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Tandem RAFT Polymerization and Click Chemistry: An Efficient Approach to Surface Modification

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Modification of Silica Nanoparticles using the “Grafting to” Approach

3 g (0.33 mmole) of free polystyrene obtained from a tandem experiment, 1.3 g of azide modified silica and 40 mL of DMF were combined in a round bottom flask and stirred for several min. The mixture was sonicated for 30 min and solutions of 0.005 g (0.031 mmole) CuSO₄ in 0.5 mL water and 0.022 g (0.11 mmole) sodium ascorbate in 1 mL water were added to that flask. This mixture was heated at 70 °C for 18 h. The silica nanoparticles were isolated as described previously.

Modification of Silica Nanoparticles using the “Grafting from” Approach

Synthesis of RAFT CTA Immobilized Silica Nanoparticles

1.5 g azide modified silica, 0.25 g (0.62 mmole) alkyne terminated RAFT CTA and 10 mL of anhydrous DMF were combined in a Schlenk flask. This mixture was sonicated for 30 min at room temperature. 0.005 g (0.031 mmole) CuSO₄ in 1 mL water and 0.012 g (0.06 mmole) of sodium ascorbate in 1 mL water were added to the flask followed by stirring for 15 h at 50 °C. The modified silica particles were obtained after centrifugation. These particles were redispersed and centrifuged to remove any

physisorbed RAFT CTA. This cycle was repeated two times with toluene, one time with water and one additional time with toluene. The silica particles were dried under reduced pressure to afford RAFT CTA modified silica nanoparticles.

Surface Mediated RAFT Polymerization on Silica Nanoparticles

1.1 g of RAFT CTA modified silica nanoparticles, 20 mL of styrene, 20 mL of toluene, 0.15 g of carboxyl terminated RAFT CTA (0.4 mmole) and 0.0067 g (0.04 mmole) of AIBN were combined in a flask under inert atmosphere. Polymerization and work up were done using the above mentioned procedure.

Table 1. Effect of Cu(I) concentration on tandem approach of surface modification

Concentration of CuBr (in ratio)	Elemental analysis		Free PS		Grafting density by elemental analysis (groups/nm ²)	Grafting density By TGA (groups/nm ²)
	Sulfur (%)	Carbon (%)	M_n (g/mole)	Polydispersity		
1	0.29	15.39	9000	1.11	0.51	0.54
10	0.52	20.76	9000	1.10	0.72	0.70