Application Note:

Preparation of Monodisperse Polymer Spheres

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Monodisperse, surfactant-free polymer spheres for use as colloidal crystal templates can be easily obtained in reasonably large quantities. Typical synthesis methods for poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) by emulsifier free emulsion polymerization are described below and yield spheres several hundred nanometers in diameter. Sphere sizes can be adjusted by altering the stirring rate, monomer concentration, reaction temperature, and amount of initiator. In both cases, the reaction is carried out in a four-necked round-bottom flask equipped with an electric stirrer with a Teflon stir blade, a water condenser, a pipet connected to a source of nitrogen, and a thermocouple probe (**Figure 1a**).

To synthesize PMMA spheres, 1600 mL of deionized water and 400 mL of methyl methacrylate (**M55909**) monomer are added to the flask. The mixture is stirred at approximately 350 rpm and bubbled with nitrogen. The temperature is increased to 70 °C and the system is allowed to equilibrate. After temperature stabilization, 1.50 g of the initiator, 2,2'-azobis (2-methylpropionamidine) dihydrochloride (**440914**), is dissolved in approximately 25 mL of deionized water and added to the flask (Figure 1b). Within several minutes, the mixture in the flask turns milky white. Over the course of the reaction (1–2 hours), the temperature rises several degrees before returning to 70 °C, signaling the end of the reaction.

The synthesis of PS spheres is very similar. 1700 mL of deionized water is added to the flask and heated to 70 °C while stirring at about 350 rpm. After the temperature has stabilized, 200 mL of washed styrene (**240869**) is added, and the temperature is allowed to equilibrate. Next, 0.663 g of the initiator, potassium persulfate (**379824**), is dissolved in 100 mL of water and heated to 70 °C before addition to the flask. The temperature is held constant, and the mixture is stirred for 28 hours.

After the polymerization reactions are complete, the polymer sphere solutions are filtered through glass wool to remove any large agglomerates from the solution. The spheres are then ordered into a colloidal crystal (Figure 1c) by one of several methods described in the text of article on p. 10 of this issue.

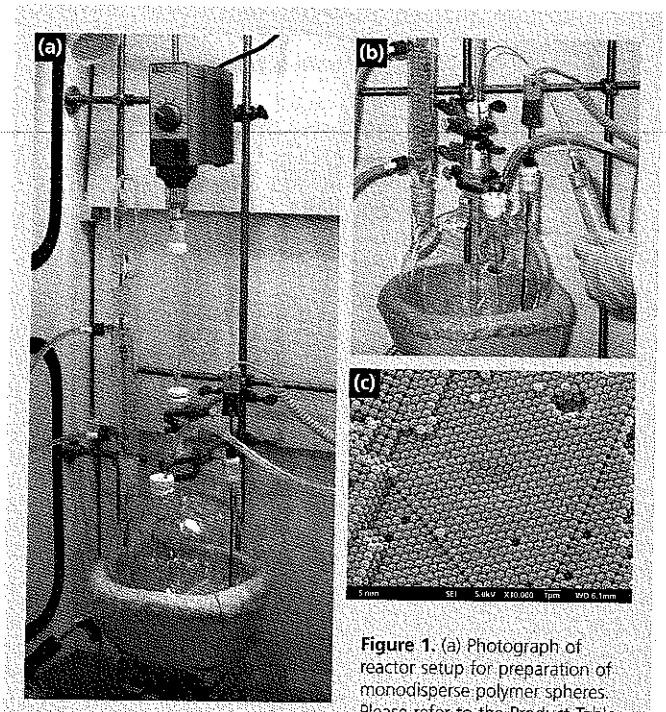

Figure 1. (a) Photograph of reactor setup for preparation of monodisperse polymer spheres. Please refer to the Product Table for list of reactor components. (b) Reagents (e.g. free-radical initiators) are added to the reaction via syringe without breaking N_2 atmosphere inside the reactor. (c) SEM image of a typical PMMA colloidal crystal with multiple layers of monodisperse PMMA spheres packed in fcc structure. Point and line defects often observed in these colloidal crystals are also visible in the micrograph.

Components for Reactor Setup

Description	Product No.
Flask, round-bottom, 4-neck, 34/45 center, 24/40 side joints	Z561096-1EA
Bubbler, 24/40 joint	Z104329-1EA
Condenser, coiled, 300 mm L, 24/40 joints	Z552356-1EA
Septa, for 24/40 joints	Z553980-10EA
Mixer, model RW 16, 115 V	Z403881-1EA
Stirrer bearing, PTFE, for 10 mm o.d. shaft, 34/45 joint	Z555614-1EA
Stirrer blade, PTFE, fits 10 mm o.d. shaft, 125 mm W	Z105740-1EA
Stirrer chuck, fits 10 mm o.d. shaft	Z136786-1EA
Stirrer shaft, polished, 10 mm o.d. x 580 mm L, with button	Z136735-1EA
Syringe needle, 304 SS, Luer connector, non-coring point, 18 gauge, 2 in. L, for nitrogen gas	Z113042-1EA
Syringe needle, 304 SS, Luer connector, non-coring point, 18 gauge, 24 in. L, for cannulation	Z100862-1EA
Syringe, 30 mL, metal Luer tip	Z181269-1EA
Needle-tubing connector, for 1/4 in. — 5/16 in. i.d. tubing, Luer connector	Z101168-4EA
Heating mantle, hemispherical, for 5 L flasks, 115 V	Z284890-1EA
Temperature controller, J-KEM® model 210, 120 V*	Z210226-1EA
Adapter, thermocouple probe, PTFE, 1/8 in. i.d. hole, 24/40 joint for J-KEM temperature controller	Z248282-1EA

*Includes Type T thermocouple probe shown in Figure 1a,b
J-KEM is a registered trademark of J-KEM Scientific, Inc.

For questions, product data, or new product suggestions, please contact Aldrich Materials Science at matsci@sial.com.