One-step seed dispersion polymerisation in supercritical carbon dioxide†

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A single step seed dispersion polymerisation is reported for the first time, in which $scCO_2$ is used simultaneously as both an antisolvent and a polymerisation medium to create polymer-C_{60} composite microparticles providing additional proof for the mechanism of dispersion polymerisation in $scCO_2$.

Composite polymer particles have attracted much attention since Hughes and Brown first investigated their physical properties.[1] The common approach to prepare composite polymer particles is through a multi-step seed emulsion or a multi-step dispersion polymerisation.[2,3] There are a great number of publications describing the preparation of sub-micron composite polymer particles. By contrast, there are very few reports of the synthesis of large composite polymer particles with micrometer-size.[4,5] The large specific surface area, high mobility, and easy recovery of such microparticles make them ideal for a wide range of applications such as adhesives, binders for fabrics, viscosity controllers and additives for paper, textiles and construction materials. More specifically, functional microparticles have attracted much attention in latex diagnostics, affinity bioseparators, drug and enzyme carriers, optical and opto-electronic studies, *etc*.[6] In this paper, we describe a one-step seed dispersion using $scCO_2$ simultaneously as both an antisolvent and a polymerisation medium to produce novel micrometer-sized polymer-C_{60} composite particles. Carbon dioxide is non-flammable, relatively non-toxic and naturally abundant, and is consequently promoted as a sustainable solvent in chemical processing. The "green" properties of carbon dioxide have provided the driving force for the development of a number of new applications.[7–11] Therefore, this process provides a technically and environmentally satisfying new method for the preparation of advanced colloid materials.

Previous work[12] has shown that $scCO_2$ is a good antisolvent for C_{60} solutions. Using rapid antisolvent precipitation, irregularly shaped submicrometer C_{60} particles have been formed in $scCO_2$. In a separate application of $scCO_2$ it has been demonstrated that $scCO_2$ is a good reaction medium for the dispersion polymerisation of styrene.[8,10] Here we demonstrate that these two $scCO_2$ processes can be combined to fabricate novel polystyrene-C_{60} composite microparticles. C_{60} was initially dissolved in styrene monomer with initiator (AIBN) and stabilizer (PDMS-ma), and was then injected into $scCO_2$. Because $scCO_2$ acted as an antisolvent, C_{60} precipitated and dispersed in $scCO_2$. The resulting particles then acted as the seeds for the dispersion polymerisation of styrene in $scCO_2$, leading to the formation of the polystyrene-C_{60} composite microparticles. After the polymerisation, upon venting CO_2, the final product was a dry, fine, free flowing brown powder (see ESI†). Overall there was a 91% styrene monomer conversion. As a comparison, neat polystyrene microparticles were prepared under precisely the same conditions but in the absence of C_{60} (see ESI†). Comparing the morphology of polystyrene-C_{60} composite microparticles obtained by SEM (Fig. 1A) to that of neat polystyrene microparticles (Fig. 1B), it can be clearly seen that the composite particles (1.2 μm in diameter with particle size distribution of 1.26) are more homogeneous than the neat polystyrene particles (a bimodal particle size distribution, 2.1 μm and 400 nm in diameter, respectively). These data clearly suggest that the dispersed C_{60} particles acted as seed nucleation centres for the particle formation during the polymerisation.

However, there is an interesting finding. TEM analyses show that the C_{60} cannot be observed in the polystyrene matrix. This is surprising since high resolution TEM should be capable of detecting a single molecule C_{60}. The polystyrene-C_{60} composite microparticles gave a diffraction pattern (see ESI†) which differs from the expected pattern for C_{60}. Powder X-ray diffraction (XRD) analysis did not find any specific peaks matching with C_{60}. These results demonstrate that the structure of C_{60} in the polystyrene-C_{60} composite microparticles has been changed. We found that this polystyrene-C_{60} composite microparticle product completely dissolves in common organic solvents such as toluene, chloroform, and THF to form a brown solution. Previously, it was demonstrated[13–15] that C_{60}-polystyrene random copolymers with fullerenes interspersed along the polymer backbone could be synthesized by free-radical copolymerisation of C_{60} with styrene in bulk or solution. In all cases, the resulting polymers were soluble in common solvents that dissolve polystyrene and formed brown solutions. This suggests that in our case C_{60} was copolymerized

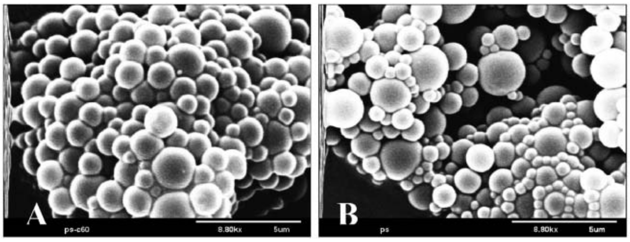

Fig. 1 SEM images (A) Polystyrene-C_{60} composite, (B) Neat polystyrene.

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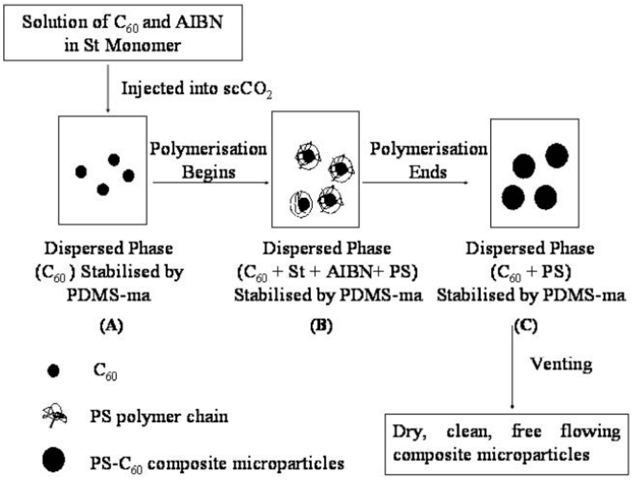
with styrene. Further characterizations were carried out to prove this point. We found that the absorption spectrum of polystyrene-C_{60} composite microparticles in solution was different from that of the parent fullerene, and moreover, the fluorescence of composite microparticles was blue-shifted and much stronger. These observations were identical to those of C_{60}-styrene copolymers in previous work.[13–15]

This interesting finding gives further understanding to the one-step seed dispersion polymerisation of styrene using C_{60} in $scCO_2$ (Scheme 1). In a dispersion polymerisation, two polymerisation loci are expected to contribute to the polymer production: the CO_2-rich continuous phase and the polymer-rich dispersed phase. One aspect currently under debate concerns which is the dominant polymerisation locus for the dispersion polymerisation in $scCO_2$.[16] The mass transport of reactants between phases is the key factor in determining the relative importance of each polymerisation locus. Since the rate of these processes is proportional to the interphase surface area, poor stabilization of the polymer particles will result in the formation of a bulky polymer phase. Poor stabilization would also significantly reduce the polymerisation rate inside the particles because of the hindered transport of monomer from the continuous phase. This is similar to the case of precipitation polymerisation, where the insoluble polymer is segregated out of the continuous phase. Because of the limited solubility of the monomer in the polymer phase, it accumulates without further significant reaction. On the other hand, when conditions corresponding to good stabilization are achieved, the reaction is effective in both loci. At the beginning, the only active locus is the continuous phase, where the first polymer chains are produced. However, as soon as particles are formed, monomer, initiator and active species are partitioned between the continuous and dispersed phases and both loci are effective. Under stable conditions, the particles very rapidly become the dominant locus. The polymerisation continues only in the polymer-rich phase, which is swollen with monomer. This mechanism is supported by most researchers. Recently, Fehrenbacher[17,18] has experimentally analyzed the initial stage of the reaction (particle formation) and shown that if a suitable stabilizer is used, a large number of small particles are obtained in a very short time. This confirms the dominant role of the reaction inside the polymer particles. The one-step seed dispersion polymerisation of styrene in $scCO_2$ provides additional proof for this mechanism. C_{60} was initially dispersed in $scCO_2$ and acted as a seed for the polymerisation of styrene. After the polymerisation began, the polystyrene chains precipitated. This led to the formation of particles containing C_{60} and styrene monomer. These particles then became the dominant locus for polymerisation. The styrene monomer dissolved C_{60} inside the particles, leading to a similar bulk reaction system as reported in previous work.[14,19] During the polymerisation, C_{60} inside the particles was copolymerised with styrene and finally incorporated into the polymer chain. Gel permeation chromatography (GPC) indicates that the polystyrene-C_{60} composite microparticle product and the polystyrene reference have almost the same molecular weight and polydispersity (Fig. 2). This apparently suggests that C_{60} did not have a significant effect on the polymerisation of styrene in $scCO_2$. However, more characterisations are under way to elucidate the complex structures of polystyrene-C_{60} composite.[20]



Scheme 1 One-step seed dispersion polymerisation.

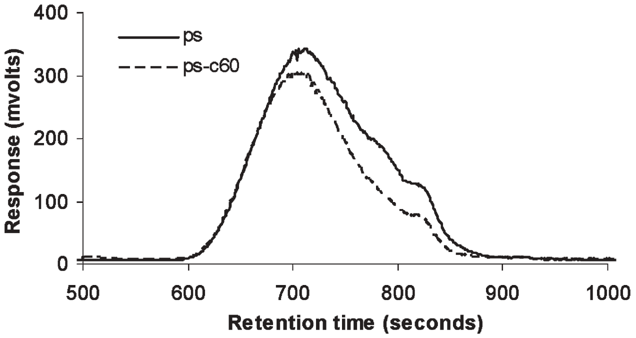


Fig. 2 GPC traces. The dashed line for polystyrene-C_{60} composite (M_w = 80300, PDI = 1.95); the solid line for neat polystyrene (M_w = 70500, PDI = 2.09).

In conclusion, polymer-C_{60} composite microparticles have been prepared through a one-step seed dispersion polymerisation method in which $scCO_2$ can be used simultaneously as an antisolvent and a polymerisation medium. This one-step seed dispersion polymerisation further proves the mechanism of dispersion polymerisation in $scCO_2$. This technically and environmentally satisfying method using CO_2 as the only solvent is applicable to many combinations of different materials and can lead to the production of a wide variety of new polymer composite microparticle materials.

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