

Electronic Supplementary Information (ESI)

Thiourea-tagged poly(octadecyl acrylate) gels as fluoride and acetate responsive polymer gels through selective complexation

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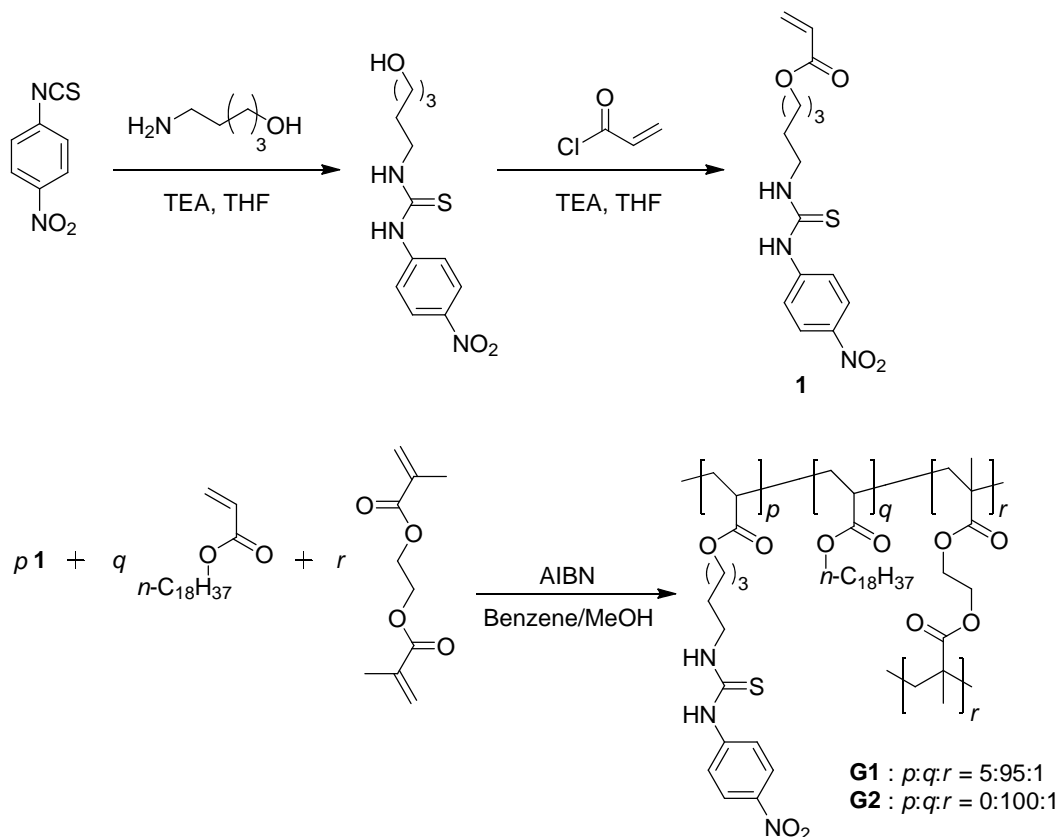
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Experimental Methods

1) Preparation of monomer **1** and polymer gel **G1** and **G2**

Monomer **1** and polymer gel **G1** and **G2** were prepared according to the following scheme.



Preparation of monomer **1**

To a stirred solution of 4-nitrophenyl isothiocyanate (3.5 g, 19.4 mmol) and 5-aminopentan-1-ol (2.0 g, 19.4 mmol) in 100 mL dry THF was added TEA (2.8 mL, 20.0 mmol). After stirring 4h at room temperature, the reaction mixture was concentrated by rotary evaporator. The residue was partitioned between ethyl acetate and water. The organic layer was successively washed with water, brine and dried over anhydrous Na₂SO₄. Filtration and evaporation by rotary evaporator furnished 1.5 g of crud *N*-(5-hydroxypentyl)-*N'*-(4-nitrophenyl)thiourea, which was used to react next step without further purification.

To a stirred solution of *N*-(5-hydroxypentyl)-*N'*-(4-nitrophenyl)thiourea (1.5 g, 5.3 mmol) in THF (50 mL) at 0 °C were added TEA (0.8 mL, 5.7 mmol) and acryloyl chloride (0.440 mL, 5.4 mmol). After stirred for 12 hr, the reaction mixture was filtered

and solvent was evaporated by rotary evaporator to furnish crud product. The crude product was purified by flash chromatography (25% hexane: ethyl acetate) to give compound **1** (1.25g, 70%). ¹H NMR (400 MHz, CDCl₃): δ 8.66 (broad-s, 1H, NH) 8.21 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.65 (broad-s, 1H, NH), 6.39 (dd, *J*₁ = 17.2 Hz, *J*₂ = 1.5 Hz, 1H), 6.15-6.06 (m, 1H), 5.85 (dd, *J*₁ = 10.3 Hz, *J*₂ = 1.5 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.66 (d, *J* = 5.7 Hz, 2H), 1.77-1.65 (m, 4H), 1.49-1.42 (m, 2H).

Preparation of G1

A typical protocol is as follows: 33.78 mg (0.1 mmol) of **1** (*p*), 617 mg (1.9 mmol) of octadecyl acrylate, 3.78 μL (0.02 mmol) of ethylene glycol dimethacrylate, and 6.57 mg (0.04 mmol) of azobisisobutyronitrile (AIBN) were dissolved in benzene (360 μL) and methanol (30 μL). The solution was degassed and then placed into sealed glass tube for copolymerization by heating for 48 h at 60°C. The formed gel was washed methanol for 48 h, then air-dried at room temperature. The sample was cut into cylinders of about 1.0 mm in length and dried *in vacuo* at 40°C.

Preparation of G2

A typical protocol is as follows: 649 mg (2.0 mmol) of **1**, 3.78 μL (0.02 mmol) of ethylene glycol dimethacrylate, and 6.57 mg (0.04 mmol) of azobisisobutyronitrile (AIBN) were dissolved in benzene (400 μL). The solution was degassed and then placed into sealed glass tube for copolymerization by heating for 48h at 60°C. The formed gel was washed methanol for 48 h, then air-dried at room temperature. The sample was cut into cylinders of about 1.0 mm in length and dried *in vacuo* at 40°C.

2) Measurement of Swelling Degrees

A sliced each dried gel was taken weight (*W*_{dry}) and it was placed in to tightly capped vials contain THF (*ε*=7.6) mixed with respective anion contain tetra(*n*-butyl)ammonium salts in the various concentrations at room temperature. After immersion for 2 days, the swelled gel was carefully transferred to another vials and weight was measured for swelled gel (*W*_{wet}). We measured *Q* of the gels, which is defined by as the following equation;

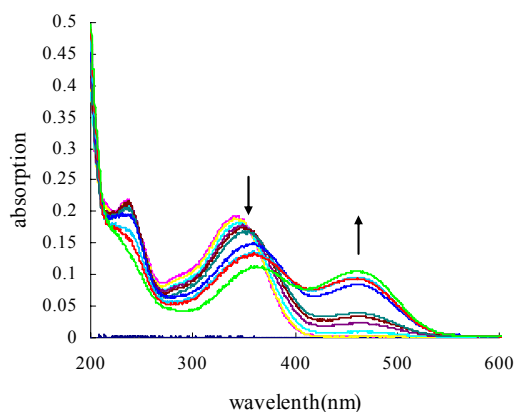
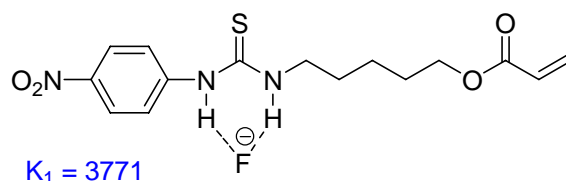
$$Q = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (\text{wt/wt})$$

where *W*_{dry} and *W*_{wet} are the weights of the dried gel and the wet gel, respectively.

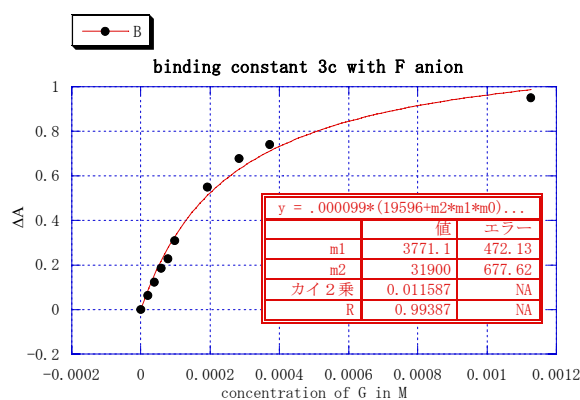
3) Titration of **1** with tetra(*n*-butylammonium) fluoride

Binding constant was determined for host with guest by UV absorption spectroscopic method.

Binding constant between thiourea monomer **1** and tetra(*n*-butyl)ammonium fluoride (TBAF) in acetonitrile.

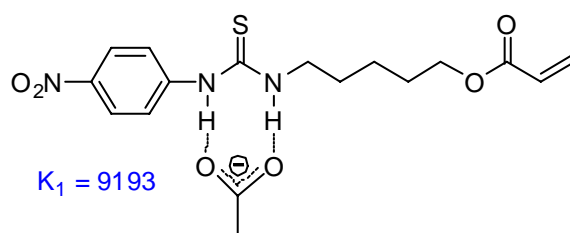


Host concentration = 0.000099M, at 343nm. TBAF used as guest

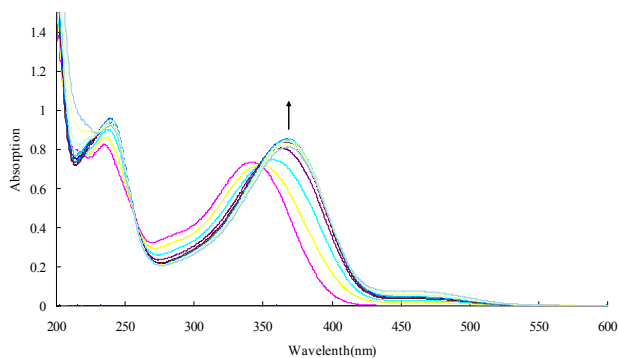


4) Titration of **1** with tetra(*n*-butyl)ammonium acetate

Binding constant between thiourea monomer **1** and tetra(*n*-butyl)ammonium Acetate (TBAOAc) in acetonitrile.



Titration Vs TBAOAc



Host concentration = 0.000029M, at 343nm. TBAOAc used as guest

