Supporting Information for:

Responsive Single-Chain Polymer Nanoparticles with Host-Guest Features

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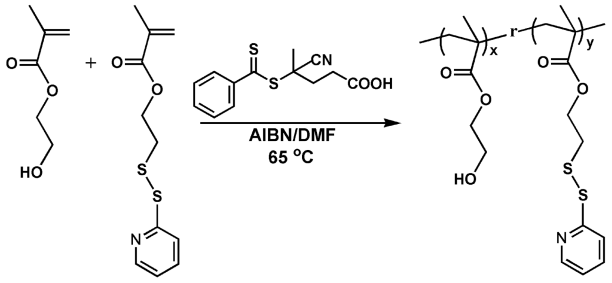
Experimental Section

Materials and Methods:

2,2-Dithiodipyridine, 2-mercaptoethanol, 2-Hydroxyethyl methacrylate (HEMA), D,L-dithiothreitol (DTT), Pyrene, Nile red, 4-Cyano-4-(phenylcarbonothioylthio)-pentanoic acid were obtained from Sigma-Aldrich and were used as received without further purification. Pyridyl disulfide ethyl methacrylate (PDSEMA) was prepared using a previously reported procedure[1]. The 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. ^{1}H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer. Atomic force microscopy (AFM) images were collected on Dimension 3000 under ambient conditions by use of silicon cantilevers. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC, DMF) using PMMA standards with a refractive index detector. Dynamic light scattering (DLS) measurements were performed using a Malvern Nanozetasizer. The emission spectra were obtained from a JASCO FP-6500 spectrofluorimeter.

Synthesis of random copolymer P(HEMA-*co*-PDSEMA) by RAFT and Schematic representation of the formation of SCPNs



To a Schlenk flask, PDSEMA (256 mg, 1 mmol), HEMA (910 mg, 7 mmol), AIBN (0.41 mg, 0.0025 mmol), and 4-cyano-4-(phenylcarbonothioylthio)-pentanoic acid (3.5 mg, 0.0125 mmol)were dissolved in 1.5 mL dry DMF. The solution mixture was subjected to three freeze-pump-thaw cycles. The sealed flask was immersed in a preheated oil bath at 65 ^{o}C. The polymerization reaction was allowed to proceed for 12 h (to polymer **1**), 20 h (to polymer **2**), 32 h (to polymer **3**), respectively. The polymerization was quenched by cooling down the flask to ambient temperature. The polymer was purified by precipitation in ethyl ether for three times.

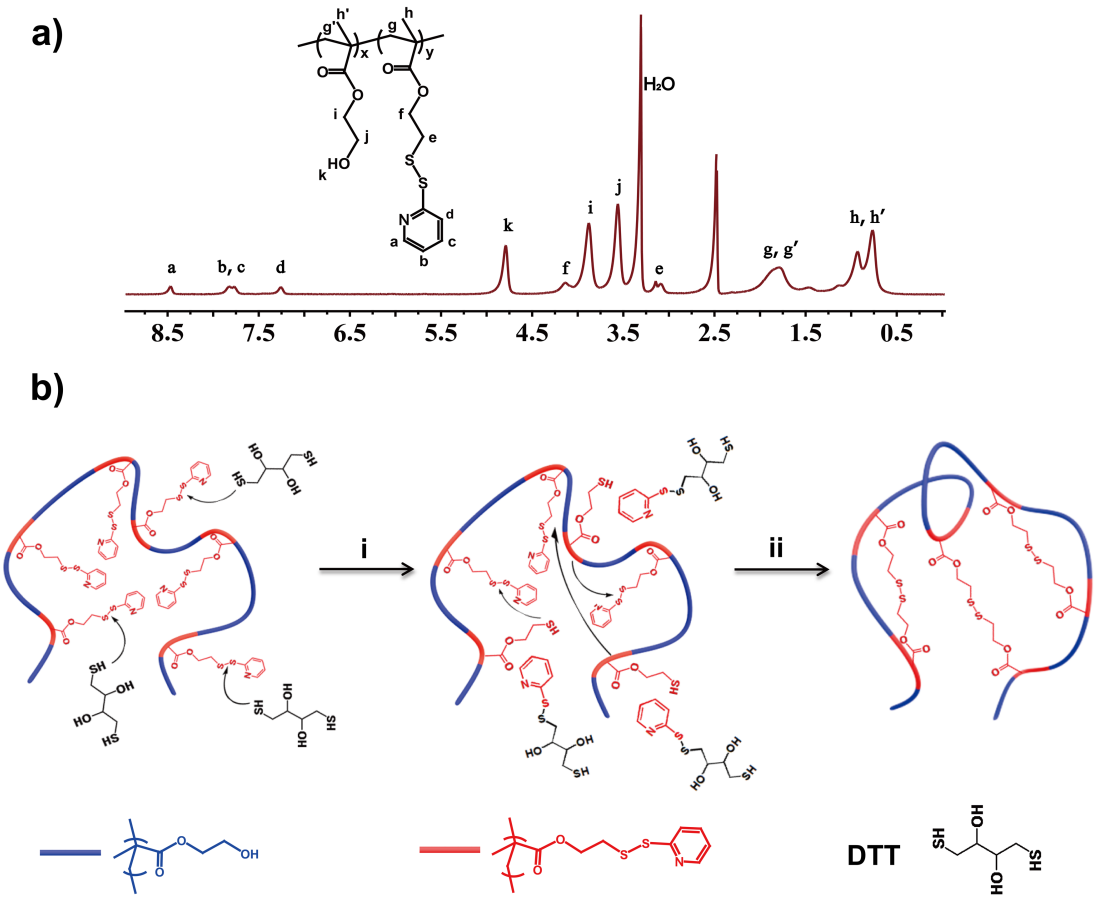


Fig. S1 (a) ^{1}H NMR of random polymer P(HEMA-*co*-PDSEMA) in $(CD_3)_2SO$. (b) Schematic representation of the formation of SCPNs: i) DTT attacks PDS groups to generate a reactive thiol unit; ii) The reactive thiols react with the remaining PDS groups to form the SCPNs.

Pyrene encapsulation

Polymer **1** was dissolved in methanol to make 0.5, 2, 5, 10, 25, and 50 mg mL^{-1} solutions. 1 mL of polymer solution was placed in a glass vial. 1 wt% of pyrene was dissolved in the vial. Then, the requisite amount of DTT (10mol% compared to PDSEMA groups), was added to polymer solution under stirring. The crosslinking reaction was allowed to proceed overnight. After that, the solution was dialyzed against water, followed by filtering through the syringe filter (0.45 μm). The final concentration of particles was diluted to 0.5 mg mL^{-1} by adding water.

Redox-responsive release for Nile red

The process of encapsulating Nile red was similar to that mentioned above. 10, 20, 30, 40, 50 mol% (against the precursor PDSEMA groups) of DTT was respectively added 1 mL of polymer 1 solution (0.5 mg mL^{-1}) containing 1wt% of Nile red under stirring overnight. Finally, the solution was dialyzed against water followed by filtrate through the syringe filter (0.45 μm). After adding 5 μM or 5 mM reductant, the spectral emission intensity of Nile red was recorded.

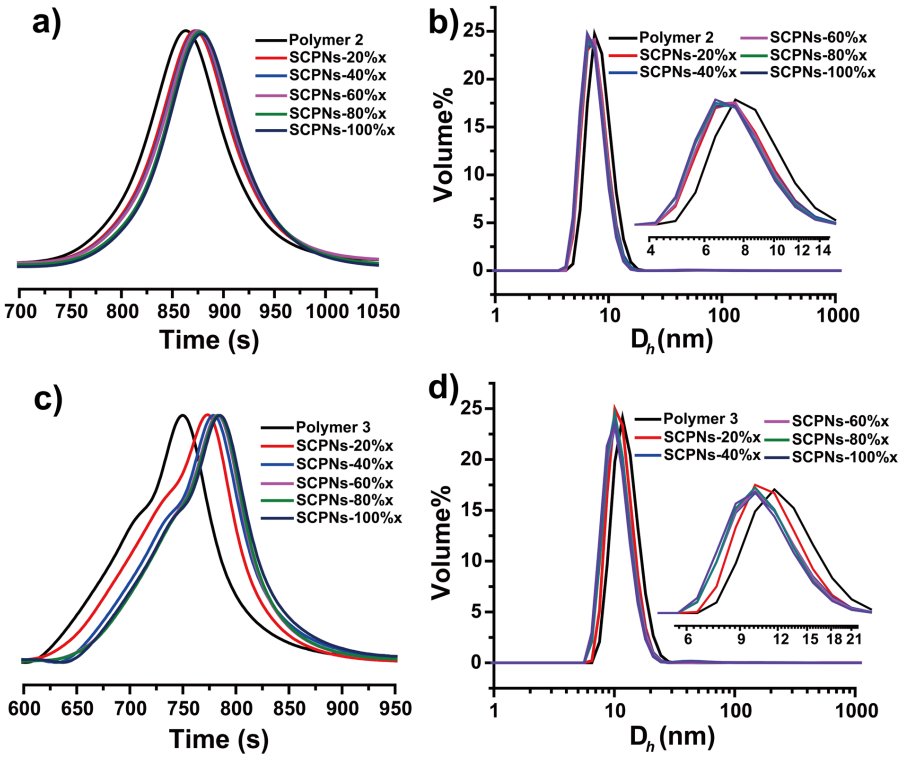


Fig. S2 (a, c) GPC and (b, d) DLS of polymer 2, polymer 3, and the corresponding SCPNs.

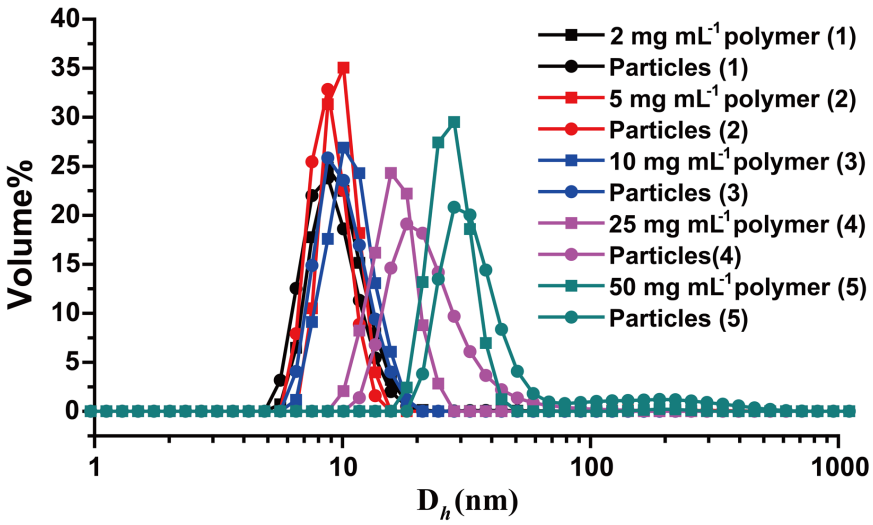


Fig. S3 DLS of polymer **1** at 2, 5, 10, 25, and 50 mg mL^{-1} and the corresponding particles by adding 10 mol% DTT.

References

S. Ghosh, S. Basu, S. Thayumanavan, *Macromolecules*, 2006, **39**, 5595-55