Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Experimental Section

MATERIALS. Styrene (S) and butyl acrylate (BA) were obtained from BASF SE, butanediol diacrylate (BDDA) from Merck KGaA, allyl methacrylate (ALMA) from Evonik Röhm GmbH and Dowfax 2A1 from Dow Chemicals. 4-(4-nitrobenzyl)pyridine (NBP) was purchased from Fisher Scientific. All other chemicals were purchased from VWR and used as received. Prior to use in emulsion polymerization, the stabilizers hydroquinone monomethylether and 4-*tert*-butylcatechol were removed from the monomers as follows. Styrene was destabilized by passing it through an aluminium oxide column and subsequent distillation under reduced pressure. BA was extracted with 1 M sodium hydroxide solution, washed with water until the solution was neutral followed by drying with sodium sulfate. ALMA and BDDA were destabilized by ion exchanger De-Hibit 200 (PolySciences Europe GmbH). For use in emulsion polymerization, deionized water was bubbled with nitrogen for at least 30 min. For the coagulation of the latices, technical grade methanol and sodium chloride were used. Vinylphenylglycidylether (VPGE) was synthesized by reacting coumaric acid with epichlorohydrin, as reported elsewhere.[1, 2]

Instrumentation. Transmission electron microscopy (TEM) was performed on a Zeiss EM10 with an operating voltage of 60 kV. For investigation of the single particles, the diluted dispersions were drop-cast on nitrocellulose-coated or carbon-coated copper grids (Plano GmbH, Germany) and dried at room temperature. All shown images were recorded with a slow-scan CCD camera obtained from TRS (Tröndle) in bright field mode. Camera control was computer-aided using the ImageSP software from TRS (Tröndle). Scanning electron microscopy (SEM) were conducted on a Philips XL30 FEG at an operating voltage of 5-25 kV. Dynamic light scattering (DLS) measurements of the particles were performed on a Nanophox photon cross-correlation spectrometer (Sympatec). The experiments on diluted dispersions of the particles after each step of the particle synthesis were carried out at an angle of 90° at 20 °C. Centrifugation was performed with a Heraeus Multifuge X3R Centrifuge from Thermo Scientific. UV/vis transmission spectra were recorded with a Lambda 40 UV-Vis (Perkin Elmer Inc.) spectrometer. DSC measurements were recorded with a Mettler Toledo DSC1 from 20 °C to 220 °C with a heating rate of 10 K min^{-1}. Contact angles were measured using the sessile-drop method with a DataPhysics OCA 35 contact angle system using 4 µL droplets of deionized water. The measurements were conducted at ambient temperature.

SYNTHESIS OF POLY(STYRENE-CO-BUTYL ACRYLATE) P(S-CO-BA) CORE PARTICLES. A 1 L flask equipped with stirrer and reflux condenser is filled at 75 °C under argon with a cold monomer emulsion of 440 g of deionized water, 3.6 g of butylacrylate (BA), 0.40 g of allyl methacrylate (ALMA) and 0.02 g of sodium dodecylsulfate (SDS). The polymerization was initiated by adding 50 mg of sodium bisulfite, 175 mg of sodium peroxodisulfate (SPS) and 50 mg of sodium bisulfite in this sequence. After 10 minutes, a monomer emulsion consisting of 75 g of styrene, 75 g of BA, 0.4 g of SDS, 0.4 g of KOH, 0.5 g of Dowfax 2A1 and 180 g of water is added continuously over 6 h. Particles as outlined above reveal an overall diameter of $D \cong 285$ nm, when prepared with exactly 0.02 g of the surfactant SDS in the seed stage.

SYNTHESIS OF P(S-CO-BA) CORE P(BA-CO-VPGE) SHELL PARTICLES. A 250 mL flask equipped with stirrer and reflux condenser is filled under argon at 75 °C with 50.0 g of P(S-*co*-BA)-core particles (20 wt% in water), 1.875 g of sodium dihydrogen phosphate (2 wt% in water) and 2.500 g of sodium hydrogen carbonate solution (2 wt% in water). After 30 min, the polymerization is initiated by adding 9 mg of sodium bisulfite, 63 mg of SPS and 9 mg of sodium bisulfite in this sequence. After additional 15 min of stirring, a monomer emulsion containing 2.350 g of BA, 2.950 g of VPGE, 0.590 g of BDDA, 0.016 g of SDS, 0.020 g of Dowfax 2A1, 0.063 g of sodium dihydrogen phosphate (2 wt% in water) and 0.125 g of sodium hydrogen carbonate (2 wt% in water) is added continuously over 300 min.

PREPARATION OF SIO_2 PARTICLES. Silica particles are prepared according to a modified stepwise Stöber process. In a 1 L flask equipped with stirring bar a mixture of 125 mL ethanol, 12 mL NH_3 solution (25 % in water) and 0.5 mL of water are added and heated to 48 °C. After 30 min, a solution of 9 mL tetraethoxysilane (TEOS) diluted in 12.5 mL ethanol is added. The mixture is stirred for further 16 h at 48 °C yielding the particle dispersion with silica content of 19 g L^{-1}. In a subsequent step, 22.5 mL of ethanol and 2.5 mL NH_3 solution are added followed by addition of a solution of 4.5 mL TEOS in 5 mL ethanol. The mixture is stirred for additional 16 h at 35 °C resulting in particles with an average diameter of 43 nm. Finally, 22.5 mL of ethanol and 2.5 mL NH_3 solution are added followed by addition of 4.5 mL of TEOS in 5 mL ethanol. The final average diameter of the silica particles is 50 nm as determined by TEM and DLS measurements. From this batch portions for further particle growth are used. In each step the dispersion has been diluted to a concentration to 11 g L^{-1} with ethanol and NH_3 solution (25 % in water). The concentration of ethanol and ammonia is kept constant. Subsequently TEOS diluted in ethanol is added up to a concentration of 19 g L^{-1} SiO_2 in the dispersion. Each day in an 8 hours interval two stages of particle growth has been started to assure an entire conversion. After 7 days, a dispersion with silica content of 19 g L^{-1} and a particle diameter of 120 nm as determined by DLS measurements is obtained.

Preparation of Amino-Functionalized SiO_2 particles. In a 100 mL flask equipped with stirring bar and reflux condenser 50 mL of the above described silica particle dispersion is heated to 60 °C. 200 µL of (3-aminopropyl)trimethoxysilane (1.15 mmol) (APTES) are added dropwise and stirred at 60 °C for additional 2 hours.

Synthesis of Raspberry-Type Core/Shell Particles. Amino-functionalized silica particles are centrifuged for 15 min at 8.000 rpm at least 5 times in order to remove unreacted compounds. 5.7 g of the silica particle are dispersed in ethanol to a silica content of 2 wt% and transferred to a 50 mL flask equipped with a stirring bar. Subsequently, 25.5 g of P(S-co-BA) core P(BA-co-VPGE) shell particles (1.2 wt% in ethanol) are added dropwise and stirred for additional 30 minutes at room temperature.

Preparation of Hydrophobized Glass Wafers. For the intended contact angle measurements, glass wafers (26 x 76 x 1 mm) are coated with the raspberry-like hybrid particles by using a doctor blade followed by exposure to oxygen plasma (100 W, 60 s). The particle film is hydrophobized by treating with a solution of dichlorodimethylsilane (1 wt% in hexane) for 5 min at 25 °C.

General Procedure for Studying Crosslinking Reactions of PVPGE-Containing Particles. For investigating the thermal crosslinking reactions of P(S-*co*-BA) core P(BA-*co*-VPGE) shell particles, the particle dispersion is centrifuged for 15 min at 15.000 rpm for at least 5 times. Prior to DSC measurements, 50 mg of the particles are transferred in a 10 mL flask and 102 mg of the curing agent isophorondiamine (IPDA) is added. After mixing the components vigorously for at least 5 minutes to ensure complete wetting of the particles, the pretreated sample (10-20 mg) are sealed in a 40 µL aluminum DSC sample pan and covered with a pierced aluminum lid.

General Procedure for Determining Epoxy-Functionalities. For the purification of the particles, P(S-*co*-BA) core P(BA-*co*-VPGE) shell dispersion (20.79 wt% in water) is introduced in a regenerated-cellulose membrane tube (molecular weight cutoff 12 - 14 kDa; Medicell International Ltd) and dialyzed against ethanol for 4 days to exchange the reaction medium and unreacted compounds. Every 24 hours the ethanol phase is removed and replaced by fresh ethanol. The final percent by weight is 1.2 wt% in ethanol. In an Erlenmeyer-flask equipped with magnetic stirrer, 2 mL of a solution of NBP in ethanol (0.1 g mL^{-1}) and a catalytic amount of NH_3-solution (25 % in water) are added to 3 mL of the particle dispersion and stirred for 3 h. For UV/vis measurements in heterogeneous particle dispersion, an isorefractive medium is a necessity to avoid dominant scattering background of the particles. For this purpose, anisole is used as a dispersion medium. For UV/vis measurements 200 µL of the surface immobilized epoxy moieties with NBP was diluted with 1 mL of anisole.

Calculation of Epoxy Functionalities at the PVPGE-Particle Surface. A quantification of the transformed epoxy moieties given as c_{chromo} after ring opening reaction could be carried out by using Lambert Beer law (eq. 1):

$$c_{chromo} = \frac{E}{\varepsilon \cdot d_{cuv} \cdot c_w} \; [\text{mol g}^{-1}] \qquad (1)$$

Where E is the absorbance, c_w the mass concentration of the particle dispersion, d_{cuv} the cuvette thickness and ε the molar extinction coefficient. The molar extinction coefficient was determined to 1537.36 cm^2 mmol at an absorption maximum of 544 nm, measuring serial dilutions of Preussmann reagent after reaction with VPGE monomer in anisole (Fig. S5). Assuming identical values of the molar extinction coefficient in solution and for the surface-anchored chromophore, the chromophore concentration, c_{chromo}, of surface-attached epoxy moieties which were capable for ring-opening reaction could be obtained. For an estimation of surface-attached epoxy-functionalities featuring the capability for reaction with the Preussmann reagent (NBP), we used the epoxy concentration c_{chromo} obtained by UV/vis measurements at an absorption maximum of 544 nm of the purified particles in anisole. c_{chromo} was determined to be $1.32 \cdot 10^{-4}$ mmol mL^{-1} for above described PVPGE-containing particles featuring an average diameter of 350 nm. Particle concentration of the measured dispersion was 0.0092 g mL^{-1} leading to a single particle mass of:

$$m \text{ (single particle)} = \rho \cdot V = \rho \cdot \frac{1}{6}\pi d^3 = 2.36 \cdot 10^{-14} \text{ g.}$$

The number of particles could be obtained by the following equation:

$$N \text{ (particles)} = \frac{0.0092 \text{ g/mL}}{2.36 \cdot 10^{-14} g} = 3.9 \cdot 10^{11} \text{ mL}^{-1}.$$

This dispersion was further diluted to $2.34 \cdot 10^{11}$ mL^{-1} and $3.9 \cdot 10^{10}$ mL^{-1}, respectively. From the finally diluted sample, c_{chromo} could be determined to be $1.32 \cdot 10^{-4}$ mmol mL^{-1}. The amount of epoxy groups per particle could be calculated by:

$$N \text{ (epoxy)} = \frac{6.022 \cdot 10^{23}\ mol^{-1} \cdot 1.32 \cdot 10^{-7}\ mol \cdot mL^{-1}}{3.9 \cdot 10^{10}\ mL^{-1}} = 2.04 \cdot 10^{6} \text{ mL}^{-1}.$$

With a particle surface calculated by π $d^2 = 3.85 \cdot 10^5$ nm^2, the amount of epoxide function per single particle could be obtained to:

$$\frac{2.04 \cdot 10^{6}}{3.85 \cdot 10^{5}\ nm^2} = 5.3 \text{ nm}^{-2}.$$

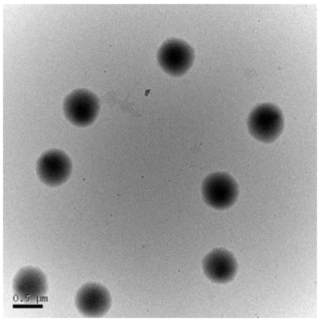

Fig. S1 TEM measurements of P(S-co-BA) core particles. The deposited particles tended to lose their spherical shape during TEM measurements, accompanied with an increase in particle diameters. Scale bars correspond to 500 nm.

Tab. S2 Comparison of hydrodynamic radii determined by using DLS and TEM measurements.

sample	d_{DLS} (nm)	d_{TEM} (nm)[a]
P(BA) Seed	67 ±8	-
P(S-*co*-BA) Core	286 ±31	490 ± 25[b]
P(S-*co*-BA) Core P(BA-*co*-VPGE) Shell Particles	348 ± 39	332 ± 48

[a] The errors for the average particle diameters were determined by taking the mean of 200 particles out of the corresponding TEM images; [b] The average diameters for the very soft core particles obtained by TEM are not meaningful as the particles tended to lose their spherical shape during the TEM measurements.

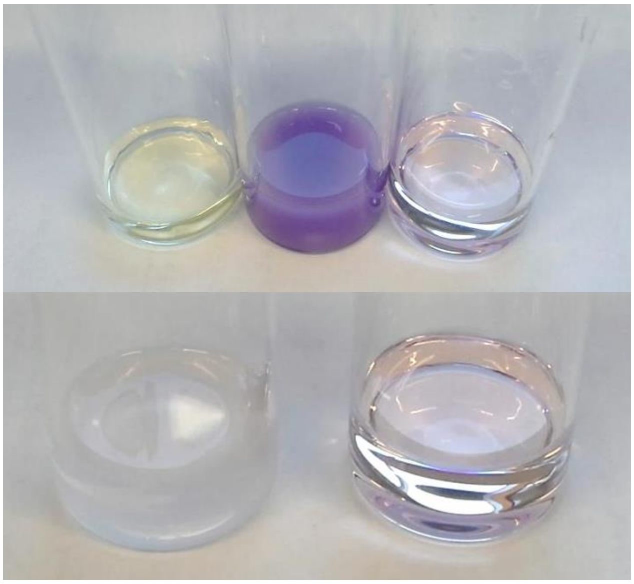

Fig. S3 Top: Images of solution of 4-(4-nitrobenzyl)pyridine (Preussmann reagent) in ethanol (left), core/shell particle dispersion after treatment with the Preussmann reagent in ethanol (middle) and the diluted particle dispersion in anisole as an isorefractive solvent (right). Bottom: direct comparison of the NBP treated particles dispersion in ethanol (left) and the particle dispersion in anisole.

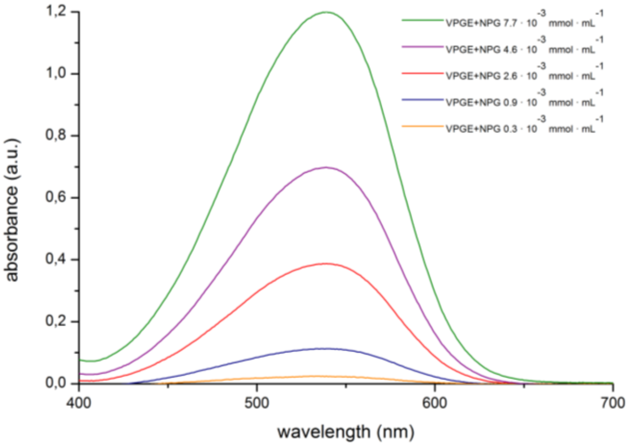

Fig. S4 UV/vis spectra of different concentrations starting with a concentration of 7.7 · 10-3 mmol mL-1 (green line) diluted down to 0.3 · 10-3 mmol mL-1 (orange line) of the monomer VPGE treated with Preussmann reagent as model reaction in anisole as isorefractive dispersion medium.

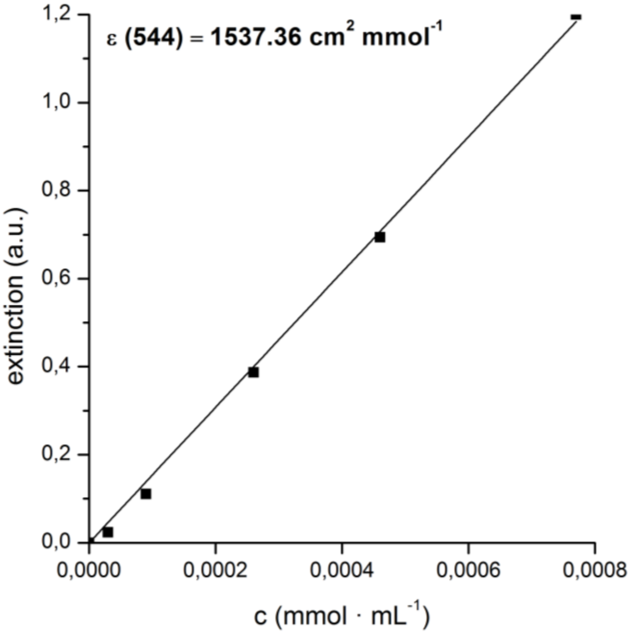

Fig. S5 Calibration plot for the determination of the molar extinction coefficient at 544 nm.

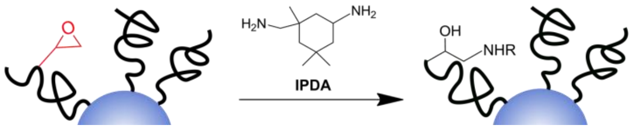

Fig. S6 Reaction of surface-immobilized epoxy moieties with 3-aminomethyl-3,5,5-trimethylcyclohexylamine (IPDA) in the DSC experiments (see main text).

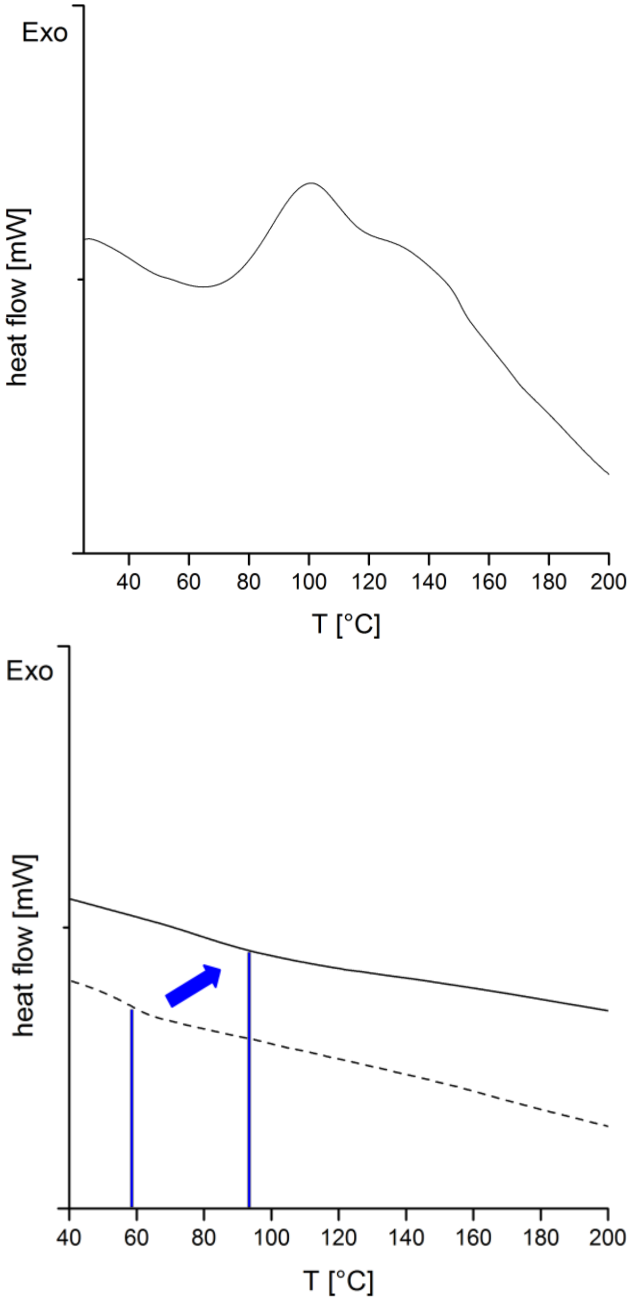

Fig. S7. DSC thermogram (first run) of a mixture consisting of IPDA and VPGE-containing core/shell particles (top) and thermogram (second run) for the same sample (bottom, solid black line) with a glass transition temperature of 95 °C. For comparison, the dotted line gives the DSC experiment for the pristine VPGE-containing particles in the absence of cross-linking reagent, featuring a glass transition temperature of 58 °C.

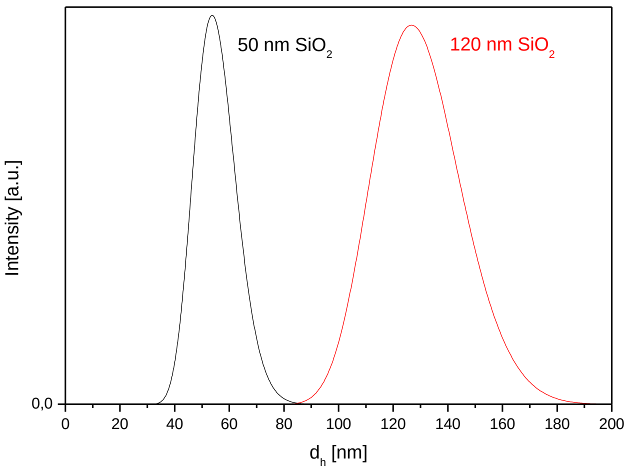

Fig. S8 DLS results for the silica particles used for the preparation of organic VPGE-core silica shell hybrid raspberry-type structures as depicted in Scheme 3.

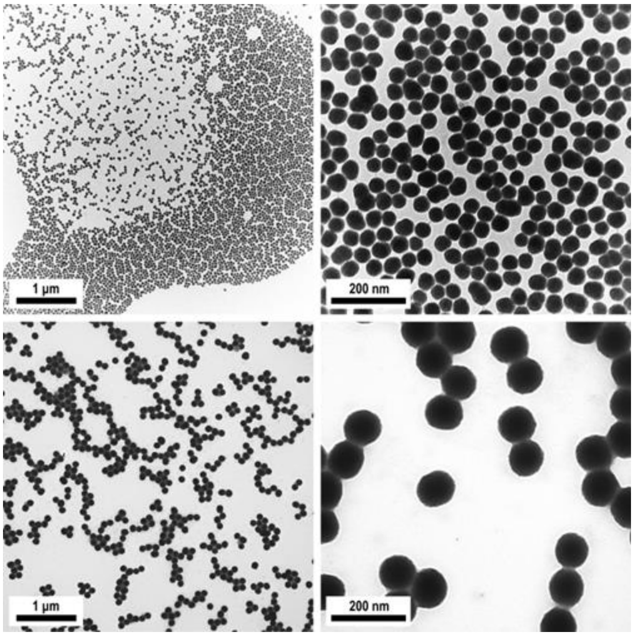

Fig. S9 TEM images of 50 nm (top) and 120 nm (bottom) silica particles used for the preparation of organic VPGE-core silica shell hybrid raspberry-type structures, as depicted in Scheme 4. Scale bars correspond to 1000 nm and 200 nm from the left to the right.

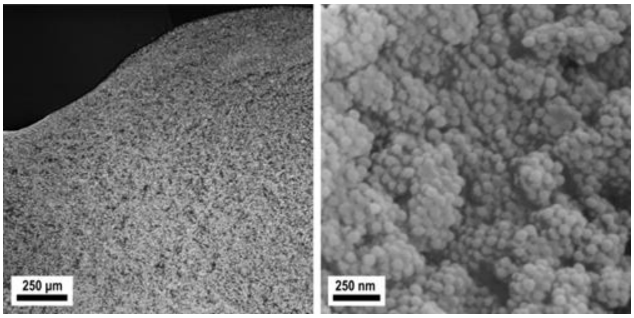

Fig. S10 Exemplary SEM image of a hydrophobic raspberry-particle film obtained after applying a vertical deposition protocol of the particle dispersion followed by treatment of oxygen plasma and dichlorodimethylsilane. Scale bars correspond to 250 µm (left) and 250 nm for the right zoom-in image.

References

1. Kunitsky, K.; Shah, M. C.; Shuey, S. W.; Wagman, M. E. *US 2008/0167433 A1* **2008**.
2. Werre, M.; Frey, H., submitted.