

Supporting Information

Click Chemistry as a Route to Surface Functionalization of Polymer Particles dispersed in Aqueous Media

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1. Materials and Reagents

Except where indicated, all chemicals were purchased from Aldrich and used without further purification. Rhodapex AB20 (28.5 wt% active, Rhodia) and Doxfax 2A1 (45 wt% active, Dow Chemical) were used as surfactants. Methyl methacrylate (MMA) was purified prior to use by washing with 2% NaOH solution to remove inhibitor, followed by washing with deionized water and then drying over anhydrous MgSO_4 . Immediately prior to use, inhibitor was removed from methacrylic acid (MAA) by stirring over fresh silica several times.

2. Core-Shell Particle Synthesis

Synthesis of the core-shell particles was achieved by adapting a procedure for synthesis of poly(methyl methacrylate) particles that was developed previously (Foster, A.B.; Lovell, P.A.; and Rabjohns, M.A.; unpublished work).

The polymerization was carried out in a 5-necked flanged glass reaction vessel fitted with a nitrogen inlet, mechanical stirrer and water-cooled condenser. The vessel was suspended in a thermostated water bath at 75 °C during polymerization. The procedure and quantities of reactants added are given in Table 1. The initial charge of surfactant solution plus seed-stage monomer was allowed to equilibrate for ten minutes whilst a flowing nitrogen atmosphere was established. Addition of the first initiator solution defined $t = 0$.

The aqueous phase of the core-shell particle dispersion was cleaned by dialysis against deionized water using a pre-soaked dialysis membrane (50,000 Dalton cut off) for two weeks, changing the deionized water reservoir at least once a day.

3. Particle Size Distribution (PSD) Analysis

PSD analysis of samples removed from the polymerization was performed by hydrodynamic chromatography at room temperature using a Polymer Laboratories Particle Size Distribution Analyser (PSDA) fitted with a Type 2 cartridge and a 20 μL injection loop using the proprietary Polymer Laboratories eluent. Calibration of the PSDA was performed using seven polystyrene latex standards (Polymer Laboratories) with particle diameters in the range 43-993 nm. Prior to injection, the latex standards and samples were diluted in the proprietary eluent (typically using 2 drops of dispersion in 5 mL of eluent); an aqueous solution of 3-nitrobenzenesulfonic acid sodium salt was automatically injected as a flow rate marker. The raw experimental data were processed into particle diameter data using the PSDA software and then exported into Microsoft Excel for calculation of particle number fraction and the number-average particle diameter, d_N .

Table 1. Emulsion Polymerization Formulation and Procedure

Comment / Action Sequence	Component	Mass / g
Seed Stage		
Initial reactor charge	Deionized H ₂ O	346.89
	AB20 (28.5 wt%)	3.51
	2A1 (45 wt%)	2.23
Monomer (added at t = -10 min)	MMA	25
Initiator solution 1 (t = 0)	Ammonium persulfate (APS)	1.08
	Deionized H ₂ O	50.04
Initiator solution 2 (t = 55 min)	APS	0.27
	Deionized H ₂ O	25.13
Dilution water (t = 60 min)	Deionized H ₂ O	274
Wait 10 min for equilibration		
Growth Stage 1		
Monomer (added at constant rate by peristaltic pump from t = 70 min to t = 220 min)	MMA	228
Initiator / surfactant solution 1 (added at constant rate by syringe pump from t = 70 min to t = 220 min)	APS	0.13
	AB20 (28.5 wt%)	3.51
	2A1 (45 wt%)	2.23
	Deionized H ₂ O	10.36
Wait 15 min after completion of the additions		
Growth Stage 2		
Monomer mixture	MMA	36.19
	MAA	7.84
Initiator / surfactant solution 2 (added at constant rate by syringe pump from t = 235 min to t = 265 min)	APS	0.03
	AB20 (28.5 wt%)	0.7
	2A1 (45 wt%)	0.45
	Deionized H ₂ O	2.07
Wait 60 min after completion of additions before cooling to room temperature		

4. Alkyne Functionalization of Core-Shell Particles

The quantities used for alkyne functionalization of particle surfaces are given in Table 2. An aqueous solution of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC-MI) was prepared and added to the particle dispersion under magnetic stirring. The propargylamine was then added and the resulting dispersion stirred for 3 days at room temperature before being transferred to a pre-soaked dialysis membrane (50,000 Dalton cut off) for purification, changing the reservoir of deionized water at least daily for two weeks.

Table 2. Reactant Quantities used for Alkyne Functionalisation of the Core-Shell Particles

Component	Mass / g	Moles
Particle dispersion (3 wt% particles)	15	–
Acid functionality	0.115	1.339×10^{-3}
EDC-MI	0.498	1.674×10^{-3}
Propargylamine	0.0812	1.473×10^{-3}
Deionized water	148	–

4. Reaction of Surface Alkyne Groups with 3-Azido-7-Hydroxycoumarin (AHC)

The quantities used for the click reaction of AHC with alkyne surface groups are given in Table 3. The latex was first adjusted to pH 8 by the addition of a small amount of dilute aqueous NaOH and was then added to a small vial followed by the sodium ascorbate, CuSO₄ solution and finally the AHC. DMF was then added to aid solubility of the AHC and the vial suspended in a temperature controlled oil bath at 35 °C for 4 days.

A small portion of the product dispersion was diluted with deionized water until almost completely transparent and then transferred to a quartz cuvette for analysis. The wavelength for maximum UV-visible absorption, λ_{max} , in the wavelength range 200-700 nm was determined first using a Varian Cary 5000 UV/Visible Spectrometer, which gave $\lambda_{\text{max}} = 333$ nm. Fluorescence analysis was then performed on a Varian Cary Eclipse Fluorescence Spectrophotometer using an excitation wavelength of 335 nm, scanning for fluorescence emission in the range 345-750 nm.

Table 2. Reactant Quantities used for Reaction of Surface Alkyne Groups with AHC

Component	Mass / g	Moles	Equivalents
Particle dispersion (3 wt% particles)	0.3927	–	–
Alkyne functionality (assuming 100% conversion of CO ₂ H)	–	3.16×10^{-6}	1
3-azido-7-hydroxycoumarin (AHC)	0.007	3.45×10^{-5}	10.9
DMF	0.0756	–	–
1 M aqueous CuSO ₄	0.0328	2.85×10^{-5}	9
Sodium ascorbate	0.0034	1.72×10^{-5}	5.4