

Thermoresponsive Oligo(ethylene glycol)-Based Polymer Brushes on Polymer Monolith for All-Aqueous Chromatography

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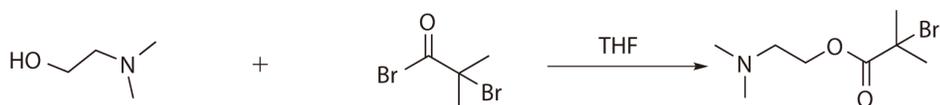
Experimental Section

Materials

2-(2-Methoxyethoxy)ethyl methacrylate (MEO₂MA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA; Mn = 475 g/mol) were obtained from Aldrich (St. Louis, Mo, USA). 2-(Dimethylamino)ethanol was supplied by Sigma Aldrich (Steinheim, Germany). Tetrahydrofuran (THF), Triethylamine, copper bromide (CuBr₂) and 2-Bromoisobutyryl bromide were obtained from Beijing Chemical Plant (Beijing, China). Pentamethyldiethylenetriamine (PMDETA) was obtained from JK Ltd (Tokyo, Japan).

Preparation of Water-soluble ATRP Initiator

Water-soluble ATRP initiator was prepared as shown in Figure S1 and procedure was described as follows: 2-(Dimethylamino)ethanol (4.0 g, 40.5 mmol) and triethylamine (5.0 g, 50.0 mmol) were added to a three necked flask with a magnetic stirrer. After the flask was purged with nitrogen for 30 min, dry THF (20 mL) was added via double-tipped needle, and the flask was cooled to -15 °C. 2-Bromoisobutyryl bromide (6.1 mL, 50.0 mmol) was then added slowly via syringe. A white precipitate formed within 5 min. The reaction solution was allowed to warm to room temperature over approximately 2 h and was stirred for further 14 h. After this time, the reaction solution was filtered to remove the white precipitate, and decolorizing charcoal was added to the yellow filtrate. This mixture was then filtered again, and the THF was removed under vacuum.



2-(dimethylamino)ethanol 2-bromoisobutyryl bromide initiator

Figure S1. Scheme for the synthesis of the water-soluble ATRP initiator.

Preparation of P(MEO₂MA-*co*-OEGMA) via ARGET ATRP

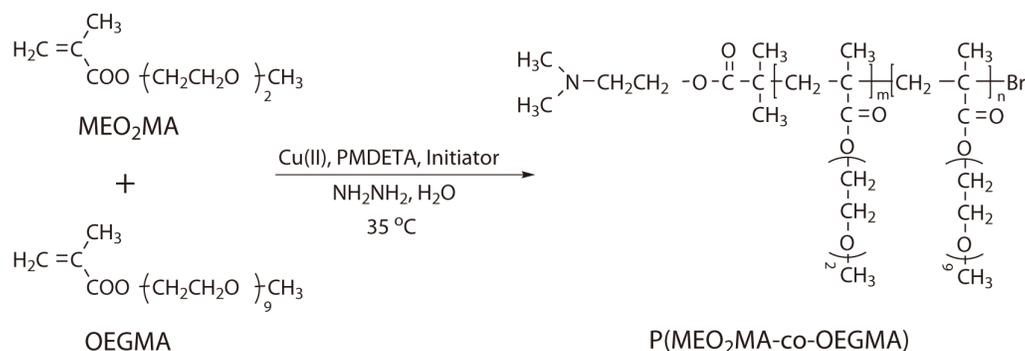


Figure S2. Scheme for synthesis of P(MEO₂MA-*co*-OEGMA) by ARGET ATRP.

P(MEO₂MA-*co*-OEGMA) was prepared as shown in Figure S2 and the detailed procedure follows: the initiator (0.02 mL, 0.02 mmol), CuBr₂ (0.0034g, 0.15 mmol), PMDETA (0.032 mL, 0.15 mmol), MEO₂MA (0.76 mL, 4.11 mmol), OEGMA (0.14 mL, 0.32 mmol) and 20 mL water were added to a flask. The resulting mixture was deoxidized by purging with argon for 5 min at room temperature. The flask was immersed in an oil bath preheated to 37 °C. Then hydrazine (0.037 mL, 0.60 mmol) was added to the above solution. The polymerization was stopped by exposing the reaction solution to the air. Subsequently, 30 mL THF was added to the reaction solution, followed by excess MgSO₄ to absorb the water. After filtration, the THF solution of P(MEO₂MA-*co*-OEGMA) was passed through an alumina column to remove residual catalyst. THF was then removed under vacuum, yielding colourless

oil.

Characterizations of the Prepared P(MEO₂MA-*co*-OEGMA) Copolymers

The prepared copolymers were analyzed by gel permeation chromatography (GPC), which was performed on a Waters 1515 HPLC solvent pump equipped with a set of Waters Styragel columns and a Waters 2414 differential refractometer detector. THF was used as eluent at a flow rate of 1.0 mL/min with polystyrene calibration. The LCST value was determined from the dependence of absorbance at 632 nm on temperature using an ultraviolet-visible light (UV-Vis) spectrophotometer (Specord 200, Analytic Jena, Germany) coupled with a temperature controller. Cloud points were determined using 1 mg/mL aqueous solutions with a heating rate of 1 °C/min.

Table S1. Characterization of the prepared P(MEO₂MA-*co*-OEGMA) copolymers

Code ^a	Preparation time (h)	MEO ₂ MA/OEGMA (Molar ratio in feed)	M _n ^b (g mol ⁻¹)	PDI ^b	LCST ^c (°C)
P3-15	3	85/15	12400	1.46	38.3
P4-15	4	85/15	13082	1.53	36.8
P8-15	8	85/15	22328	1.47	34.9
P4-10	4	90/10	8391	1.80	25.7
P4-20	4	80/20	12762	1.59	44.1

^aAbbreviated as Px-y where x and y represent reaction time and feed mole ratio of OEGMA, respectively.
^bMeasured by GPC with PS standard. ^c Defined as the temperature at 50% transmittance in Milli-Q water.

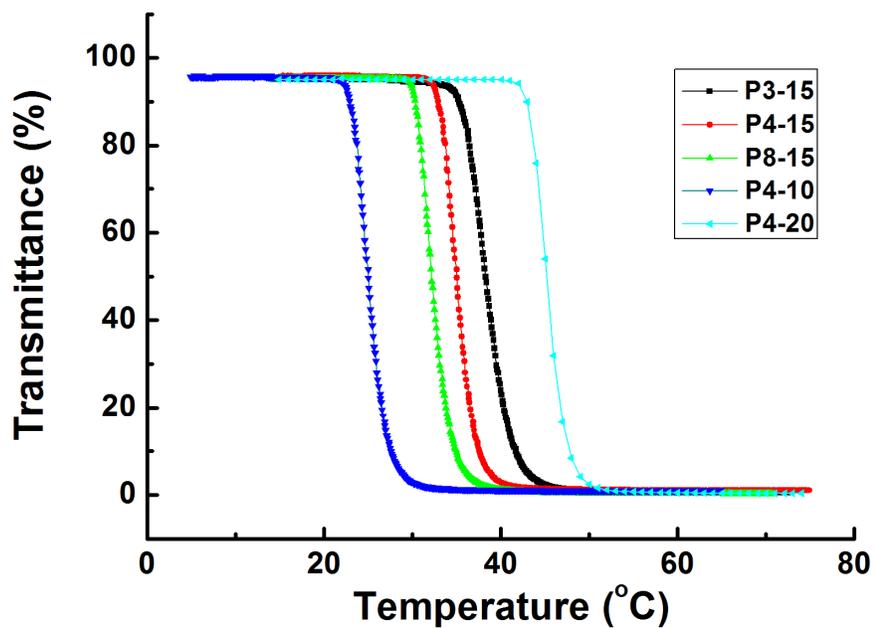


Figure S3. Phase transition profiles of P3-15, P4-15, P8-15, P4-10 and P4-20 in Milli-Q water.

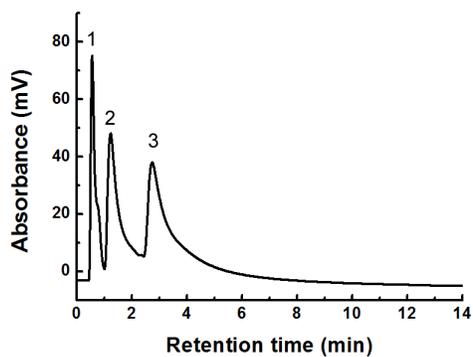


Figure S4. Chromatogram of the three-steroid mixture. Peak 1 represents hydrocortisone; 2, testosterone; 3, medroxyprogesterone acetate. Conditions: column, polymer monolith prepared with 12 h of grafting time in 100 mm x 4.6 mm I.D. column; mobile phase, Milli-Q water; flow rate, 3.0 mL/min; temperature, 40 °C.