

# Synthesis of sulfur-rich nanoparticles using self-assembly of amphiphilic block copolymer and a site-selective cross-linking reaction



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## ABSTRACT

Water soluble sulfur-rich nanoparticles (S-NPs) having the sulfur content of more than 80 wt% were synthesized using a self-assembled block copolymer structure comprising 4-bromophenyl vinyl sulfide (BPVS) and *N*-isopropyl acrylamide (NIPAM), and a site-selective cross-linking reaction in selective aqueous solution. The core cross-linking reaction of sodium polysulfide with 1,2,3-trichloropropane as a cross-linker in the presence of poly(BPVS-*b*-NIPAM) was conducted in water, in which the site selective reaction takes place inside the micelles. DLS analysis demonstrated the formation of stable S-NPs with uniform sizes, which could be controlled by the nature of the cross-linking agents and reaction conditions ( $D_h = 140\text{--}170$  nm in  $\text{CHCl}_3$ ). UV-vis, fluorescence, and cyclic voltammetry measurements led to the optical and electrochemical properties derived from polysulfide units and incorporated cross-linked units in the resulting products, supporting the successful preparation of desired S-NPs. The S-NPs exhibited LCST behavior around 32 °C, which stems from the poly(NIPAM) shell.

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## 1. Introduction

Cross-linked block copolymer micelles have been attracted significant attention, because the cross-linking stabilization and tailoring of nanostructures can be achieved using a range of chemistries within the assembly [1–13]. Core cross-linking is one of the most useful strategies to fix the micelle structures, which can afford the structural stability of assembled structures and introduce additional functional units into the core moiety. A wide range of chemistries have been employed to afford core cross-linked polymeric nanoparticles (NPs) with various core-shell structures [1–7,9,10]. Depending on the nature of the cross-linking reactions, reagents used for the reactions, and reactive sites in the block copolymers, the chemical and physical properties and functions of resulting core cross-linked NPs can be tuned by manipulating the chemical structures of the cores, degree of the cross-linking, and size and shape of resulting NPs. The solubility and dispersibility of

the core-shell NPs and their interaction with the environment are governed by the chemical structure of the shell, which consists of solvated blocks of the copolymer. Recently, we have developed an efficient strategy for the synthesis of core cross-linked core-shell NPs with various optoelectronic functions, involving  $\pi$ -conjugated polymer [14–16],  $\pi$ -conjugated [17], fluorescent [18], and electron-deficient (acceptor-type) units [19], in the cores via the self-assembly of block copolymers with cross-linkable segments. In these systems, an *in situ* Suzuki coupling reaction [14–17], Buchwald-Hartwig coupling reaction [17], formation of imine linkages [18], and imidization [19] were employed to incorporate desired functional units into the block copolymer micelles.

In recent years, there has been renewed interest in sulfur-rich materials derived from elemental sulfur, because of their potential applications such as Li-S batteries, IR imaging technology, and self-healing materials [20,21]. In particular, much attention has been paid to “inverse vulcanization” as a useful methodology to create chemically stable and processable polymeric materials through the direct copolymerization of elemental sulfur with vinylic monomers [22]. Polymeric NPs consisted of sulfur-containing units have been the focus of intense research [23–28],

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as they exhibit a variety of interesting properties, such as high specific surface area, good solubility and processability, and characteristic sulfur-based properties. A variety of sulfur-based NPs have been designed with desirable chemical structures, sizes, topologies, and interfaces, which were synthesized by radical polymerization of bis(4-vinylthiophenyl)sulfide [23], ring-opening polymerization of propylene sulfide [24,27], and thiol-ene polymerization in water [25]. Recently, Pyun et al. reported the synthesis of water-dispersible polymer NPs with high sulfur content (>75 wt%) by interfacial polymerization between 1,2,3-trichloropropane and sodium polysulfide in water [28].

Herein, we reported a facile and convenient way to prepare novel sulfur-rich nanoparticles (S-NPs) with good solubility in organic solvent and water and characteristic thermoresponsive property (Scheme 1). For the purpose, we employed sodium polysulfide originated from elemental sulfur, a cross-linking agent, and amphiphilic block copolymer composed of 4-bromophenyl vinyl sulfide (BPVS) and *N*-isopropyl acrylamide (NIPAM), which can assemble into micelle in aqueous solution. Four different halogen compounds were selected as cross-linking agents, including 1,2,3-trichloropropane, 1,2-dibromoethane, 2,5-dibromothiophene, and 1,4-dibromobenzene, which afford core cross-linked S-NP(C3), S-NP(C2), S-NP(Th), and S-NP(Bz), respectively. The core-shell NPs with sulfur-based cross-linked cores and thermoresponsive poly(NIPAM) shell were prepared by the reaction of the halogen compound and sodium polysulfide, which can also react with Br groups in the assembled block copolymer in water. In this study, we selected sodium polysulfide and halide compounds as the functional monomers, which are similar to those used for the synthesis of disulfide and polysulfide polymers [29,30]. Distinct from Pyun's work [28] and synthetic method for polysulfide polymers, which are known as Thiokol [29–31], we employed functional block copolymer as a starting material, by which additional functionality can be incorporated into the core cross-linked NPs. In this work, the thermo-responsive property due to poly(NIPAM) block was introduced into the resulting S-NPs. Amphiphilic block copolymers with reactive Br groups in the hydrophobic segment were chosen as polymeric surfactants, because the large block lengths in the copolymers may allow for efficient steric stabilization in water. The

feasibility to incorporate various functionalities, depending on the structures of functional block copolymers and cross-linkers, and formation of stable core-shell structures are attractive features of our system for developing novel sulfur-based advanced materials.

## 2. Experimental section

### 2.1. Materials

Sulfur (Aldrich), sodium sulfide nonahydrate (Aldrich, >98%), 1,2,3-trichloropropane (TCI, >98%), 1,2-dibromoethane (TCI, >99%), 2,5-dibromothiophene (TCI, 95%), and 1,4-dibromobenzene (Aldrich, >98%) were used as received. Amphiphilic block copolymers composed of 4-bromophenyl vinyl sulfide (BPVS) and *N*-isopropyl acrylamide (NIPAM), poly(BPVS-*b*-NIPAM), were synthesized by RAFT polymerization according to our previous study [17]. The detailed procedure and synthetic results of the block copolymers are shown in Supporting Information (Table S1).

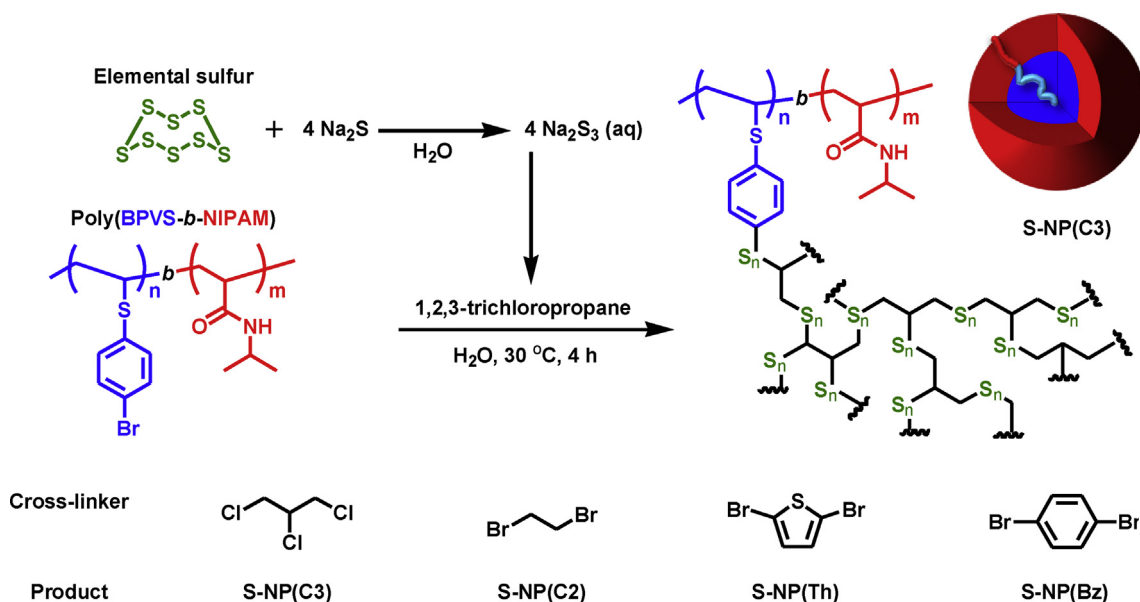
### 2.2. Sodium polysulfide

Sodium polysulfide stock solution was prepared according to the literature [28]. Elemental sulfur (641 mg, 20 mmol) was dissolved in a solution of Na<sub>2</sub>S (780 mg, 10 mmol) in 8 mL of water in a septum-sealed flask under nitrogen. The mixture was diluted by addition of water until the volume of the stock solution was 10 mL.

Note that Na<sub>2</sub>S<sub>3</sub> was commonly considered as a main structure of the resulting product obtained by the reaction between S<sub>8</sub> and Na<sub>2</sub>S under condition [28]. Whereas, Na<sub>2</sub>S<sub>x</sub> was frequently employed as the structure of the mixed products obtained by the reaction between S<sub>8</sub> and Na<sub>2</sub>S, depending on the feed ratio and conditions [31].

### 2.3. Sulfur-rich nanoparticles (S-NPs) by site-selective cross-linking reaction

A typical procedure for S-NP(C3) obtained from 1,2,3-trichloropropane is as follows: The aqueous solution (10 mL) of poly(BPVS-*b*-NIPAM) (0.042 g, 0.02 mmol based on the bromide



**Scheme 1.** Synthesis of sulfur-rich nanoparticles (S-NPs), S-NP(C3), S-NP(C2), S-NP(Th), and S-NP(Bz), from 1,2,3-trichloropropane, 1,2-dibromoethane, 2,5-dibromothiophene, and 1,4-dibromobenzene, respectively.

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