SYNTHESIS OF MACROPOROUS POLYMER BEADS BY SUSPENSION POLYMERIZATION USING SUPERCRITICAL CARBON DIOXIDE AS A PRESSURE-ADJUSTABLE POROGEN

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Introduction

Herein we describe the preparation of macroporous polymer beads by oil-in-water (O/W) suspension polymerization using supercritical carbon dioxide ($scCO_2$) as the porogenic solvent. Carbon dioxide is an inexpensive, non-toxic, and non-flammable solvent alternative for polymer synthesis and processing.[1] Unlike liquids, supercritical fluids (SCFs) are highly compressible and the density (and therefore solvent properties) can be varied over a wide range by changing pressure. In principle, this allows control over variables such as phase behavior, and should permit 'tuning' of certain chemical reactions and polymerizations.[2] DeSimone and others have shown that $scCO_2$ is a versatile medium for both homogeneous and heterogeneous polymerization.[3] Previously, we synthesised cross-linked divinylbenzene-based polymers in $scCO_2$ by free-radical precipitation polymerization and dispersion polymerization.[4]

Macroporous polymers are important in a wide range of applications such as ion-exchange resins, chromatographic separation media, solid-supported reagents, and supports for combinatorial synthesis.[5,6] Unlike gel-type polymers which swell in the presence of an appropriate solvent, the cross-link density in macroporous polymers is sufficient to form a permanent porous structure which persists in the dry state. Macroporous polymers are usually synthesized as beads (typical diameter = 10–1000 μm) by O/W suspension polymerization[7] in the presence of a suitable porogen (*i.e.*, an additive which induces pore formation in the polymer matrix). The porogen may be an organic solvent which is miscible with the monomers[8] or a linear polymer which is soluble in the monomer phase.[9] However, to achieve *fine* control over porosity is not always straightforward. For one thing, the porous structure which develops can be remarkably sensitive to small changes in polarity of the porogenic solvent (or solvent mixture) employed. This has also been noted in the synthesis of continuous macroporous polymer monoliths.[10] Thus, the development of alternative methods for controlling porosity in macroporous polymers may offer distinct advantages. In this work the possibility of preparation of macroporous polymer beads by oil-in-water (O/W) suspension polymerization using supercritical carbon dioxide ($scCO_2$) as the porogenic solvent was investigated.

Experimental

Materials

Trimethylol propane trimethacrylate (TRIM), methyl methacrylate (MMA), poly(vinyl alcohol), and CO_2 (99.9995%, Messer Greisheim) were all used as received. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol.

O/W Suspension Polymerization

Polymerizations were conducted in a stainless steel autoclave (volume = 57.5 cm^3, New Ways of Analytics) equipped with a vertically mounted, 2-blade impeller stirrer. In a typical polymerization, the reactor was charged with a mixture of monomer(s), initiator (AIBN), and an aqueous solution of stabilizer [poly(vinyl alcohol)]. The system was purged with a slow flow of CO_2 at room temperature for 20 min with gentle stirring. The reactor was then pressurized with liquid CO_2 to 140 bar or below, and the reaction mixture was heated to 60 °C. More CO_2 was added was added close to the reaction temperature if necessary to make up the pressure to the desired level. After 6h , the reactor was cooled and the CO_2 vented. The polymer was recovered by filtration and washed twice with warm water and then twice with acetone. The product was then filtered and dried under vacuum at 50 °C to yield a free-flowing, white powder.

Polymer Analysis

Polymer morphology was investigated using a Hitachi S2460-N scanning electron microscope. Samples were sputter coated with gold before analysis. Mean particle sizes and particle size distributions were calculated by measuring at least 100 particle diameters.

Nitrogen adsorption/desorption (BET) measurements were carried out using a Micromeritics Tristar 3000 insturment.

Mercury intrusion porosimetry data were obtained using a Micromeritics Autopore 9220 mercury porosimeter.

Results and Discussion

Table 1 summarises the results of a series of polymerizations carried out under various conditions. In the absence of CO_2, the O/W suspension polymerization of TRIM led to polymer beads with an average diameter of 180 μm (entry 1). Analysis by scanning electron microscopy (SEM), mercury intrusion porosimetry, and N_2 adsorption / desorption (BET) showed that the beads were non-porous, as reflected by the low surface area (<5 m^2/g).

Table 1. Suspension Polymerization of TRIM using $scCO_2$ as the Porogen

Entry	Pressure (bar)	intrusion volume (ml/g)[a]	median pore diameter (nm)[a]	surface area (m^2/g)[b]
1	1	0.00	[c]	<5
2	100	0.28	(19)[d]	<5
3	200	1.05	2206	222
4	300	1.23	110	253
5	400	0.69	40	478
6	300	0.42	(84)[d]	<5
7	300	1.13	735	366
8[e]	300	0.93	102	37

Reaction conditions: 20% w/v TRIM based on volume of H_2O, AIBN (2% w/v), 0.5% w/w PVA (80% hydrolyzed, M_w = 10,000 g/mol), 50°C, 6 h. [a] Measured by mercury intrusion porosimetry over the pore size range 7 nm-20 μm. [b] Measured by N_2 adsorption desorption using the Brunauer-Emmett-Teller method. [c] Non-porous sample. [d] Sample has a relatively low pore volume and exhibits a broad, flat pore size distribution. Thus, the median pore diameter does not provide much useful information in this case. A significant proportion of fractured beads and 'fines' was also observed. [e] Monomer mixture = TRIM (20% v/v) + MMA (80% v/v).

This reaction was repeated in the presence of $scCO_2$ over a range of pressures while keeping all other variables constant (entries 2–5). Macroporous polymer beads were formed when CO_2 was added to the reaction mixture (Figure 1). Moreover, our preliminary results suggest that the degree of porosity, the average pore size, and the surface area in the beads can be tuned over a wide range by varying the CO_2 density. Observations of the phase behavior of the system at low pressure (100 bar) showed that the monomer phase and the CO_2 phase were not fully miscible. This resulted in the formation of porous beads but the pore volume was relatively low (0.28 ml/g), as was the surface area of the sample. By contrast, at higher pressure the monomer was completely miscible with CO_2, and a homogeneous monomer / CO_2 mixture was dispersed as droplets throughout the aqueous phase. As a result, the beads were found to have increased pore volume and much higher surface area. This can be explained by the fact that the pore volume in the materials tended to increase with pressure whereas the median pore diameter decreased significantly as the pressure was raised (Table 1). The combination of these two trends resulted in a sharp rise in polymer surface area as a function of CO_2 pressure (Figure 2). We attribute this behavior to variation in the CO_2 solvent strength as a function of density. We believe that the variation in pore diameter (and the associated change in surface area) in the beads can be rationalized by the fact that the system is very sensitive to the porogen solvent quality, as found with more conventional porogenic solvents.[7-10] The trends observed support this interpretation, with higher CO_2 density (*i.e.*, increased solvent strength) leading to smaller pores and larger surface areas.

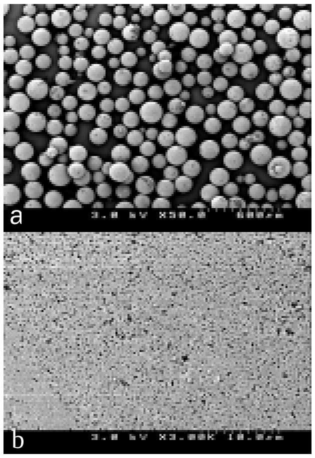

Figure 1. Electron micrographs of macroporous polymer beads synthesized using $scCO_2$ as the porogen (300 bar) (a) Scale bar = 600 µm; (b) Magnification of bead surface showing porous structure, scale bar = 10 µm

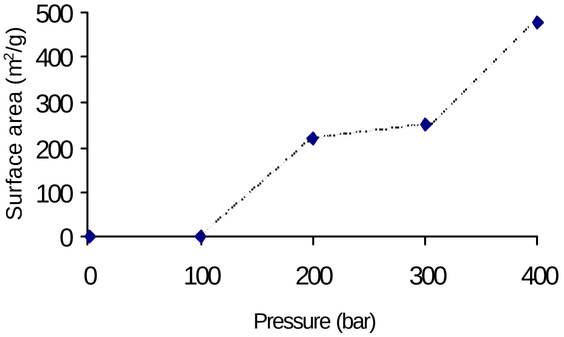

Figure 2. Variation in BET surface area of the macroporous beads as a function of reaction pressure, as measured by N_2 adsorption/desorption.

In addition to varying the CO_2 density, we are also investigating the influence of more standard reaction parameters such as stirring speed, monomer / cross-linker concentration, stabilizer morphology, and stabilizer concentration. As might be expected,[8,11] the level of cross-linking also has a strong effect on the properties of macroporous polymers prepared by this route (entry 8).

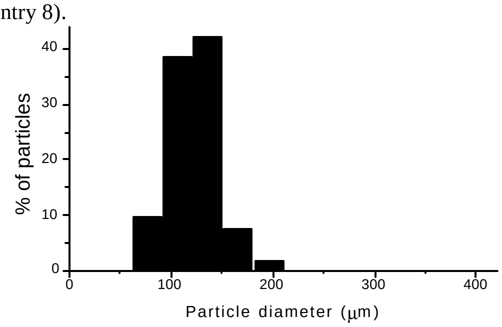

Figure 3. Particle size distribution as calculated (>100 particles) from SEM for macroporous particles produced at a reaction pressure of 400 bar.

Conclusions

In conclusion, we have demonstrated that well-defined macroporous polymer beads can be synthesized in the absence of any organic solvents using $scCO_2$ as the porogen. These preliminary results are perhaps the most dramatic example yet of a system where polymer properties can be 'tuned' by varying the supercritical fluid solvent density.

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