confirmed that the number average molecular weight (M_n) and polydispersity index (PDI) of the copolymer was 17,300 g/mol and 1.61, respectively.
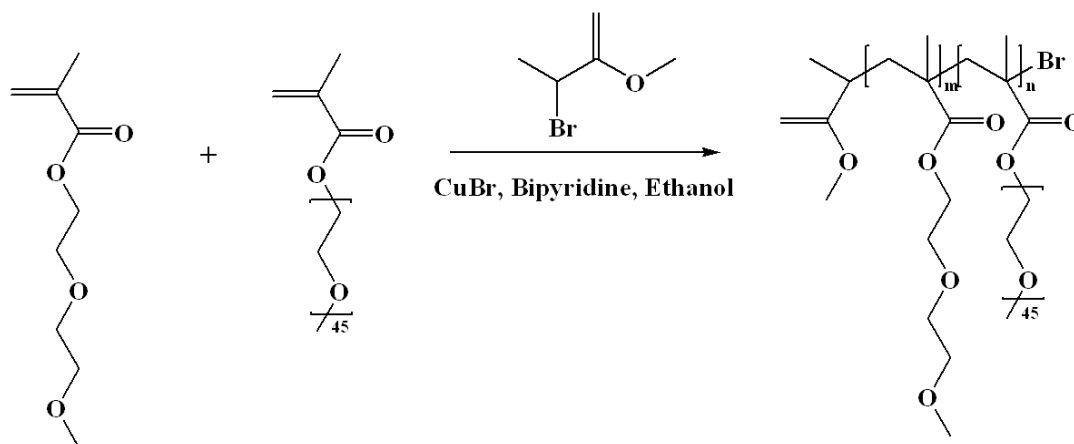

Figure S1. Synthetic Scheme of P(MEO$_2$MA-*co*-PEGMA$_{2080}$).

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H NMR spectra were recorded in CDCl$_3$ on a Bruker AV300 NMR spectrometer operating in the Fourier transform mode. All analyses were performed at 25 °C. The ^{1}H NMR

spectra of P(MEO$_2$MA-*co*-PEGMA$_{2080}$) is shown in Figure S2, and all the peaks corresponding to the protons on the copolymer are assigned correctly as reported in literature.[1]
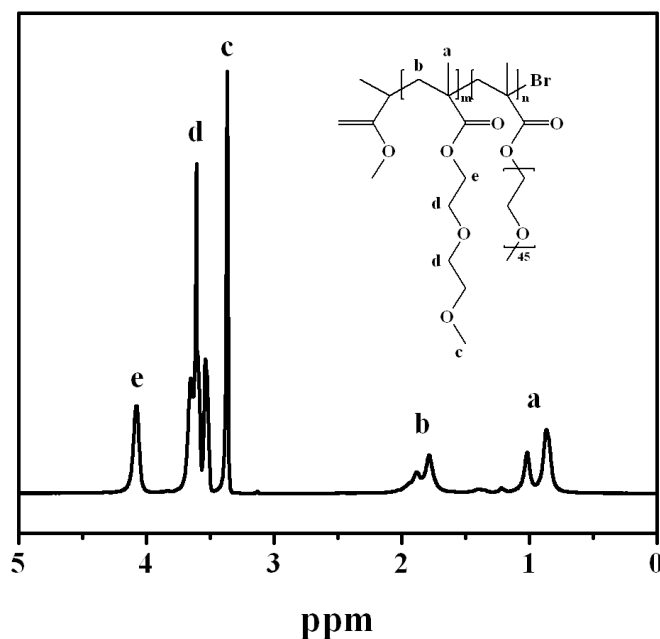

Figure S2. ^{1}H NMR spectra of P(MEO$_2$MA-*co*-PEGMA$_{2080}$) in CDCl$_3$ at 25 ^{o}C.

Gel Permeation Chromatography (GPC)

Molecular weight and molecular weight distribution were determined by OmniSEC GPC system equipped with a ViscoGel Column, a RI and light scattering detectors. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. For calibration, linear polystyrene standards (PSS) were used. The GPC results, shown in Figure S3, indicate the copolymer with number average molecular weight of 17,300 g/mol was synthesized with a polydispersity index (PDI) of 1.61. The PDI is somewhat larger than normally expected for an ATRP process, however it has been previously reported that the polymerization of OEGMA-based monomer using CuBr catalyst generally yielded a PDI of between 1.5-1.8.[2, 3] However, molecular weight

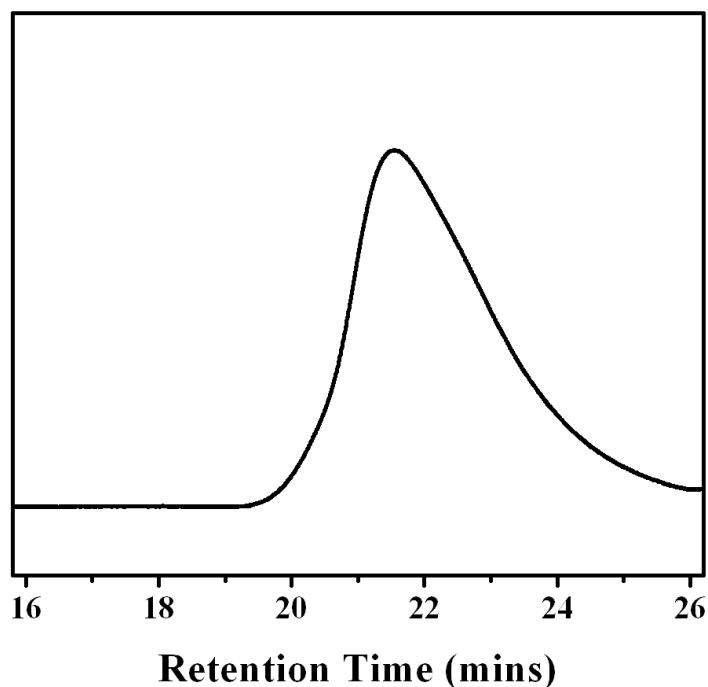distribution was found to have no significant effect on phase transition for copolymers of comparable composition.[3]

Figure S3. GPC profile of P(MEO$_2$MA-*co*-PEGMA$_{2080}$) at 25 $^{\circ}$C.

UV-Visible Spectroscopy

The thermal responsive measurements were performed on a Varian (Carey 100 Bio) UV-visible spectrophotometer equipped with a temperature controller. Transmittance of the copolymer solutions with concentration of 0.3, 0.5, 1.0 wt% were monitored as a function of temperature. All the measurements were performed at a heating rate of 1 $^{\circ}$C/min and at a visible wavelength of 500 nm.

Dynamic and Static Light Scattering

Light scattering measurements were performed on a Brookhaven BI-200SM goniometer and BI-9000AT digital correlator equipped with an argon-ion laser. A 0.45 μm filter was used to remove dust prior to all the measurements, and the experimental temperature was controlled by a PolyScience water-bath. For dynamic light scattering (DLS), the time correlation function of the scattering intensity $G_2(t)$ is defined as $G_2(t) = I(t) I(t + \Delta t)$, where $I(t)$ is the intensity at time t and Δt is the lag time, and the inverse Laplace transform of REPES in the Gendist software package was used to analyze time correlation functions with the probability of reject set at 0.5. Thus, the apparent hydrodynamic radius R_h can be determined from the Stocks-Einstein equation:

$$R_h = \frac{kTq^2}{6\pi\eta\Gamma} \qquad\qquad (1)$$

where k is the Boltzmann constant, q is the scattering vector ($q = 4\pi n \sin(\theta/2)/\lambda$, where n is the refractive index of solvent, θ is the scattering angle, and λ is the wavelength of the incident laser light in vacuum), η is the solvent viscosity, and Γ is the decay rate.

For static light scattering (SLS), it can be used to measure the average radius of gyration (R_g) and weight-average molar mass (M_w) of the aggregates. In this experiment, the M_w of the micelles can be obtained from SLS measurements based on the Debye equation:

$$\frac{KC}{R(q)} = \frac{1}{M_w}\left(1 + \frac{1}{3}R_g^2 q^2\right) + 2A_2C \qquad\qquad (2)$$

where K is an optical parameter ($K = [4\pi^2 n_{tol}^2(dn/dc)^2]/N_A\lambda^4$ where n_{tol} is the refractive index of toluene (1.494), dn/dc is the refractive index increment of the polymer measured using BI-DNDC, N_A is Avogadro's constant, and λ is the wavelength), C is the concentration of the polymer solution, $R(q)$ is the Rayleigh ratio, q is the scattering vector, and A_2 is the second virial

coefficient. The absolute excess time-averaged scattered intensity, i.e., Rayleigh ratio $R(q)$, is expressed by the equation:

$$R(q) = R_{tol,90}\left(\frac{n}{n_{tol}}\right)^2 \frac{I-I_0}{I_{tol}} \sin\theta \qquad (3)$$

where $R_{tol,90}$ is the Rayleigh ratio of toluene at scattering angle 90° with a value of 40×10^{-6} cm^{-1}, n is the refractive index of the solvent, I, I_0, and I_{tol} are the scattered intensities of the solution, solvent, and toluene, respectively, and θ is the scattering angle. In our case, the concentration of the polymer solution is sufficiently low (0.02 wt%), and the $2A_2C$ term in Eq. 2 is expected to be negligible. Therefore, the intercept of the plot of $KC/R(q)$ against q^2 yields the inverse of the apparent weight-average molar mass (M_w^{app}); consequently, the aggregation number of the micelle can be evaluated using the equation $Z = M_w^{app}/M_w$, where M_w is the molar mass of the single polymer chain.[4, 5]

Transmission Electron Microscopy (TEM)

Transmission electron microscopic studies were performed using a Philips CM10 electron microscopy. The TEM samples were prepared by depositing one drop of 0.02wt% particle suspensions onto carbon coated TEM copper grid, which was placed on a filter paper. The excess liquid was absorbed by filter paper and the remaining liquid was allowed to air-dry overnight at room temperature.

References

(1) Lutz, J.-F.; Weichenhan, K.; Akdemir, Ö.; Hoth, A. *Macromolecules* **2007**, *40,* 2503-2508.

(2) Matyjaszewski, K., Davis, T. P., Eds.; *Handbook of Radical Polymerization;* Wiley Interscience: Hoboken, NJ, 2002; p 920.

(3) Lutz, J.-F.; Hoth, A. *Macromolecules* **2006**, *39*, 893-896.

(4) Ravi, P.; Wang, C.; Tam, K. C.; Gan, L. H. *Macromolecules* **2003**, *36,* 173-179.

(5) Wang, C.; Wyn-Jones, E.; Sidhu, J.; Tam, K. C. *Langmuir* **2007,** *23,* 1635-1639.