ELECTRONIC SUPPORTING INFORMATION

Understanding particle formation in surfactant-free waterborne coatings prepared by emulsification of pre-formed polymers

Maria Jose Gonzalez-Alvarez,[a] Jan Paternoga,[a, ‡] Katharina Breul,[a, ‡] Hyungjun Cho,[a] Mahtab Z. Roshandel,[a] Mohsen Soleimani*[,b] and Mitchell A. Winnik*[,a]

a. Department of Chemistry, University of Toronto, Toronto ON, Canada.
b. BASF Corporation, Advanced Material and Systems Research, Wyandotte, Michigan, USA.

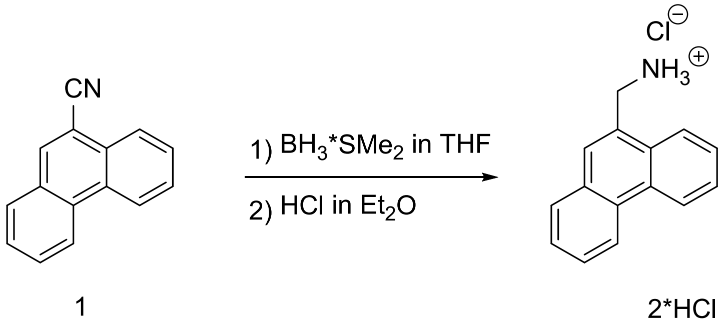
‡ These authors contributed equally to this paper.

* Corresponding authors: mohsen.soleimani@basf.com, mwinnik@chem.utoronto.ca.

ADDITIONAL RESULTS AND DISCUSSION

Synthesis of 9-aminomethylphenanthrene hydrochloride

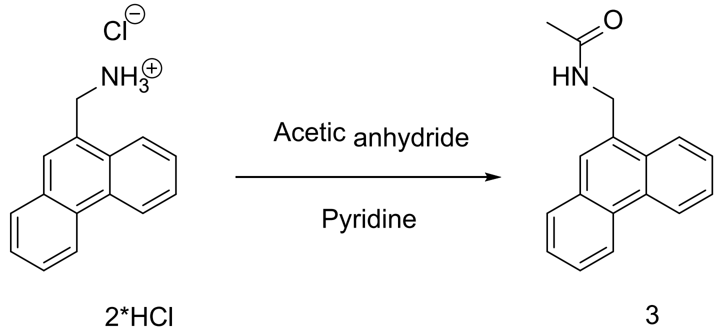
9-Aminomethylphenanthrene (**2**) was synthesized by reduction of 9-cyanophenathrene (**1**) with borane-dimethyl sulfide in THF as shown in Scheme S1. Treatment with HCl in diethylether yielded in the hydrochloride salt in an overall yield of 64%. The ^{1}H NMR spectra is presented in Figure S1 and the mass spectrum of the product is shown in Figure S2.

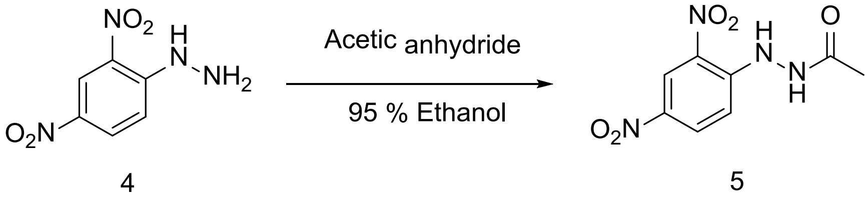


Scheme S1

Acetamide model compounds

To obtain the molar extinction coefficients for the dyes attached to the polymer, acetamide derivatives of 9-aminomethylphenanthrene (**2**) and 2,4-dinitrophenylhydrazine (**4**) were prepared as model compounds by treating small samples of the dyes with an excess of acetic anhydride.





Scheme S2

Calculation of the extinction coefficients of the different dyes

Extinction coefficients were calculated by measuring the absorbance at different concentrations in ethyl acetate at λ_{max} of both acetamide derivatives (**3**) and (**5**) (Figures S3, S4) and also at 370 nm for the DNP derivative. Values of ε were obtained as the slopes of plots of absorbance versus the concentration. The extinction coefficients obtained are $\varepsilon_{296} = 1.1 \times 10^4$ $M^{-1}cm^{-1}$ for *N*-(phenanthren-9-ylmethyl) acetamide (**3**), and $\varepsilon_{331} = 1.6 \times 10^4$ and $\varepsilon_{370} = 7.6 \times 10^3$ for *N*-acetamido-2,4-dinitrophenylhydrazine (**5**).

Determination of the dye content of the polymers by UV-Vis measurements

Solutions of the polymers in ethyl acetate were prepared by weighing samples with a microbalance. Absorbance values were measured at λ_{max} for each sample (1 cm cells). Molar dye concentrations were calculated as [dye] = A(λ)/ε. In this way, we found 2.0×10^{-4} mol phenanthrene / g for Pol-Phen and 2.0×10^{-4} mol 2,4-DNP / g for Pol-DNP. Using a value of Mn = 5,000 for the polymer, we estimate 1.0 dye molecules per polymer for both samples.

EXPERIMENTAL

Materials

9-Cyanophenanthrene (Aldrich, 97%); borane dimethyl sulfide complex (Aldrich, 10M), methanol (Aldrich, ACS reagent); diethyl ether and hydrogen chloride solution (Aldrich. 4.0 M in dioxane) were used as received. Tetrahydrofuran (inhibitor free, Aldrich) was dried with a PureSolve Micro® purification system.

9-Aminomethylphenanthrene (**2**). Under nitrogen 9-Cyanophenanthrene (**1**) (1.50 g, 7.4 mmol, 1 eq.) was dissolved in dry THF (40 mL) and $BH_3{\cdot}SMe_2$ (1.68 g, 22.1 mmol, 3 eq.) was added dropwise. The yellow reaction mixture was stirred at reflux (70 °C) for 30 h. The solution was cooled to room temperature, and methanol (2.4 g, 75 mmol, 10 eq.) was added slowly (over 20 min). The resulting solution was refluxed for another 0.5 h. The solvent was removed under reduced pressure. The residue was dispersed in a mixture of diethyl ether (75 mL) and water (25 mL). The resulting suspension was filtered and the organic layer was separated. The organic layer was washed with water (10 mL), brine (35% NaCl, 10 mL) and water (10 mL) and dried with anhydrous Na_2SO_4. The resulting solution was treated directly, while stirring, with HCl (4 M in dioxane, 0.3 g, 8.2 mmol, 1.1 eq.). After 2 h, the precipitated coulourless solid was collected by filtration and washed with diethyl ether (5 mL), chloroform (5 mL) and acetone (5 mL). Yield: 1.15 g (4.8 mmol, 64%). ^{1}H NMR (DMSO-d6, δ in ppm): 4.6 (s, $CH_{2,}$ 2H), 7.6 - 8.9 (m, Ar-H, 9H), see Fig S1. Mass spectrum (DART): m/e = 208.1 [Phe-CH_2-NH_3]$^+$, 191.1 [PheCH_2]$^+$, see Fig S2.

N-(phenanthren-9-ylmethyl) acetamide (**3**). 9-aminomethylphenanthrene hydrochloride (**2**)*HCl (70 mg, 0.29 mmol, 1 eq.) was dissolved in pyridine (13 mL). Acetic anhydride (900 mg, 8.8 mmol, 30 eq.) was added dropwise at room temperature and the resulting solution was stirred at 30 ˚C for 12 h. The excess solvent was evaporated under reduced pressure, and the resulting solid redissolved in chloroform (30 mL). The organic layer was washed with 10 mL HCl (1 M) and 10 mL PBS buffer (pH 7.4). The organic layer was collected and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the product was obtained as a coulourless solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.63 (dd, 2H); 7.99 (dd, 1H); 7.79 (dd, 1H); 7.58 (m, 5H); 5.56 (s, 1H); 4.86 (d, 2H); 1.97 (s, 3H).

l-Acetyl-2-(2,4-dinitro)phenylhydrazine (**5**). 2,4-Dinitrophenylhydrazine (**4**) (100 mg, 0.5 mmol, 1 eq.) was dispersed in 95% ethanol (2 mL) and the mixture was heated to reflux. A mixture of acetic anhydride (1.9 g, 18.9 mmol, 38 eq.) and 95% ethanol (1.8 mL) was added dropwise. The mixture was refluxed for 1 h, then cooled with an ice bath. The yellow crystalline product was recrystallized from 95% ethanol and yellow needles were obtained. ^{1}H NMR (500 MHz, CD_3CN, δ in ppm): 9.39 (broad s, 1H); 8.94 (d, 1H); 8.52 (broad s, 1H) 8.25 (dd, 1H,); 7.26 (d, 1H,); 2.02 (s, 3H).

SUPPORTING FIGURES

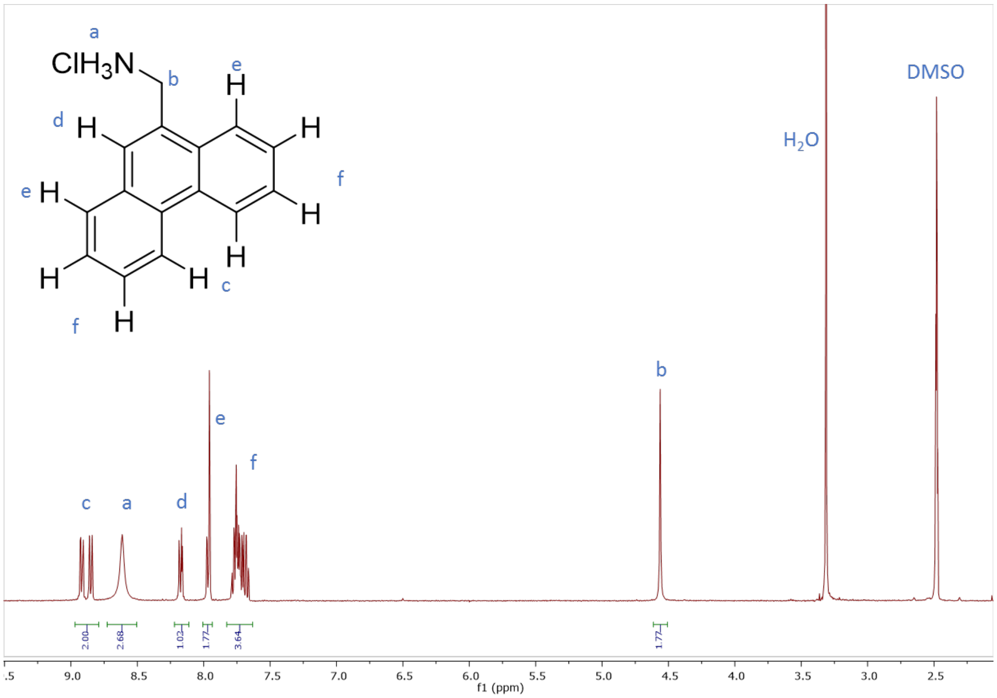


Figure S1. ^1H NMR of 9-aminomethylphenanthrene hydrochloride (**2**)*HCl in DMSO-d6.

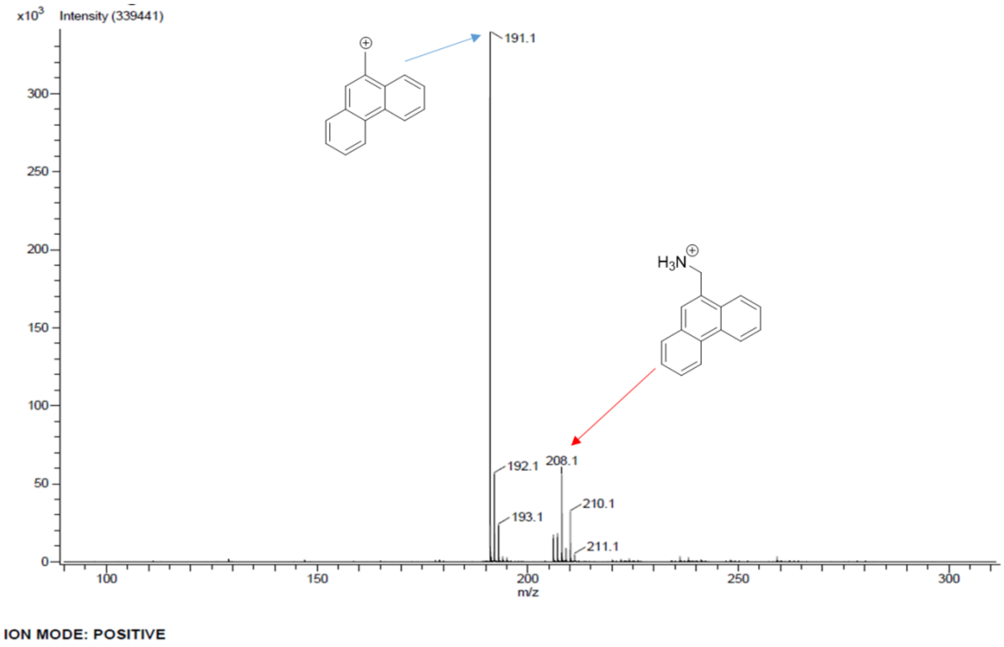


Figure S2. MS spectra (DART) of 9-aminomethylphenanthrene hydrochloride (**2**)*HCl.

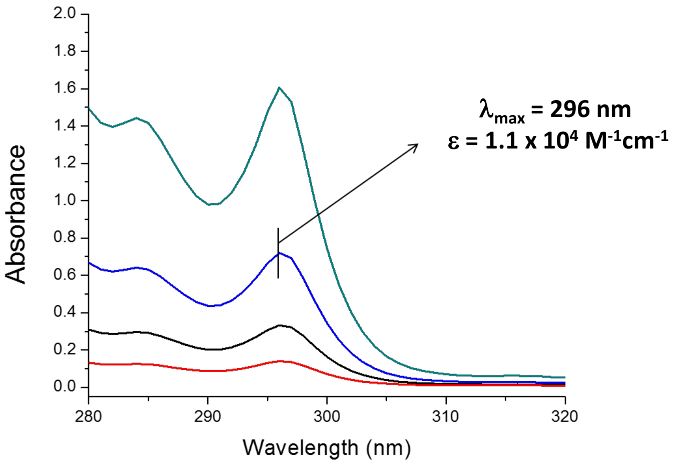


Figure S3. UV-vis spectra of *N*-(phenanthren-9-ylmethyl) acetamide (**3**) at different concentrations in ethyl acetate. The extinction coefficient was determined at 296 n .

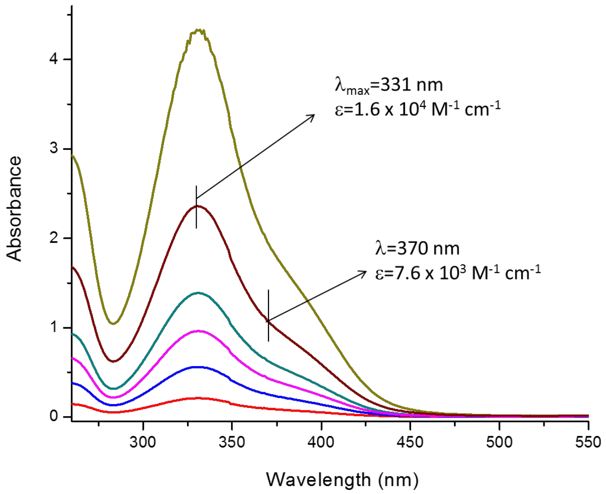


Figure S4. UV-vis spectra of 1-Acetyl-2-(2,4-dinitro)phenylhydrazine (**5**) at different concentrations in ethyl acetate. The extinction coefficients were determined at 331 and 370 nm.

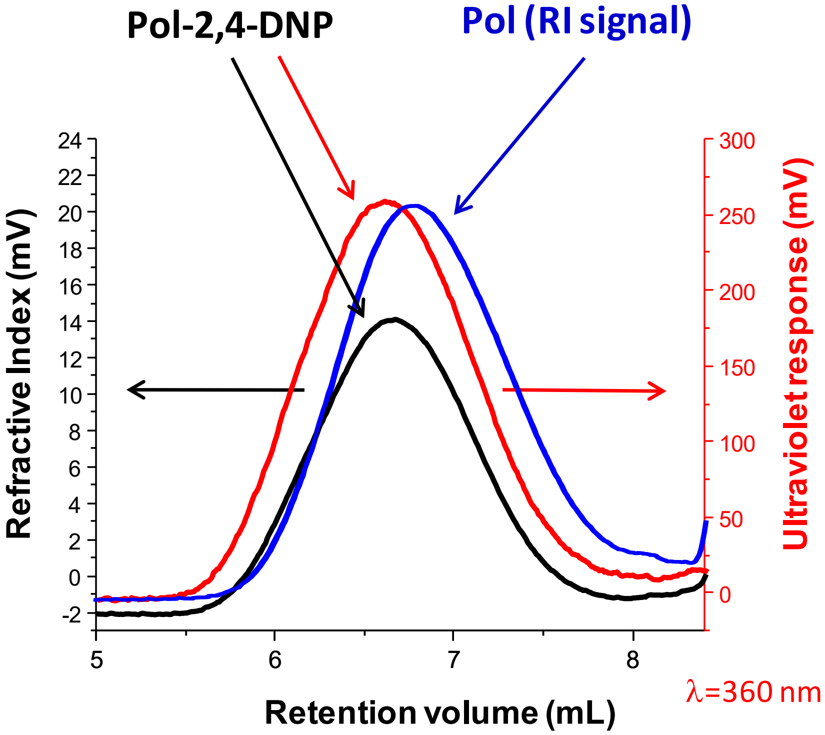


Figure S5.GPC Trace for unlabeled polymer (blue, RI signal) and for the labeled 2,4-DNP-Pol (red: UV signal and black: RI signal). The GPC solvent was THF + salts (Tetra-*n*-butylammonium bromide) and the concentration of the samples were 2 mg mL^{-1}.

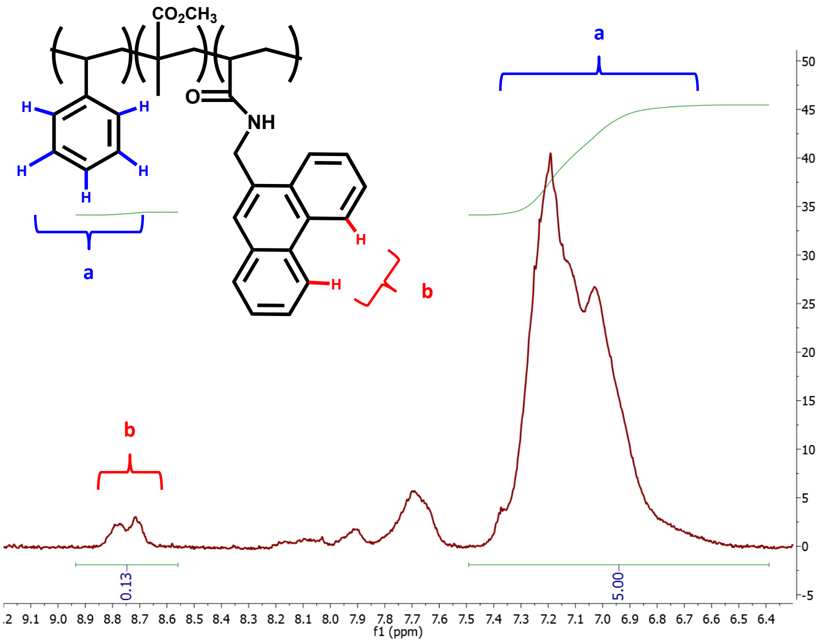


Figure S6. ^{1}H NMR of the aromatic region of **Pol-Phen** in deuterated DCM

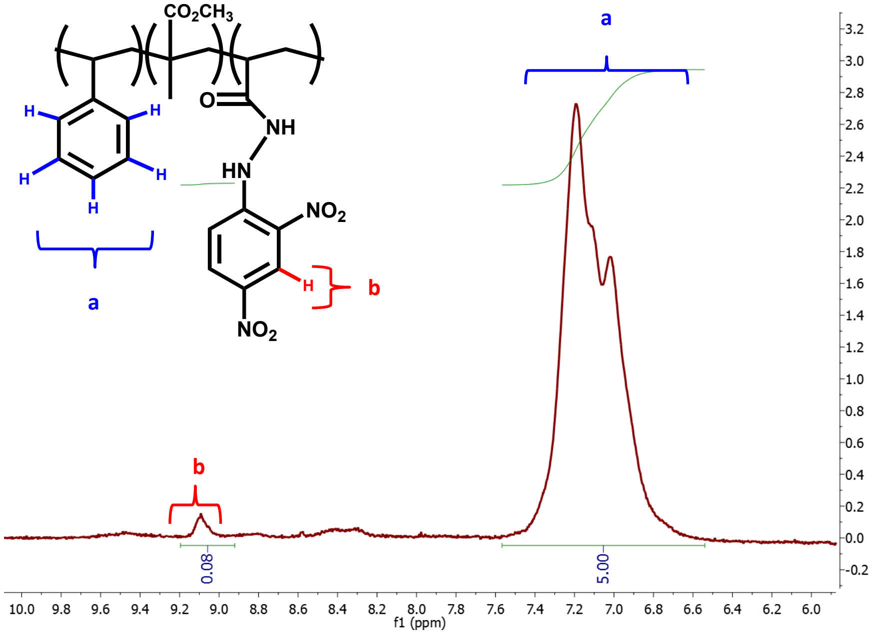


Figure S7. ^{1}H NMR of the aromatic region of **Pol-2,4-DNP** in deuterated DCM.

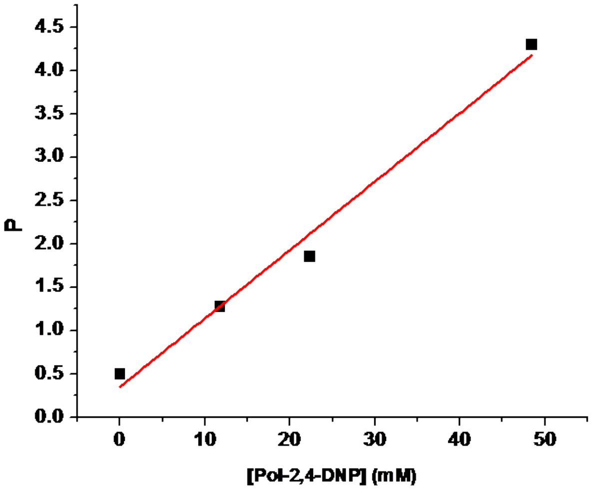
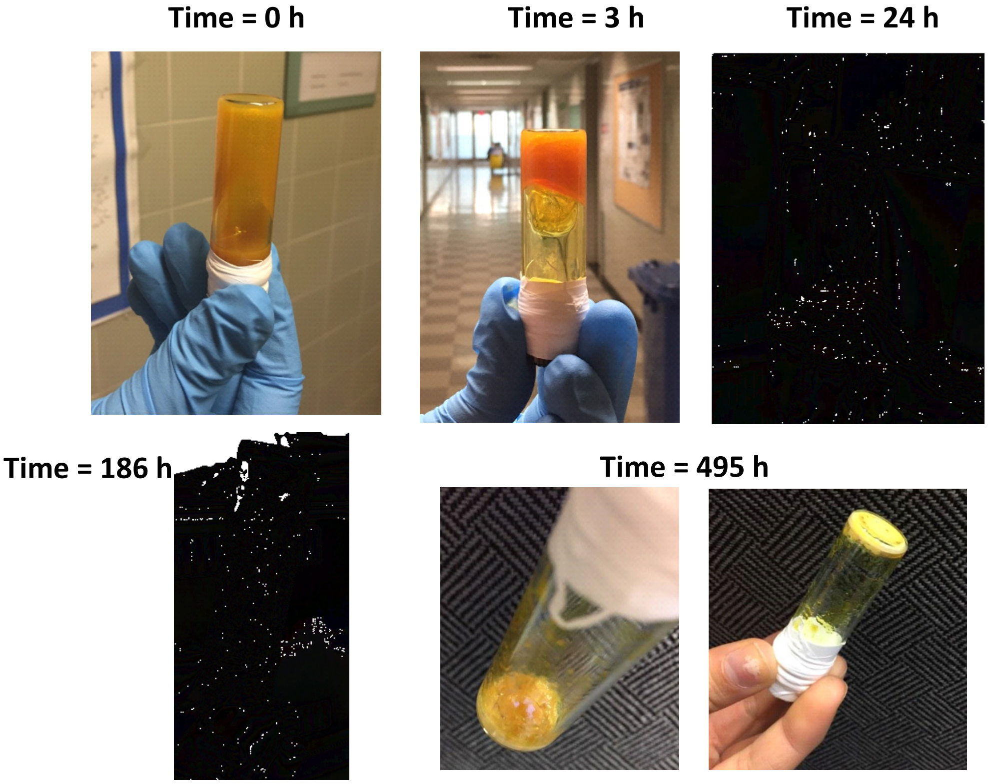


Figure S8. Plot of P vs [Pol-2,4-DNP, mM] for fully mixed solvent-cast films prepared from **Pol-Phen** and varying amounts of **Pol-2,4-DNP**. The P values were obtained by fitting individual Phe decay curves to equation (2) (main text with τ_D fixed at 45 ns). From the slope of the plot, we calculate R_0 = 2.75 nm.



Time = 0 h

Time = 3 h

Time = 24 h

Time = 186 h

Time = 495 h

Figure S9. Mother dispersion (37 wt% solids) made from a 1:9 **Pol-Phen/Pol-2,4-DNP** dispersion mixture after annealing at 60 °C for different periods of time. The pictures show the appearance of the sample after removal from the oven and cooling to room temperature after annealing at 60 °C for different periodes of time. We observed an increase of the viscosity of the sample over time.

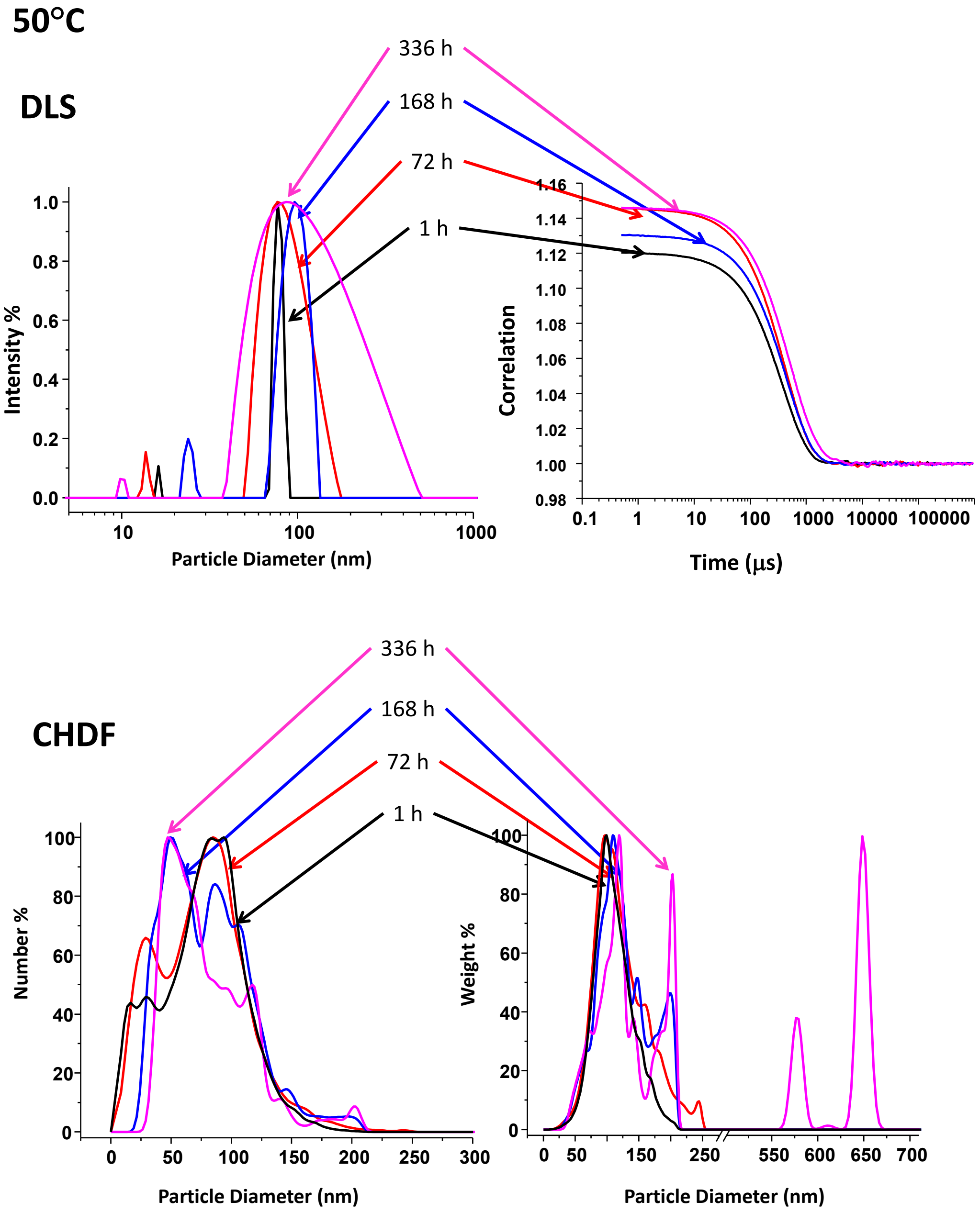
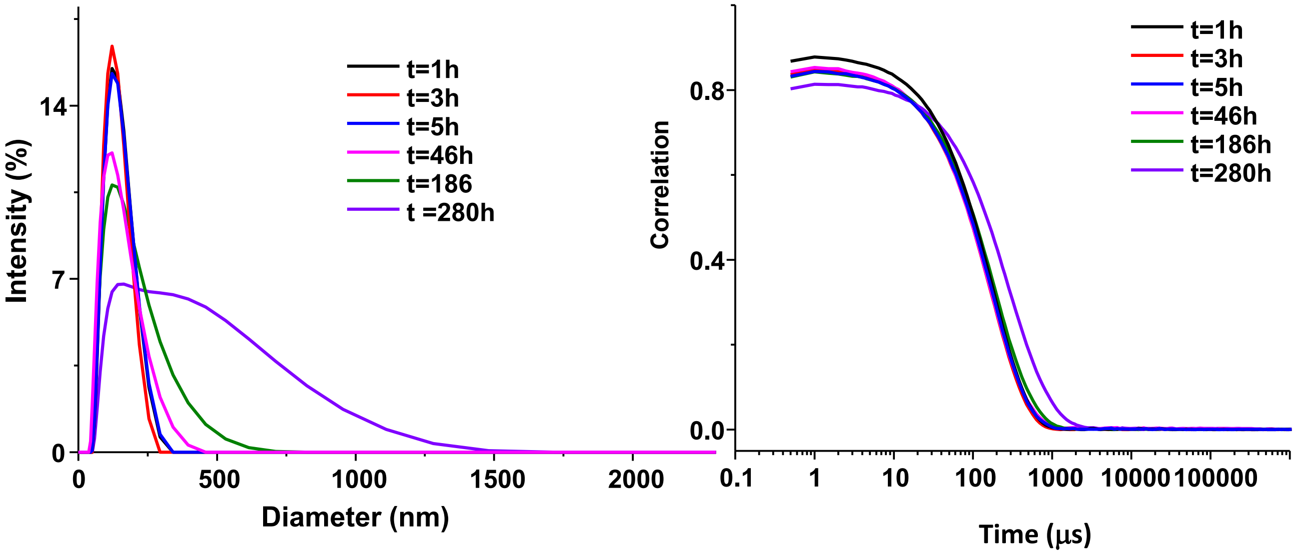


Figure S10. Particle size analysis by DLS (CONTIN intensity distributions and autocorrelation decay profiles) and by CHDF (number and weight distributions) for a dispersion consisting of a 1:9 **Pol-Phen**/**Pol-2,4-DNP** mixture at different annealing times at 50 °C.

60°C

DLS



CHDF

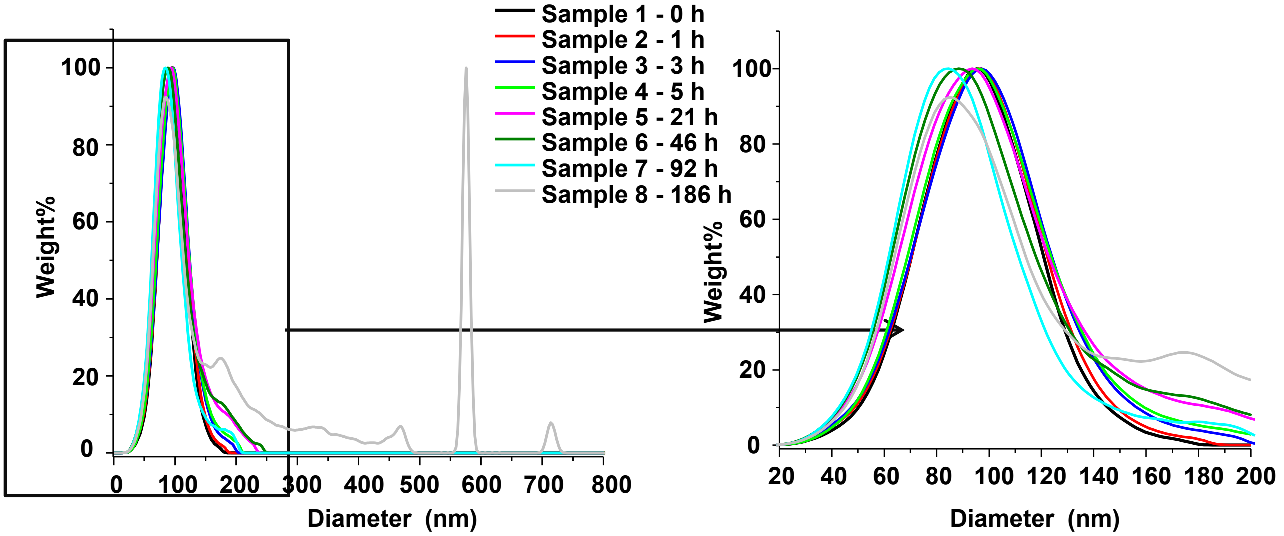


Figure S11. Particle size analysis by DLS (CONTIN intensity distributions and autocorrelation decay profiles) and by CHDF (weight distributions) for a dispersion consisting of a 1:9 **Pol-Phen**/**Pol-2,4-DNP** mixture at different annealing times at 60 °C.

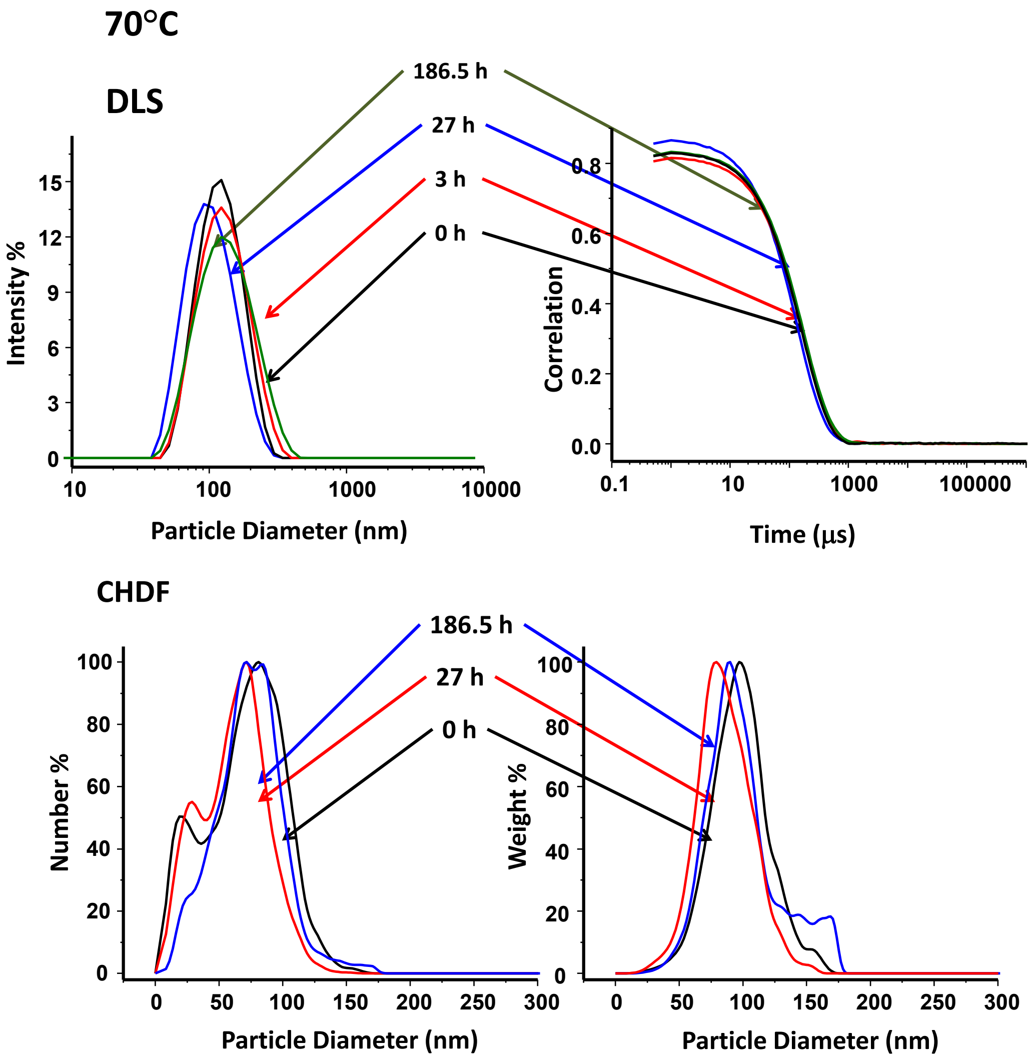


Figure S12. Particle size analysis by DLS (CONTIN intensity distributions and autocorrelation decay profiles) and by CHDF (number and weight distributions) for a dispersion consisting of a 1:9 **Pol-Phen**/**Pol-2,4-DNP** mixture at different annealing times at 70 °C.

SUPPORTING TABLE

Table S1. Particle size and polydispersity measured by DLS for the emulsification of a 1:9 mixture of **Pol-Phen** and **Pol--2,4-DNP** comparing Batch 1 and Batch 2.[a]

BATCH 1 [b]			**BATCH 2** [c]		
Time (min)	**d_h (nm)**	**PDI**	**Time (min)**	**d_h (nm)**	**PDI**
0	**302**	**0.34**	**0**	**102**	**0.41**
10	**232**	**0.30**	**10**	**107**	**0.12**
20	**144**	**0.13**	**20**	**88**	**0.09**
30	**134**	**0.11**	**30**	**95**	**0.11**
45	**142**	**0.09**	**45**	**100**	**0.07**
60	**142**	**0.05**	**60**	**103**	**0.05**
80	**138**	**0.06**	**80**	**109**	**0.09**
110	**146**	**0.05**	**110**	**114**	**0.06**
140	**160**	**0.01**	**140**	**112**	**0.10**
170	**162**	**0.06**	**170**	**117**	**0.09**

a. Solid polymers **Pol-Phen** with **Pol-2,4-DNP** were mixed in a 1:9 ratio. As described in the main text, the sample was partially neutralized with ammonia and dispersed in hot water (37 wt% solids).

b. Batch 1: Stirring was stopped and aliquots at different times were taken from the bottom of the flask. These were diluted with water and the particle diameters d_h were measured by DLS.

c. Batch 2: Stirring was stopped, and after 10 s, an aliquot was taken from the upper part of the liquid in the flask. Each aliquot was diluted with water, centrifuged to remove any possible large aggregates, and the particle diameters d_h were measured by DLS.