Design of smart polyacrylate showing thermo-, pH-, and CO₂-responsive feature

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Experimental section

Materials

N-isopropylacrylamide (NIPAM; TCI, 98%), methacryloyl chloride (Innochem, 97%), acryloyl chloride (Aladdin, 96%), 2-(methylamino)ethanol (Aladdin, 99%) and 2-(ethylamino)ethanol (Aladdin, 98%) were used as received. 2’-Azobis(isobutyronitrile) (AIBN; Sinopharm Chemical Reagent, 99%) was purified by recrystallization from ethanol. Tetrahydrofuran (THF, Shanghai Chemical Reagent Co., 99%) was refluxed with sodium chips under N₂ until dry and freshly distilled before use. Dichloromethane (Shanghai Chemical Reagent Co., 99%) was distilled over CaH₂ before use. 2-(Dodecylsulfanylthiocarbonylsulfanyl)-2-methyl propionic acid
(DDMAT) was synthesized according to literature procedures. Other reagents were all analytical grade and used as received. Deionized water was used in the present experiment.

Syntheses of the monomer 2-((3-(isopropylamino)-3-oxopropyl)(methyl)amino)ethyl acrylate (IMA) and its analogues

NIPAM (6.0 g, 53 mmol) and 2-(methylamino)ethanol (3.6 g, 48 mmol) were dissolved in 30 mL of ethanol under vigorous stirring, and the reaction mixture was refluxed at 80 °C for 2 days. The solvent was evaporated under reduced pressure to give 9.5 g of the crude product as a yellow oil. The crude product (9.5 g) and triethylamine (5.8 g, 58 mmol) were added to 30 mL of dichloromethane, and the solution was cooled in an ice bath. Subsequently, acryloyl chloride (5.2 g, 58 mmol) in 15 mL of dichloromethane was added dropwise to the solution over 30 min. The mixture was stirred for 12 h at room temperature. The mixture was diluted with 200 mL of dichloromethane and wash with NaOH aqueous solution (75 mL, 1 mol/L). The organic layer was dried over anhydrous Na₂SO₄. After filtration, the volatiles were removed and the crude product was purified by column chromatography on silica gel with ethanol/ethyl acetate (19:1) to give IMA as a yellow oil (6.2 g, 53% overall yield). ¹H NMR (CDCl₃), δ (TMS, ppm): 1.12 (6H, CH(CH₃)₂), 2.33 (5H, NCH₃ and CH₂CONH), 2.68 (2H, COOCH₂CH₂), 2.74 (2H, CH₂CH₂CONH), 4.03 (1H, CH(CH₃)₂), 4.28 (2H, COOCH₂), 5.86 (1H, trans-CH=CH₂), 6.14 (1H, CH=CH₂), 6.43 (1H, cis-CH=CH₂), 7.66 (1H, CONH). ¹³C NMR (CDCl₃), δ (TMS, ppm): 22.78,
The other three monomers of 2-((3-(isopropylamino)-3-oxopropyl)(ethyl)amino)ethyl acrylate (IEA), 2-((3-(isopropylamino)-3-oxopropyl)(methyl)amino)ethyl methacrylate (IMM) and 2-((3-(dimethylamino)-3-oxopropyl)(methyl)amino)ethyl acrylate (DMA) were synthesized with the similar procedures of IMA.

**RAFT homopolymerization of IMA**

A stock solution in THF (6 mL) comprising IMA (1.5 g, 6.2 mmol), DDMAT (11.3 mg, 31 μmol) and AIBN (1.3 mg, 8 μmol) was prepared. Aliquots (1 mL) were transferred to ampules, degassed by three freeze-pump-thaw cycles, sealed under N2, and heated at 70 °C. After the predetermined intervals, the sealed ampule was cooled in an ice bath. Small portions of the solution were withdrawn for $^1$H NMR analysis and GPC measurement. The polymer was isolated by precipitated in petroleum ether, and further purified by repeated dissolution in THF and precipitation in petroleum ether followed by drying under vacuum as a yellowish oil.

**Characterization**

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 400MHz spectrometer. The number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) were measured by gel permeation chromatography (GPC) against PMMA standard in LiBr-added DMF ([LiBr] = 50 mM) at a flow rate of 1.0
mL min\(^{-1}\) at 35 °C on three Waters Styragel columns (measurable molecular weight range: 100-5000, 500-30 000, and 5000-600 000) connected to a Waters 1515 pump and a Waters 2414 refractive index detector. The LCST of the polymers were determined by turbidity analysis on a PGENERAL TU-1901 UV/vis spectrophotometer at a wavelength of 500 nm. The operation was conducted at a heating rate of 1 °C min\(^{-1}\). The lower critical solution temperature (LCST) values were determined at the half of the maximal and minimal transmittance. Dynamic light scattering (DLS) measurements were conducted at 25 °C on a Brookhaven BI-200SM apparatus with a BI-9000AT digital correlator and a He-Ne laser at 532 nm. The data were analyzed by using the CONTIN algorithm.

**Additional Results**

![Figure S1. \(^1\)H NMR spectrum of PIMA.](image)
Figure S2. Temperature-dependent DLS results of PIMA\textsubscript{82} (1.0 wt%).

Figure S3. \textsuperscript{1}H NMR spectrum of IEA
Figure S4. $^{13}$C NMR spectrum of IEA.

Figure S5. $^1$H NMR spectrum of IMM.
Figure S6. $^{13}$C NMR spectrum of IMM.

Figure S7. $^1$H NMR spectrum of DMA.
Figure S8. $^{13}$C NMR spectrum of DMA.

Figure S9. Thermo-response of PIMA and its analogues (1.0 wt%).
Figure S10. pH titration curve of 1.0 wt% PIMA$_{82}$ at 50 °C.

References