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Ionic Hydrocarbon Surfactants for Emulsification and Dispersion Polymerization in Supercritical CO_2

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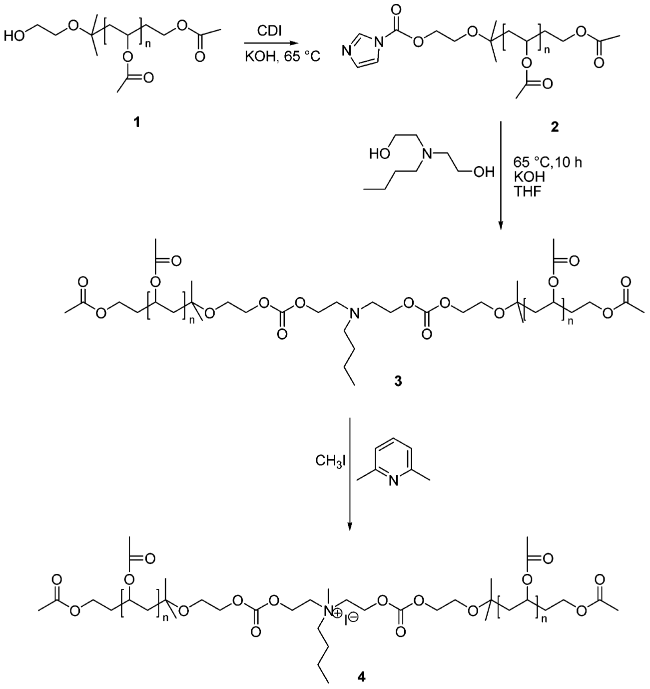
Supercritical carbon dioxide ($scCO_2$) has been promoted recently as a sustainable solvent because it is nontoxic, nonflammable, and naturally abundant.[1] In particular, $scCO_2$ has been shown to be a versatile solvent for polymer synthesis and processing.[2−5] A technical barrier to the wider use of $scCO_2$ is the lack of inexpensive CO_2-soluble (and preferably biodegradable) surfactants, ligands, and phase transfer agents. The majority of systems reported so far have been highly fluorine-substituted,[3,4] and the associated costs and low biodegradability may prohibit industrial-scale use in key applications. The discovery of inexpensive CO_2-soluble materials or "CO_2-philes" is therefore an important challenge.[6] Inexpensive poly(ether carbonate) (PEC) copolymers have been reported to be soluble in CO_2 under moderate conditions.[7,8] Similarly, sugar acetates are highly soluble and have been proposed as renewable CO_2-philes.[9] Such materials could, in principle, function as CO_2-philic building blocks for inexpensive ligands and surfactants, but this potential has not yet been realized and numerous practical difficulties remain. For example, CO_2 solubility does not in itself guarantee performance in the various applications of interest and specific designed molecular architectures may be required, as in the case of water-based surfactants.

Recently, we have demonstrated the use of end-functionalized poly(vinyl acetate) (PVAc) oligomers as a CO_2-philic building block.[10] Poly(vinyl acetate) is an inexpensive, high-tonnage bulk commodity polymer which, unlike most vinyl polymers, is moderately biodegradable and has been used in pharmaceutical excipient formulations. PVAc has also been shown to exhibit anomalously high solubility in CO_2 with respect to other vinyl hydrocarbon polymers,[11,12] although the polymer is soluble only at relatively low molecular weights under conditions of practical relevance (P < 300 bar, T < 100 °C). Previously, we synthesized a number of nonionic H_2O-soluble diblock and triblock PVAc-*b*-PEG surfactant architectures and showed that these surfactants could stabilize highly concentrated CO_2-in-water (C/W) emulsions.[10] Likewise, Fan et al. used a similar method to prepare a PVAc-based CO_2-soluble ionic surfactant,[13] and very recently, a twin-tail PVAc analogue of Aerosol-OT was shown to form water-in-CO_2 microemulsions.[14]

In this new study, a novel twin-tail quaternary ammonium hydrocarbon surfactant was synthesized using oligovinyl acetate (OVAc) as the CO_2-philic unit. It was then shown that this stabilizer is an emulsifier for water and an efficient stabilizer for the dispersion polymerization of pyrrole in $scCO_2$.

Scheme 1. Synthesis of OVAc-Based Ionic Hydrocarbon Surfactant



Our synthetic strategy was based on the preparation of monohydroxyl-functionalized PVAc by free-radical polymerization in the presence of a chain-transfer agent, 2-isopropoxyethanol (IPE).[15,16] The bulk PVAc-OH material was then fractionated by supercritical fluid extraction (CO_2 pressure 70−300 bar) to produce a series of end-functionalized OVAc-OH materials with number-average molecular weights, M_n, ranging from 800 to 4000 g/mol (see Supporting Information). The fractionated OVAc-OH samples exhibited relatively narrow molecular weight distributions (M_w/M_n) in the range 1.14−1.40. These fractions were shown to be soluble in CO_2 up to significant concentrations: for example, a fraction with M_n of 840 g/mol and M_w of 1048 g/mol was found to be soluble at 11.8 wt % in liquid CO_2 (25 °C) at a pressure of 100 bar.

The OVAc-OH species were modified by using carbonyldiimidazole (CDI) coupling, as exploited previously for the synthesis of dendrimers and hyperbranched polymers (Scheme 1).[17] First, the OVAc imidazolide ester, **2**, was produced by reaction of OVAc-OH with an excess of CDI. Next, the imidazolide ester was coupled with *n*-butyldiethanol amine to produce polymer **3**. Last, the tertiary amine functionality was converted to the quaternary ammonium cation by reaction with methyl iodide under mild conditions to produce a "twin-tail" ionic surfactant, **4** (M_n = 2280 g/mol, PDI = 1.25). The structure of **4** was confirmed by NMR and GPC (see Supporting Information). As such, surfactant **4** is designed to have CO_2-philic OVAc tails and a polar ionic headgroup either to interact with a dispersed polymer phase (in the case of dispersion polymerization) or to impart surface activity (in the case of emulsification).

Surfactant **4** was shown to be soluble in CO_2, and the cloud pressure point pressure was determined at 25 °C to be 4200 psi at a concentration of 0.6 wt %. White, milky water-in-CO_2 (W/C) emulsions could be formed with 0.6 wt % **4** (4400 psi, 25 °C, continuous 600 rpm stirring, H_2O:CO_2 = 1:4 v/v; Figure 1). However, in comparison with concentrated C/W emulsions formed using nonionic surfactants,[10] the W/C emulsions formed using **4** showed much poorer stability. Once stirring was ceased, the emulsions exhibited partial phase separation after ∼1 min

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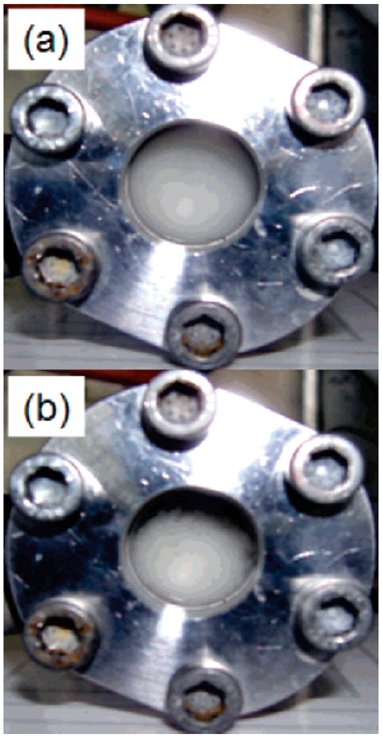

Figure 1. Water-in-CO_2 (W/C) emulsion prepared using PVAc-QA-PVAc ionic hydrocarbon surfactant **4** (0.06 g **4**, 2.0 mL of H_2O, 8 mL of CO_2, 600 rpm stirring, 20 °C, 4400 psi). (a) W/C emulsion formed during stirring. (b) Partial phase separation 1 min after stirring was ceased.

(Figure 1b), in contrast to the C/W emulsions[10] which were stable without stirring for >48 h. Conductivity measurements confirmed that W/C emulsions rather than C/W emulsions were formed with **4**. While long-term emulsion stability is a prerequisite for some applications, the preparation of transiently stable "breakable" W/C emulsions is of interest for applications such as phase-transfer catalysis where subsequent separation of the phases is of key importance.

Conducting polymer particles are of significant recent interest because of their potential in such as optoelectronic devices, electrochemical displays, electrode coatings, and sensors.[18−22] In particular, polypyrrole (PPy) has attracted much attention because of its good electrical conductivity, redox properties, and environmental stability.[23] Conducting polymer nanoparticles have prepared by surfactant stabilized dispersion polymerization.[24−26] Typically, these particles are 100−200 nm in diameter. Previously, polypyrrole[27−31] and other conducting polymers[32−35] have been synthesized using $scCO_2$ as a solvent or processing adjunct. Polypyrrole (PPyr) has been prepared using $scCO_2$ as precipitated aggregates and in fibrillar morphologies,[27] electrochemically as films,[28−30] and in composites.[35] There are no reports, however, on the preparation of well-defined spherical PPyr particles by such methods, and thus the dispersion polymerization of pyrrole in CO_2 was carried out using stabilizer **4** under a variety of reaction conditions (Table 1, entries 1−3). As a comparison, the polymerization was also carried out using methanol as the medium which is also a good solvent for PVAc and a nonsolvent for PPyr (Table 1, entries 4 + 5). In the first case (entry 1), a 10 cm^3 stainless steel view cell reactor was charged with pyrrole (0.5 mL) and stabilizer **4** (0.05 g). The reactor was then pressurized with CO_2 (45 °C, 100 ± 5 bar), and stirring was commenced (magnetic stir bar, 600 rpm). When all of the monomer and stabilizer were dissolved to form a single homogeneous phase, a controlled volume of $FeCl_3$/methanol solution was added to the vessel at a rate of 1 cm^3 min^{-1} using an HPLC pump at 150 bar. A homogeneous black dispersion was formed almost immediately (Supporting Information, Figure S5) with no clear evidence of bulk precipitation of the PPyr product. The CO_2 was vented 90 min after the addition of the $FeCl_3$. The product was recovered as a fine, free-flowing black powder which was dried by air. As isolated directly from the reactor, the particles showed a degree of physical aggregation because they were imbedded in a matrix of stabilizer **4** (Figure S6). It was found however that uniform, separated spherical PPy particles were formed upon washing and redispersing in MeOH, as evidenced by SEM imaging (Figure 2a). From the SEM images, the average particle size was in the range 200−1000 nm, which agrees well with the particle size distribution as determined by laser particle sizing (Figure S7) for dispersions in MeOH (average particle size = 295 nm; HALO LM10 Nano Particle Analysis System, NanoSight Limited, UK). By contrast, no uniform spherical particles were observed when the polymerization was carried out in the absence of **4** (Figure 2b), as observed previously by Armes and co-workers.[27] This confirms that the ionic stabilizer plays a vital role in preventing particle aggregation during synthesis.

Table 1. Reaction Conditions for Polymerization of Pyrrole

	pyrrole (mL)	surfactant **4** (g)	methanol (mL)	$FeCl_3$ (g)
1[a]	0.5	0.05	0.5[c]	1.164[c]
2[a]	0.5	0	0.5[c]	1.164[c]
3[a]	0.5[d]	0.05	0.5	1.164
4[b]	0.5	0.05	9.0	1.164[c]
5[b]	0.5	0.05	8.0	1.164[c]

[a] Synthesis carried out in $scCO_2$, 10 cm^3 reaction vessel, 2200 psi. [b] Reaction carried out using MeOH as the continuous phase. [c] Catalyst added slowly to reaction mixture as a MeOH solution. [d] Monomer added slowly to reaction mixture.

It was found that the order of addition of the reagents was important. Spherical particles could not be formed when the reverse addition method was used (entry 3; Figure S9), that is, when stabilizer **4**, $FeCl_3$, MeOH, and CO_2 were added to the view cell followed by slow injection of pyrrole monomer.

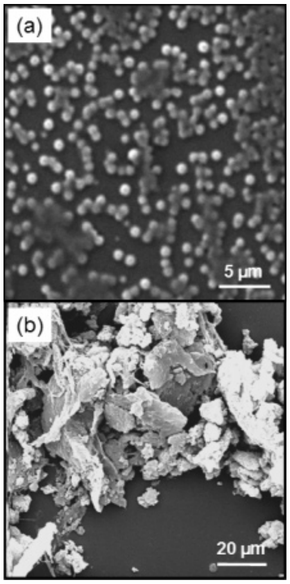

Figure 2. Electron micrographs of polypyrrole (PPyr) produced by polymerization in CO_2. (a) PPyr nanoparticles produced by dispersion polymerization in CO_2 in the presence of surfactant **4** (Table 1, entry 1). (b) PPyr produced in CO_2 in the absence of stabilizer **4**. Both samples were washed with MeOH prior to analysis by SEM.

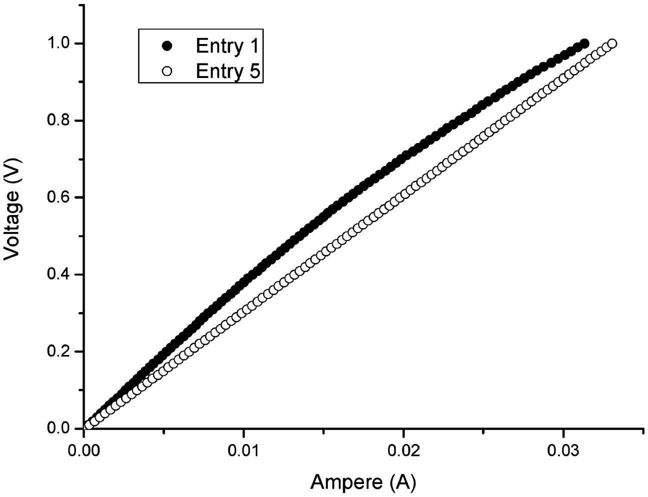

Figure 3. Plot of voltage vs current for PPyr produced in CO_2 (entry 1, filled symbols) and MeOH (entry 5, open symbols).

Similarly, attempts to carry out the dispersion polymerization using neat MeOH as continuous phase instead of CO_2 (entries 4 + 5) did not lead to the formation of uniform spherical PPyr nanoparticles but formed instead undefined precipitated products (Figures S10 + S11), suggesting that CO_2 is the better reaction medium in this case in terms of morphology control. By contrast, the sample prepared by dispersion polymerization in $scCO_2$ with stabilizer **4** (entry 1) exhibited a lower electrical conductivity (0.107 S/cm, Figure 3) in comparison with the sample prepared in methanol (0.152 S/cm; entry 5), possibly because the very different product morphologies lead to differences in the pressed-pellet conductivity measurement.

In conclusion, we have developed a novel ionic hydrocarbon surfactant which can be use as an emulsifier and as a stabilizer for dispersion polymerization in $scCO_2$. This is the first example of the use of a hydrocarbon surfactant for dispersion polymerization in CO_2. The significantly lower cost and enhanced biodegradability of such hydrocarbon stabilizers suggest that these materials may have uses in applications where the cost or environmental issues associated with fluorocarbon materials are prohibitive.

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Supporting Information Available: Experimental methods, GPC data, NMR data, and additional SEM and particle sizing. This material is available free of charge via the Internet at http://pubs.acs.org.

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