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Qualitative sensing of mechanical damage by a fluorogenic click reaction

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Supporting Information

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1. Abbreviations

ATMS	allyltrimethylsilane
CuAAC	copper(I)-catalyzed alkyne-azide "click" cycloaddition reaction
DCM	dichloromethane
DCTB	*trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile
DETA	diethylenetriamine
DGEBA	diglycidylether of bisphenol A
DMAP	*N*,*N*-dimethylpyridine-4-amine
EA	ethyl acetate
EDC · HCl	*N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride
LCCP	living carbocationic polymerization
NaTFA	sodium trifluoroacetate
PIB	poly(isobutylene)
SDS	sodium dodecyl sulfate

2. Materials

All materials, chemicals and solvents, which were used for the here described synthesis were obtained from Sigma-Aldrich and were used without further purification if not mentioned otherwise. Deuterated chloroform ($CDCl_3$) as well as deuterated dimethyl sulfoxide (DMSO-d_6) were purchased from Chemotrade, oxalyl chloride from Merck and EDC · HCl from Alfa Aesar. DCM was predried over calcium chloride and freshly distilled over calcium hydride under a nitrogen atmosphere prior use.

3. Methods

3.1. NMR spectroscopy

NMR spectra were recorded on a Varian Gemini 2000 (400 MHz) at 27 °C. Deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) was used as solvent. All chemical shifts

were given in ppm and all coupling constants in Hz. MestRec-C software (version 4.9.9.6) was used for interpretation of the NMR-spectra.

3.2. ATR-IR spectroscopy

ATR-IR spectra (32 scans) were performed on a Bruker Tensor VERTEX 70equipped with a Golden Gate Heated Diamond ATR Top-plate. Opus 6.5 was used for analyzing data.

3.3. GPC

*Gel permeation chromatography (GPC)*measurements were performed on a Viscotek GPCmax VE 2002 from Viscotek^{TM}using a H_{HR}H Guard-17369 and a GMH_{HR}-N-18055 column in THF at 40 °C *via* detection of the refractive index with a VE 3580 RI detector of Viscotek^{TM}. For external calibration PIB-standards (320 g/mol to 578000 g/mol) from Viscotek^{TM} were used. For UV/Vis-detection of polymers GPC spectra were recorded on a GPCmax VE 2001 from Viscotek^{TM} equipped with a column set of a H_{HR}-H Guard-17369 column, a CLM30111 column and a G2500H_{HR}-17354 column in THF (1 mL/min) at 35 °C. Therefore a UV-detector (model 2501) from Viscotek^{TM} was applied at 330 nm. For evaluation of data OmniSEC software (V 4.5.6) was used. The concentration of all samples was 3 mg/mL and the flow rate was 1 mL/min.

3.4. Rheology

*Rheological measurements*were performed on an oscillatory plate rheometer MCR 101 / SN 80753612 from Anton Paar (Physica). For all measurements a PP08 measuring system (parallel plated, diameter 8 mm) was used. Measurements were performed at 20 °C and for regulating the sample temperature thermoelectric cooling / heating in a Peltier chamber under dry oxygen was applied. For sample preparation a 1 : 1 mixture (100.0 mg) of a trivalent azido-functionalized PIB and a trivalent alkyne-functionalized PIB as well as coumarin-functionalized PIB (1 wt%) were placed in a flask and were dissolved in THF (approximately 3.0 mL). The solvent was removed and the sample was dried in high vacuo. The copper(I) catalyst (0.1 equiv per functional group) was dissolved in $CHCl_3$ (40.0 µL) and was added as a stock solution to all investigated polymer mixtures. Subsequently, the reaction mixture was mixed with a spatula and was immediately put on the rheometer plate. Every ten minutes a frequency sweep was performed within the LVE. Therefore, the strain γ was adjusted to 0.1 % with an angular frequency ω ranging from 100 to 1 rad·s^{-1}. The gelation time was determined as crossover of the storage (G') and the loss modulus (G''). For evaluation of data the RheoPlus / 32 software (V 3.40) and OriginPro7 was used.

3.5. ESI-ToF-MS

ESI-TOF MS measurements were performed on a Focus micro TOF by BrukerDaltonics. Therefore the sample was dissolved in methanol (HPLC grade) at a concentration of 1 mg·mL^{-1}and 100 µL of a sodium iodide solution in acetone (HPLC grade, 20 mg·mL^{-1}) were added. For analysis direct infusion (180.0 µL/h) and detection in positive mode was used.

3.6. MALDI-ToF-MS

Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-ToF-MS) experiments were performed on a Bruker Autoflex III system operating in linear mode. For data evaluation flexAnalysis software (version 3.0) was used. Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064 ± 6.5 nm; 3 ns pulse width; up to 2500 Hz repetition rate), accelerated by a voltage of 20 kV, and detected as positive ions. As matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used and was dissolved in THF (HPLC grade) at a concentration of 20 $mg \cdot mL^{-1}$. The investigated PIB as well as sodium trifluoroacetate (NaTFA) was dissolved in THF (HPLC grade) at a concentration of 20 $mg \cdot mL^{-1}$. Solutions of the applied matrix, the polymer, and the salt were mixed in a volume ratio of 25:5:1. Smoothing and baseline subtraction of the recorded MALDI-ToF-MS spectrum was performed using a three point Savitzky–Golay algorithm.

3.7. UV-Vis spectroscopy

UV-Vis measurements were performed on a Perkin-Elmer Lambda 18 UV-Vis spectrometer or on a FluoroMax-2 of JOBIN YVON·SPEX Instruments S.A., Inc. equipped with a 150W continuous Xe-lamp. HPLC grade THF was used as solvent. The sample concentration was 0.33 mg/mL. For evaluation of data Origin Pro8G (v. 8.0951) was used.

3.8. Fluorescence spectroscopy

Fluorescence measurements were performed on a FluoroMax-2 of JOBIN YVON·SPEX Instruments S.A., Inc. equipped with a 150W continuous Xe-lamp and a resolution of 0.3 nm or on a Cary Eclipse Fluorescence Spectrophotometer from Agilent Technologies. For all measurements an excitation wavelength of 333 nm was applied and emission spectra were recorded from 350 to 650 nm every ten minutes. The sample concentration was 0.33 mg/mL THF (HPLC grade). For evaluation of data the Cary Eclipse Scan Applications Software (v. 1.2, 147) and Origin Pro8G (v. 8.0951) was used.

For investigation of the fluorogenic click-reaction in solution a 1: 1 mixture (100.0 mg) of a trivalent azido-functionalized PIB and a trivalent alkyne-functionalized PIB as well as coumarin-functionalized PIB (**1**, 1 wt%) were dissolved in THF (3 mL, HPLC-grade). After dissolving the polymers the solution was transferred in a closable quartz cuvette equipped with a magnetic stir bar and the copper(I) catalyst (0.1 eq. per functional group) was added. Experiments were run at room temperature (20 °C) under vigorous stirring.

For investigation of the fluorogenic click-reaction in the solid state a 1: 1 mixture (100.0 mg) of a trivalent azido-functionalized PIB and a trivalent alkyne-functionalized PIB as well as coumarin-functionalized PIB (**1**, 1 wt%) were placed in a flask and were dissolved in THF (3 mL, HPLC-grade). The solvent was removed and the sample was dried in high vacuo. The copper(I) catalyst (0.1 equiv per functional group) was added to the polymer mixture and was mixed with a spatula. The so obtained mixture was immediately put between two quartz glass plates which were fixed within a solid state sample holder.

Epoxy specimen with separately encapsulated trivalent azido-functionalized PIB and coumarin-functionalized PIB **1**as well as trivalent alkyne-functionalized PIB and uniformly dispersed $CuBr(PPh_3)_3$ was scratched with a razor plate. The specimen was subsequently put between two quartz glass plates and was fixed within a solid state sample holder. Measurements within the epoxy matrix were performed every 10 minutes over a course of 48 hours. In case of control experiments (unscratched specimen) measurements were performed every 10 minutes over a course of 12 hours.

3.9. DLS

The *hydrodynamic diameter* of the nanocapsules was measured on the dispersions with a Nicomp 380 Submicron Particle Sizer (PSS-Nicomp) equipped with a laser wavelength of λ = 635 nm as a light source at an angle of 90° (DLS) for 300 s.

3.10. Electron microscopy (TEM and SEM)

The morphology of the nanocapsules was examined with a *transmission electron microscope (TEM)* (JEOL 1400) operating at an accelerating voltage of 120 kV and a LEO 1530 Gemini *scanning electron microscope (SEM)* operating at 350 V. 10 µL of the diluted dispersions were placed on small silicon wafers for SEM. For TEM measurements, the nanocapsules dispersion was centrifuged at 8000 rpm for five minutes and the pellet was then redispersed in water. *N*-hexane was added to extract the core and to examine the nanocapsules core-shell morphology. After removal of *n*-hexane 10 µL of the dispersions were placed on copper grids for TEM investigations.

3.11. Freeze drying

For *freeze drying* of PIB-nanocapsules a freeze dryer type P4K-S80 of Dieter Piatkowski Forschungsgeräte was used.

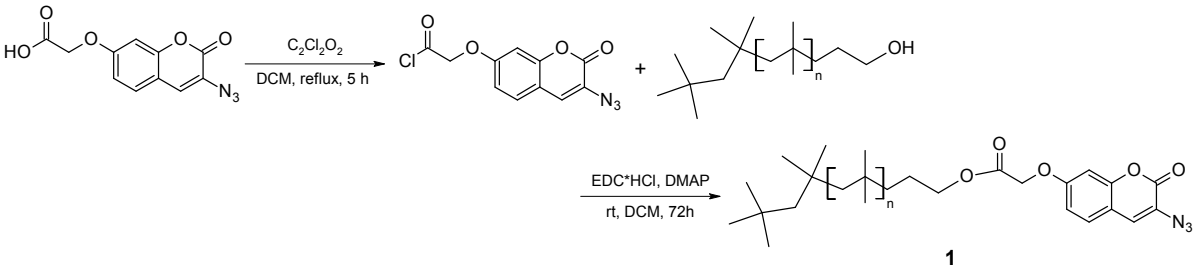
3.12. DMA measurements

The self-healing properties of epoxy specimens (35x5x2 mm) containing 15 wt% nanocapsules filled with trialkyne[1] and triazide[2] separately and $CuBr(PPh_3)_3$ as catalyst (5 mol%) were evaluated *via* dynamic mechanical analysis (DMA) through single-notch impact testing of damaged and healed specimens. The specimens were investigated by applying a three-point bending mode, where DMA measurements were conducted to check the tensile storage modulus (*E'*) at low amplitude. Therefore, *E'* was evaluated for notched specimens, specimens after crack penetration, as well as after healing at room temperature and different time intervals. An impulsive load of 7N was applied to the specimens *via* tensile force in three-dimensional bending mode in order to propagate a crack along the notched plane. Notching was performed using CEAST, manual NOTCHVIS.

4. Synthesis

The synthesis of 3-azido-7-hydroxycoumarin was carried out according to literature.[3] 3-Azido-7-(tert-butylcarboxymethoxy)coumarin as well as 3-azido-7-carboxymethoxycoumarin were prepared according to a synthesis protocol of Dirks et al.[4] For the synthesis of hydroxy-functionalized PIB allyl-functionalized PIB which was prepared *via* living carbocationic polymerization (LCCP) was hydroborinated followed by oxidation. The according synthesis procedures were published elsewere.[5] Trivalent azido- and alkyne-telechelic PIBs were prepared *via* living carbocationic polymerization (LCCP) following the literature.[6]

4.1. Synthesis and characterization of coumarin-functionalized PIB **1**



1

The synthesis of **1** was done *via* esterification of hydroxy-functionalized PIB with 3-azido-7-carboxymethoxycoumarin in a two-step one-pot reaction. First, [(3-azido-2-oxo-2*H*-chromen-7-yl)oxy]acetyl chloride was prepared *in situ*. Therefore, 3-azido-7-carboxymethoxycoumarin (112.5 µmol, 30.0 mg, 3.0 eq.) was dissolved in dry DCM (5 mL) and was treated with oxalyl chloride (112.5 µmol, 9.7 µL, 3.0 eq.). Under a dry atmosphere of argon the reaction mixture was heated under reflux for five hours. After cooling down to room temperature hydroxy-functionalized PIB (37.5 µmol, 150.0 mg, 1.0 eq.) and DMAP (21.0 µmol, 2.7 mg, 0.56 eq.) was dissolved in dry DCM (1 mL) and the so prepared solution was added to the reaction mixture. The reaction mixture was further cooled down to 0 °C and EDC · HCl (0.06 mmol, 11.4 mg) was added followed by stirring for 72 hours at 40 °C. After removing the solvent in vacuo the crude product was dissolved in *n*-hexane (20 mL) and was washed with methanol (five times 15 mL each) as well as with saturated NH_4Cl-solution (20 mL). The isolated *n*-hexane phase was dried over Na_2SO_4 and the solvent was removed in vacuo after filtration of the drying agent. After drying in high vacuo **1** was obtained as an orange, highly viscous polymer in a yield of 67 % (25.0 µmol, 107.0 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (H_4, s, 1H), 7.33 (H_5, d, $^3J_{H,H}$ = 8.7 Hz, 1H), 6.81 (H_8, d, $^4J_{H,H}$ = 2.3 Hz, 1H), 6.90 (H_6, dd, $^4J_{H,H}$ = 2.5, $^3J_{H,H}$= 8.6 Hz, 1H), 4.68 (H_9, s, 2H), 4.18 (H_{12}, t, $^3J_{H,H}$ = 6.6, 2H), 1.42 (H_{13}, repetitive unit, n · CH_2), 1.11 (H_{14}, repetitive unit, 2n · CH_3), 0.99 (H_{15}, s, 15H). IR (cm^{-1}): 2950.4, 2897.4, 2124.0, 1737.2, 1617.6, 1470.6, 1389.2, 1365.4, 1302.5, 1229.8, 1168.5, 949.4, 923.7, 689.5, 629.3.

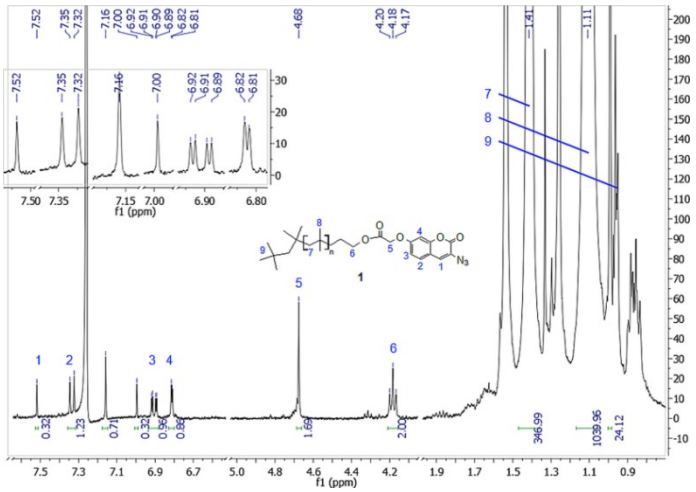


Figure S1: ^{1}H-NMR-spectrum of coumarin-functionalized PIB **1**.

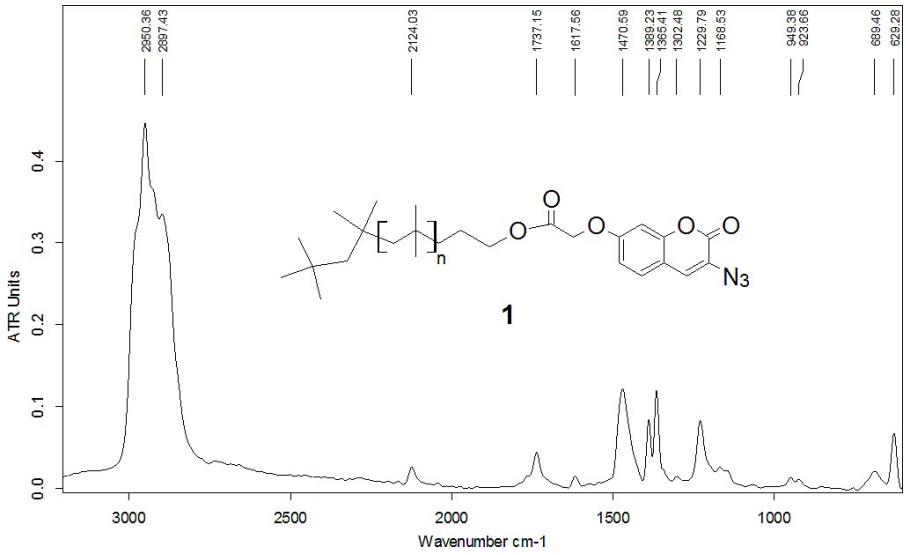


Figure S2: FTIR-spectrum of coumarin-functionalized PIB **1**.

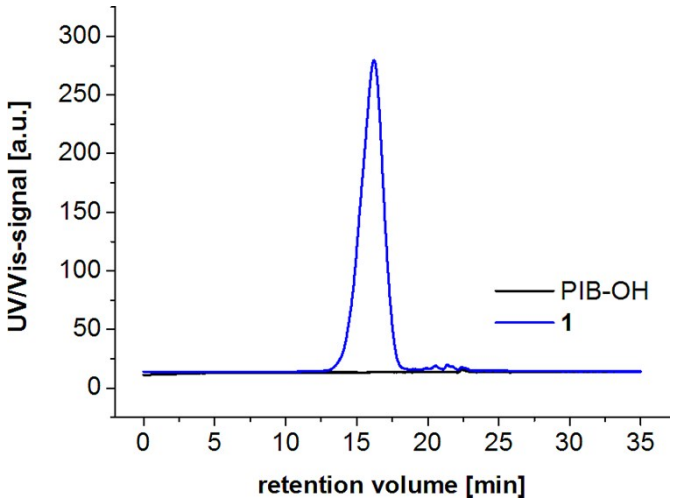


Figure S3: Gel permeation chromatographic curves of PIB-OH and coumarin-functionalized PIB **1** detected by UV detector at 330 nm.

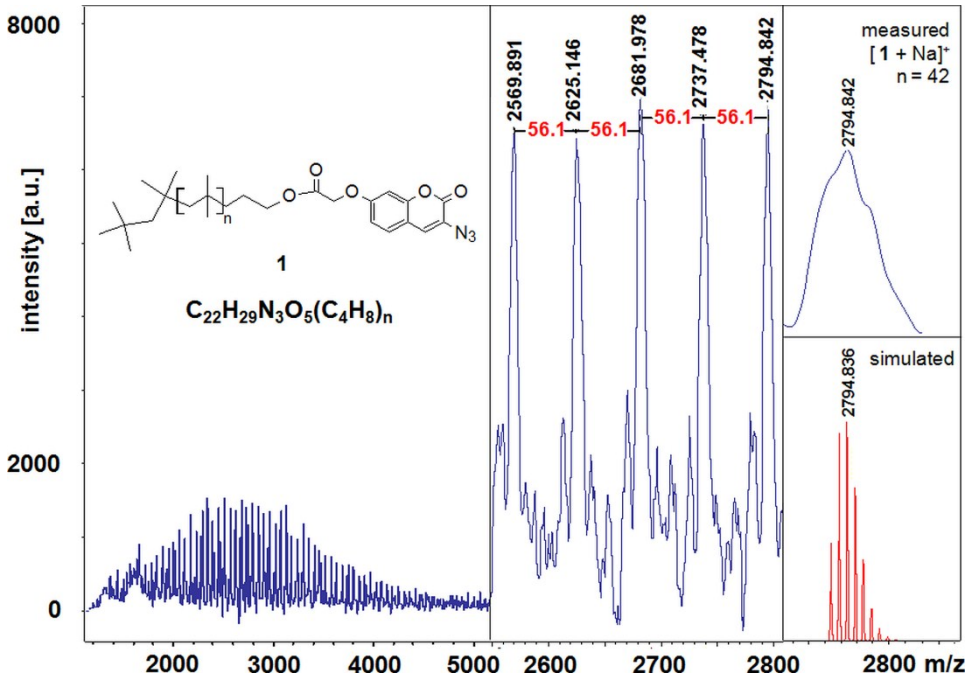
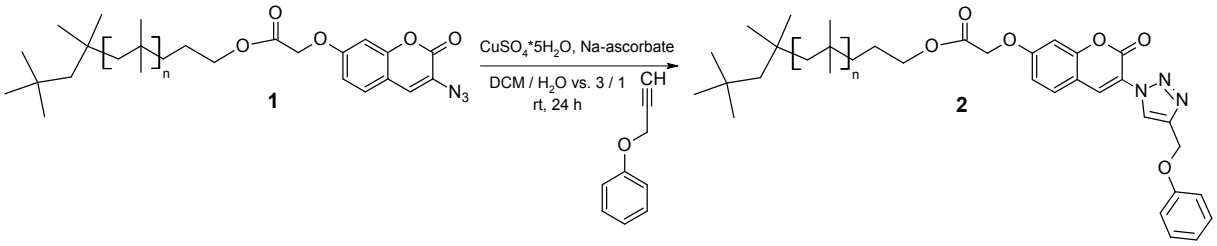


Figure S4: MALDI-ToF mass spectrum of coumarin-functionalized PIB**1** and simulation of the sodium adduct of coumarin-functionalized PIB **1** with n = 42 units of isobutylene.

4.2. Click-reaction of coumarin-functionalized PIB **1** with phenyl propargyl ether - synthesis and characterization



Coumarin-functionalize PIB (**1**, 6.3 µmol, 25.0 mg, 1.0 eq.) was converted with phenyl propargyl ether *via* click-chemistry in order to obtain polymer **2**. Therefore, **1** was dissolved in a solvent mixture of DCM and water (3:1, 4 mL) and was purged with argon for 30 minutes. Phenyl propargyl ether (6.9 µmol, 0.89 µL, 1.1 eq.), sodium ascorbate (31.5 µmol, 5.2 mg, 5.0 eq.) and $CuSO_4 \cdot 5\ H_2O$ (6.3 µmol, 1.6 mg, 1.0 eq.) was added and the reaction mixture was vigorously stirred at room temperature for 24 hours. After complete conversion (TLC, *n*-hexane, R_f = 0.05) the reaction mixture was diluted with DCM (30 mL) and extracted with saturated NH_4Cl-solution (two times 50 mL each) followed by water (two times 50 mL each). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo after filtration of the drying agent. After drying in high vacuo the product **2** was obtained as an orange, highly viscous polymer in a yield of 74 % (5.1 µmol, 21.0 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31, 7.00, 5.13, 4.69, 4.20, 1.42 (H_{13}, repetitive unit, n · CH_2), 1.11 (H_{14}, repetitive unit, 2n · CH_3), 0.99 (H_{15}, s, 15H). IR (cm^{-1}): 2949.8, 2895.4, 1739.8,

1714.7, 1667.0, 1620.2, 1546.5, 1470.8, 1389.3, 1365.6, 1229.4, 1168.5, 1114.4, 949.2, 922.4, 856.0, 779.2, 731.1, 631.5.

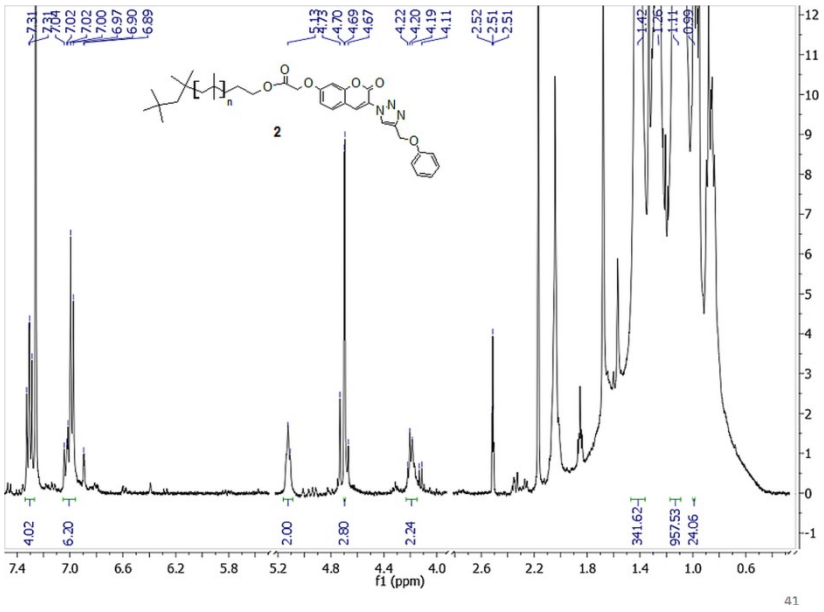


Figure S5: ^{1}H-NMR-spectrum of **2**.

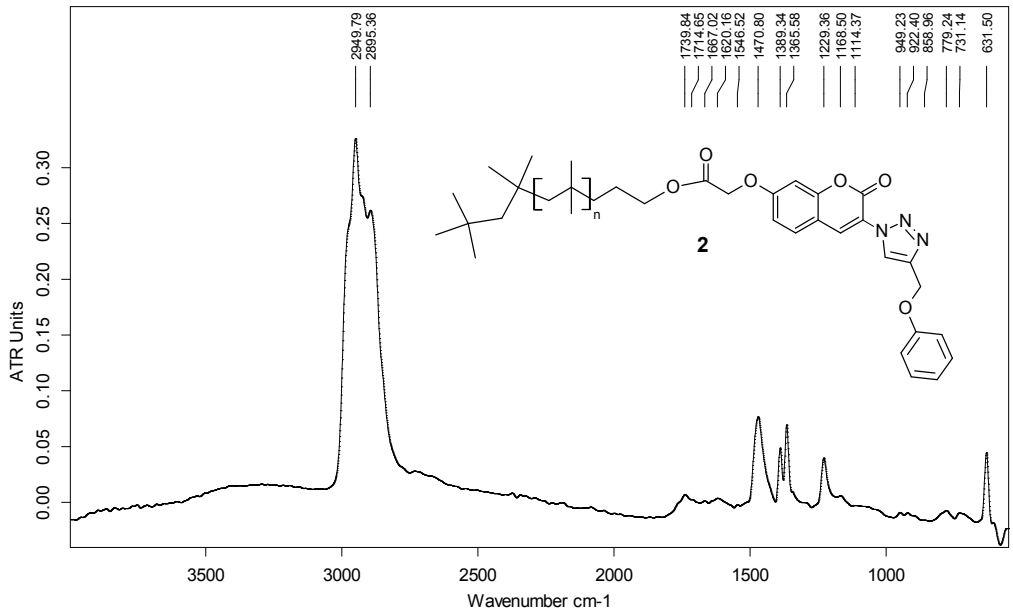


Figure S6: FTIR-spectrum of **2**.

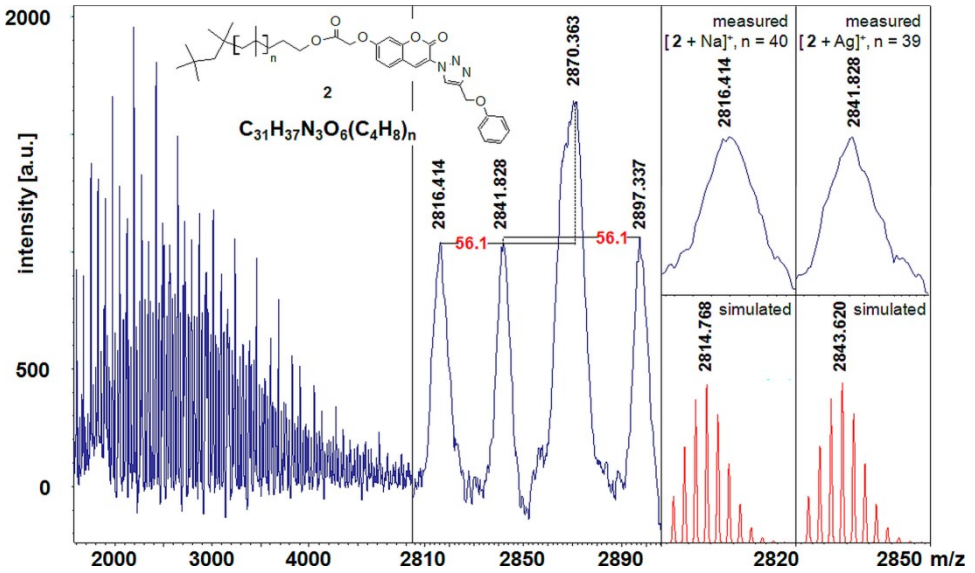
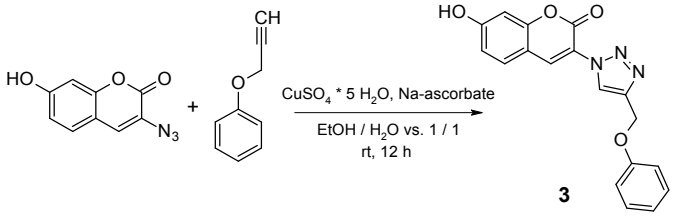


Figure S7: MALDI-ToF mass spectrum of PIB **2**, simulation of the sodium adduct of **2** with n = 40 units of isobutylene and simulation of the silver adduct of **2** with n = 39 units of isobutylene.

4.3. Synthesis and characterization of 7-hydroxy-3-[4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl]-2H-chromen-2-one **3**



3-Azido-7-hydroxycoumarin (345.0 µmol, 70.0 mg, 1.0 eq.) and phenyl propargyl ether (345.0 µmol, 39.5 µL, 1.0 eq.) was dissolved in a solvent mixture of ethanol and water (1:1, 10 mL). After purging with nitrogen for 15 minutes a 1 M solution of sodium ascorbate (69.0 µL) and a solution of $CuSO_4 \cdot 5\ H_2O$ (7.5 wt%, 57.3 µL) was added to the reaction mixture. After purging with nitrogen for further 10 minutes the reaction mixture was vigorously stirred in the dark for 24 hours at room temperature. After complete conversion (TLC, EA / *n*-heptane 1 : 2, R_f = 0.2) ethanol was removed in vacuo and the reaction mixture was diluted with water (10 mL). The so obtained mixture was cooled down to 0 °C and the desired product precipitated. The crude product was separated by filtration followed by washing with water. Afterwards the crystals were dissolved in acetone and the solvent was removed in vacuo to obtain **3** as a brown powder in a yield of 30 % (100.0 µmol, 33.0 mg)

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (H_9, s, 1H), 8.61 (H_4, s, 1H), 7.76 (H_5, s, 1H), 7.31 (H_{13}, t, $^3J_{H,H}$ = 7.9, 2H), 7.08 (H_{12}, d, $^3J_{H,H}$ = 8.0, 2H), 6.98-6.85 ($H_{6,8,10,14}$, m, 4H), 5.25 (H_{11}, s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 158.0, 156.3, 154.9, 154.4, 142.9, 136.5, 131.7, 129.5, 129.4, 125.5, 120.9, 119.2, 114.7, 110.3, 60.6. IR (cm^{-1}): 3194.8, 3169.6, 3105.3, 3067.0, 2957.9, 2928.1, 2873.7, 2854.0, 1732.4, 1704.7, 1613.1, 1595.8, 1518.5, 1488.5, 1460.4, 1421.6, 1384.9, 1339.0, 1295.0, 1221.3, 1170.3, 1116.8, 1085.5, 1054.1, 1031.5,

1011.4, 924.3, 858.7, 824.9, 757.0, 695.4, 654.3, 632.7. ESI-ToF-MS (MeOH) m/z: 358.116 (M + Na^+, measured), 358.303 (M + Na^+, simulated)

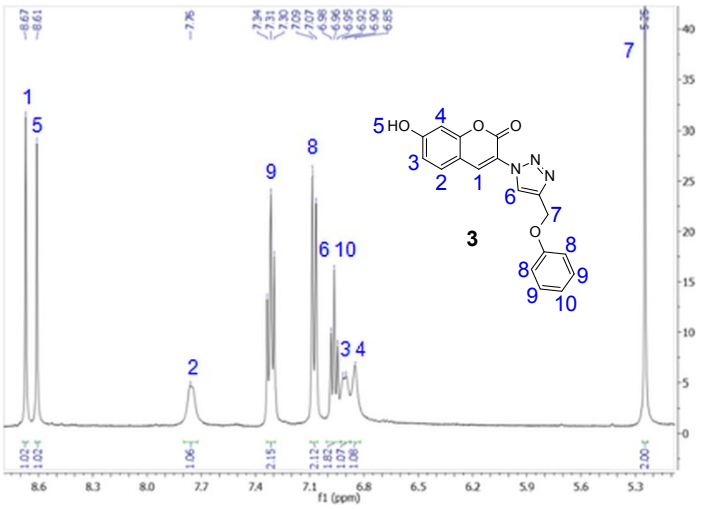


Figure S8: ^{1}H-NMR-spectrum of **3**.

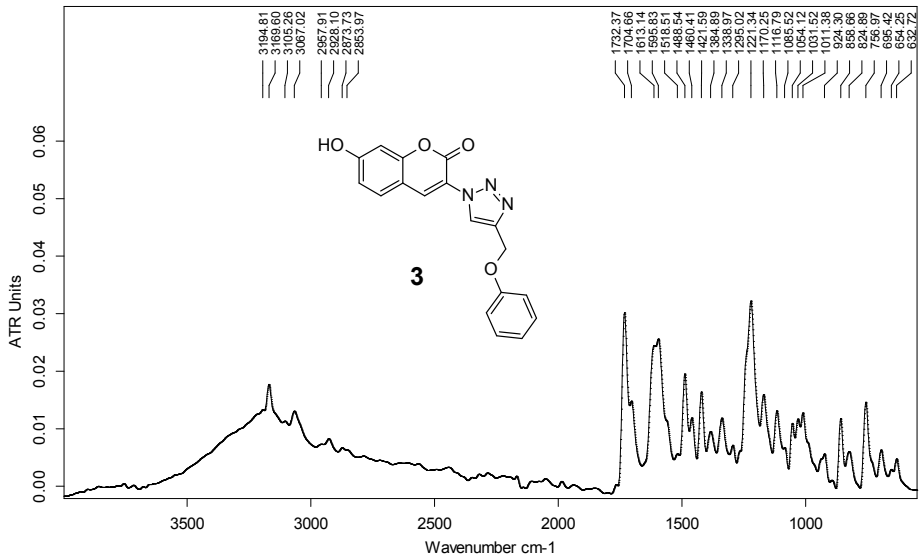


Figure S9: FTIR-spectrum of **3**.

4.4. Encapsulation of polymers *via* miniemulsion solvent evaporation technique

Miniemulsion solvent evaporation was used for the preparation of nanocapsules.[7] 100 mg of PIB (three-arm star PIB-alkyne or three-arm star PIB-azide + 1wt% PIB **1**) and 100 mg of poly(vinyl formal) (PVF) were dissolved in 2 mL of chloroform. The organic phase was added to 10 mL of an aqueous solution with concentrations of 0.5 mg mL^{-1} of either sodium dodecyl sulfate (SDS) or a mixture of SDS and Lutensol AT50. The mixture was stirred at 1100 rpm for 1 h in a closed glass vial to obtain a macroemulsion. The emulsion was then subjected to ultrasonication under ice-cooling for 2 min in a 30 s pulse/15 s pause regime

(Branson W450-D sonifier with a 1/2 in. tip). Afterward, the chloroform was evaporated at 40 °C while stirring at 500 rpm for 12 h.

4.5. Preparation of epoxy nanocomposites - embedding procedure of PVF/PIB nanocapsules

The epoxy nanocomposite was prepared according to literature.[8] Therefore, 500 mg of diglycidylether of bisphenol A (DGEBA, EPON 828 epoxy resin) and diethylenetriamine (DETA, 12 pph) were first manually mixed together for 10 minutes, and then degassed to eliminate trapped air. The calculated amount of nanocapsules (15 wt%) and catalyst ($CuBr(PPh_3)_3$, 0.3 equ.) were then manually stirred into the mixture, followed by mixing using vortex and bath sonicator for 15 minutes. A second degassing procedure was followed to remove any further air bubbles. The final mixture was poured into a silicon mold (30x5x2mm) and specimens were cured at room temperature for 24 hours, followed by 24 hours at 35 °C.

5. UV-Vis and fluorescence spectroscopy investigations

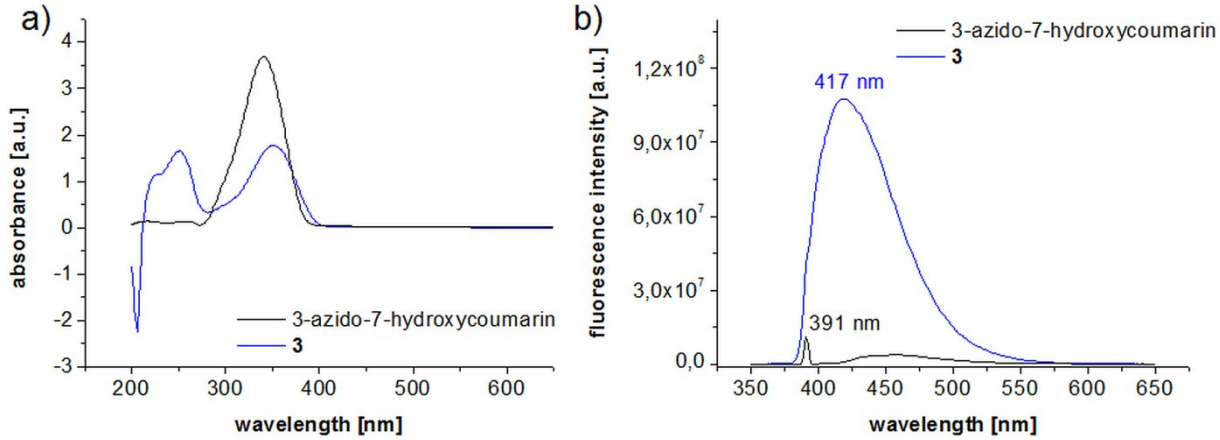


Figure S10: a) UV/Vis-spectra and b) fluorescence spectra of 3-azido-7-hydroxycoumarin and **3** (0.33 mg/mL THF, HPLC grade).

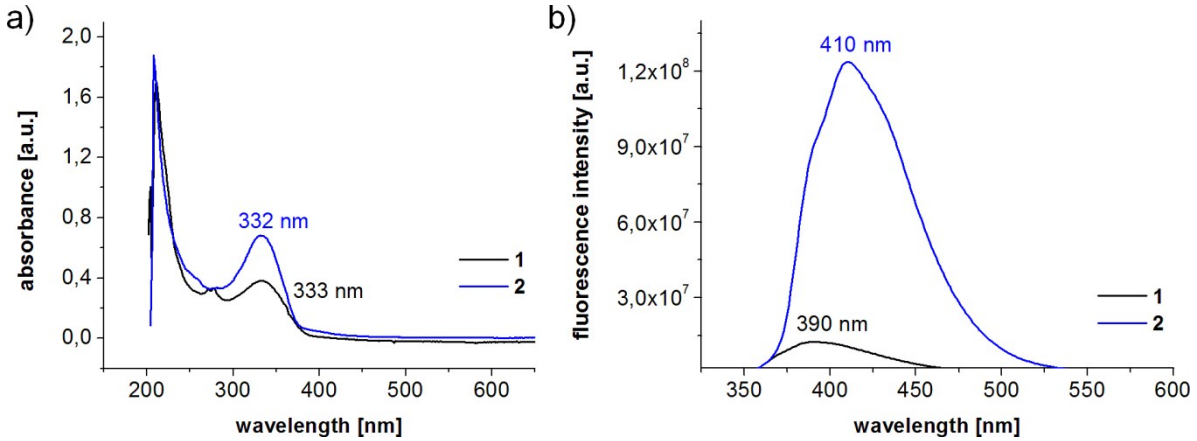


Figure S11: a) UV/Vis-spectra and b) fluorescence spectra of **1** and **2** (0.33 mg/mL THF, HPLC grade).

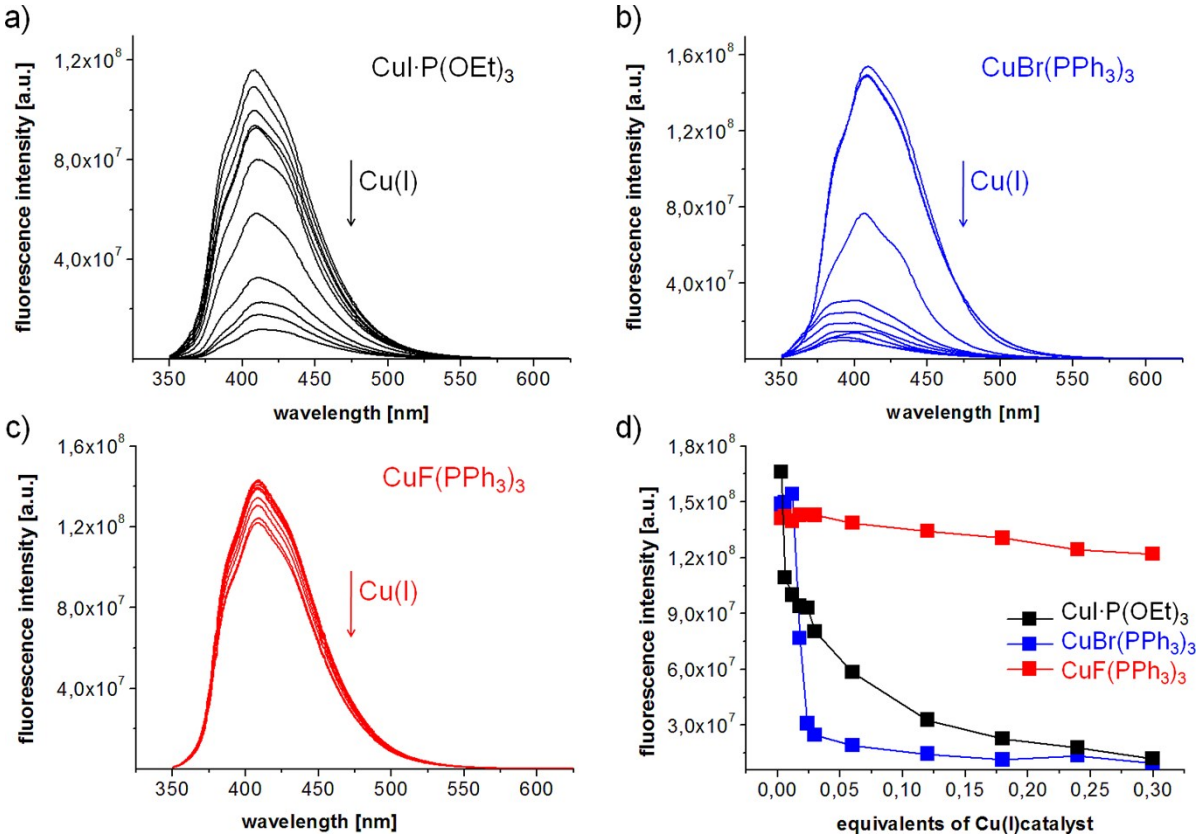


Figure S12: Fluorescence spectra of **2** (0.33 mg/mL THF, HPLC grade) in the presence of increasing equivalents of a) CuI·P(OEt)$_3$, b) CuBr(PPh$_3$)$_3$ and c) CuF(PPh$_3$)$_3$. d) Overview of the effect of increasing equivalents of different copper(I) catalysts on the fluorescence intensity of **2** (0.33 mg/mL THF, HPLC grade).

6. Rheology investigations

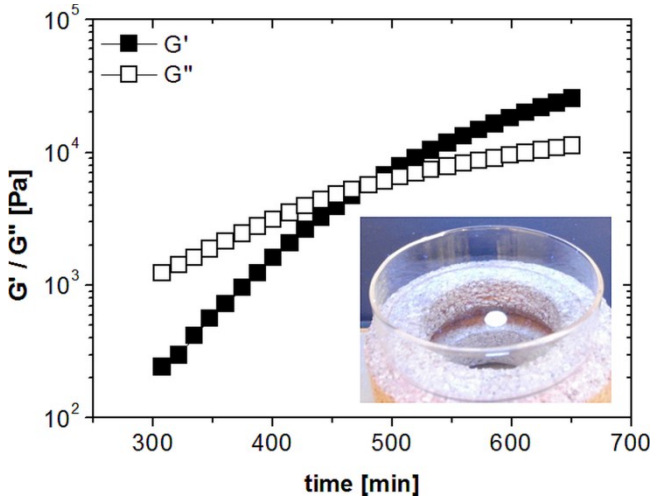


Figure S13: Fluorogenic click reaction between three-arm star PIB-azide and -alkyne and fluorogenic probe **1** (1 wt%) directly on the rheometer plate at 20 °C using 0.3 equ. of CuBr(PPh$_3$)$_3$.

7. Encapsulation results and TEM and SEM micrographs

Table S1: Hydrodynamic diameter and yield of the core-shell nanoparticles prepared with different surfactant ratios.

Surfactant(s)		Hydrodynamic diameter D_h [nm]	Size distribution [%]	Yield [%]
SDS [%]	Lutensol AT50 [%]			
0	100	---[a]	---[a]	---[a]
25	75	393.2	33	53
50	50	294.7	22	50
75	25	246.8	15	40
100	0	203.7	23	24

[a]No encapsulation observed.

In order to tune the size of the obtained nanodispersion as well as the yield of the prepared PVF/PIB nanocapsules the influence of the nature of the surfactant was investigated in detail. Therefore, the concentration of the surfactant or surfactant mixture was kept at 0.5 mg/mL showing the best encapsulation efficiency for PIBs as described earlier.[7] Thus, five different mixtures of sodium dodecyl sulfate (SDS) and Lutensol AT50, a non-ionic $C_{16}H_{18}$ fatty alcohol ethoxylate surfactant (degree of ethoxylation = 50), ranging from 0 % to 100 % SDS were prepared. Subsequently, the hydrodynamic diameter of the dispersed nanoparticles as well as the recovery of the capsules after freeze-drying (yield) has been determined. Furthermore, TEM and SEM micrographs of prepared PVF/PIB nanocapsules before and after extraction of the PIB-core with *n*-hexane have been recorded (see Figure S13).

While no successful encapsulation was observed for pure Lutensol AT50, nanocapsules with an average size of 393 nm and with a relatively broad size distribution (+/- 131 nm) and a yield of 53% were obtained for Lutensol AT50 : SDS *vs.* 75 : 25. By further increasing the amount of SDS the hydrodynamic diameter of the obtained nanocapsules consequently decreased up to 204 +/- 46 nm going along with a stepwise decrease of the yield up to 24%. Independently on the investigated surfactant mixture, core-shell morphologies were observed. This morphology is highlighted by TEM micrographs after extraction of the PIB-core with *n*-hexane (see Figure S14). Thus, the size of the nanocapsules was tuned by adjusting the Lutensol AT50:SDS ratio for obtaining the PVF-PIB nanocapsules in good to moderate yields after freeze-drying.

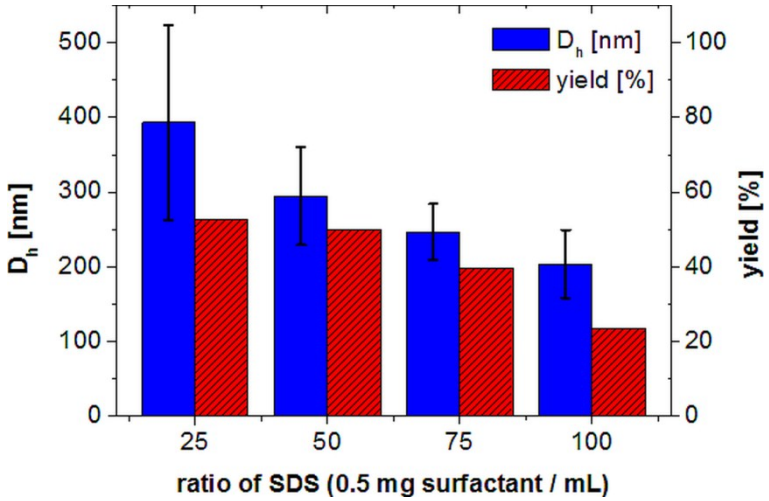


Figure S14: Influence of the surfactant ratio (0.5 mg surfactant/mL) on the diameter of the nanocapsules containing PIB determined by DLS measurements and on the encapsulation yield.

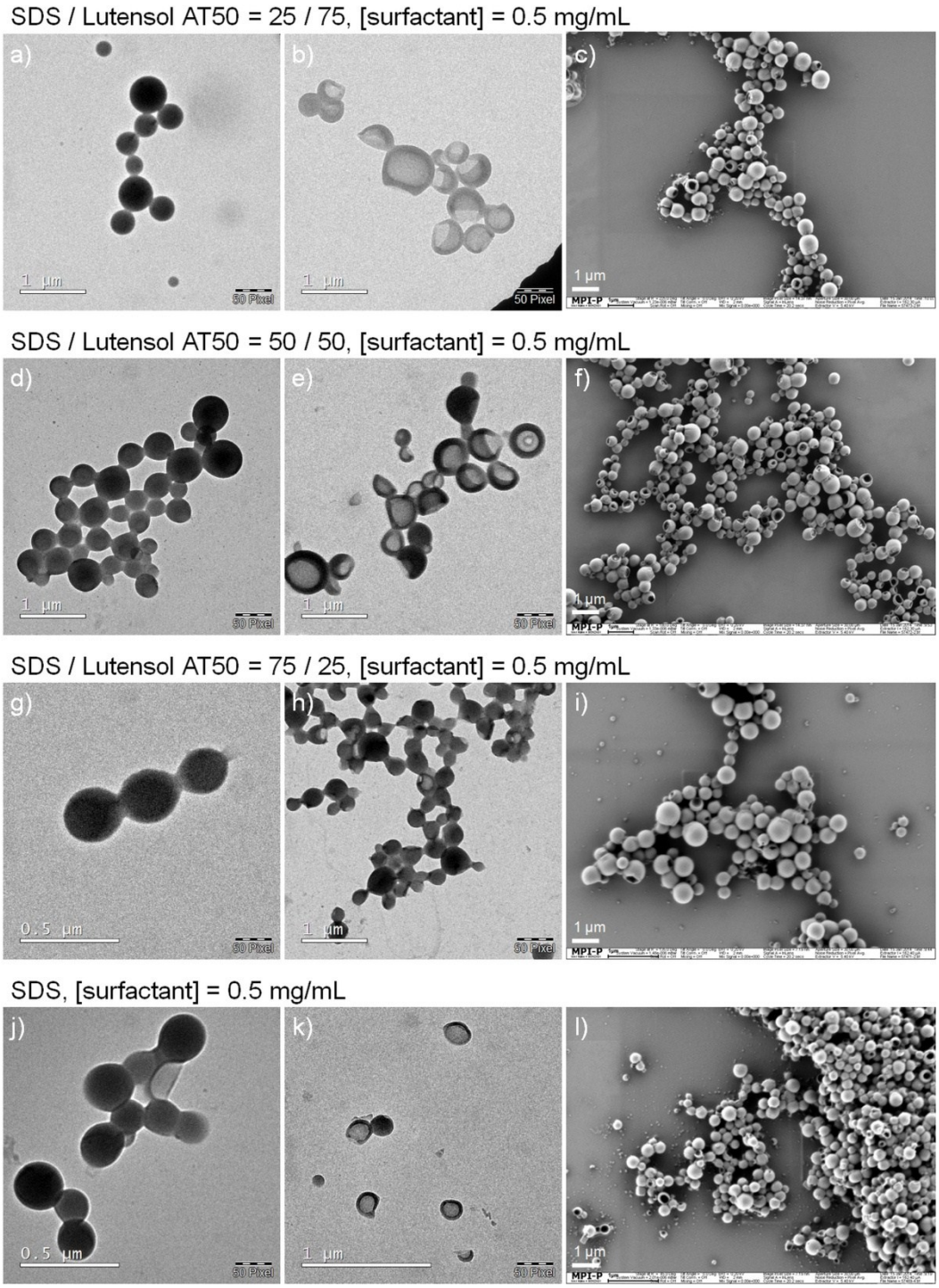


Figure S15: TEM micrographs of PVF/PIB nanocapsules before a) and after b) extraction of the PIB core with *n*-hexane. c) SEM micrograph of the nanocapsules after extraction of the core with *n*-hexane (scaling bar: 1 µm). a) to c) SDS / Lutensol AT50 = 25 / 75, [surfactant] = 0.5 mg/mL.TEM micrographs of PVF/PIB nanocapsules before d) and after e) extraction of the PIB core with *n*-hexane. f) SEM micrograph of the nanocapsules after extraction of the core with *n*-hexane (scaling bar: 1 µm). d) to f) SDS / Lutensol AT50 = 50 / 50, [surfactant] = 0.5 mg/mL.TEM micrographs of PVF/PIB nanocapsules before g) and after h) extraction of the PIB core with *n*-hexane. i) SEM micrograph of the nanocapsules after extraction of the core with *n*-hexane (scaling bar: 1 µm). g) to i) SDS / Lutensol AT50 = 75 / 25, [surfactant] = 0.5 mg/mL.TEM micrographs of PVF/PIB nanocapsules before j) and after k) extraction of the PIB core with *n*-hexane. l) SEM micrograph of the nanocapsules after extraction of the core with *n*-hexane (scaling bar: 1 µm). j) to l) [SDS] = 0.5 mg/mL.

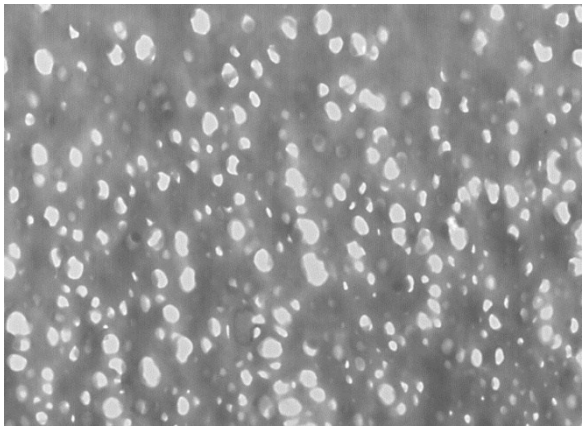


Figure S16: TEM micrographs of PVF/PIB nanocapsules embedded within the epoxy matrix.

8. Self-healing investigations

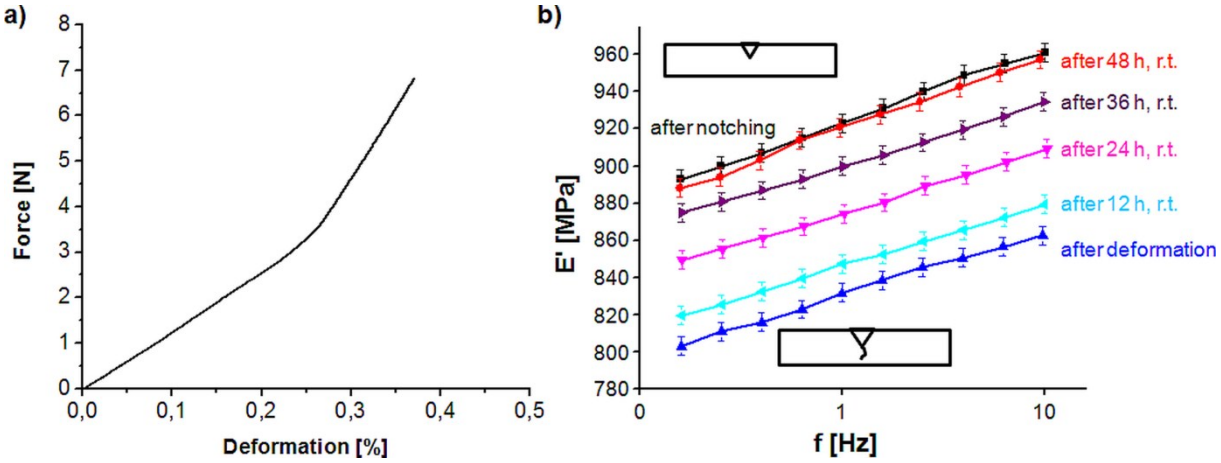


Figure S17: a) Load *vs.* crack opening displacement curve. b) DMA measurements of prepared specimens containing 15 wt% nanocapsules filled with trialkyne and triazide separately and $CuBr(PPh_3)_3$ as catalyst (5 mol%) after notching before applying force (black curve) and after crack penetration and deformation (blue curve) including healing at room temperature (r.t.) for 12 h (turquoise curve), 24 h (pink curve), 36 h (purple curve) and 48 h (red curve), respectively.

9. Literature

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