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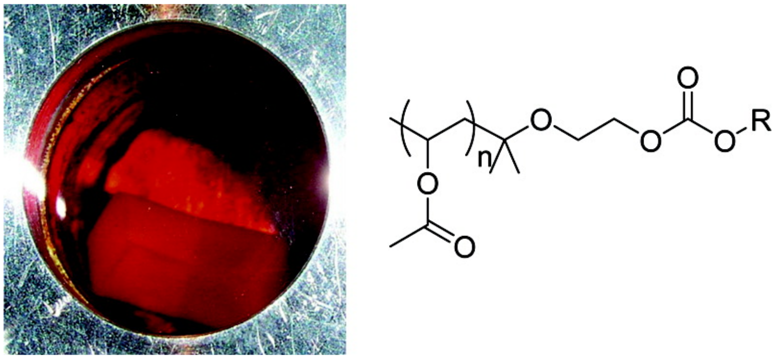

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Functional Oligo(vinyl acetate) CO_2-philes for Solubilization and Emulsification

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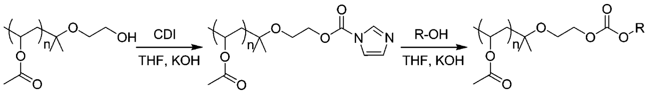
Supercritical carbon dioxide ($scCO_2$) is an inexpensive, nontoxic, and nonflammable medium for materials synthesis and processing[1] and is a potential replacement solvent for applications such as dry-cleaning, bioprocessing, lithography, and precision cleaning.[2] Carbon dioxide is a relatively weak solvent: important classes of materials which tend to exhibit low solubility in $scCO_2$ include polar biomolecules, pharmaceutical actives, and high-molecular weight polymers.[1−3] Such issues are not unique to CO_2—indeed, an enormous variety of surfactants and phase transfer agents have been developed to disperse poorly soluble molecules in water. A technical barrier to the use of $scCO_2$ is the lack of an equivalent range of inexpensive CO_2-soluble (and preferably biodegradable) surfactants, ligands, and phase transfer agents. The majority of systems reported thus far have been highly fluorine-substituted,[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.[5] Inexpensive poly(ether carbonate) (PEC) copolymers have been reported to be moderately soluble in CO_2.[6] Similarly, sugar acetates have been proposed as renewable CO_2-philes.[7] 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. Effective surfactants, in particular, tend to require specific asymmetric topologies such as diblock copolymers.[8] This in turn necessitates a flexible and robust synthetic methodology to produce well-defined architectures for specific applications.

In this study, we have used end-functionalized poly(vinyl acetate) oligomers (OVAc) as CO_2-philic building blocks. Poly(vinyl acetate) (PVAc) is an inexpensive, high-tonnage bulk-commodity polymer which, unlike most vinyl polymers, is moderately biodegradable and has been used in pharmaceutical excipient formulations.[9] PVAc has also been shown to exhibit anomalously high solubility in CO_2 with respect to other vinyl hydrocarbon polymers,[10] although the polymer is soluble only at relatively low molecular weights under conditions of practical relevance ($P < 300$ bar, $T < 100$ °C). PVAc has been used previously in CO_2-soluble fluorocarbon−hydrocarbon block copolymers[11] but as the CO_2-*phobic* block rather than as the CO_2-philic solubilizing functionality.

Our synthetic strategy is based on the preparation of monohydroxyl functionalized PVAc (Scheme 1) by free-radical polymerization in the presence of a chain-transfer agent, 2-isopropoxyethanol (IPE).[12] 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.

Scheme 1



These fractions were 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 soluble at 11.8 wt % in liquid CO_2 (25 °C) at a pressure of 100 bar (see Supporting Information). A "high throughput" solubility screen established that the maximum (kinetic) solubility in CO_2 was observed for the underivatized monohydroxyl materials at a M_w of around 2000 g/mol.[13]

We have utilized carbonyldiimidazole (CDI) coupling, as exploited previously for the synthesis of dendrimers and hyperbranched polymers[14] (Scheme 1), to form functional CO_2-philic architectures by end-group modification.

This route has a number of advantages. First, the OVAc-imidazolide intermediate can be isolated, purified, and then coupled with a wide range of alcohols (or amines) to produce a variety of structures. Second, the route introduces a carbonate linkage that may further enhance CO_2 solubility[6] and could also improve the biodegradability of the resulting materials.

To illustrate the use of OVAc as a solubilizing group, an organic dye, Disperse Red 19 (DR19), was functionalized with OVAc (M_n = 1070 g/mol, M_w = 1430 g/mol) to produce **1** (Figure 1). The stoichiometry of the reaction was controlled such that one OVAc chain was attached to each DR19 molecule, as confirmed by GPC and ^1H NMR. DR19 itself had negligible solubility in CO_2 up to pressures of 300 bar/25 °C (no color was observed in the CO_2 phase).[15] By contrast, the functionalized dye, **1**, was found to be soluble in CO_2 (100−200 bar) at least up to concentrations of around 1 wt % (Figure 1). This suggests that fractionated OVAc has potential as a less expensive and more biodegradable replacement for the highly fluorinated materials used previously to solubilize species such as dyes, catalysts, proteins, and nanoparticles in CO_2.[4,16]

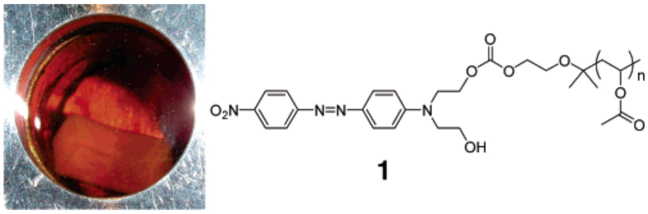


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Figure 1. Photograph showing the dissolution of an OVAc-functionalized dye, **1**, in CO_2 (200 bar, 20 °C, 0.77 wt %).

Another important area in $scCO_2$ technology is the formation of water-in-CO_2 (W/C) and CO_2-in-water (C/W) emulsions and microemulsions.[16,17] The same CDI route was used to couple OVAc with poly(ethylene glycol) monomethyl ethers (HO-PEG-OMe) and

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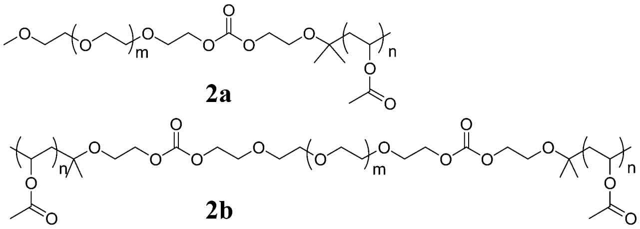

Figure 2. Structures of CO_2-philic surfactants for C/W emulsion formation: OVAc−*b*-PEG diblock polymer (**2a**) and OVAc−*b*-PEG−*b*-OVAc triblock polymer (**2b**).

poly(ethylene glycol) diols (PEG) to produce diblock (Figure 2, **2a**) and triblock (**2b**) copolymers, respectively.

The solubility behavior of these materials can be controlled by varying the overall molecular weight and the molar ratio of OVAc to PEG. It was found that both CO_2-soluble and H_2O-soluble structures can be synthesized in this way. A range of H_2O-soluble diblock and triblock architectures was produced, and it was found that both structures could stabilize highly concentrated C/W emulsions (Figure 3).

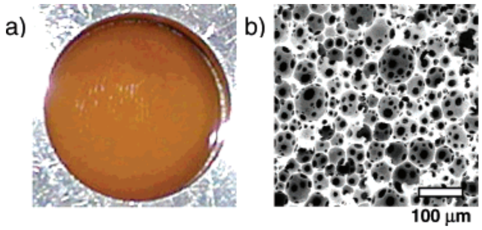

Figure 3. (a) Photograph of highly concentrated CO_2-in-water (C/W) emulsion (97% v/v CO_2) stabilized by a triblock copolymer surfactant, **2b** (200 bar, 20 °C, 1.6 wt % **2b** based on total emulsion, $M_n = 7030$ g/mol, $M_w = 8270$ g/mol, $m \approx 60$, $n \approx 30$). A water-soluble dye, methyl orange, was included in the aqueous phase. (b) Emulsion-templated poly(acrylamide) material synthesized by polymerization of a concentrated C/W emulsion (90% v/v CO_2) stabilized with a diblock surfactant **2a** ($M_n = 3020$ g/mol, $M_w = 3300$ g/mol, $m \approx 60$, $n \approx 9$).

For example, an OVAc−*b*-PEG−*b*-OVAc triblock surfactant (type **2b**, $m \approx 60$, $n \approx 30$) was found to emulsify up to 97% v/v CO_2 in water and to form a uniform, opaque emulsion which was stable for at least 48 h (Figure 3a).[18] The remarkable stability of these emulsions was further demonstrated by polymerization of the continuous aqueous phase to give porous, cross-linked poly(acrylamide) (PAM) materials, as produced previously from C/W emulsions stabilized with perfluoropolyether (PFPE) ammonium carboxylate surfactants.[19] Figure 3b shows an electron micrograph of such a material formed from a 90% v/v C/W emulsion stabilized using an OVAc−*b*-PEG diblock copolymer surfactant, **2a**. The structure demonstrates unambiguously that the emulsion was C/W as opposed to W/C. The macropore volume in this material was determined by mercury porosimetry to be 8.7 cm^3/g (bulk density $= 0.057$ g/cm^3, median pore diameter $= 10.85$ μm). This material was found to be more porous than any produced using PFPE surfactants,[19] which can be attributed to the very concentrated and stable C/W emulsion from which it was formed. By contrast, it was not possible to generate stable 90% v/v C/W emulsions using PFPE in the presence of acrylamide. Similar results were obtained with water-soluble OVAc−*b*-PEG−*b*-OVAc triblocks. This suggests that OVAc-based diblock and triblock surfactants are functionally superior to perfluorinated materials for this application, in addition to being much less expensive and potentially biodegradable.

In conclusion, we present here a simple and generic method for producing inexpensive, functional hydrocarbon CO_2-philes for solubilization, emulsification, and related applications. We have shown that these structures can outperform perfluorinated analogues in specific applications.[19] This synthetic route should allow the design of a wide range of related CO_2-philic materials.

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Supporting Information Available: Experimental preparations for materials, GPC data for SCF fractionation, and mercury intrusion porosimetry data for porous structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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