



## Supporting Information

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### Dye-Loaded Mechanochromic and pH-Responsive Elastomeric Opal Films

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### **Dye-Loaded Mechanochromic and pH-Responsive Elastomeric Opal Films**

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*Materials:* Ethyl acrylate (EA, 99.5 %), butyl acrylate (BuA, 99+ %), 2-(hydroxyethyl) methacrylate (HEMA, 97 %), methyl methacrylate (MMA, 99 %), allyl methacrylate (ALMA, 98 %), butanediol diacrylate (BDDA, 90 %) and styrene (S,  $\geq 99$  %) were purchased from Sigma Aldrich. Before the emulsion polymerization and free radical polymerization, the radical inhibitors were removed from the monomers by passing through an alumina column (basic, 50 200  $\mu\text{m}$ ). Sodium dodecyl sulfate (SDS,  $\geq 98.5$  %) was obtained from Sigma Aldrich and Dowfax 2A1, a surfactant having a dual polar sulfonate head group and a non-polar C12 alkyl chain, from Dow Chemicals. The blocked isocyanate cross-linker Crelan EF403 was donated by Bayer Materials Science, phenolphthalein (P,  $> 99$  %) by Fisher Scientific, and congo red by abcr. For use in emulsion polymerization, deionized water was degassed by a constant nitrogen flow for at least 30 min. All other chemicals were purchased from Sigma Aldrich and VWR and used as received, if not otherwise mentioned.

*Instrumentation:*  $^1\text{H}$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer working at 400 MHz. NMR chemical shifts are referenced relative to the used solvent (pyridine- $d_5$ ). Dynamic light scattering (DLS) measurements of the particle dispersions (solid content of 0.12 ppm,  $1.2 \times 10^{-7}$  wt.%) were performed with a Zetasizer ZS90 (Malvern Instruments) equipped with a 4 mW, 633 nm HeNe Laser. We carried out the measurements at 25 °C at an angle of 90° with a three-fold determination of 15 runs and an equilibration time of 120 s. Automated data acquisition was carried out using a cumulant fit. For the calculations, the z weight average hydrodynamic diameters were used.

Transmission electron microscopy (TEM) was done with a JEOL JEM 2100 electron microscope at an operating voltage of 200 kV. To investigate polymer-based particles, diluted dispersions were drop casted on a nitrocellulose coated copper grid. The shown TEM images were recorded in bright field mode by a Gatan Orius SC1000 CCD camera. The control of the camera was computer resisted using Gatan Microscopy Suite software.

For evaluation of the thermal properties of the synthesized core-interlayer-shell particles, differential scanning calorimetry (DSC) was carried out with a DSC 214 F1 Polyma from Netzsch in a temperature range of -140 °C to +140 °C and a heating rate of 10 K min<sup>-1</sup> in a nitrogen atmosphere.

Reflection spectra were recorded using a fiber FLAME T VIS NIR ES spectrometer from Ocean Optics combined with a high powered tungsten halogen lamp HL 2000 HP FHSA (output power 20 W) and a 400 µm premium fiber QP400 2 VIS BX. Strain  $\epsilon$  dependent reflection measurements were carried out using a custom-built goniometer setup. The strain range was varied from  $\epsilon=0\%$  to  $\epsilon=60\%$ .

UV/vis-measurements of the liquid residues were performed on a Evolution 220 UV-Visible Spectrophotometer by Thermo Scientific. All spectra were recorded in a wavelength range from 280 to 700 nm.

*Synthesis of Cross-Linked Polystyrene Core Particles:* Cross-linked polystyrene (PS) core particles were synthesized in a 5 L double-wall reactor equipped with a stirrer and a reflux condenser under an argon atmosphere at 75 °C. For this purpose, the vessel was filled with a monomer emulsion (ME) of 18 g styrene (S), 2 g butanediol diacrylate (BDDA), 1400 g deionized water, and 1.2 g sodium dodecyl sulfate (SDS) and stirred at 300 rpm. The polymerization was subsequently initiated by the addition of 0.18 g sodium disulfite (NaDS), 2.59 g sodium persulfate (NaPS), and 0.18 g NaDS (each component was dissolved in 5 g of deionized water). After 15 min reaction time, a monomer emulsion (ME1) containing 1.67 g

SDS, 2.92 g potassium hydroxide (KOH), 1.6 g Dowfax 2A1, 513 g S, 51.3 g BDDA and 659 g deionized water was added continuously with a flow rate of 6 mL min<sup>-1</sup> using a rotary piston pump reglo-CPF digital, RH00 (Ismatec, Wertheim, Germany). After the complete addition of ME1 the reaction was kept at a constant temperature for an additional 45 min, resulting in a solid content of the particle dispersion of 16.4 wt.%, respectively. The average hydrodynamic diameter of the cross-linked PS core particles was 203.2 ± 7.8 nm determined by dynamic light scattering (DLS).

*Free Radical Polymerization of P(EA<sub>82</sub>-co-HEMA<sub>18</sub>):* For the free radical polymerization (FRP) of P(EA<sub>82</sub>-co-HEMA<sub>18</sub>), 70 mg azobisisobutyronitrile (AIBN), 1.5 mL HEMA, 8.5 mL ethyl acrylate (EA), and 100 mL tetrahydrofuran (THF) were transferred into a 250 mL round bottom flask equipped with a reflux condenser. The mixture was degassed using a constant nitrogen flow for at least 30 min and then heated to 90 °C overnight while continually stirring. The resulting polymer (Yield: 6.8 g) was isolated by removing the solvent under reduced pressure and characterized via <sup>1</sup>H-NMR spectroscopy (400 MHz, pyridine d<sub>5</sub>, δ in ppm): 4.95 (1H, HEMA-CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH), 4.55 (2H, HEMA-CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH); 4.24 (2H, HEMA-CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH, 2H EA-CH<sub>2</sub>-CH<sub>3</sub>); 1.28 (3H, EA-CH<sub>2</sub>-CH<sub>3</sub>, 3H HEMA-CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH) (**Figure S1**).

*Polymer analogous reaction for the preparation of dye-loaded Copolymer:* Before use, dimethylformamide (DMF) was dried overnight by molecular sieve (3 Å). For the polymer analogous reaction, 4 g of P(EA-co-HEMA) was dissolved in 250 mL DMF, and 0.82 g carbonyldiimidazole (CDI) was added to the solution. The resulting mixture was stirred overnight at a temperature of 90 °C followed by the addition of 3.53 g of congo red. After 6 h of reaction time at 90 °C the dye-loaded copolymer was isolated by removing the solvent under reduced pressure.

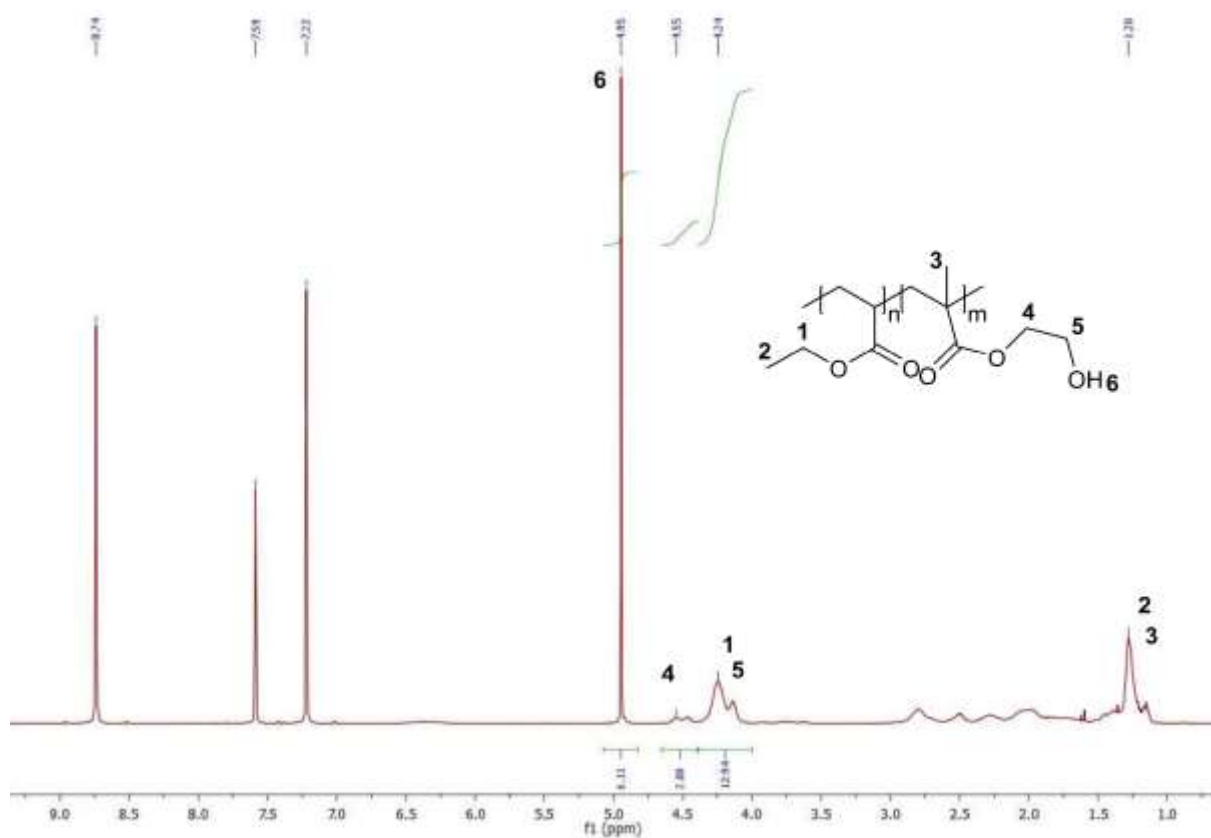


Figure S1.  $^1\text{H-NMR}$  spectrum of  $\text{P}(\text{EA}_{82}\text{-co-HEMA}_{18})$  in  $\text{pyridine-}d_5$ .

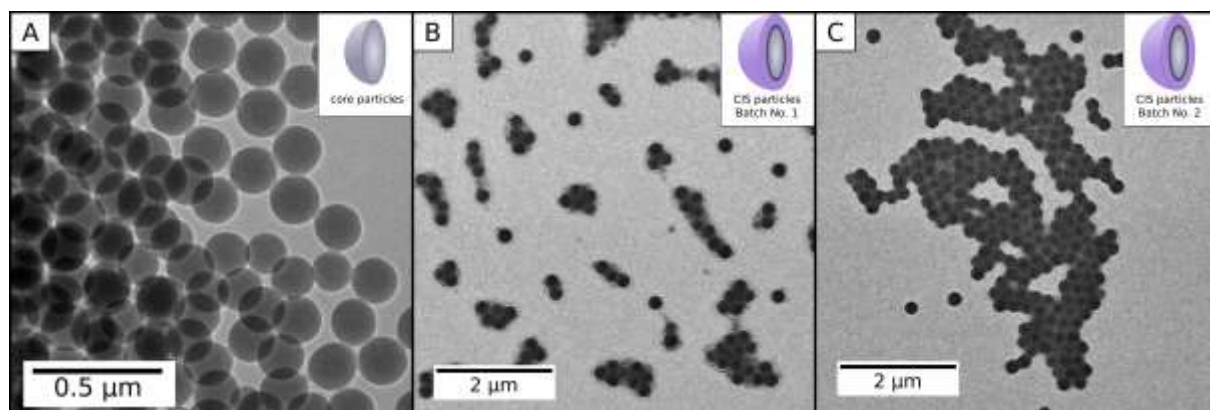


Figure S2. Transmission electron micrographs of A) poly (styrene-*co*-butanediol diacrylate) core particles and core-interlayer-shell (CIS) particles of B) batch No. 1 and C) batch No. 2.

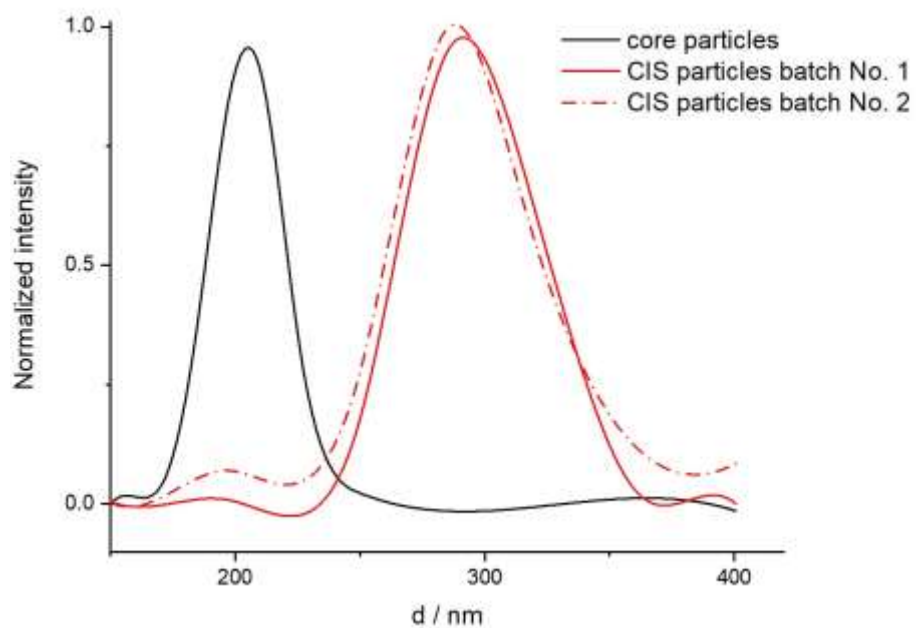


Figure S3. Dynamic light scattering (DLS) measurements after each step of semicontinuous emulsion polymerization to investigate the hydrodynamic diameters as well as size distribution for batch No. 1 (left) and batch No. 2 (right).

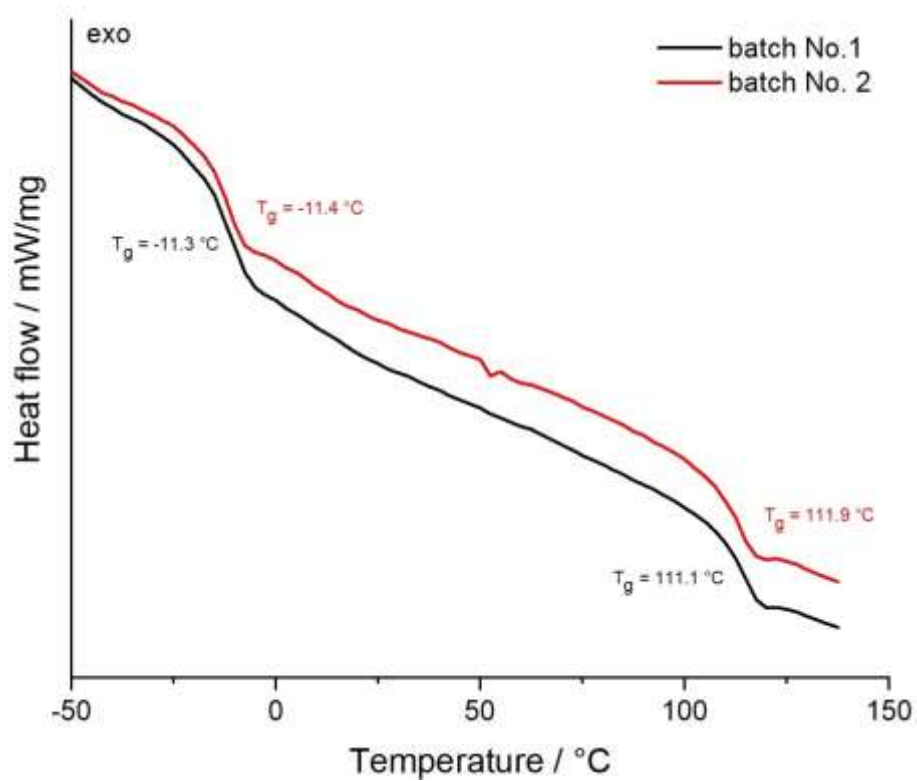


Figure S4. Differential scanning calorimetry (DSC) thermograms of P(S-co-BDDA)@P(MMA-co-ALMA)@P(EA-co-BuA-co-HEMA) core-interlayer-shell particles of batch No. 1 (black line) and batch No. 2 (red line).

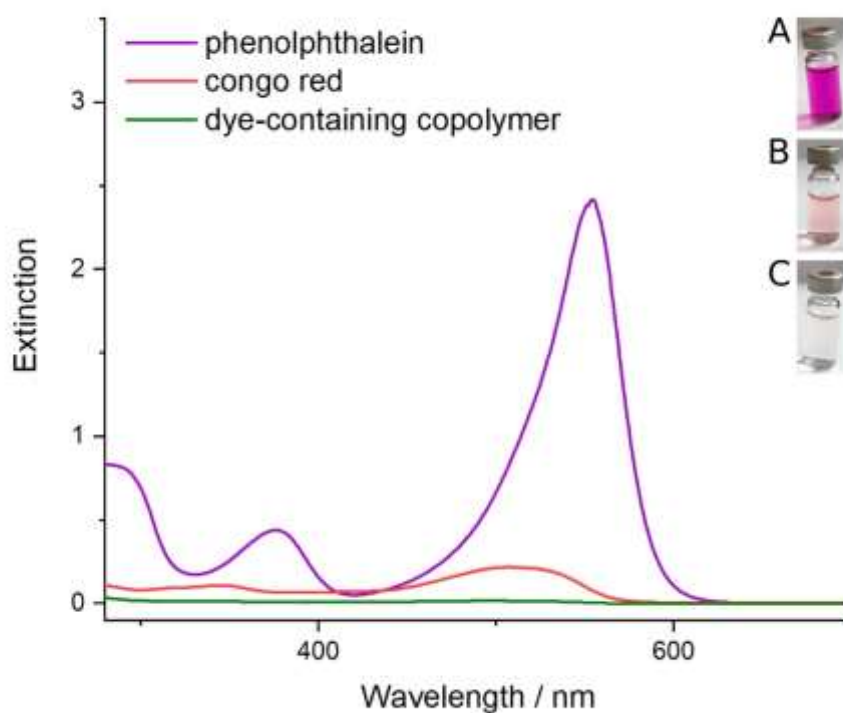


Figure S5. UV/vis-spectra and corresponding photographs of each liquid residue belonging to the different opal films. Residues of the (A) phenolphthalein, (B) congo red, and (C) dye-containing copolymer loaded opal film.