Supporting Information:

Aggregation-induced Microgelation: a New Approach 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 (Me₆TREN) 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 × 10⁴, 1 × 10³ and 500 Å pore sizes). Monodisperse polystyrene standards were used for calibration. The NMR spectra were recorded in CDCl₃ on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer.

Hydrolysis of Polyvinyl Acetate-b-PNIPAm to Obtain Polyvinyl Acetate-b-PNIPAm.

n-Propylamine (1 mL, 12 mmol) was added to the methanol solution (20 mL) of Polyvinyl Acetate-b-PNIPAm₄₅ (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 5 (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 1H NMR (Fig S2); the signals corresponding to the two blocks were clearly observed. The block lengths were determined by 1H NMR. The results are summarized in Table S1.

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ GPC (10^3)</th>
<th>$M_n$ NMR (10^3)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAcBr</td>
<td>27.2</td>
<td>15.0</td>
<td>1.22</td>
</tr>
<tr>
<td>PVAc170-b-PNIPAm85</td>
<td>36.5</td>
<td>24.6</td>
<td>1.20</td>
</tr>
<tr>
<td>PVAc170-b-PNIPAm155</td>
<td>46.0</td>
<td>32.5</td>
<td>1.25</td>
</tr>
<tr>
<td>PVAc170-b-PNIPAm370</td>
<td>78.4</td>
<td>56.8</td>
<td>1.40</td>
</tr>
</tbody>
</table>

GPC data were based on polystyrene standard calibration.

Fig. S3 shows the CONTIN results of PVA170-b-PNIPAm370 at 36, 37 and 38 °C during the heating process. Only one component is observed in the solution, and the polydispersity is similar.

![CONTIN results of PVA170-b-PNIPAm370 at 36, 37 and 38 °C during the heating process. C= 2.0×10^-4 g/mL.](image)

Fig. S4 shows the CONTIN results of PVA170-b-PNIPAm85 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 PVA170-b-PNIPAm85.

![CONTIN results of PVA170-b-PNIPAm85 with 1.0M urea at selected temperatures during the heating and cooling processed. C= 2.0×10^-4 g/mL.](image)