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Supplementary Information

A Facile Approach for the Synthesis of Cyclic Poly(N-isopropylacrylamide) Based on Anthracene-Thiol Click Reaction

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Experimental

Materials

N-isopropylacrylamide (NIPAM) (Across, 99%) was recrystallized from hexane and dried under vacuum prior to use. *2,2'*-azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Toluene and tetrahydrofuran (THF) were dried by and distilled over benzophenone-Na under a nitrogen atmosphere. All other chemicals used were of at least analytical grade and used as received.

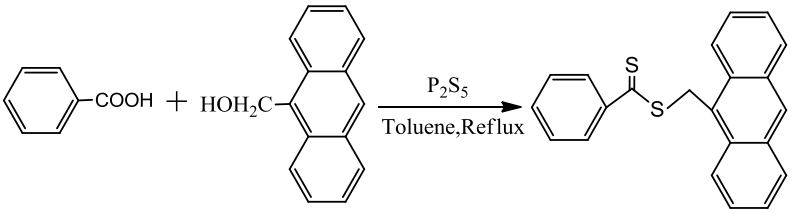
Characterization

Gel permeation chromatography (GPC) measurements were performed on a Waters 410 apparatus. Dichlormethane was used as eluent at a flow rate of 1.0 mL/min at 35

^{o}C under 2.0 g/L concentration. The apparent molecular weights and polydispersities were determined with a calibration based on linear polystyrene standards. Temperature-dependent turbidimetry was recorded on a Shimadzu UV-1650 equipped with GPS-240A temperature controller. ^{1}H NMR spectra were recorded at room temperature on a Bruker-400 spectrometer using tetramethylsilane as internal reference. UV–Vis spectra were recorded using a CARY 300 spectrophotometer

Synthesis

Anthracene-9-ylmethyl benzodithioate (AMB). AMB was prepared according to a slightly modified literature procedure (Scheme s1).[s1]



Scheme s1. Synthesis of anthracene-9-ylmethyl benzodithioate.

Benzoic acid, anthracen-9-ylmethanol, P_4S_{10} and toluene were added to a 100 ml three-necked round flask. The mixture was stirred at room temperature for half an hour and then heated to reflux for 20 hours under argon atmosphere. The reaction solution was filtrated after cooling and the filtrate was washed with deionized water. The organic solution layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evacuated off to yield a dark red solid. The crude product was purified by column chromatography on silica using mixed petroleum ether and dichlormethane (15:1) as eluent. ^{1}H NMR spectrum of the product matches with that reported on the literature[s1]. ^{1}H NMR (400HMz, $CDCl_3$), 5.54 (s, 2H); 7.34～8.20 ppm (m, 14).

Elemental analysis Calcd (%) C 76.73, H 4.65; Found (%) C 76.69, H 4.84.

Poly(*N*-isopropylacrylamide) (PNIPAM) end-capped with anthracene group by RAFT polymerization. PNIPAM end-capped with anthracene group was prepared according to a modified literature procedure[s1]. To a 50 mL three-necked round-bottom flask was added NIPAM, AIBN, and AMB (equiv to AIBN), and the reaction mixture was degassed by three freeze pump-thaw cycles and left in an argon atmosphere. Then 10 mL of toluene was added with syringe and placed in an oil bath at 90 °C for 48 h. The resulting polymerization mixture was diluted with THF and precipitated with hexane. The polymer was purified by dissolving the crude polymer in THF and then precipitated into hexane for three cycles. The pink polymer obtained was dried for 24 h in a vacuum oven at 30 °C.

***Linear*-PNIPAM-SH.** *Linear*-PNIPAM-SH was prepared according to a modified literature procedure[s2]. The PNIPAM end-capped with anthracene group was dissolved in THF under an argon flow. After complete dissolution of the polymer, 85% hydrazine hydrate (5-fold molar excess with respect to the thiocarbonylthio moiety) was degassed and added in the polymer solution with syringe. The reaction mixture was stirred for 3 days at room temperature. During this period, the originally pink solution became dark green. The reaction mixture was precipitated from hexane three times and the resulting aminolysis product (*linear*-PNIPAM-SH) was dried under vacuum.

***Cyclic*-PNIPAM.** The *linear*-PNIPAM-SH was dissolved in THF at a concentration of 0.05 g/mL. AIBN was introduced into the flask under a protection of argon flow. The

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reaction mixture was allowed to stir for 24 h at 70 ^{o}C. After the mixture was cooled to room temperature, an excess of hexane was added to precipitate the *cyclic*-PNIPAM. This purification cycle was repeated three times. The obtained product was dried overnight under vacuum for 24 h.

Temperature-Dependent Turbidimetry.

The optical transmittance of the aqueous solution of *linear*- or *cyclic*-PNIPAM at a wavelength of 500 nm was recorded.[s3] The heating rate was 0.2 °C min^{-1}. The lower critical solution temperature (LCST) and the cloud point (CP) were defined as the temperatures corresponding to 1% and 50% decreases of transmittance, respectively.

References

s1. Zhou, N. C.; Lu, L. D.; Zhu, X. L.; Yang, X. J.; Wang, X.; Zhu, J.; Zhou, D. *Polym. Bull*, **2006**, *57*, 491-498.

s2. Qiu, X. P.; Winnik, F. M. *Macromol. Rapid. Commun.* **2006**, *27*, 1648–1653.

s3. Xu, J.; Ye. J.; Liu, S. Y. *Macromolecules*, **2007**, *40*, 9103-9110.

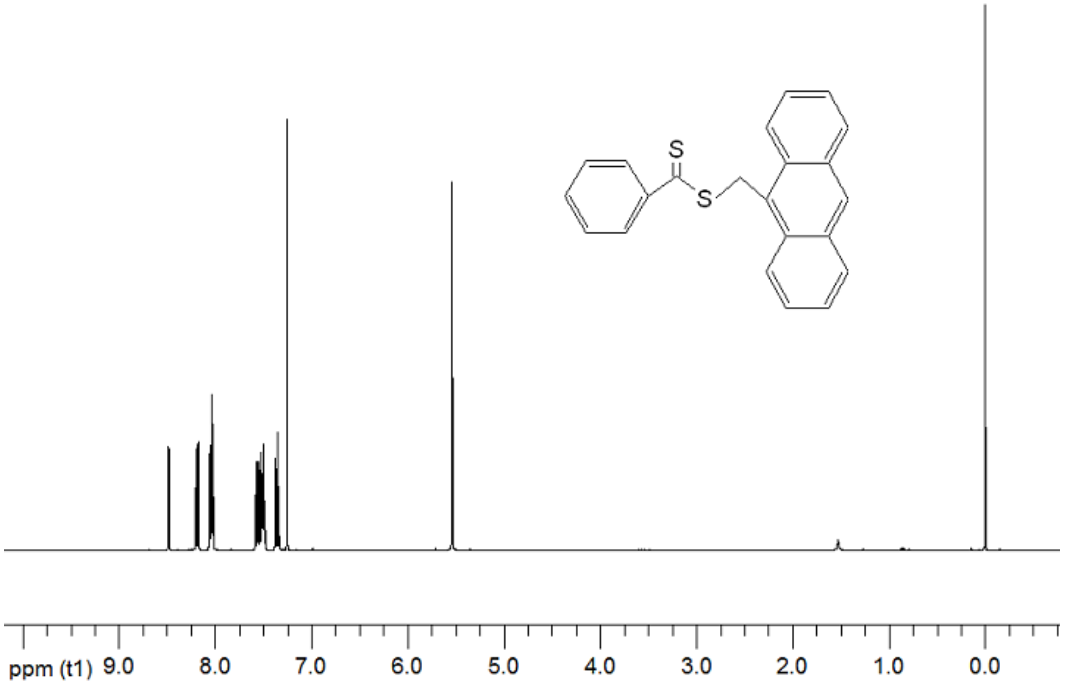

Figure S1. ^{1}H NMR spectrum of AMB.

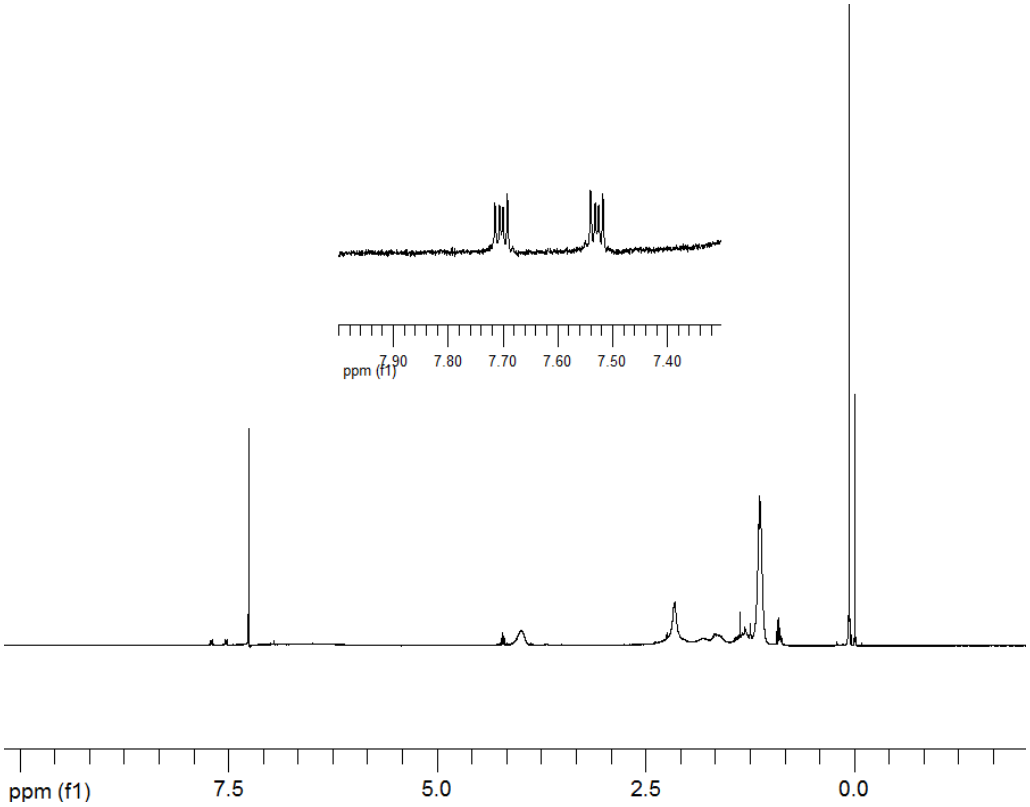

Figure S2. The typical ^{1}H- NMR spectrum of linear-PNIPAM-SH.

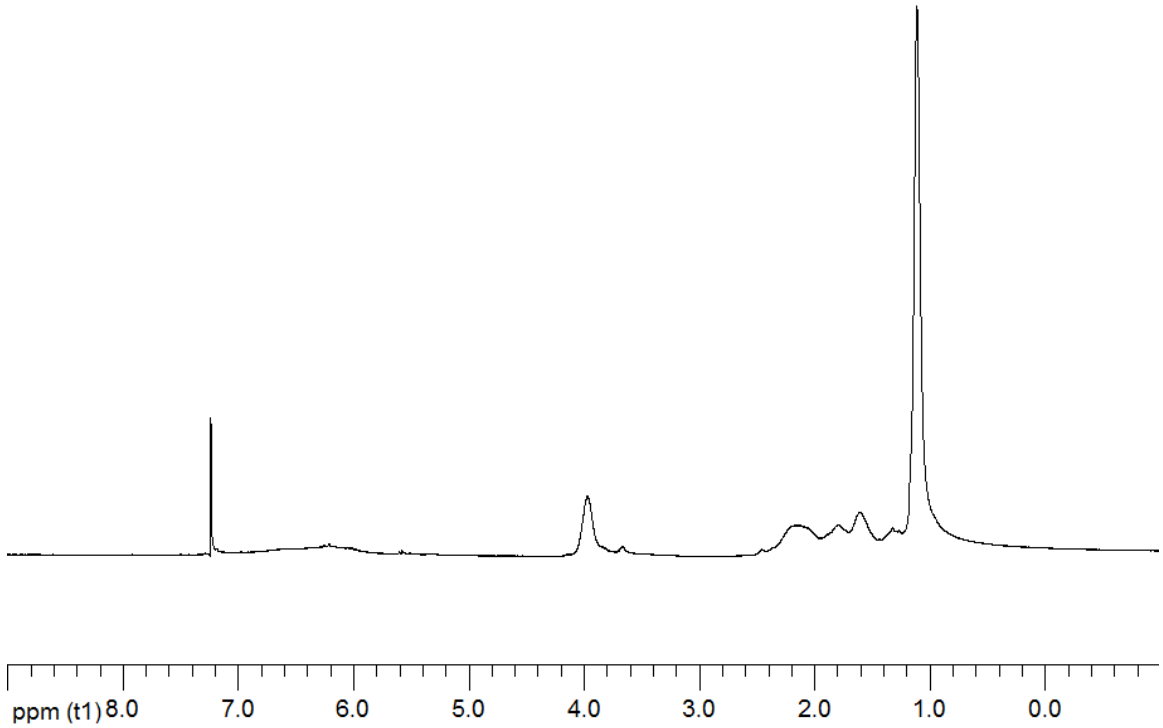

Figure S3. The typical ^{1}H NMR spectrum of cyclic-PNIPAM.