Synthesis of Monodisperse Fluorescent Poly (Butyl Acrylate) Microspheres

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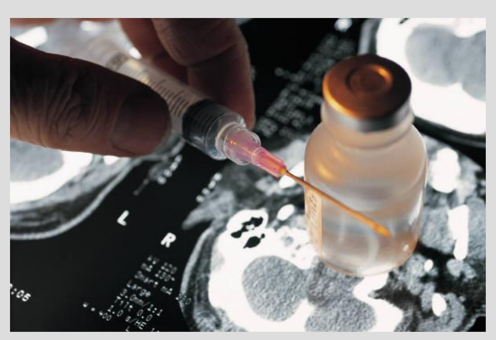
Abstract

Two methods were investigated to synthesize crosslinked, fluorescent poly (butyl acrylate) (PBA) latex spheres via dispersion polymerization. The first method involved one step in which the fluorescent dye was reacted with the butyl acrylate monomer, initiator, crosslinker, and polymeric stabilizer within a methanol/water solution. The initiator enables polymerization of the monomer, the crosslinker links the polymers together to form solid particles, and the stabilizer mitigates particle aggregation. The second method involved two steps in which the dye was added after the particles were formed. The materials synthesized from the first and second methods were characterized with optical microscopy, dynamic light scattering (DLS), scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM).



Introduction

Monodisperse, or uniform, one-size polymer spheres are used in diverse applications such as latex paints, polymeric coatings, and delivery of drugs. Specifically, butyl acrylate (PBA) particles have been copolymerized with other polymers to encapsulate drugs and attach peptides. Copolymerizing PBA with other polymers is advantageous as PBA is rubbery and copolymerizing butyl acrylate with polymers such as styrene can result in stiffer materials. Moreover, crosslinking butyl acrylate with fluorescent dyes enables the synthesis of particles whose fluorescence can be used to track their position, enabling novel studies to quantify the interactions of particles in complex environments such as polymer solutions or melts, which are ubiquitous in the processing of paints, coatings, or pharmaceuticals.

Objective

- **To determine the best method to synthesize monodisperse fluorescent poly (butyl acrylate) microspheres**.
- ***Method One - One Step Synthesis***: Add the fluorescent dye at the beginning of the reaction to form the butyl acrylate latexes.
- ***Method Two - Two Step Synthesis***: Add the fluorescent dye after the butyl acrylate latex particles have been formed.

Methods and Materials

Method One - One Step Synthesis

All reagents were reacted together, consisting of the monomer (butyl acrylate), fluorescent dye (2-[methyl-(7-nitro-2,1,3-benzooxadiazol)-4-ylamino]ethyl 2-methyl methacrylate, NBD-MMA), initiator (2,2'-azodiisobutyronitrile, AIBN), cross-linker (allyl methacrylate) and stabilizer (polyvinylpyrrolidone, PVP) in a solution of 90% methanol and 10% water by mass. These reactants were added into a Schlenk flask which was placed in an oil bath at 70°C for 24 hours. The resulting product was analyzed with optical microscopy, dynamic light scattering (DLS), scanning electronic microscopy (SEM) and confocal laser scanning microscopy (CLSM).

Method Two - Two Step Synthesis

All of the reagents except the fluorescent dye (NBD-MMA) were reacted in a Schlenk flask to form particles, followed by the addition of the dye. The product was again analyzed with optical microscopy, dynamic light scattering (DLS), scanning electron microscopy (SEM), and confocal laser scanning microscopy (CLSM).

Results

Method One - One Step Synthesis (Fig. 1a): Copolymerizing the fluorescent dye with butyl acrylate leads to the incorporation of the dye into the latex, but produces clumpy particles that vary widely in size and shape. Based on Fig. 1b, fluorescence can be detected with confocal microscopy, but Fig. 1c shows a clumpy polymer with a wide distribution in particle sizes. Nuclear magnetic resonance spectroscopy (NMR) of dye (NBD-MMA) indicates a significant amount of impurities; thus, refining the synthesis of NBD-MMA may lead to uniform particles.

Method Two - Two Step Synthesis (Fig 2a): Monodisperse particles, 1 micron in diameter, were produced as shown in the optical microscope image in Figure 2b and the SEM image in Figure 2c. The fluorescent dye, NBD-MMA, was added after particles were formed, leading to monodisperse fluorescent microspheres (Figure 2d). Thus, the two step synthesis can be used to produce fluorescent butyl acrylate microspheres.

Method One - One Step Synthesis

Figure 1a. Reaction with method one

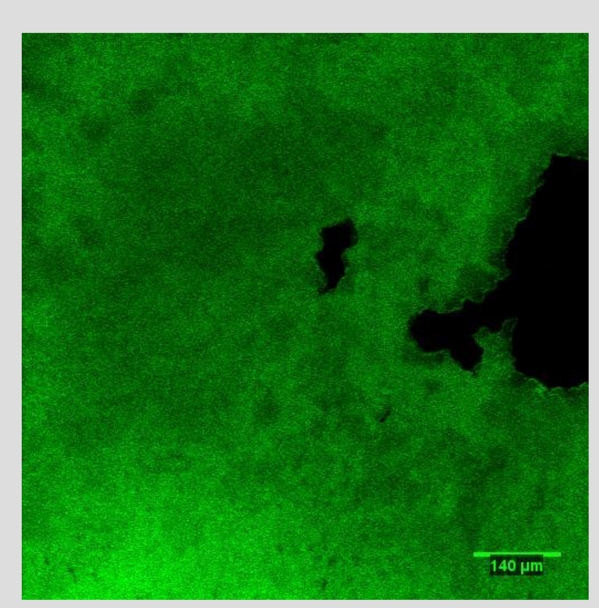


Figure 1b. Confocal microscopy of fluorescent butyl acrylate polymer (10X magnification)

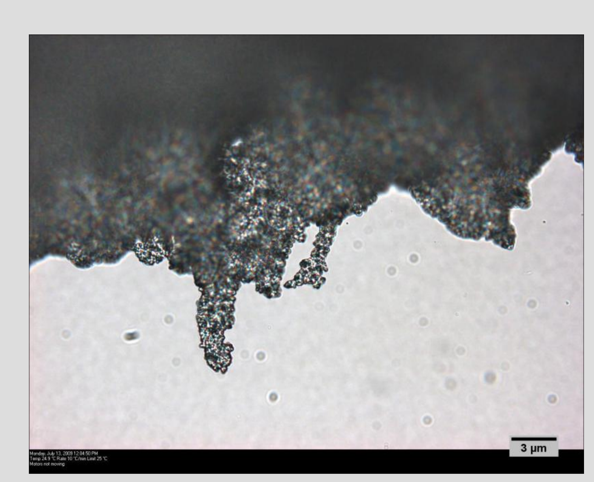


Figure 1c. Optical microscope image of clumpy butyl acrylate polymer (50X magnification)

Method Two - Two Step Synthesis

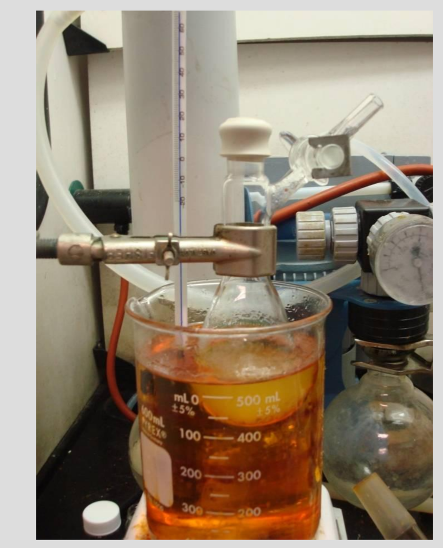


Figure 2a. Reaction with method two

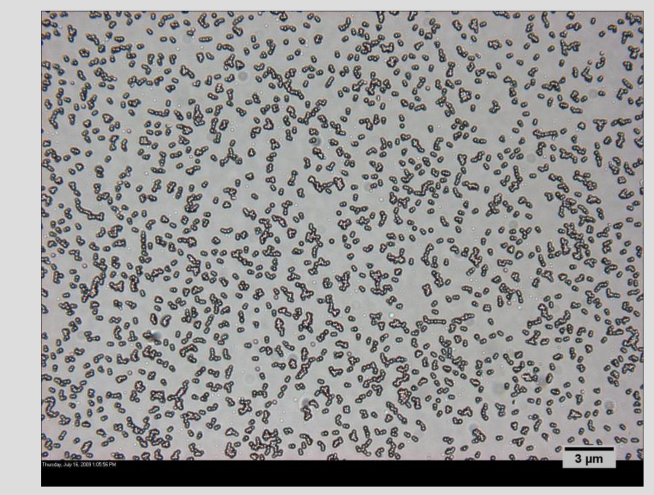


Figure 2b. Optical microscope image of butyl acrylate particles (50X magnification).

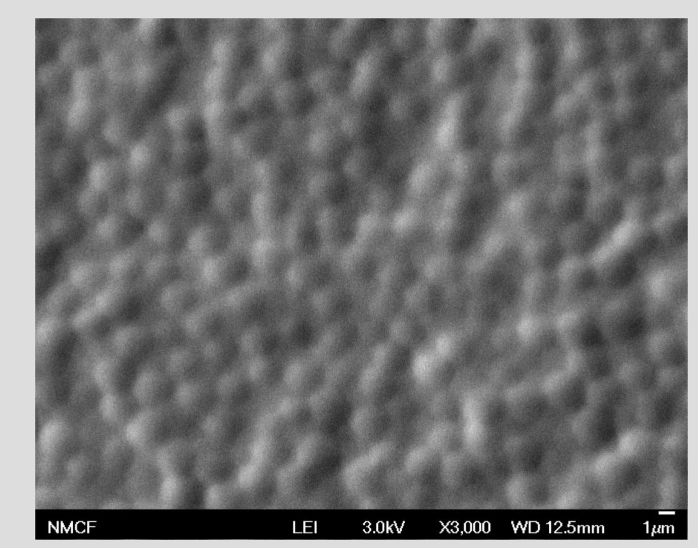


Figure 2c. SEM image of butyl acrylate particles

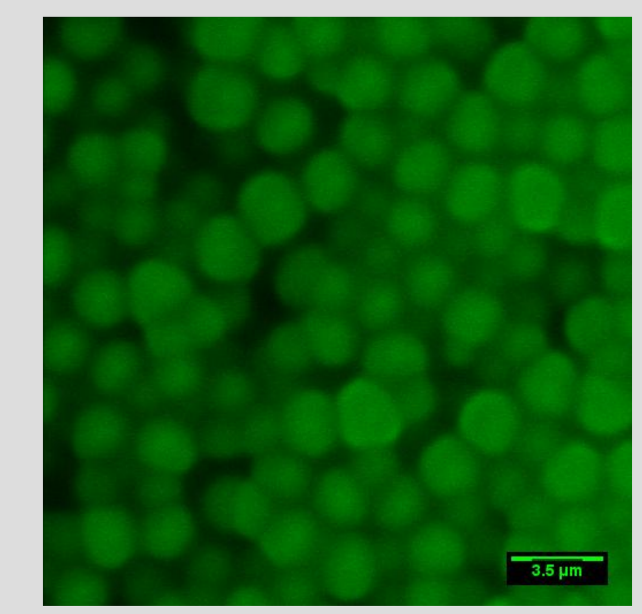


Figure 2d. Confocal microscope image of fluorescent butyl acrylate particles (Close up image at 60X magnification).

Conclusions

The one step synthesis of Method 1 in which the fluorescent dye was added at the beginning of the reaction, leads to fluorescent butyl acrylate latex that varies widely in size and shape. The two step synthesis of Method 2 in which the dye is added subsequent to particle formation, leads to fluorescent, monodisperse, butyl acrylate spheres, which could be observed with confocal laser scanning microscopy (CLSM). Our future investigations will involve the development of a semi-batch reaction to produce larger quantities of fluorescent particles using the two step synthesis. We are also refining the synthesis of the fluorescent dye.

Acknowledgements

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