

Supporting Information

A synthetic strategy for the preparation of sub-100nm functional polymer particles of uniform diameter

Kato L. Killops,^{a*} Christina G. Rodriguez,^{b,c} Pontus Lundberg,^d Craig J. Hawker,^c and Nathaniel A. Lynd^{b,c,e*}

^a U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010. Email: kathryn.l.killops.civ@mail.mil

^b Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

^c Materials Research Laboratory, University of California, Santa Barbara, CA 93106.

^d Life Sciences Solutions, Thermo Fisher Scientific, Svellevæien 29, 2001, Lillestrøm, Norway.

^e McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712. Email: lynd@che.utexas.edu

Chemicals. All chemicals were purchased from Sigma Aldrich and used without further purification, unless otherwise stated. Allyl glycidyl ether was purchased from TCI America. Styrene was degassed by three freeze-pump-thaw cycles and purified by stirring over dibutylmagnesium at 0°C and distilling into receiving flasks. Ethylene oxide and allyl glycidyl ether were degassed by three freeze-pump-thaw cycles and purified by stirring over butylmagnesium chloride at 0°C and distilling into receiving flasks. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories. Potassium naphthalenide was prepared by dissolving recrystallized naphthalene (10 g) in dry THF (250 mL) and then adding potassium metal (3 g) under positive argon pressure. The system was closed with a septum and allowed to stir overnight with a glass-coated stir-bar. Basic aluminum oxide was used to remove the inhibitor present in the styrene monomer prior to emulsion polymerization.

Instrumentation. NMR (¹H, ¹³C) spectra were recorded on a Bruker DMX-300 MHz spectrometer at room temperature. Chemical shifts are reported in parts per million (δ) relative to CHCl₃ (7.24 ppm for ¹H), DMSO (2.50 ppm for ¹H), or DMF (8.03 ppm for ¹H) as internal reference. Gel permeation chromatography was performed in chloroform with 0.25% triethylamine on a Waters 2695 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Scanning electron microscopy was performed on a FEI XL30 Sirion FEG Digital Electron Scanning Microscope at 3.0 to 5.0 keV. Dynamic light scattering was performed on a Wyatt Möbius instrument at ambient temperature in Milli-Q water. BCP and latex samples were diluted and filtered through a 1.6 μm glass filter before DLS measurement. Particle size and polydispersity were derived from the regularization fit of the correlation function, and scattering intensities < 3% were not included. Confocal microscopy of the particles was performed on an Olympus BX40 microscope. Fluorescence spectroscopy was performed on a Horiba Jobin Yvon fluorometer. Coefficient of variation (CV) was determined from measuring at least 30 particles from the SEM image for each sample, and the standard deviation in particle diameters was divided by the sample mean. The measurements were made using ImageJ software. N_p was determined according to the equation:¹

$$N_p = \frac{6\tau}{\rho\pi D^3}$$

where N_p is the number of particles per unit volume, τ is the solids content in the dispersed phase (g L^{-1}), ρ is the density of the polymer (g mL^{-1}), and D is the diameter of the particles measured by either SEM or DLS (D_h).

*PS-*b*-P(EO-co-AGE)*. The synthesis was performed according to procedures found in Killops, *et al.*²

Particle synthesis. A general procedure was used and scaled accordingly: 10 wt. % styrene in water, 5-20 wt. % block copolymer (BCP) (relative to styrene), and 0.8 wt. % (relative to styrene) potassium persulfate (KPS). Reactions were typically conducted in water (25 to 100 mL). First, styrene was suspended with vigorous stirring in half of the total volume of water in a three-neck flask fitted with a condenser. The BCP was dissolved in the other half of water. The BCP micelle solution was added dropwise to the stirring styrene suspension. The mixture was sparged with N_2 for 30 minutes at RT, then heated to 70°C under N_2 flow. In a separate vial fitted with a septum, KPS was dissolved in a small amount of water and sparged with N_2 for 10 minutes. The solution was transferred via cannula to the reaction mixture. The emulsion polymerization was stirred at 80°C for 6-16 hours.

4-((2-mercaptoethoxy)methyl)-6,7-dimethoxycoumarin. In a vial, 4-bromomethyl-6,7-dimethoxycoumarin (307 mg, 1.03 mmol) was dissolved in DMF. Mercaptoethanol (100 mg, 1.28 mmol) and potassium carbonate (160 mg, 1.16 mmol) were then added. The reaction was left to stir overnight at room temperature. The solution was diluted with CH_2Cl_2 and washed twice with H_2O , then brine, and dried over anhydrous MgSO_4 . The crude product was purified over a silica plug with ethyl acetate and evaporated to dryness. Product was recovered as a light yellow solid (248 mg, 82% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.05 (s, 1H), 6.83 (s, 1H), 6.23 (s, 1H), 3.92 (s, 6H), 3.79 (m, 4H), 2.71 (t, 2H, $J=6$ Hz), 2.05 (bt, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 153.1, 151.3, 150.2, 146.3, 112.5, 110.6, 105.5, 100.4, 61.2, 56.5, 34.8, 32.7. ESI-TOF MS ($M + \text{H}^+$) calculated for $\text{C}_{14}\text{H}_{16}\text{O}_5\text{S}$: 297.0791; found: 297.0809.

Synthesis of coumarin-labeled particles. The solvent for the as-synthesized alkene-functional (M3 15 wt.% BCP) particles (H_2O) was replaced by MeOH via three centrifugation, solvent-exchange cycles. The thiol-functional coumarin (100 mg, 0.423 mmol) was dissolved in MeOH (7 mL) and added to a vial containing 1 mL of the particles in MeOH (0.114 mmol ene). AIBN (9 mg, 0.055 mmol) was added as the thermal initiator, the vial was capped with a septum, and the solution was sparged with N_2 for 10 minutes. The solution was heated at 60°C overnight. The solution was diluted with MeOH (10 mL), and centrifuged to purify. The supernatant was removed and replaced with MeOH five times to ensure complete removal of the unreacted coumarin, the point at which the fluorescence spectrum showed no coumarin absorption.

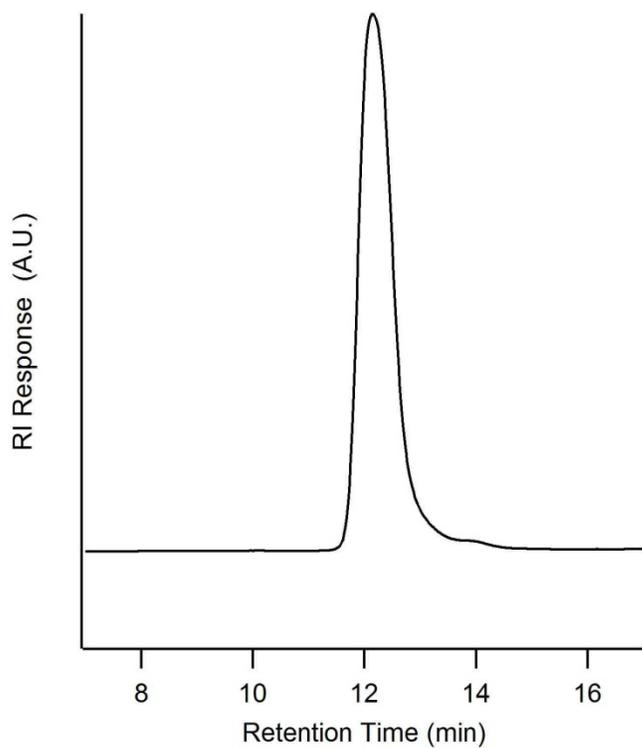


Figure S1. Size exclusion chromatograph of **M3** in THF.

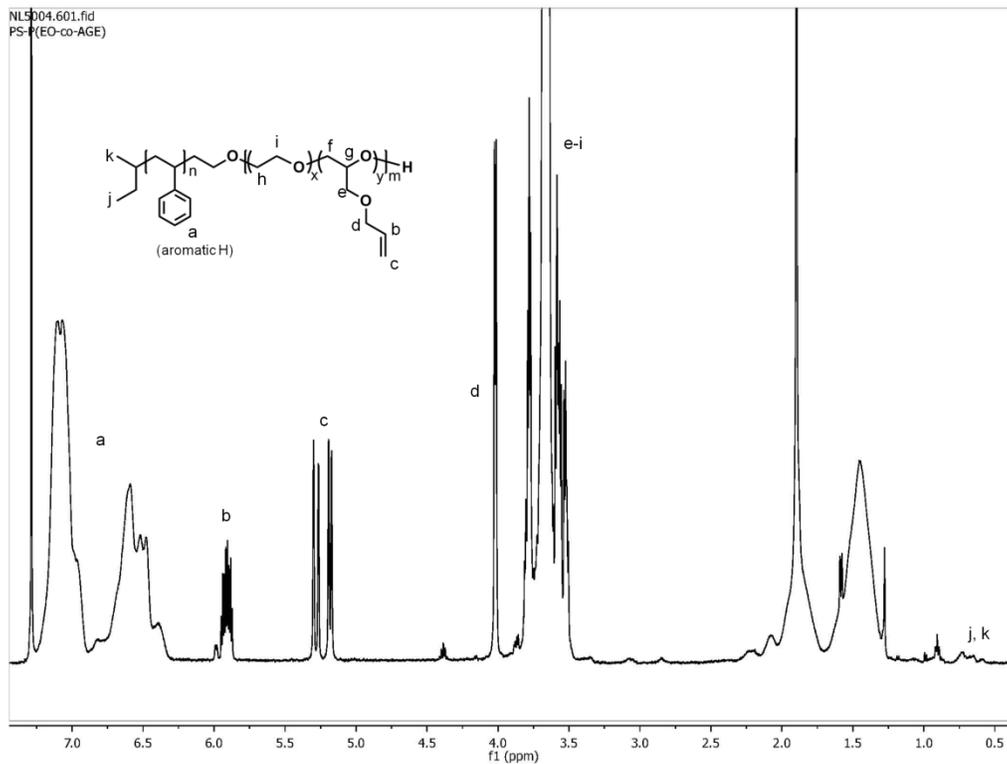


Figure S2. ¹H NMR of **M3**.

Table S1. Diameters of block copolymer structures in aqueous solution from DLS

Polymer	D_h (nm)	% PD
S3	156	45
M1	246	31
M3	229	41
M5	262	37
L3	12, 389	19, 69

Size and polydispersity (PD) determined using the regularization fit of the correlation function from Dynamics software from Wyatt; average of three measurements, each containing 10 acquisitions.

Table S2. Diameters of monomer-swollen block copolymer structures in aqueous solution from DLS

Polymer	D_h (nm)	% PD
S3	130	32
M1	182	75
M3	132	35
M5	156	56
L3	154	23

Size and polydispersity (PD) determined using the regularization fit of the correlation function from Dynamics software from Wyatt; average of three measurements, each containing 10 acquisitions.

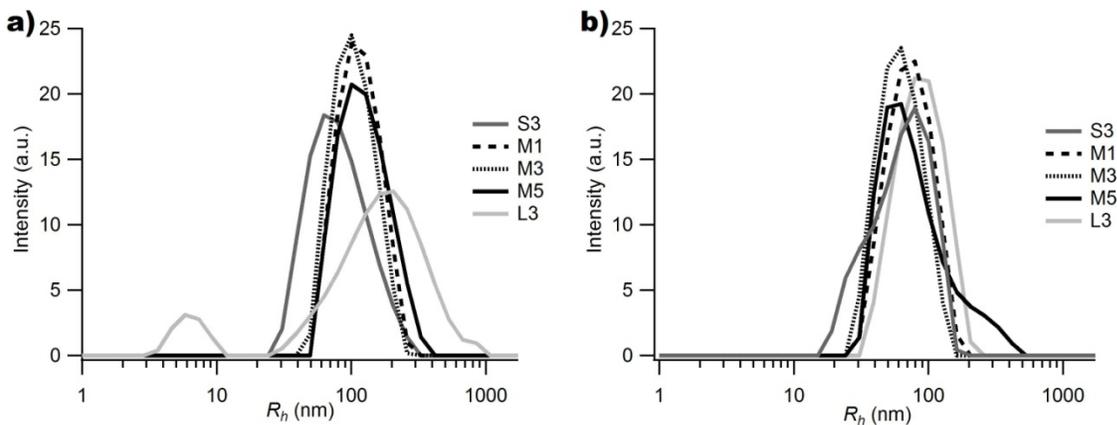


Figure S3. Dynamic light scattering of (a) aqueous BCP solutions and (b) BCP solutions after swelling with styrene. Representative histograms from the regularization fit of the correlation function from Wyatt Dynamics software.

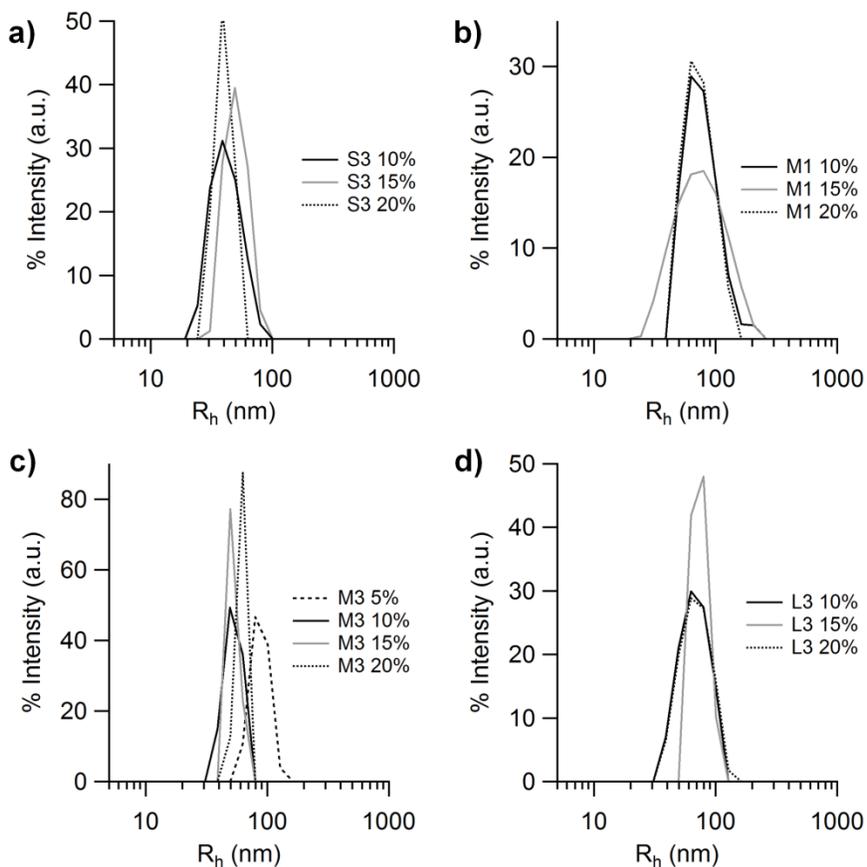


Figure S4. Representative DLS histograms of a) **S3**, b) **M1**, c) **M3**, d) **L3** series of particles determined from the regularization fit of the correlation function in Dynamics software from Wyatt.

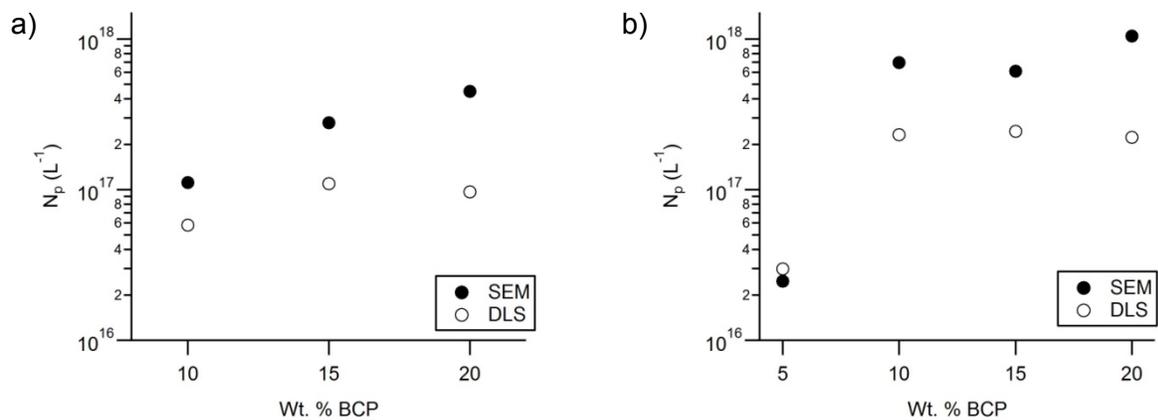


Figure S5. Plots of number of particles (N_p) versus weight % BCP for (a) **L3** and (b) **M3**. Filled circles represent N_p calculated from particle diameters measured by SEM and open circles represent N_p calculated from particle diameters measured by DLS. Both measurements include the mass of the total solids.

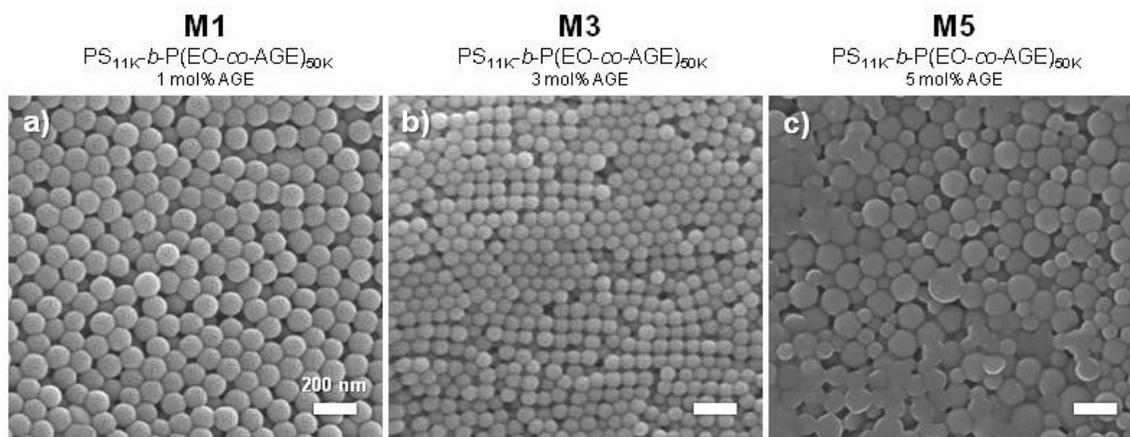


Figure S6. SEM images of particles synthesized with 10 wt% of BCP stabilizers with varying incorporations of AGE comonomer.

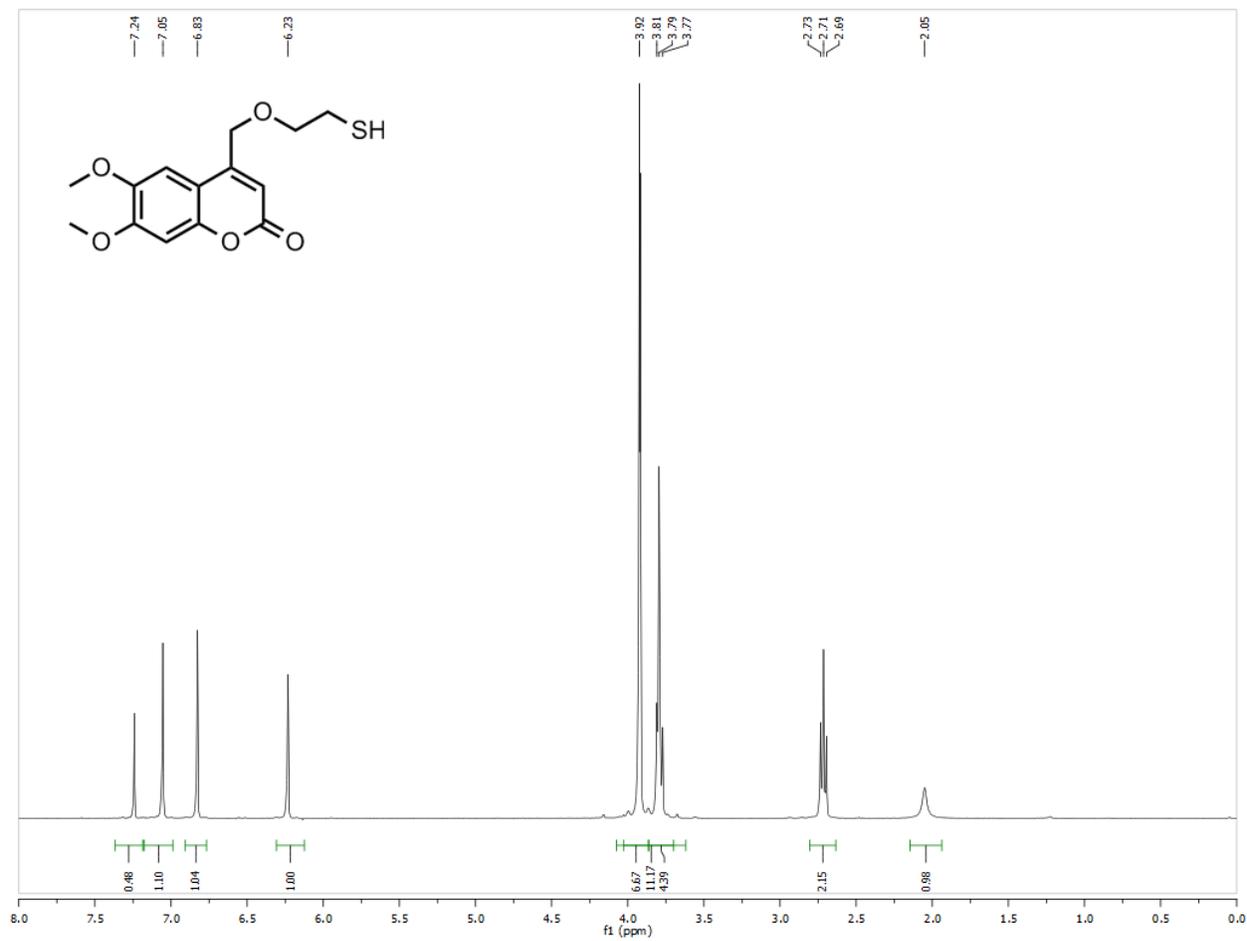


Figure S7. Chemical structure and ¹H NMR spectrum of 4-((2-mercaptoethoxy)methyl)-6,7-dimethoxycoumarin in CDCl₃.

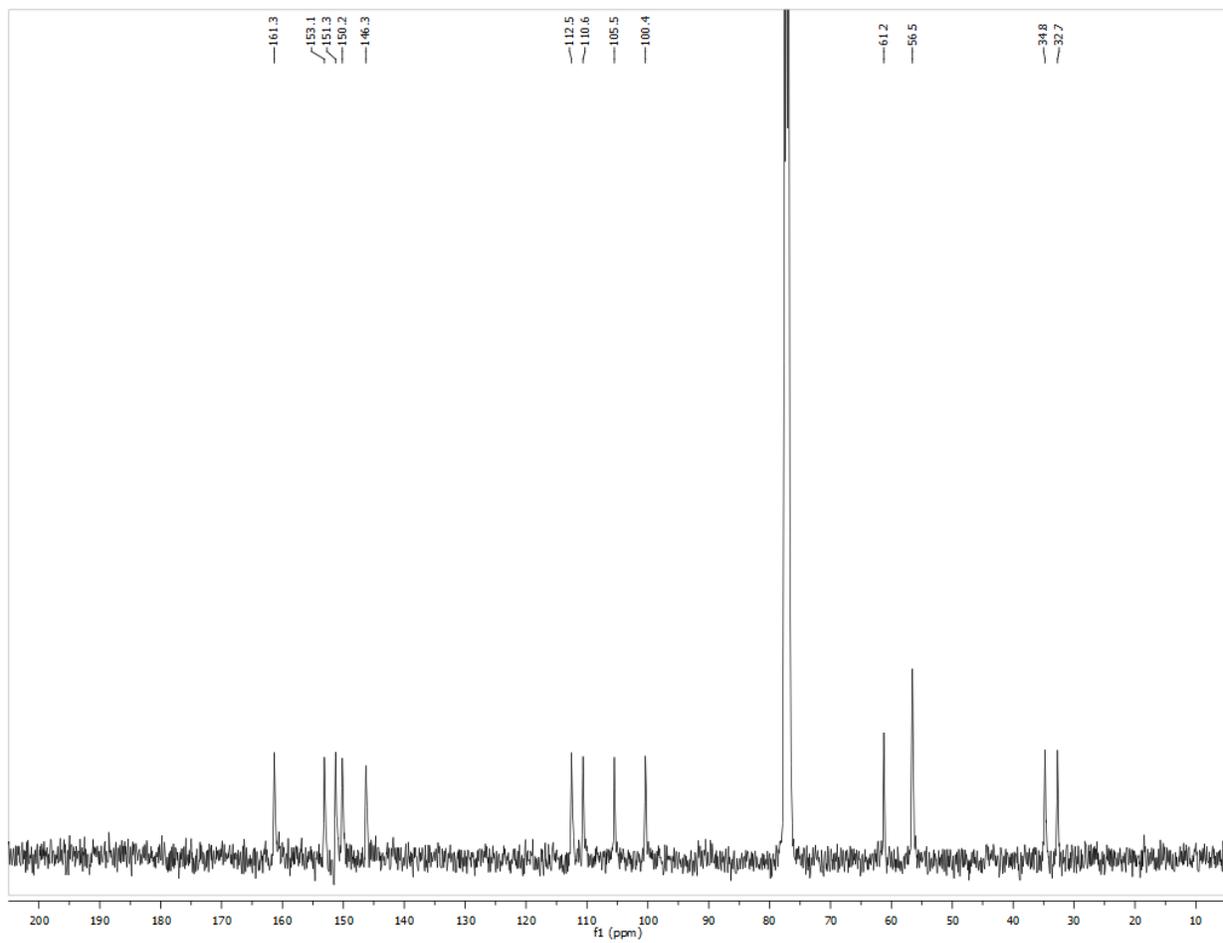


Figure S8. ¹³C NMR spectrum of 4-((2-mercaptoethoxy)methyl)-6,7-dimethoxycoumarin in CDCl₃.

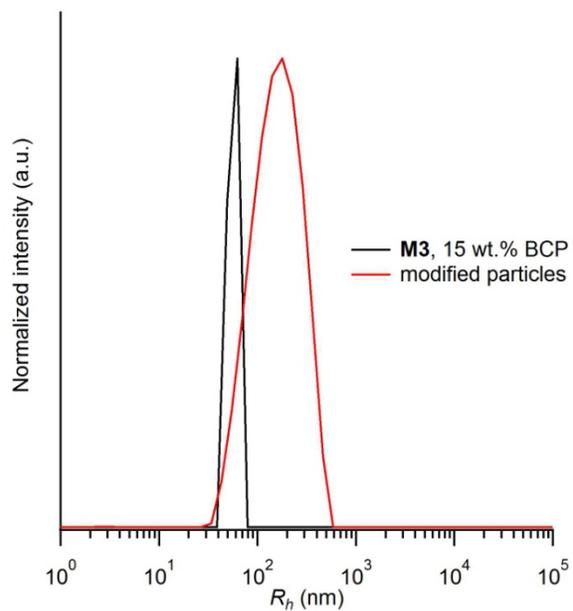


Figure S9. Dynamic light scattering of **M3** (15 wt.% BCP) particles before (black) and after (red) thermal thiol-ene click reaction with coumarin.

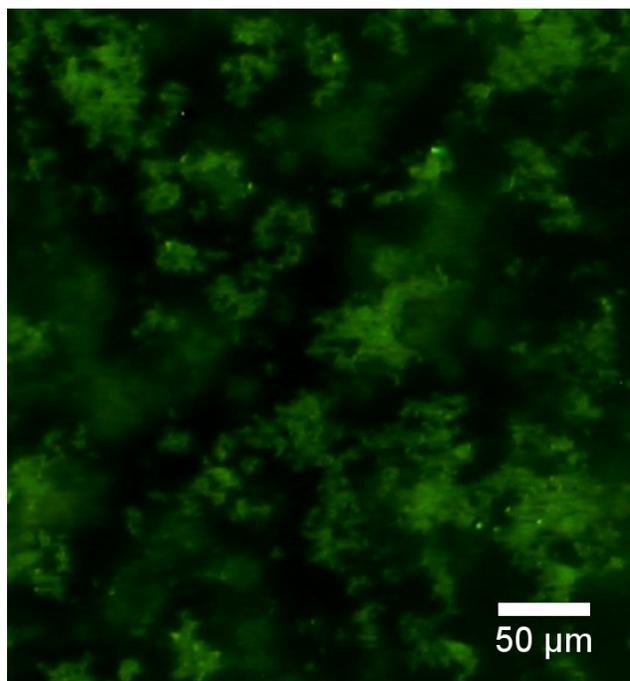


Figure S10. Fluorescence microscope image (10x magnification) of particles functionalized with coumarin.

1. I. Chaduc, M. Girod, R. Antoine, B. Charleux, F. D'Agosto and M. Lansalot, *Macromolecules*, 2012, 45, 5881-5893.
2. K. L. Killops, N. Gupta, M. D. Dimitriou, N. A. Lynd, H. Jung, H. Tran, J. Bang and L. M. Campos, *ACS Macro Letters*, 2012, 1, 758-763.