

Sulfur-rich polymer nanoparticles prepared by miniemulsion polymerization

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Electronic Supplementary Information

Synthesis of sulfur-rich polymer nanoparticles

Sulfur-rich polymer nanoparticles (SPNPs) were prepared in miniemulsion. The sulfur-rich dispersed phase was composed of sulfur (3.9 mmol of S₈), a comonomer (from 0.78 mmol to 7.8 mmol), an initiator or activator (0.25 mmol), and dipropyl sulfide (0.31 mmol). To produce different SPNPs, the comonomer used was either benzyl methacrylate, 1,3-diisopropenylbenzene, α -methyl styrene, limonene, or cyclododecene. The preferred mechanism of initiation was investigated by using different additives and initiators such as *N*-methylimidazole (NMI), or di-*tert*-butylperoxide (DTBP).

The mixture of sulfur, comonomers, and additives was heated and stirred at 130 °C for ca. 30 min to melt the sulfur and homogenize the mixture. The continuous phase was prepared by dissolving 0.4 g of polyglycerol polyricinoleate in 20 mL of glycerol. The glycerol mixture was heated to 130 °C and combined with the dispersed phase. The biphasic mixture was sonicated 4 min with a Branson SFX 550 sonifier or 10 min with a Branson SFX 250 sonifier equipped with a ¼" tip oscillating at 70% amplitude. After emulsification, the mixture was reacted for 4h (unless noted otherwise) at either 130 or 180 °C.

Synthesis of bulk sulfur-rich polymers

The synthesis of polymer in bulk was performed by heating for 4h (unless noted otherwise) a mixture of sulfur (3.9 mmol of S₈), comonomer (from 0.78 mmol to 7.8 mmol) and an initiator or activator (0.25 mmol). The mixture was heated at either 130 °C or 180 °C.

Characterization of the SPNPs

The hydrodynamic diameter and size distribution of the SPNPs were measured by dynamic light scattering (DLS) at 25°C using a Malvern NanoS90, working at an angle of 90° or a Delsa Nano S from Beckman Coulter working at an angle of 165°. The average hydrodynamic diameter and the polydispersity index (PDI) of the SPNPs suspension were obtained from the CONTIN analysis of the DLS correlation curve. Morphological studies were performed by scanning electron microscopy (SEM) with a 1530 Gemini LEO (Zeiss) microscope. For sample preparation, one drop of a diluted aqueous suspension of SPNPs was placed onto a silica wafer and dried under ambient conditions. Infrared spectroscopy was performed by using a Perkin-

Elmer Spectrum BX FT-IR spectrometer. For nuclear magnetic resonance (NMR) analysis, ^1H spectra were recorded with a Bruker Avance spectrometer operating at a frequency of 300 MHz.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler-Toledo DSC 823 or a Mettler-Toledo DSC1 at a heating rate of 10 K/min under N_2 atmosphere.

Size exclusion chromatography experiments were performed using an Agilent Technologies 1260 instrument consisting of a pump, auto sampler, and column oven. A column set composed of 3 columns: SDV 10^6 Å, SDV 10^4 Å and SDV 500 Å (PSS Standards Service GmbH), all of 300 x 8 mm and 10 μm average particle size were used at a flow rate of 1.0 mL/min and a column temperature of 30 °C. THF was used as eluent. The injection volume was 100 μL . Detection was accomplished with a RI detector and a UV detector at 254 nm wavelength (Agilent Technologies). Calibration was carried out by using polystyrene (PSS Polymer Standards Service).

Absorbance spectra of sulfur-rich polymer films were collected for a spectral range of 300 to 800 nm using an Agilent Cary 60 UV/vis spectrometer.

Cyclic voltammetry measurements were carried out on a Metrohm Autolab PGSTAT204 potentiostat/galvanostat with a three-electrode-cell system, glassy carbon electrode as the working electrode, Hg/HgCl_2 electrode as the reference electrode, platinum wire as the counter electrode, and Bu_4NPF_6 (0.1 M in acetonitrile) as the supporting electrolyte, with a scan rate of 100 mVs^{-1} in the range of -1.5 eV to 3 V.

Powder X-Ray Diffraction (PXRD) measurements were obtained on a Rigaku Ultima IV x-ray diffractometer equipped with a copper X-ray source. The diffraction was recorded in a range of $2\theta = 3-90^\circ$ at a scan rate of 2°min^{-1} with a tube voltage of 40 kV and 44 mA current.

NMR was performed either on a Bruker Avance III 300 spectrometer or a Bruker Avance 500 spectrometer.

S_8 Conversion

To calculate the conversion of S_8 during the reaction, differential scanning calorimetry was used (Figure S1). The heat (Q_{S_8}) of fusion of crystalline S_8 was measured for a sample of pure sulfur of mass m_{S_8} . Then the heat of fusion (between 100 and 125 °C) of unreacted S_8 (Q_{sample}) in a polymer sample of mass (m_s) was measured after polymerization in order to calculate the mass of unreacted S_8 in the polymer sample (m_u). The composition of the reacted polymer was assumed to be the same as the feed (using the weight fraction of the comonomer in the feed (WR)).

$$m_u = \frac{Q_{sample}}{Q_{S_8}/m_{S_8}} \quad (\text{eq. S1})$$

$$m_s = m_p + m_u = m_{S_8,reacted} + m_{comonomer} + m_u = m_{S_8,reacted} + WR \cdot m_{S_8,reacted} + m_u \quad (\text{eq. S2})$$

$$SC = \frac{m_{S_8,reacted}}{m_{S_8,reacted} + m_u} 100 = \frac{m_s - m_u}{m_s + WR \cdot m_u} 100 \quad (\text{eq. S3})$$

where SC is the percentage of S_8 conversion, m_s the mass of the sample analyzed by DSC, m_p the mass of copolymer in the sample, m_u the mass of unreacted S_8 in the sample, $m_{S_8,reacted}$ the mass of reacted S_8 in the copolymer, $m_{comonomer}$ the mass of comonomer in the copolymer.

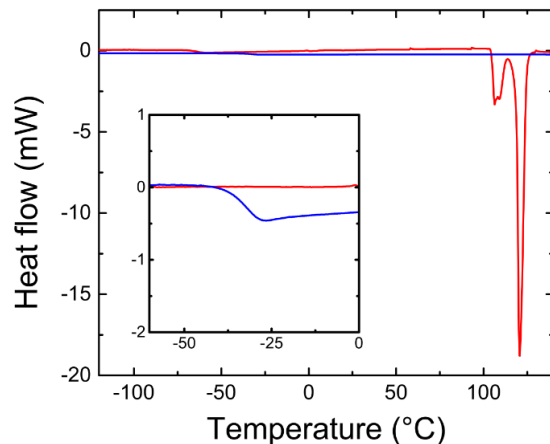


Figure S1. Thermogram of pure sulfur (red) and SPNPs (blue). The inset display the region where the glass transition temperature of the polymer can be observed.

Selected samples were analyzed by both DSC and powder X-Ray diffraction (PXRD). Both DSC and PXRD show the conversion of crystalline elemental sulfur into an amorphous material containing unreacted crystalline S_8 . To purify the sulfur-rich copolymer, the SPNPs were dissolved, the unreacted and insoluble sulfur was removed, and the polymer recovered and dried. The DSC and PXRD analysis were performed before and after the purification of the polymers. Both DSC and PXRD analysis of the purified polymers shows that the purified material is completely amorphous. The PXRD spectra were used to qualitatively measure the presence, if any, of amorphous unreacted S_8 . To do so, the contribution of the purified polymer was subtracted from the PXRD spectra of the raw unpurified SPNPs. Then, the area of the peak corresponding to crystalline S_8 was integrated (I_{crys}), and the total spectrum was also integrated (I_{total}) to provide an approximation of the degree of crystallinity of the sulfur present in the unpurified sample given by: $Crystallinity\%_{S8} = I_{crys} / I_{total} \times 100$.

In every sample measured, the crystallinity of the unreacted S_8 was > 98%.

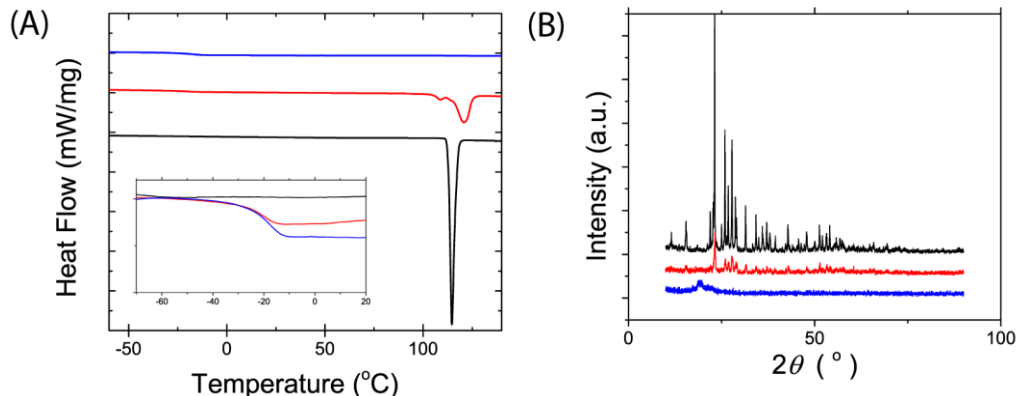


Figure S2. Analysis of conversion of S_8 for the reaction of an equimolar mixture of S_8 and α -MSt. (A) Thermogram of elemental sulfur (black), as prepared SPNPs (red), and purified sulfur copolymer (blue). (B) Powder x-ray diffraction profile for elemental sulfur (black), as prepared SPNPs (red), and purified sulfur copolymer (blue).

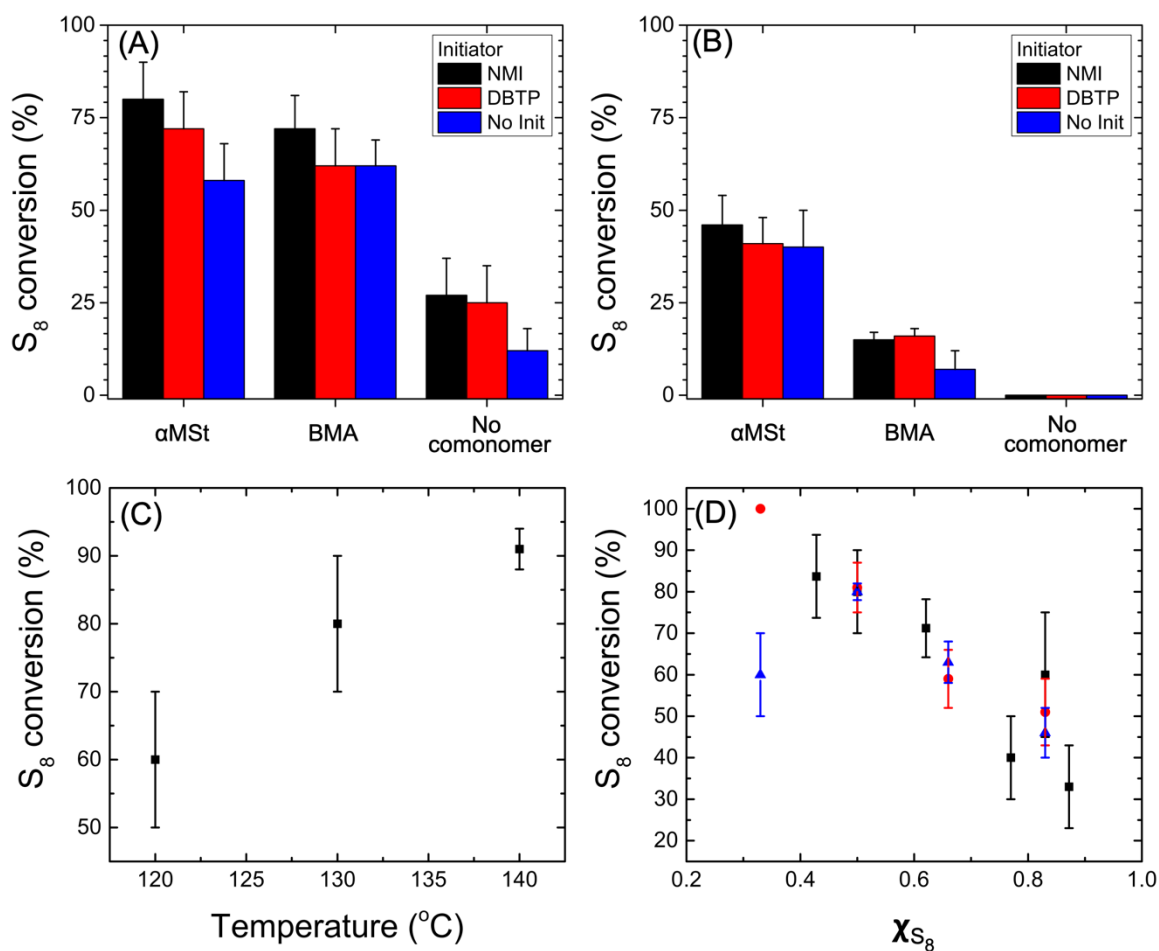


Figure S3. Conversion of S_8 during copolymerization measured by DSC. (A) Conversion measured for reaction performed at 130 °C in miniemulsion with an equimolar amount of S_8 and comonomer. (B) Conversion measured for reaction performed at 130 °C in bulk with an equimolar amount of S_8 and comonomer. (C) Effect of the temperature on the conversion of S_8 during miniemulsion polymerization for an equimolar mixture of S_8 and α -methyl styrene initiated with NMI. (D) Effect of the composition of the monomer feed on the conversion of S_8 for copolymerization performed in the presence of NMI at 130 °C with α -methyl styrene (■), limonene (●) and cyclododecene (▲).

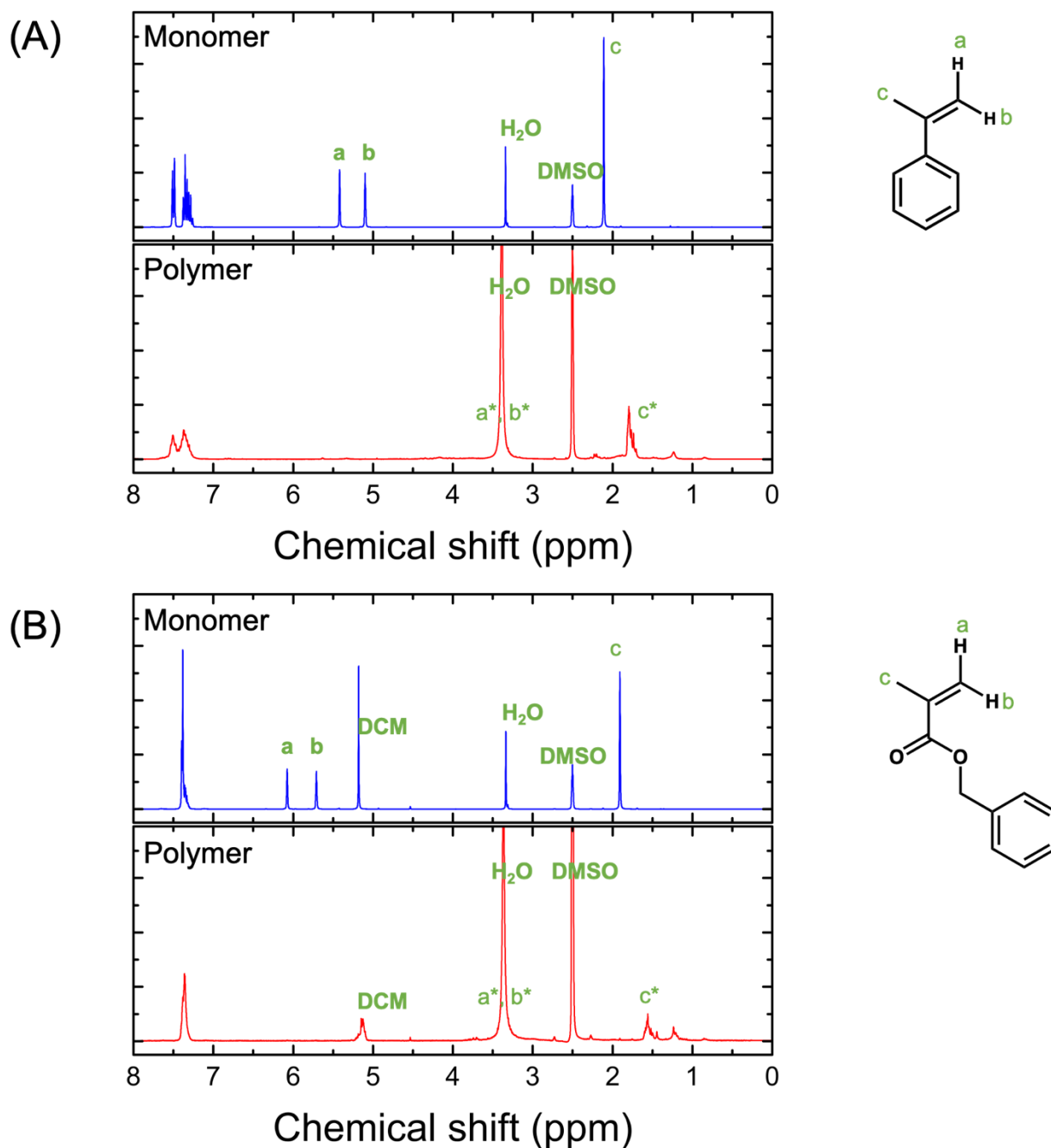


Figure S4. ^1H NMR spectra of the comonomer and the resulting sulfur-rich polymers displaying the inclusion of the comonomer in the final polymer material. (A) copolymerization of S_8 with α -methyl styrene in the presence of NMI; (B) copolymerization of S_8 with benzyl methacrylate in the presence of NMI. In the purified copolymer nanoparticles, no signal of unreacted comonomer is present, but DSC showed the unconverted S_8 (Figure S2).

Polymerization mechanisms

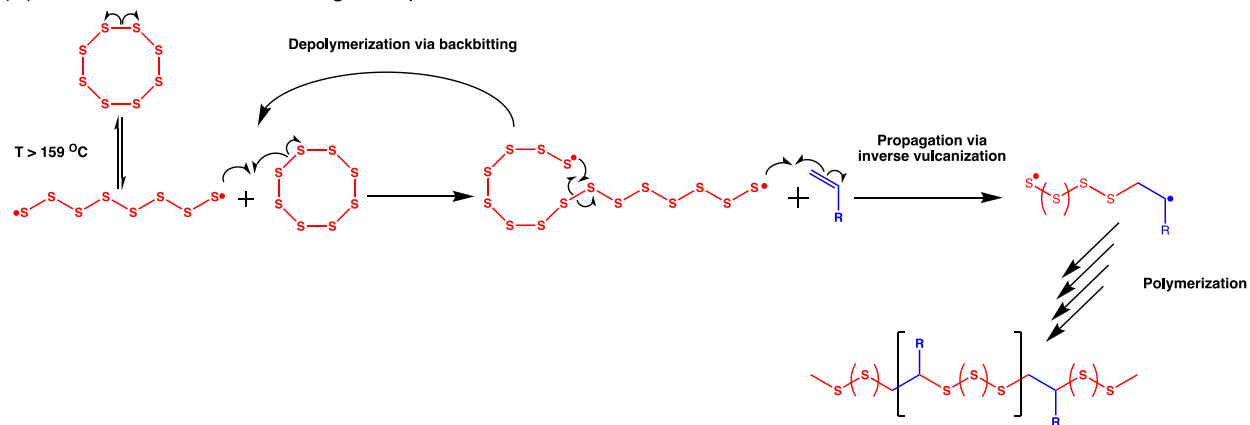
The copolymerization of S₈ was carried out in the presence of different comonomers and using different initiators or activators.

In the absence of any initiator, the polymerization follows the classical inverse miniemulsion mechanism (Figure S5.A). Molten elemental sulfur is heated above 159°C, at this temperature, homolytic cleavage of S-S bond leads to the formation of a sulfur diradical, which can undergo radical polymerization. Then, the growing chain is stabilized against depolymerization by the reaction between the terminal sulfur radical and an -ene comonomer because pure poly(sulfur) chains are prone to depolymerization via backbiting.⁵¹

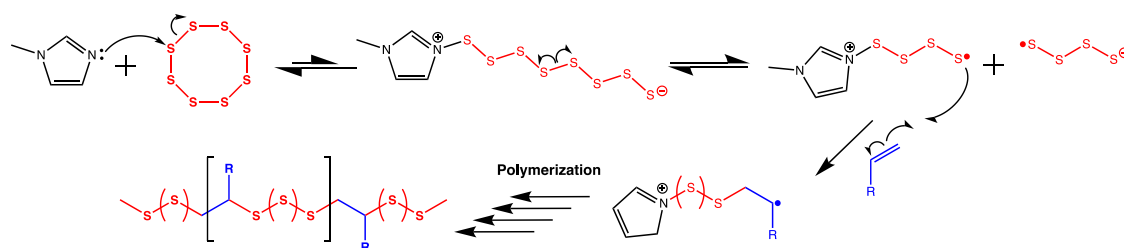
Alternatively, N-methyl imidazole (NMI) can be used as an activator to perform inverse vulcanization at a lower temperature (Figure S5.B). NMI performs a nucleophilic attack on the S₈ molecule, leading to the formation of a thiolate. The linear polysulfide segment formed is prone to homolytic scission, which leads to the formation of thiyl radicals, which can undergo polymerization either by attacking another S₈ molecule or reacting with a comonomer.⁵²

Sulfur is commonly used as an inhibitor or retarder during free radical polymerizations.^{53,54} The growing radical chain can react with the S₈ molecule, forming a thiyl radical. The rate of addition of the monomer to the thiyl radical is slower than the rate of addition to the initial radical, leading to a decrease in the apparent polymerization rate. Furthermore, it was demonstrated that the rate of addition of S₈ to the growing chain of methyl acrylate occurs at a rate similar to the addition of a new methyl acrylate, and the rate of addition of a methyl acrylate monomer to the thiyl radical occurs faster than the termination.⁵⁵ After the formation of radicals by the thermal degradation of the free radical initiator (Figure S5.C), the comonomer reacts with a radical. Then, the growing chains can either undergo the addition of another comonomer unit or the addition of a S₈ molecule, leading to the formation of the sulfur-rich copolymer.

(A) Inverse vulcanization at high temperature



(B) inverse vulcanization in the presence of a nucleophilic activator



(C) inverse vulcanization in the presence of a radical initiator

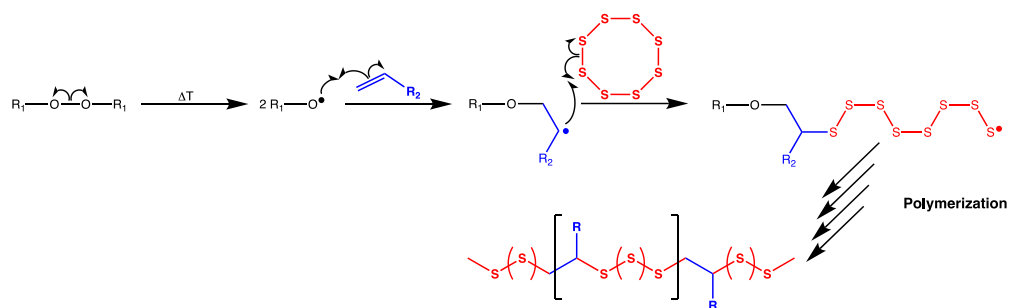


Figure S5. Suggested mechanisms for the copolymerization of S_8 . (A) Inverse vulcanization at high temperature. (B) Inverse vulcanization catalyzed by nucleophilic activation with NMI. (C) Inverse vulcanization initiated with a free-radical initiator.

Polymer Characterization

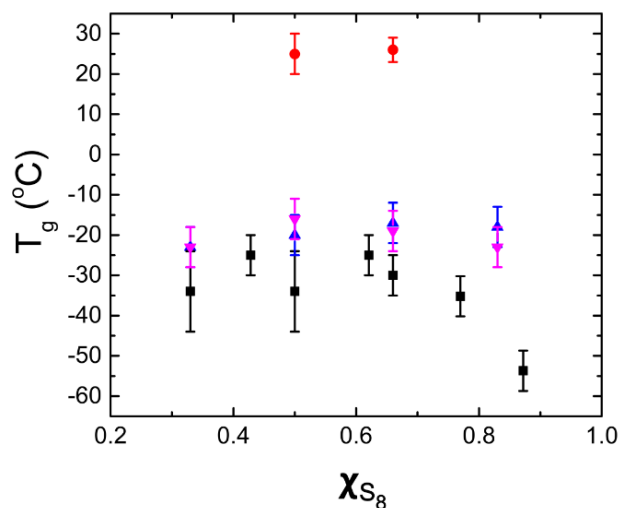


Figure S6. Glass transition temperature of the SPNPs produced with different molar fractions of S_8 on the monomer feed. For copolymer prepared in miniemulsion in the presence of NMI using (■) α -methyl styrene, (●) 1.3-diisopropenylbenzene, (▲) limonene, or (▼) cyclododecene as comonomer.

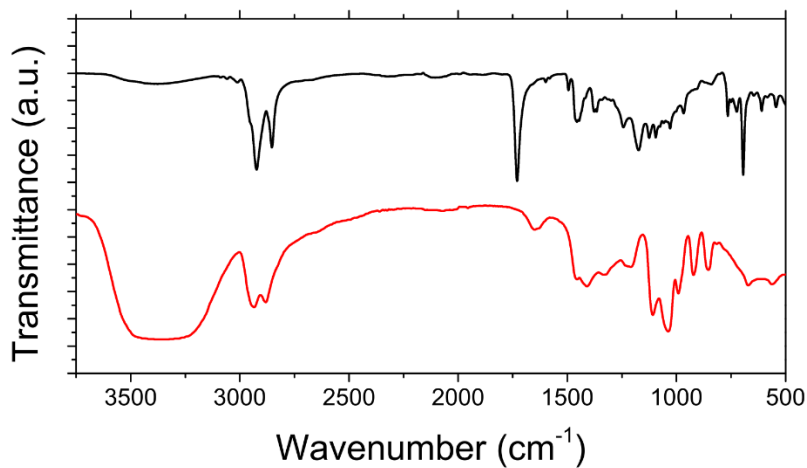


Figure S7. FTIR spectra of dried SPNPs (black) from an aqueous suspension (transferred to water from the as prepared glycerol suspension) and concentrated suspension of SPNPs in glycerol (red). FTIR shows that the SPNPs were fully washed from the glycerol used during synthesis during the water transfer.

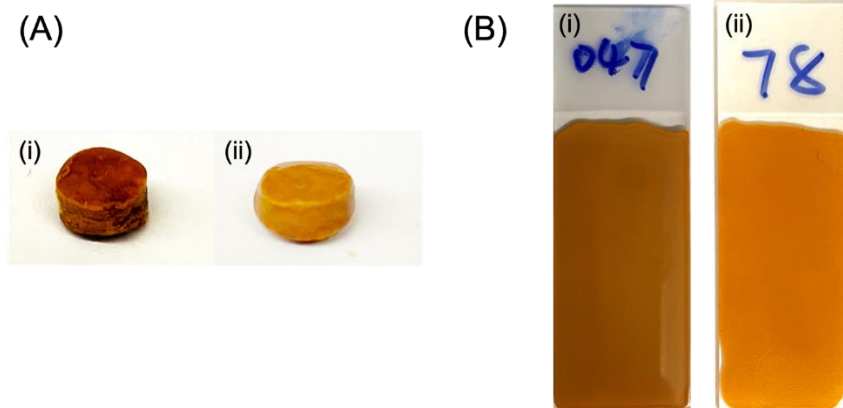


Figure S8. Processing of the SPNPs latex. (A) Monolith prepared by the room temperature molding of SPNPs prepared with a monomer feed composition i) of 1 molar eq of S_8 , 1 molar eq of α -methyl styrene and 0.1 molar eq of 1.3-diisopropenylbenzene and ii) of 1 molar eq of S_8 , 1 molar eq of limonene. (B) Films casted from a 10 wt% aqueous suspension of SPNPs prepared with a monomer feed composition i) of 1 molar eq of S_8 , 1 molar eq of α -methyl styrene and 0.1 molar eq of 1.3-diisopropenylbenzene and ii) of 1 molar eq of S_8 , 1 molar eq of cyclododecene.

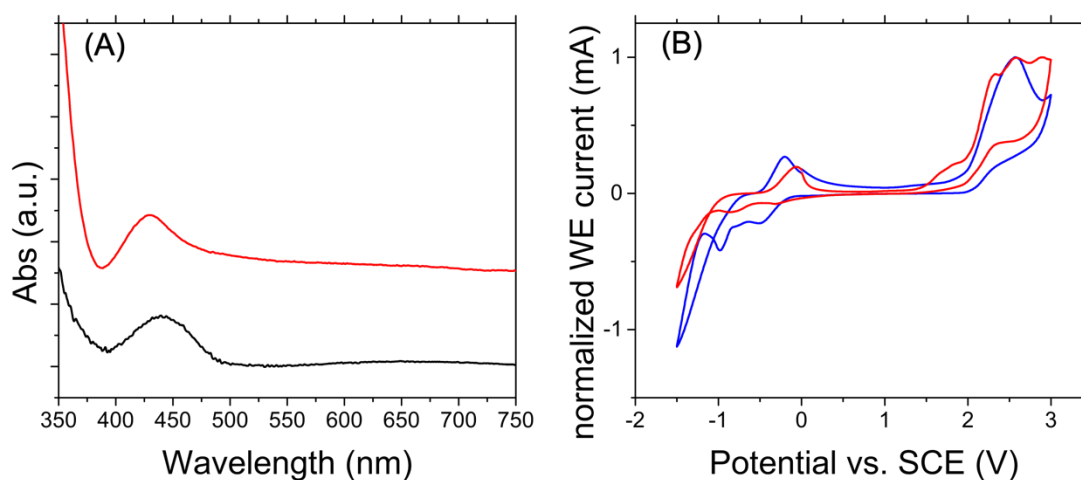


Figure S9. Optical and electrochemical properties of SPNPs. (A) UV-vis spectra of sulfur-rich polymer prepared in miniemulsion (black) and in bulk (red) with an equimolar feed composition of S_8 and α -methyl styrene. (B) Cyclic voltammogram of S_8 (red) and SPNPs (blue) prepared with an equimolar feed composition of S_8 and α -methyl styrene.

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