

SYNTHESIS OF HIGHLY CROSS-LINKED POLYMERS BY OIL-IN-OIL EMULSION POLYMERISATION IN SUPERCRITICAL CARBON DIOXIDE

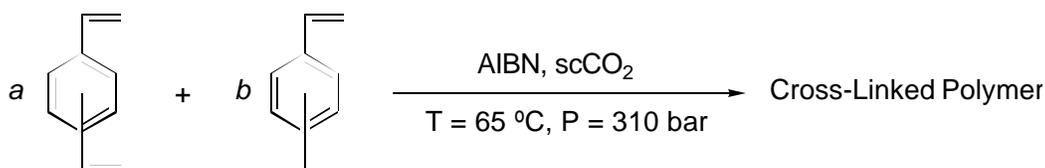
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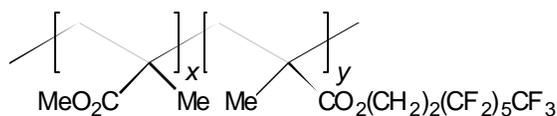
Abstract: Supercritical carbon dioxide (scCO₂) is an attractive solvent for polymer chemistry because it is inexpensive, non-toxic, and non-flammable.^{1,2} Unlike conventional liquid solvents, supercritical fluids are highly compressible and the solvent density (and therefore solvent properties) can be tuned over a wide range by varying pressure.³ DeSimone and others have shown that CO₂ is a versatile solvent for both homogeneous⁴ and heterogeneous⁵⁻⁷ polymerisations. In particular, CO₂-soluble surfactants have been developed for the free radical dispersion polymerisation of styrene and methyl methacrylate (MMA) in scCO₂, thus allowing the formation of regular polymer microspheres.⁸⁻¹⁵ The development of CO₂-based emulsion or suspension polymerisation techniques has received much less attention, probably because most monomers studied so far have been found to be quite soluble in scCO₂. Adamsky and Beckman investigated the inverse emulsion polymerisation of acrylamide in biphasic water / scCO₂ mixtures, both with and without added surfactants.¹⁶ In more recent studies, Super and Beckman chose 2-phase conditions for copolymerisation of CO₂ and cyclohexene oxide, however surfactants were not used and emulsification of the monomer was not reported.^{17,18} There has, in fact, been relatively little data in the literature concerning the formation of monomer emulsions in scCO₂, however the stabilisation of certain polymer emulsions in CO₂ has been described recently in detail.^{19,20}

In this paper, we report the formation of highly cross-linked polymers based on divinylbenzene (DVB), using scCO₂ as the polymerisation medium.



Scheme 1: Polymerisation of divinylbenzene (DVB) in scCO₂. a = 0.55-0.8, b = 0.2-0.45.

Rather surprisingly, DVB was found to be much less soluble in CO₂ than comparable monomers, such as styrene or MMA. This has allowed us to carry out unstabilized, suspension-type polymerisations in the absence of surfactants.²¹ For emulsion polymerisation in CO₂, a CO₂-soluble, diblock copolymer surfactant (**1**) was synthesized by a modified screened anionic polymerisation technique.¹³



Scheme 2: Structure of surfactant **1**. Molar ratio $x:y = 1:1$ by ¹H NMR. Calculated $\overline{M}_n = 74.5$ kg/mol.

In the presence of surfactant **1**, emulsification of the DVB monomer mixture in CO₂ was observed, giving rise to an emulsion-type polymerisation (Table 1).

	w/w % surfactant 1 ^a	polymer morphology	particle size ^b (μ m)	phase behaviour ^c	yield (%)
a	0	powder	1-5	US	89
b	0.25	powder	0.5-2.5	E	90
c	1	powder	0.4-1.6	E	87
d	3	microspheres	0.41	E	96

Table 1: Reaction conditions: 2.0g monomers (55 w/w % DVB, 'DVB55'), AIBN (8 w/w %), 310 ± 10 bar, 65 °C, 24 h.

^a Weight % based on monomer. ^b Determined by SEM. ^c US = unstabilized suspension, E = emulsion.

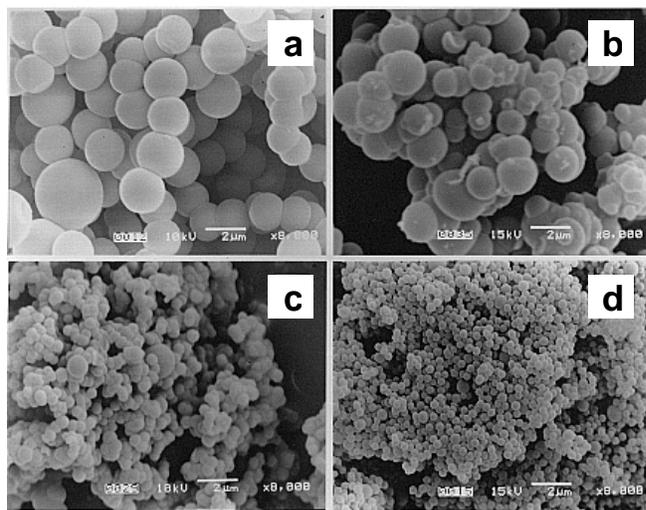


Figure 1: Scanning electron microscope (SEM) images of particles formed by the polymerisation of 55 w/w % DVB (DVB55) in the presence of various amounts of surfactant **1**. (a) 0 w/w %, (b) 0.25 w/w %, (c) 1.0 w/w %, (d) 3.0 w/w %. (Scale bar = 2 μ m in all images.)

The morphology of the highly cross-linked polymers was very sensitive to surfactant concentration. In the absence of **1**, a cloudy suspension of monomer in CO₂ was formed, and spherical polymer particles were formed which exhibited significant agglomeration (Table 1, Figure 1a).²¹ However, in the presence of 0.25-3.0 w/w % **1**, an opaque, white emulsion of monomer-in-CO₂ was observed upon pressurisation of the reactor. This appearance persisted throughout the polymerisation, and the polymer particles obtained were considerably

smaller than those produced in the absence of surfactant (Fig. 1b-d). At relatively low surfactant concentrations (0.25-1.0 w/w % **1**), the polymer particles had broad size distributions and showed signs of agglomeration (Fig. 1b,c). At higher surfactant concentrations (3 w/w % **1**), uniform, unagglomerated microspheres were obtained with relatively narrow size distributions, suggesting that the emulsion was effectively stabilized under these conditions (Fig. 1d, Fig. 2).

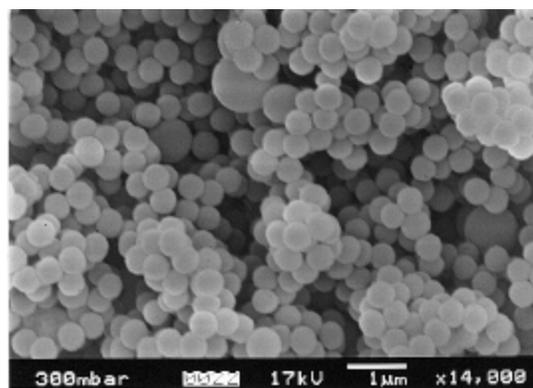


Figure 2: SEM of cross-linked polymer microspheres synthesized by oil-in-oil emulsion polymerisation in $scCO_2$. (Scale bar = 1 μm .)

It not likely that the initiator, AIBN, was exclusively soluble in either the monomer or in the CO_2 continuous phase, thus making it difficult to classify these polymerisations according to common conventions based on partitioning of initiator during polymerisation.²² In the absence of more detailed mechanistic evidence, we have classified the stabilized reactions as ‘oil-in-oil emulsion polymerisations,’ based on the observed phase behaviour and the final particle morphology.

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