Self-assembly of core-shell nanoparticles for self-healing materials

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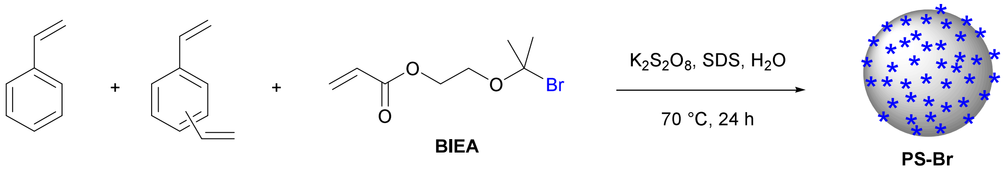
Supporting Information

General information

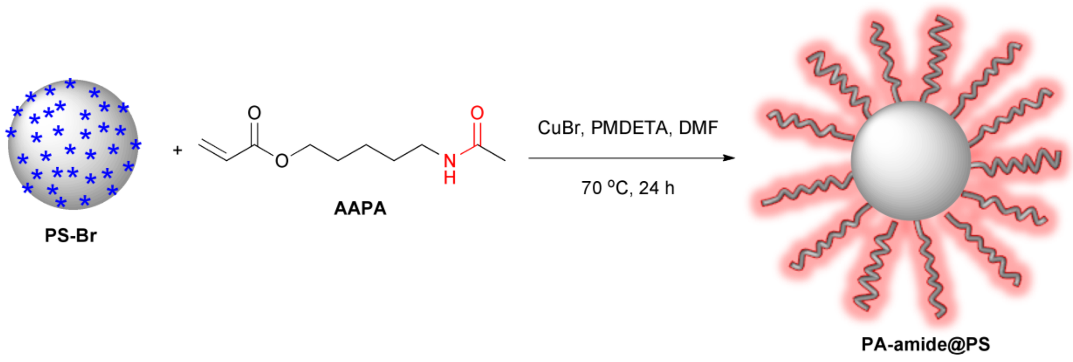
Chemicals were purchased from Sigma-Aldrich, VWR or Fisher Scientific and used without further purification. Solvents used in reactions were from alumina filtration system. 2-(2-Bromoisobutyryloxy)ethyl acrylate (**BIEA**) was prepared according to the literature.[1] The acrylate amide monomer 5-acetylaminopentyl acrylate (**AAPA**) was reported in literature.[2] All glassware was flame dried before use, and reactions were carried out under nitrogen atmosphere. Extraction solvents were commercial grade. Flash Chromatography was performed using forced flow of the indicated solvent systems over Fisher silica gel (230 - 400 mesh). ^{1}H NMR spectra were taken on a 500 MHz Bruker instrument. NMR chemical shifts were reported as values in ppm relative to deuterated solvents DMSO-*d6* (2.50). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hz and integration. Multiplets were reported over the range (in ppm) it appeared. ^{13}C NMR spectra were taken on a 125 MHz Bruker instrument. Carbon NMR data were recorded relative to the solvent signals of DMSO-d_6 (39.51). Mass spectral data (ESI/MS) were obtained on a Micromass auto spec spectrometer. The average diameters of the nanoparticle were measured by Dynamic Light Scattering (DLS) using a Zetasizer Nano Series (Malvern Instrument, Model: ZEN3600) at 25 °C**.** Molecular weights of the linear polymer were determined by size-exclusion chromatography (SEC) in methanol (1.0 mL/min) coupled with a Dawn DSP18 multi-angle light scattering detector (MALS, laser wavelength $\lambda = 632$ nm, Wyatt Technology, Santa Babara, CA) and a Refractometric Index (RI) detector (an Agilent 1100 SEC system with a Shodex OHpak SB 803-HQ column).

Synthesis of cross-linked polystyrene (PS) nanoparticles



The cross-linked PS nanoparticles **PS-Br** were prepared by emulsion polymrization.[3] Styrene (4.166 g, 40.0 mmol), divinylbenzene (0.260 g, 2.0 mmol), **BIEA** (0.530 g, 2 mmol) and the surfactant sodiumdodecyl sulfate (SDS) (0.100 g) were mixed in deionized water (48 mL). The mixture was stirred under nitrogen for 1 hour at room temperature. Then the temperature was raised to 70 °C for 1 hour. After the injection of potassium persulfate solution in water (0.015 g in 2 mL H_2O), the mixture was stirred under nitrogen at 70 °C for 24 hours. After cooling down, the size of the nanoparticles was measured by dynamic light scattering in water suspension. The nanoparticles were purified by centrifugation and washing with acetone (3 times) and water (3 times). After lyophilization, 3.256 g (65% yield) of nanoparticles **PS-Br** was obtained.

Synthesis of self-healing core-shell nanopaticles



The core-shell nanoparticles were prepared by ATRP polymerization[4] using **(PA-amide)-204@PS** as an example. The cross-linked nanoparticles **PS-Br** (0.176 g, 0.071 mmol Br), 5-

acetylaminopentyl acrylate (**AAPA**) (5.677 g, 28.5 mmol) and PMDETA (0.026g, 0.150 mmol) were mixed in DMF (14 mL). The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (0.011 g, 0.076 mmol), the mixture was heated at 70 °C for 24 h. The monomer conversion (51%) was determined by ^{1}H NMR spectroscopy. Upon cooling, the polymer was precipitated three times in ether to thoroughly remove any residual monomer. Catalyst was removed by passing a solution of the polymer in methanol over a basic alumina plug. The dried polymer (2.973 g) was obtained by evaporating the methanol solution under vacuum at 110 °C.

TEM studies

TEM was performed on a FEI/Philips CM-20 conventional TEM operated at an accelerating voltage of 200 kV. For samples requiring staining, the samples were stained by floating the TEM grid on a 0.5 wt % aqueous solution of uranyl acetate for 1 minute, followed by removing excess solvent by placing the sample on filter paper.

Differential scanning calorimetry (DSC)

DSC was performed on a TA Instruments Q2000 using standard heat-cool-heat experiments on ~5 mg of sample between -80 and 200 °C. The heating rate was 10 °C/min. The glass transition temperatures (T_g) were reported at the inflection point of the heat capacity jump of the second heating run.

Mechanical studies

Storage moduli of the polymers were obtained by the time sweep experiment on a rheometer (AR-G2 from TA Instruments) equipped with 20 mm parallel plates at the conditions of 1%

strain, 1 Hz and 25 °C. Samples for the tensile tests were prepared by hot-pressing the samples into Teflon moulds (30 mm x 7 mm x 2 mm). The specimens were extended at 100 mm/min at room temperature. Each measurement was repeated at least three times. Self-healing specimens were prepared by cutting the film in half, gently pushing two interfaces together for a minute and letting the fixed film heal for a certain time.

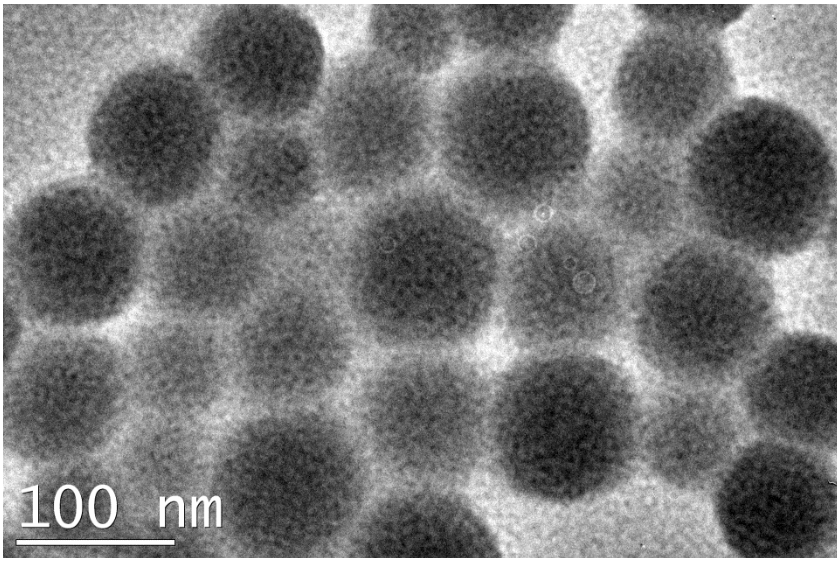


Figure S1. TEM image of the polystyrene nanoparticles **PS-Br**.

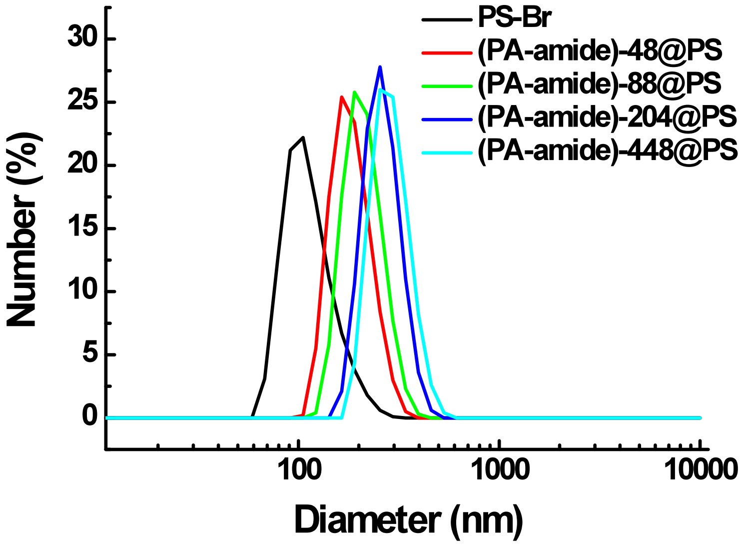


Figure S2. The size distribution of the cross-linked PS nanoparticle **PS-Br** (in chloroform) and the core-shell nanoparticles **(PA-amide)@PS** (in methanol) determined by dynamical light scattering.

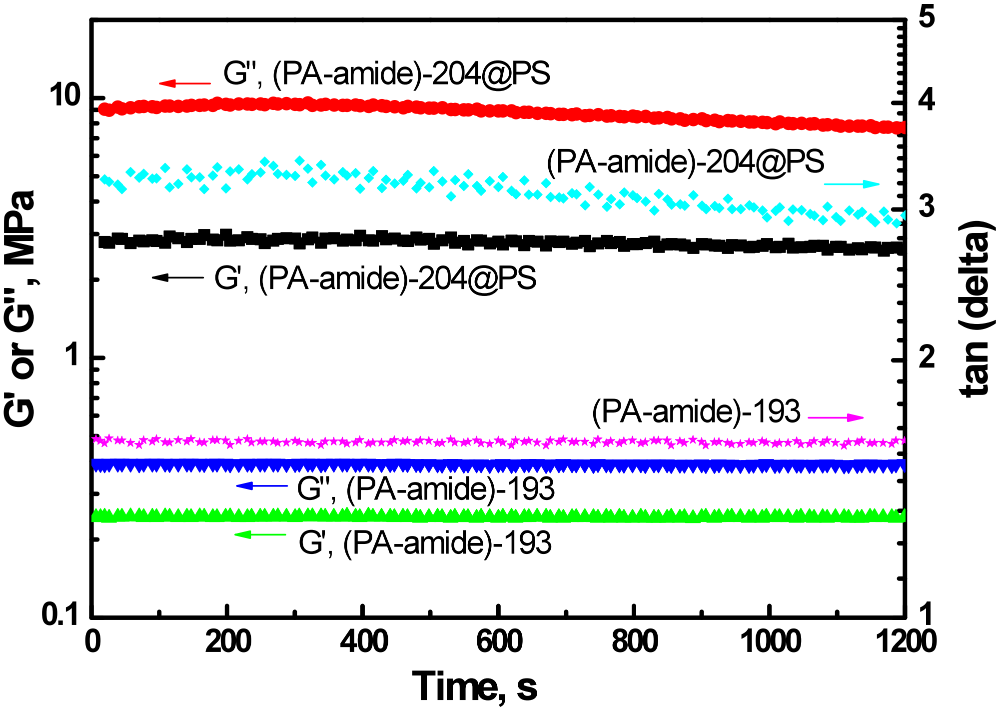


Figure S3. Time sweep rheological measurements of **(PA-amide)-193** and **(PA-amide)-204@PS**.

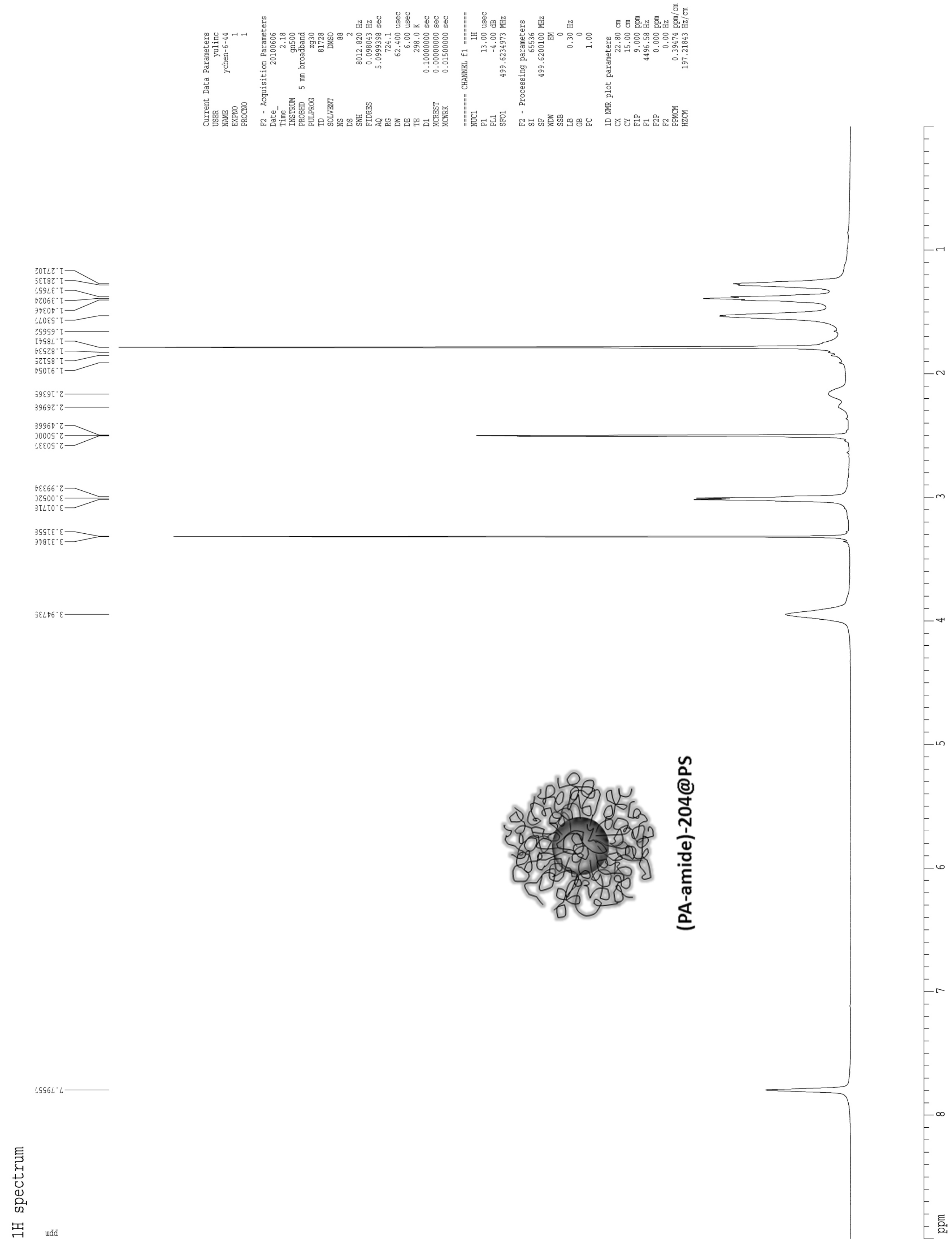


Figure S4. ^{1}H NMR spectrum of the core-shell nanoparticles **(PA-amide)-204@PS**.

References

1. Matyjaszewski, K.; Pyun, J.; Gaynor, S. G. *Macromol. Rapid Commun.* **1998**, *19*, 665.

2. Chen, Y.; Kushner, A. M.; Williams, G. A. ; Guan, Z. *Nat. Chem.* **2012**, *4*, 467.

3. Zhang, M.; Liu, L.; Zhao, H.; Yang, Y.; Fu, G.; He, B. *J. Colloid Interface Sci.* **2006**, *301*, 85.

4. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.