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Low-temperature polymerization of methyl methacrylate emulsion gels through surfactant catalysis

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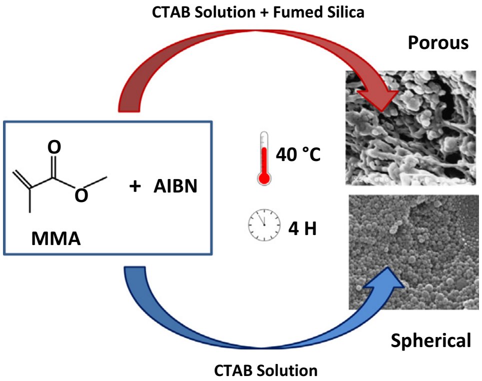
HIGHLIGHTS

- Surfactant catalysis allows AIBN-initiated free radical polymerization at 40 °C.
- Surfactant partially covers silica surfaces, remainder in surfactant–polymer mixture.
- Silica particle mainly covered with poly(methyl methacrylate).
- Fumed silica acts as an inhibitor for free radical polymerization.
- Porous composites were produced in the presence of fumed silica.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(methyl methacrylate) (PMMA)/silica/cetyltrimethylammonium bromide (CTAB) composites were prepared through surfactant catalyzed free radical polymerizations at 40 °C. Fumed silica particles controlled the morphology of the polymeric composites producing porous structures. The internal structures of the porous composite were determined using temperature-modulated differential scanning calorimetry (TMDSC). The fumed silica particles were encapsulated by an incompletely covered CTAB monolayer, with a crystallization temperature, $T_{C,CTAB} = 76$ °C, and a mixed PMMA/CTAB shell, with $T_{C,CTAB} = 63$ °C. The fumed silica surfaces acted as inhibitors for PMMA free radical polymerizations. Much of the PMMA formed in the composites was adsorbed on the silica, as evidenced by its elevated glass transition temperature compared to bulk. The enhanced decomposition of the initiator was catalyzed by CTAB and resulted in free radical polymerization of PMMA at 40 °C, which is considerably lower than the temperatures normally used for PMMA synthesis by free radical means with thermal initiation. These lowered polymerization temperatures allow energy efficient production of composites, which can incorporate temperature sensitive materials.

1. Introduction

Interfaces in colloidal systems may play a major role in terms of chemical reactions. One example of this effect is in the free radical polymerization used to synthesize polymers and polymeric

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composites from vinyl monomers. These polymerizations are often conducted well above room temperature (>60 °C) in order for sufficient numbers of initiator molecules to thermally decompose. A good example of such a process is that with 2,2′-azobis(isobutyronitrile) (AIBN) [1,2]. These temperatures, however, are too high for many temperature-sensitive molecules, including biomolecules [3], which limit the applications of free radical polymerization in the presence of many biomaterials. A low-temperature polymerization (<40 °C), therefore, is preferred for the *in-situ* preparation of polymers with biomaterials. Free radical polymerizations at low temperatures also showed narrower polydispersities [4,5], different tacticities [6], and structures compared with higher temperature polymerizations. Conducting free radical polymerizations at low temperatures is important, and can be achieved by using metallic catalysts [7], redox initiators [8], irradiation [4], or, more recently, emulsion gels [9–11]. It is the later which is the focus of this work.

Surfactant catalysis in emulsions can be a simple, cost-effective and environmental-friendly approach for low temperature polymerizations. Tauer and Oz have shown that a few different thermal initiators, including water and oil soluble species, decomposed at room temperature with assistance of surfactants [12]. Kinetics data from the cationic surfactant, cetyltrimethylammonium bromide (CTAB) and AIBN system suggested that the AIBN and CTAB formed a complex [10], which accelerates the decomposition of AIBN. Therefore, it is possible to conduct the free radical polymerization at lower than normal temperatures [9,11]. For example, emulsion gels containing 90% of styrene monomers were polymerized at 21 °C in 24 h through CTAB catalysis, and mono-dispersed polystyrene(PS)/CTAB/silica nanoparticles were obtained [9].

Poly(methyl methacrylate) (PMMA) and its porous composites are considered among the most important materials for medicine [13,14] and tissue engineering [15,16], due to their good biocompatibility. Polymerizations of MMA at low temperatures not only allowed the retention of the activity of immobilized biomolecules during and after the polymerization, but it also enhanced the thermal properties of the resulting materials [6,17]. In this paper, we extend our prior work on the low temperature polymerization of styrene to MMA [9]. Because of the differences in polarity of MMA compared with styrene, the polymerization show some complications not observed in the styrene systems. Nevertheless, we describe a surfactant-catalyzed radical polymerization of MMA from fumed silica-containing emulsion gels at low temperature (40 °C). The resulting PMMA/silica/CTAB composites have different morphologies than PMMA composites made by other techniques.

2. Materials and methods

2.1. Materials

Methyl methacrylate (MMA, Aldrich Chemical, Milwaukee, WI) was purified by washing with an NaOH solution, followed by distillation under reduced pressure. AIBN (Eastman Kodak) was purified by recrystallization from methanol. The purified materials were dried in a vacuum oven for 48 h to eliminate any solvent residue. Cetyltrimethylammonium bromide (CTAB, Eastman Kodak T5650) was used as received. Cab-O-Sil M-5P fumed silica (Cabot Corp., Tuscola, IL), with a specific surface area of 200 m^2/g, was used. The fumed silica particles were dried for 24 h at 300 °C before use. In order to reduce moisture, the dried fumed silica was kept in a vacuum desiccator after heat treatment.

2.2. Preparation of composites

For each sample, 2 ml of MMA and 0.04 g of AIBN was introduced into a 10 ml sample vial with or without 0.105 g of fumed silica. The mixtures were shaken for 1 min with a vortex mixer. An aqueous solution of CTAB with a concentration of 0.25 or 0.50 M was then introduced into the mixture. For some samples, a stable emulsion gel formed after shaking the final mixture for about 1 min. The polymerizations were conducted without stirring at 40 °C in an oil bath for 4 h. All samples were dried under ambient conditions for 24 h and then under vacuum for 24 h.

2.3. Characterization of composites

The extracted PMMA from the polymerized composites were obtained by mixing the composites with tetrahydrofuran (THF). After shaking for 12 h and centrifuging for 20 min, the silica-free upper layer was taken out and mixed with distilled water to precipitate PMMA. The precipitated products were washed several times with distilled water with sonication to remove the surfactants. The extracted polymers were dried in air and then under vacuum for 24 h.

Molecular mass was determined using gel permeation chromatography (GPC) in THF, with a Wyatt Optilab DSP differential refractometer and a Wyatt DAWN EOS light scattering detector (Wyatt Technologies, Santa Barbara, CA) at 690 nm. The dn/dc value of PMMA in THF, 0.088 mL/g, was used. Proton NMR spectra of the extracted PMMA in deuterated chloroform were recorded with a Gemini 2000 (300 MHz) spectrometer. Scanning electron micrographs of the gold-sputtered samples were taken with Hitachi S-4700 SEM operated at acceleration voltage of 20 kV in a secondary electron mode. Thermogravimetric analysis (TGA) measurements were carried out using a TA Instruments 2950 TGA (TA Instruments, New Castle, DE) with a heating rate of 20 °C/min in an air atmosphere. Temperature modulated differential scanning calorimetry (TMDSC) measurements were taken with a TA Instruments model 2920 TMDSC with nitrogen as a flow gas. The heating and cooling scans were taken from 30 to 180 °C, with a rate of 3 °C/min, and a modulation amplitude of ±1.0 °C with a period of 60 s. The reported enthalpies measured by TMDSC were the mean value of 6 replicates.

In order to separate the glass transitions from PMMA and the melting/crystallization transitions from CTAB in the composites thermograms, a DSC temperature modulation mode was used. The total heat flow, in this mode, was separated into reversing and non-reversing components [18]. The former contributes from the glass transitions and the latter corresponds to melting/crystallization transitions.

3. Results and discussion

3.1. Gel stability and polymerization

The optical photographs of typical fumed silica-containing systems (sample vials inverted) are shown in Fig. 1, and their compositions are listed in Table 1. Sample 1, consisting of fumed silica and MMA, was translucent and did not flow (i.e., it was gel-like). A mixture of fumed silica and water was liquid-like, as seen in sample 2. A mixture of MMA/water/fumed silica remained gel-like, but less translucent (sample 3). The mixtures of MMA/water/fumed silica with different concentrations of CTAB are shown for samples 4 –7. These CTAB-containing mixtures (0.10, 0.25 and 0.50 M) were white and gel-like; they are ‘‘emulsion gels”. With increased concentration of CTAB to 0.70 M (sample 7), an emulsion gel did not form as some flow was observed when the vial was inverted.

The gel formation in MMA/fumed silica (sample 1 in Fig. 1) occurred because of the presence of three-dimensional networks of fumed silica particles in MMA dispersions [9,19]. The MMA/fumed silica gel was translucent because the refractive index of