STRUCTURAL CONTROL IN POLYMERIC MATERIALS USING SUPERCRITICAL CARBON DIOXIDE

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Introduction

Carbon dioxide is an inexpensive, non-toxic, and non-flammable solvent alternative for polymer synthesis and processing [1,2]. Unlike liquids, supercritical fluids (SCFs) are highly compressible and the solvent properties can be varied over a wide range by changing the density [3]. In principle, this should permit 'tuning' of certain polymerization reactions and allow one to achieve fine control over polymer properties. However, there have been few convincing examples of polymerization reactions in dense CO_2 where polymer properties can be controlled in a predictable manner just by varying the solvent density. Previously, we synthesized non-porous cross-linked divinylbenzene-based polymers in supercritical CO_2 ($scCO_2$) by free-radical precipitation polymerization and dispersion polymerization [4,5]. More recently, we showed that these reaction conditions can be modified to generate well-defined macroporous polymer monoliths, thereby using $scCO_2$ as a porogenic solvent [6]. We have now shown that this technique can be extended to the synthesis of macroporous polymer beads *via* suspension polymerization [7]. No organic solvents are required in this process: just water and CO_2. Furthermore, we have demonstrated that the porosity in the beads can be controlled by varying the CO_2 density. In this lecture we will discuss the mechanism by which the porous structure develops and how this is affected by the SCF solvent density.

Experimental

In a typical reaction, a mixture of monomer [trimethylolpropane trimethacrylate (TRIM)], initiator [2,2´-azobisisobutyronitrile (AIBN)], and $scCO_2$ was suspended in water with stirring in the presence of a stabilizer [0.5% w/v poly(vinyl alcohol)] to inhibit droplet coalescence [7]. All polymerizations were carried out in a stainless steel high-pressure vessel fitted with an impeller stirrer (manufactured by New Ways of Analytics, Germany). Tandem reactions were carried out in a high-pressure view cell equipped with a sapphire window for observation of phase behavior [4–6]. This allowed us to ascertain the degree of miscibility of the monomer phase with CO_2.

Results and Discussion

In this study, we have synthesized macroporous polymer beads using $scCO_2$ as the porogenic solvent. We have also exploited the fact that the solvent strength of the fluid can be tuned continuously over a significant range by varying the density. As such, $scCO_2$ can be thought of as a 'pressure-adjustable' porogen. In the absence of CO_2, the O/W suspension polymerization of TRIM led to non-porous polymer beads with an average diameter of 180 μm and low surface areas (<5 m^2/g). When the reaction was repeated in the presence of $scCO_2$ over a range of pressures, macroporous polymer beads were formed with surface areas up to a maximum of 480 m^2/g. 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 (see Figure 3).

Figure 1

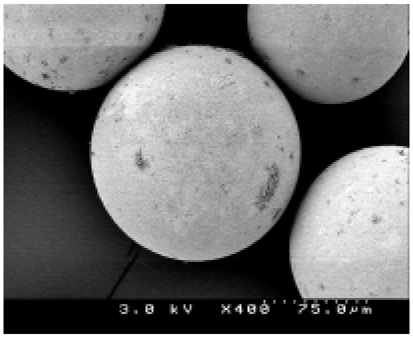

Figure 2

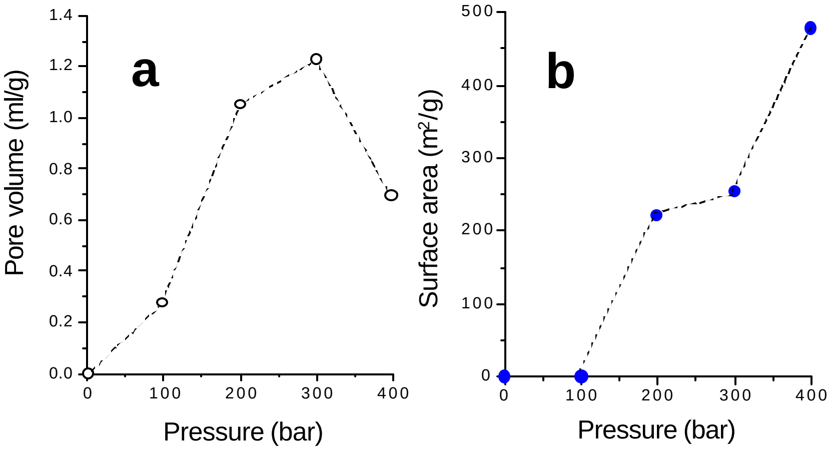

Figure 3

Figure 1. *High pressure stainless steel autoclave used for suspension polymerizations (manufactured by New Ways of Analytics, Lörrach, Germany). The autoclave has a total internal volume of 60 ml and is fitted with a vertically mounted impeller stirrer.*

Figure 2. *Macroporous polymer beads synthesized using $scCO_2$ as the porogen. Scale bar = 75 μm. Reaction conditions: 20% w/v trimethylolpropane trimethacrylate (TRIM), 2,2´-azobisisobutyronitrile (AIBN, 2% w/v), poly(vinyl alcohol) (0.5% w/v based on volume of H_2O, M_w = 88,000 g/mol, 88% hydrolyzed), 60 °C, 400 bar, stirring speed = 600 rpm, 6 h.*

Figure 3. *(a) Variation in pore volume of the macroporous beads as a function of reaction pressure, as measured by mercury intrusion porosimetry over the pore size range 7 nm–20 μm. (b) Variation in BET surface area of the macroporous beads as a function of reaction pressure, as calculated from N_2 adsorption / desorption isotherms.*

Phase Behaviour: At lower pressures (<100 bar, 60 °C), we observed that the monomer phase and the CO_2 phase were not fully miscible. As the pressure was increased, more CO_2 was dissolved in the monomer–rich droplets. This caused a change in the composition of the polymerization mixture and influenced polymer phase separation. The significant difference in morphology observed for the polymers synthesized at 100 bar and 200 bar may be attributed to this effect. However, at pressures in excess of 200 bar, we observed what appeared to be a single dispersed phase in the reaction vessel (*i.e.*, the monomer and CO_2 were fully miscible). Clearly, as the pressure was increased from 200 bar to 400 bar, more CO_2 was dissolved in the monomer droplets. However, in all of these experiments, the volumetric ratio of water to monomer was kept constant, while the CO_2 pressure was varied. Given that the surrounding water phase was relatively incompressible, then the combined *volume* of compressed CO_2 and monomer (*i.e.*, the total volume of the dispersed phase) was approximately constant at the beginning of each experiment. This holds true even though the *molar* ratio of monomer to CO_2 varies dramatically – an unusual feature of experiments involving highly compressible solvents. As phase separation proceeds and the monomer is depleted, a CO_2 rich phase is formed which finally becomes the porous structure in the beads. The variation in pore diameter (and the associated change in surface area) in the beads is therefore affected by the *density* of the CO_2 phase [8,9]. The trends observed support this interpretation, with higher CO_2 densities (*i.e.*, increased solvent strength) leading to smaller pores and larger surface areas. Broadly similar trends have been seen for porous monolithic polymers synthesized in scCO_2, although direct comparison is difficult because one would expect differences in swelling behavior and polymer shrinkage phenomena due to interfacial effects which are present in the case of the suspension polymerizations [10].

Conclusions

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.

References

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