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Synthesis of polymeric microcapsules by interfacial-suspension cationic photopolymerisation of divinyl ether monomer in aqueous suspension†

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Polymeric microcapsules have been synthesised with a markedly more hydrophillic monomer than previously reported, triethylene glycol divinyl ether, using cationic photopolymerisation in an aqueous environment. Characterisation by NMR and SEM show that the particles are formed with low dispersity with a size of approximately 1 μm in spite of the expected inhibition in aqueous conditions. Furthermore, supercritical carbon dioxide has been used to generate silver nanoparticles which distribute throughout the shell of the microcapsules further illustrating the structure of these capsules with characterisation by TEM and SAXS.

The synthesis of polymeric micro and nanoparticles is the focus of many applications including drug delivery, reinforcement in processed polymers and self-healing systems.[1,2] As a consequence of the promising applications of particles, there are numerous methods for their production. It is possible to make a preliminary distinction between two different approaches; the first one is based on the processing of pre-formed polymers, while the second one involves the polymerization of a monomer.

The production of the macroparticles is carried out starting from one or more monomers. On the basis of the method used to produce the emulsion and on the average size of dispersed droplets, it is possible to distinguish between micro-emulsion and mini-emulsion techniques.[3] In a micro-emulsion, the reaction takes place inside micelles obtained adding high concentrations of surfactant,[4] while in a mini-emulsion polymerization the reaction takes place inside the droplets of the dispersed phase and requires low surfactant concentrations.[5,6] A common way to synthesize polymeric capsule is to prepare a double emulsion (*e.g.*, water/oil/water) using a two-stage emulsification.[7]

The production of a double emulsion is difficult to achieve and the size of particles cannot precisely be controlled. For this reason, we have already developed in previous study[8] an innovative method to synthesize core–shell polymeric microcapsules that do not require the creation of a double emulsion. By inducing separation between the monomer and the initiator, adding the former in the continuous aqueous phase and the latter in the dispersed hydrophobic one, the polymerization reaction does not occur within the droplet, but at the interface between the dispersed and the continuous phase. It follows that the liquid droplet acts as a template on which surface the polymeric shell can grow, producing a core–shell structure.

While mini-emulsion free-radical chain growth polymerization has been widely reported,[9] a single manuscript shows cationic photopolymerisation of microspheres in aqueous media *via* suspension photoinitiated ring-opening polymerisation.[10] This synthetic method used a cationic photopolymerisation process, as well as conventional cationic vinyl and ring-opening polymerization, to realise a reaction that is well-known to be water sensitive.[11] Vinyl ethers are widely used in polymerisations for their ability to form networks with high efficiency for applications such as coatings, lithography *etc.*[9] Sangermano *et al.*[12] showed that the presence of water was particularly advantageous for the photopolymerization of multifunctional vinyl ether monomers. Water can provide a means of maintaining the mobilization of the propagating cationic species normally hindered through vitrification.[13] Conversely, the presence of a large amount of water, as is the case of a water-suspension polymerization, will cause a marked inhibition of polymerization. Crivello *et al.*[11] report the synthesis of epoxy functionalized microspheres by cationic photopolymerization in aqueous conditions. It is important to underline that the typical water suspension polymerization comprises hydrophobic monomers, in which droplets (oil phase) are emulsified with surfactants in a continuous phase of water. The polymerization occurs in the hydrophobic

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latex particles that form at the beginning of the polymerization process.

We present a modification of the classical emulsion microparticle polymerization to polymerize triethylene glycol divinyl ether (DVE3). In order for the cationic polymerization process in water to be successful we tailored the system to include the oil phase *n*-hexadecane which provides the interface with water, where the monomer can polymerize since the cationic photoinitiator is soluble in the hydrophibic solvent. The triarylsulfonium salt, used as the cationic photoinitiator, possesses aryl groups which impart sufficient lipophobic character allowing the photoinitiator to be readily soluble in the oil phase (see Fig. 1). The DVE3 monomer employed in this study, is amphiphilic therefore it reacts at the interface between water and *n*-hexadecane. This affords an interfacial polymerization that leads to the formation of microcapsules. Note the monomer is crosslinked as long as the polymerization proceeds at the interface between the aqueous and the oily phase and the polymeric shell surrounding the hexadecane liquid core is generated. Note that the particles do not dissolve and maintain structural integrity even after the drying process.

A DVE3 suspension in water was prepared, Fig. S1† shows the monomers used, and polymerization initiated through irradiation with UV-light then characterised by NMR and SEM (see ESI† for experimental details).

When compared to the typical radical miniemulsion polymerization, a change is made that the monomer's addition before the creation of the miniemulsion *via* ultrasonication. In radical miniemulsion photopolymerization the monomer is directly added to the aqueous phase composed by water. In the preliminary phase of the present study, this configuration was tested but, as expected, it did not lead to the crosslinking of the monomer and generation of a core–shell structure. In effect, cationic photopolymerization is inhibited by water and adding the monomer directly to the aqueous phase was proven not to be a successful procedure. To overcome this problem, the monomer was added in the dispersed phase. DVE3 is an intermediate polarity monomer, therefore, once the dispersed phase was added to the aqueous one, DVE3 tend spontaneously to move towards the interface between hexadecane and water. In this way the monomer in direct contact with the hexadecane core containing the photoinitiator.

The conversion of vinyl ether double bonds during UV-irradiation was determined by ^{1}H-NMR (Fig. 2 bottom). The peaks monitored prior to and post- photopolymerization are related to the vinyl double bond functionality: the peak at 6.42 ppm, related to the CH_2=, the peaks at 3.93 ppm and 4.11 ppm, relate to the =CHO. The complete vinyl ether double bond conversion was achieved after 10 min of irradiation compared to before irradiation (Fig. 2 top). The ^{1}H-NMR of the solvent, *n*-hexadecane, was recorded as a reference (Fig. S2†).

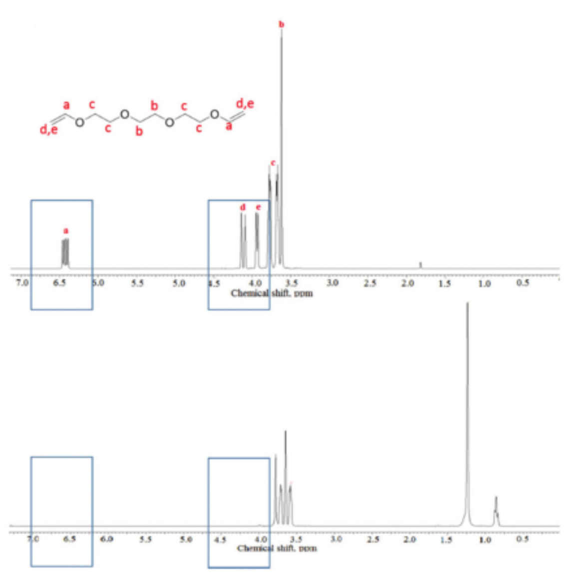

Fig. 2 ^{1}H-NMR of the polymer (bottom) produced through UV curing from DVE3 (top), note that the vinyl double bond peaks have disappeared leaving only the polymer backbone.

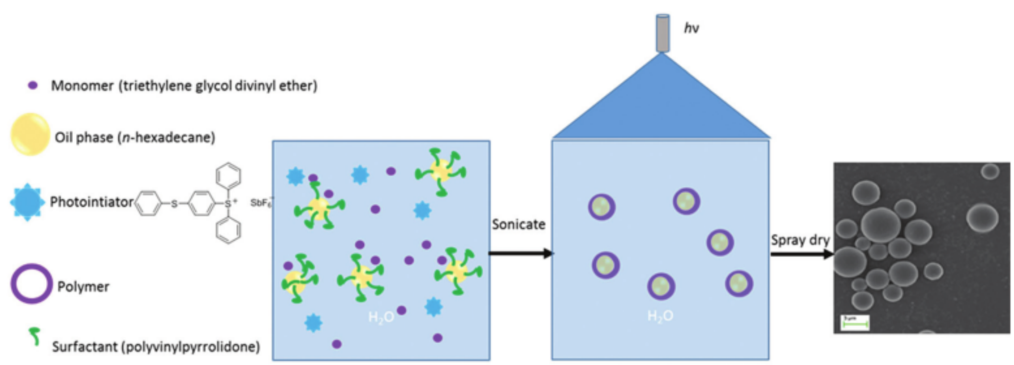

Fig. 1 Schematic detail of the reaction steps that produce macroparticles.

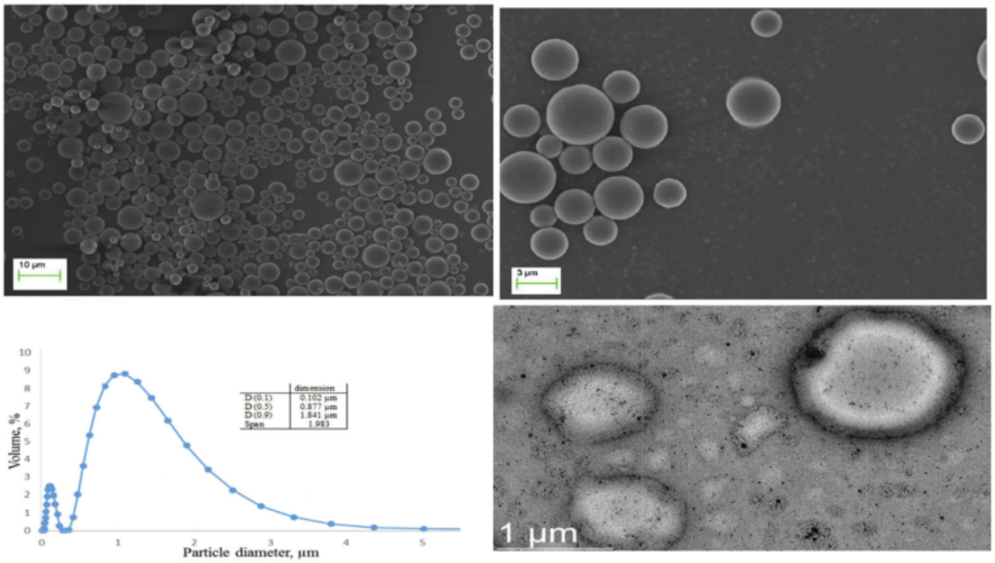

Fig. 3 (a) SEM image of the size dispersion of the microspheres (b) enlargement of representative sample, (c) DLS including size distribution table (d) TEM after impregnation with AgNPs showing the nanoparticle decoration of the polymer microcapsules.

The polymeric particles are approximately 1 µm. Particle size analyses were performed initially *via* laser diffraction in order to evaluate the average particle dimension achieved. This average size is consistent with the previous work reported,[10] and explained if we take into account the DVE3 monomer droplet is in contact with water, where chain transfer and inhibition reactions occur predominantly over polymerization at this interface. In the interfacial process the polymerization reactions occur at the oil–water interface. If the diameter of the oil droplet decreases, the ratio of the monomer surface area to volume *vs.* the water interface dramatically increases. The reaction at the water interface becomes increasingly significant as the droplet size decreases. It has been reported that, if the average diameter of the droplets falls below 1 µm, the side reactions dominate over propagation in the bulk of the droplets, and solid particles do not form. As a result, only larger particles can be formed under aqueous suspension cationic photopolymerization conditions. The volume percentage *vs.* average diameter of the polymeric particles are reported in Fig. 3c and the distribution parameters are collected in table (Fig. 3c inset).

Spherical particles with homogeneous distributions were obtained then spray dried prior to further characterisation through SEM and SAXS. A volumetric distribution calculated by using a software image from the SEM showed an average volumetric size distribution of approximately 1 µm, in agreement with the particle size measurements *via* light scattering. In Fig. 3a and b some selected SEM images of the synthesized particles are shown.

To further investigate the morphology of the microparticles supercritical carbon dioxide ($scCO_2$)[14] was employed to firstly generate silver nanoparticles (AgNPs) *in situ*; then the $scCO_2$ used to impregnate the microparticles with the AgNPs to provide further information about the composite particles by TEM and SAXS. Note that the lack of binding groups for the silver to adhere to means that the silver should be more uniformly dispersed within the matrix.[15]

By fitting the SAXS curve the radius of gyration, RG, value of 501 nm was obtained. The average diameter of the polymeric particles is calculated to be 1292 nm, using eqn (S1),† which is in good agreement with the Mastersizer measurements and SEM measurements. The Guinier plot obtained after SAXS analyses for the synthesized particles are reported in Fig. S3,† where ln of intensity I *vs.* q^2 is plotted (see ESI† experimental). By using the software Easy SAXS the probability density and distribution function (PDDF) curve for the polymer particles was obtained.

The shape of the PDDF curve is typical of a core–shell structure. The D_i = 78.1 nm, representing the inner diameter of the core–shell structure, and the D_0 = 1.335 µm representing the outer diameter of the core–shell, giving rise to a shell thickness of 0.628 µm. Further proof of the shell thickness can be seen by TEM when the AgNPs are present (Fig. 3d) showing that the AGNPs evenly distribute through the shell and cannot be seen inside the particles. Note that the size of the AgNPs by both SAXS and TEM was seen to be approximately 70 nm.

Conclusions

A novel way to synthesise hydrophilic microcapsules with a size of approximately 1–2 µm has been realised. The particles have low polydispersity and have been shown to maintain stability when impregnated with AgNPs using supercritical carbon dioxide; the addition of AgNPs could confer anti-microbial activity.[16]

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