Supporting Information:

Aggregation-induced Microgelation: a New Approch to Prepare Gels in Solution

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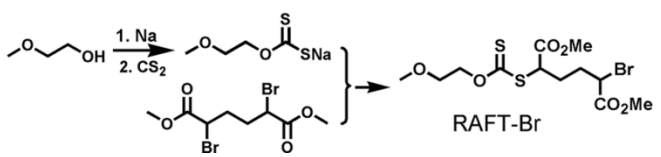
Materials.

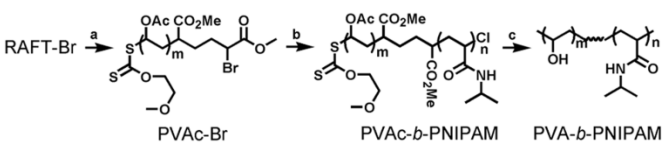
Vinyl acetate (AR, Beijing Chemicals Co.) was dried over calcium hydride and distilled under nitrogen. 2, 2′-Azobisisobutyronitrile (AIBN, AR, Beijing Chemicals Co.) was recrystallized from methanol. *N*-isopropylacrylamide (NIPAm, Aldrich, 97%) was recrystallized from benzene/hexane. All other reagents, including adipic acid (AR, Sinopharm Chemical Reagent Co.), copper(I) chloride (CuCl, 99.995+%), ethylene glycol monomethyl ether (AR, Beijing Chemicals Co.) were used as received. Dimethyl 2, 5-dibromoadipate and tris (2-dimethylaminoethyl)amine (Me_6TREN) were prepared as described in the literature[1, 2].

Characterization.

Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) (flow rate: 1 mL/min) at 35 ºC with a Waters 1525 binary HPLC pump equipped with a Waters 2414 refractive index detector and three Waters Styragel HR columns (1×10^4, 1×10^3 and 500 Å pore sizes). Monodisperse polystyrene standards were used for calibration. The NMR spectra were recorded in $CDCl_3$ on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer.



Scheme S1. Synthesis of difunctional compound with an active halide group and a xanthate group in the molecule



a: VAc, AIBN, 60 °C; b: NIPAm, CuCl, Me_6TREN, THF/iPrOH = 1:1 (w/w), 25 °C; c: n-propylamine, NaOH, methanol.

Scheme S2. General procedure for the preparation of PVA-*b*-PNIPAm

Synthesis of Dimethyl 2-Bromo-5-(2-methoxy-ethoxythiocarbonylsulfanyl) Adipate (RAFT-Br).

Sodium (0.4 g, 17 mmol) was added to ethylene glycol monomethyl ether (10 mL, 0.13 mol) until disappearance of sodium. Carbon disulfide (2 mL, 33 mmol) was slowly added, and the mixture was stirred at room temperature for 6 h. The obtained solution was added to the solution of dimethyl 2, 5-dibromoadipate (5.6 g, 17 mmol) in THF (60 mL), and the mixture was stirred for 12 h at room temperature. The precipitate was isolated by filtration and the solvent was removed under reduced pressure. The product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 15/1, v/v) to get a pale yellow liquid in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.01-2.14 (m, 4H, –CH_2CH_2–), 3.38 (s, 3H, CH_3OCH_2–), 3.70-3.76 (m, 8H, –$COOCH_3$, CH_3OCH_2–), 4.24 (t, 1H, BrCH–), 4.40 (t, 1H, –SCH–), 4.68 (t, 2H, –CH_2C(S)S–). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 28.8, 31.8 (–CH_2CH_2–), 44.4 (t, 1H, BrCH–), 51.4 (t, 1H, –SCH–), 52.8, 52.9 (–COOCH_3), 58.9 (CH_3OCH_2–), 69.4 (CH_3OCH_2–), 73.0 (–CH_2C(S)S–), 160.5, 170.5 (–COOCH$_3$), 211.5 (–C(S)S–).

Typical Procedure for the RAFT[3] Polymerization of VAc.

A mixture of RAFT-Br (0.467 g, 1.16 mmol), AIBN (20 mg, 0.12 mmol), and vinyl acetate (25 g, 291 mmol) was degassed by three freeze–pump–thaw cycles, sealed under nitrogen, and heated at 60 ºC. After the prescribed time, the reaction mixture was dissolved in THF and precipitated in petroleum ether to recover the PVAc-Br.

Typical Procedure for the ATRP of NIPAm.

CuCl (16 mg, 0.16 mmol) was added to a mixture of NIPAm (2.6 g, 23 mmol), PVAc-Br ($M_{n,NMR}$ = 14900, PDI = 1.22, 1 g, 0.067 mmol), Me_6TREN (37 mg, 0.16 mmol) and THF/*i*POH (4 g, w/w = 1:1) degassed by three freeze–pump–thaw cycles. The mixture was sealed under nitrogen and heated at 25 ºC. After the prescribed time, the reaction mixture was condensed, dissolved in THF, passed through a short neutral aluminum oxide column, and precipitated in diethyl ether to recover the block copolymer.

Hydrolysis of PVAc-*b*-PNIPAm to obtain PVA-*b*-PNIPAm.

n-Propylamine (1 mL, 12 mmol) was added to the methanol solution (20 mL) of $PVAc_{170}$-*b*-$PNIPAm_{85}$ (0.5 g, 3.5 mmol of vinyl acetate units) and stirred for 0.5 h, then the methanol solution (10 ml) of sodium hydroxide (0.16 g, 4.0 mmol) was added, and the mixture was stirred at room temperature for 6 h. The precipitate was filtered and dissolved in water. The solution was dialyzed and the product was obtained by freeze-drying.

Our group[3] and Matyjaszewski's group[4] have reported that block polymers of vinyl acetate and other monomers (styrene, (meth)acrylates) can be synthesized by combination of RAFT[3] (Reversible Addition-Fragmentation chain Transfer) polymerization and ATRP (Atom Transfer Radical Polymerization)[4, 5] with a halide-xanthate initiator. But block

copolymers of PVA could not be obtained using the reported initiator. A new initiator (RAFT-Br) was synthesized, and the xanthate group is connected to the ATRP initiator group by a carbon-carbon linkage (**Scheme S1**). Following the same polymerization procedure as reported, PVAc-*b*-PNIPAm was synthesized by the sequential RAFT polymerization of VAc and ATRP of PNIPAm (**Scheme S2**), hydrolysis of which under basic conditions in methanol led to PVA-*b*-PNIPAm.

The GPC curves of PVAc-*b*-PNIPAm with different molecular weights are shown in **Fig S1**. The block copolymers were analyzed by ^{1}H NMR (**Fig S2**); the signals corresponding to the two blocks were clearly observed. The block lengths were determined by ^{1}H NMR. The results are summarized in **Table S1**.

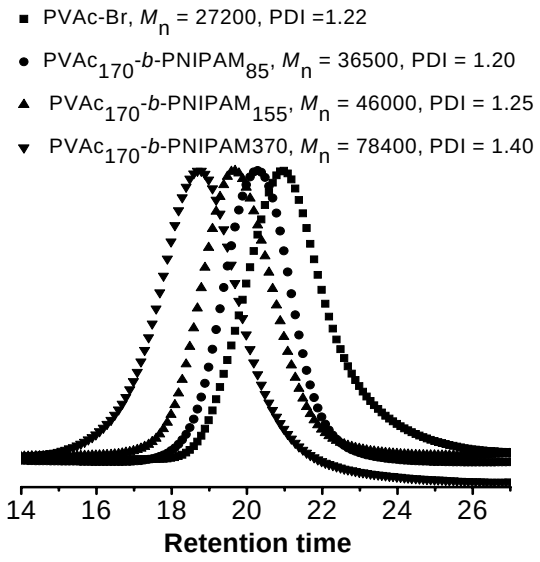


Fig. S1 GPC curves of PVAc-Br and PVAc-*b*-PNIPAm.

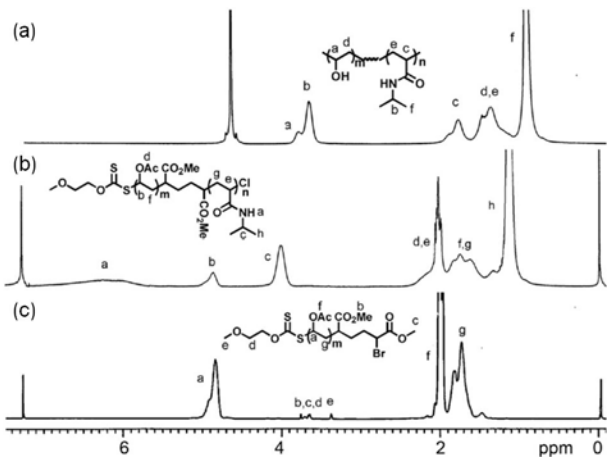


Fig. S2 (a) ^{1}H NMR (300 MHz) spectra of PVAc-Br ($M_{n,GPC}$ = 27200, PDI = 1.22) in $CDCl_3$, (b) PVAc-*b*-PNIPAm ($M_{n,GPC}$ = 78400, PDI = 1.40) in $CDCl_3$, (c) PVA-*b*-PNIPAm in D_2O.

Table S1. Synthesis of PVAc-*b*-PNIPAm with different molecular weights.

Polymer	$M_{n,GPC}$[a] (10^3)	$M_{n,NMR}$ (10^3)	PDI[a]
PVAc$_{170}$-Br	27.2	15.0	1.22
PVAc$_{170}$-*b*-PNIPAm$_{85}$	36.5	24.6	1.20
PVAc$_{170}$-*b*-PNIPAm$_{155}$	46.0	32.5	1.25
PVAc$_{170}$-*b*-PNIPAm$_{370}$	78.4	56.8	1.40

[a]: GPC data were based on polystyrene standard calibration.

Fig. S3 shows the CONTIN results of PVA$_{170}$-*b*-PNIPAm$_{370}$ at 36, 37 and 38 °C during the heating process. Only one compoment is observed in the solution, and the polydispersity is similar.

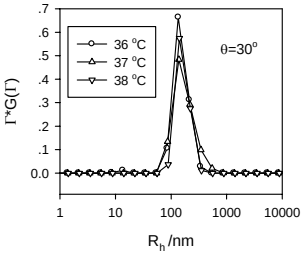


Fig. S3 CONTIN results of PVA$_{170}$-*b*-PNIPAm$_{370}$ at 36, 37 and 38 °C during the heating process. C= 2.0×10^{-4} g/mL.

Fig. S4 shows the CONTIN results of PVA$_{170}$-*b*-PNIPAm$_{85}$ with 1 M urea at selected temperatures during the heating and cooling processed. From the figure, we could find that no apparent bimodal distribution or mode split is observed (Fig. 8C), indicating that 1.0M urea changes the aggregation behavior of PVA$_{170}$-*b*-PNIPAm$_{85}$.

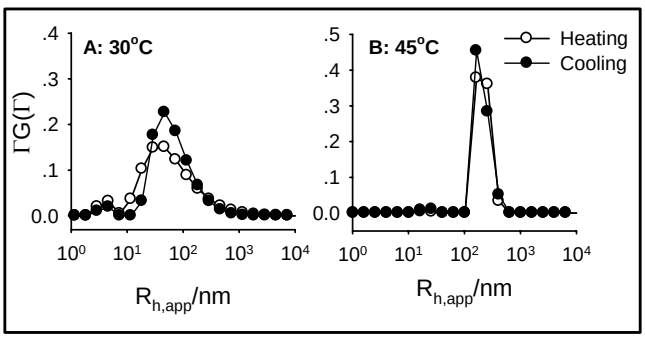


Fig. S4 CONTIN results of PVA$_{170}$-*b*-PNIPAm$_{85}$ with 1.0M urea at selected temperatures during the heating and cooling processed. C= 2.0×10^{-4} g/mL.

1. H. A. Watson and B. T. Oneill, *J. Org. Chem.*, 1990, **55**, 2950-2952.
2. M. CIAMPOLINI and N. NARD1, *Inorg. Chem.*, 1966, **5**, 41-44.
3. J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559-5562.
4. J. S. Wang and K. Matyjaszewski, *J Am Chem Soc*, 1995, **117**, 5614-5615.
5. M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721-1723.