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Supporting Information

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Stimuli-Responsive Transport of Nanoparticles Across Water-Oil Interfaces

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Synthesis of disulfide based ATRP Initiator

2,2’-dithiobis[1-(2-bromo-2-methyl-propionyloxy)ethane] (DTBE) was prepared by the acrylation of bis(2-hydroethyl) disulfide and 2-bromo-2-methylpropionyl bromide following procedures previously described in the literature.[S1]

Synthesis of homopolymers and random copolymers of MEO_2MA and OEGMA

Copolymers of MEO_2MA, and OEGMA were synthesized with slight modifications to the method of Lutz et al.[25] The details of an example polymerization are briefly presented here. The following reagents were placed in a 100 mL roundbottom flask to form a clear solution: 115 mg of DTBE, 1.19 mL OEGMA, 4.50 mL MEO_2MA, and 54.7 mg 2,2’ bipyridyl with 7.11 mL ethanol (absolute) as solvent. The reagents and solvent were then degassed with argon under stirring for 20 minutes. 37 mg CuBr catalyst was then added to the reaction mixture, which immediately turned deep brown in color. The reaction flask was then capped with a rubber septum, sealed with parafilm, purged with argon for an additional minute, and placed in a temperature controlled oil bath at 60 °C ± 5° C for 2.5 hours, at which point the reaction mixture turned green and became viscous. The reaction flask was brought to room temperature, and exposed to air before adding 5 mL ethanol to the reaction products. The resulting ethanol/polymer solution was passed through a short silica column to remove CuBr. The eluent from the column was reduced via rotary evaporation and the concentrated polymer solution was dialyzed twice (SpectraPor, Cutoff M_W = 8 000) overnight against ethanol (absolute) to remove unpolymerized monomers from the reaction products. The resulting polymers were characterized by their lower critical solution temperature (LCST) and gel permeation chromatography (GPC) with tetrahydrofuran as eluent. For the polymer synthesis detailed here LCST = 37.6°C, Mn = 19 700 (Poly methyl methacrylate equivalents), Polydispersity = 1.27.

Calculation of the interfacial energy of gold planar surfaces coated by Poly (MEO_2MA), Poly (OEGMA-*co*-MEO_2MA) and Poly (OEGMA).

Surface energy measurements were made according to the van Oss-Chaudhury-Good (VOCG) model of surface energy.[S2,S3] According to the VOCG model, the surface energy of a solid can be considered to consist of the components detailed in Equations (1) and (2), and the Young-Dupré Equation can be written as shown in Equation (3).

$$\gamma = \gamma^{LW} + \gamma^{AB} \qquad (1)$$

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \qquad (2)$$

$$(1+\cos(\theta))\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right) \qquad (3)$$

In Equations (1) and (2) γ is the overall surface energy, γ^{LW} is the Lifshitz-van der Waals component of the surface energy, γ^{AB} is an acid-base interaction comprised of γ^{+}, the electron acceptor parameter and γ^{-}, the electron donor parameter. In Equation (3) θ is the contact angle of a liquid with the substrate, γ_L is the overall surface tension of the liquid, and the subscripts S and L denote the surface energy components of the solid and the liquid respectively.

To fully model the interaction between Poly (MEO_2MA), Poly (OEGMA-*co*-MEO_2MA) and Poly (OEGMA) capped gold NPs with water, salty water and toluene, the interfacial energy of the surface grafted polymers with these solvents was also determined using the VOCG model. The overall interfacial energy can be expressed as shown in Equation (4).

$$\gamma_{SL}^{tot} = \left(\left(\gamma_S^{LW}\right)^{\frac{1}{2}} - \left(\gamma_L^{LW}\right)^{\frac{1}{2}} \right) + 2\left(\left(\gamma_S^{+}\gamma_S^{-}\right)^{\frac{1}{2}} + \left(\gamma_L^{+}\gamma_L^{-}\right)^{\frac{1}{2}} - \left(\gamma_S^{+}\gamma_L^{-}\right)^{\frac{1}{2}} - \left(\gamma_S^{-}\gamma_L^{+}\right)^{\frac{1}{2}} \right) \quad (4)$$

The literature values used for γ^{LW}, γ^{+}, and γ^{-} of the three liquids are presented in Table S1. The values for γ_{SL}^{tot} calculated using Equation (4) are presented in Table 1.

Preparation of gold planar substrates coated by PEGylated methacrylic polymers.

Disulfide functionalized Poly (MEO_2MA), Poly (OEGMA-*co*-MEO_2MA) (10 % OEGMA, LCST ~ 37°C) and Poly (OEGMA) were grafted to gold coated silicon wafers and used as model substrates for estimating the surface energy of the gold NPs capped with these polymers. The polymers were grafted to the gold substrates by incubating gold coated silicon wafers with 10 mg/mL polymer solutions in methanol for 24 hours. After cleaning, the advancing contact angles of water, ethylene glycol (EG) and α-bromonapthalene (α-BrN) on the polymer functionalized surfaces were measured (Table S2) and the surface energy components were calculated from Equation (3).

Table S1. Surface tension components (mN/m) used in employing the van Oss-Chaudhury-Good model of surface energy.

Solvent	γ^{LW}	γ^{+}	γ^{-}
Water[a]	21.8	25.5	25.5
Ethylene Glycol[a]	48	1.92	47
α-Bromonapthalene[a]	44	0	0
Toluene[a]	28.5	0	2.3
0.5 M NaCl[b]	21.1	21	33

a. Data from reference S4.

b. Data from reference S5. The value for γ^{LW} in 0.5 M NaCl solutions was calculated based on the condition that γ_L = 73.7 mN/m for a 0.5 M aqueous solution of NaCl.

Table S2. Relevant contact angles (θ) of the surface grafted polymers with water, ethylene glycol (EG) and α-bromonapthalene (α-BrN). The error values represent a 95 % confidence interval.

	MEO_2MA	**OEGMA-*co*-MEO_2MA (10:90)**	**OEGMA**
θ_{Water} (°)	55.1 ± 0.6	51.4 ± 0.4	44.4 ± 0.8
θ_{EG} (°)	41.2 ± 0.2	42.0 ± 0.2	34.9 ± 0.5
$\theta_{\alpha\text{-BrN}}$ (°)	22.2 ± 0.5	23.3 ± 0.7	17.0 ± 0.6

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