

## Dendritic Core–Shell Macromolecules Soluble in Supercritical Carbon Dioxide

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Supercritical carbon dioxide has found strong interest as a reaction medium recently.<sup>1,2</sup> As an alternative to organic solvents, compressed carbon dioxide is toxicologically harmless, nonflammable, inexpensive, and environmentally benign.<sup>3</sup> Its accessible critical temperature and pressure ( $T_c = 31\text{ }^\circ\text{C}$ ,  $P_c = 7.38\text{ MPa}$ ,  $\rho_c = 0.468\text{ g cm}^{-3}$ )<sup>4</sup> and the possibility of tuning the solvent-specific properties between the ones of liquid and gas are very attractive. However, the low solubility of many polar or ionic molecules, even at dense liquid or supercritical conditions,<sup>5</sup> is problematic. For this reason, low-molecular-weight and particularly polymeric surfactants have been studied. A limited, but increasing, number of surfactant types are known to date.<sup>6</sup>

In the general context of micellar structures, the concept of unimolecular micelles is attractive and has found strong interest. By contrast to unimolecular micelles, micelles formed by aggregation of a larger number of traditional surfactant molecules vary strongly in their aggregation number and thus properties depending on their concentration and the solute employed. Amphiphilic molecules with a highly branched dendritic polar scaffold as a core and an apolar periphery which provides solubility in a given medium have been demonstrated to form unimolecular micelles in organic solvents.<sup>7–11</sup> Such molecules can host otherwise insoluble organic molecules (e.g., dyes) or metal ions and serve as a template for the synthesis of metal nanoparticles which they also stabilize effectively.<sup>9–13</sup>

In view of the aforementioned considerations on carbon dioxide as a solvent, the report of a soluble dendrimer that also behaves as a unimolecular micelle was met with strong interest.<sup>14</sup> Despite a considerable interest also in the solubility of polymers in general in compressed carbon dioxide,<sup>15</sup> the only examples of soluble dendritic polymers reported to date are restricted to a perfluorooligoether- and perfluoroalkyl-modified poly(propylene imine) dendrimer (and even for these cases the solubility has not been quantified).<sup>14,16</sup> We now report on the synthesis of dendritic polymers with different types of solubilizing shells and on systematic studies of their solubility in compressed  $\text{CO}_2$ .

As a dendritic scaffold, hyperbranched poly(ethylene imine) (PEI) was employed. By contrast to the multistep synthesis of dendrimers,<sup>17</sup> hyperbranched polymers can be readily accessible.<sup>18</sup> A hyperbranched poly(ethylene imine) with  $M_w$  5000  $\text{g mol}^{-1}$  ( $M_w/M_n = 1.1$ ) with a degree of branching (DB) of ca.

Scheme 1. Synthesis of the Core–Shell Macromolecules

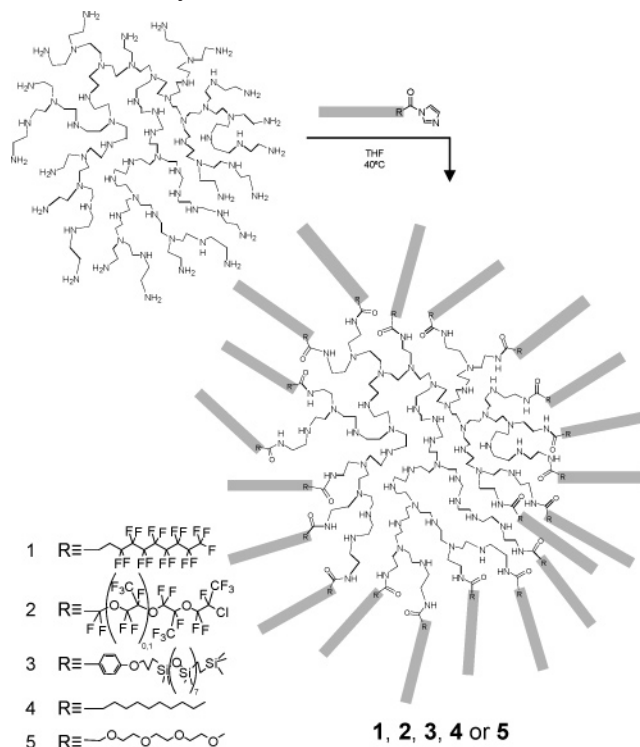


Table 1. *B* Data and Solubility Values in Supercritical  $\text{CO}_2$  at  $40\text{ }^\circ\text{C}$  and  $\rho = 0.88\text{ g cm}^{-3}$  (25 MPa)

|   | type of core  | <i>B</i> | solubility (wt %) |
|---|---------------|----------|-------------------|
| 1 | hyperbranched | 3.2      | 0.3               |
| 2 | hyperbranched | 3.2      | 0.6               |
| 3 | hyperbranched | 5.9      | 1.0               |
| 4 | hyperbranched | 1.6      | <0.001            |
| 5 | hyperbranched | 1.4      | <0.001            |
| 6 | dendrimer     | 4.6      | 0.5               |

60%<sup>8</sup> was utilized (linear polymer DB = 0%; perfect dendrimer DB = 100%).<sup>19</sup>

Different  $\text{CO}_2$ -philic moieties<sup>20–23</sup> were introduced by amidation. By comparison to a poly(propylene imine) dendrimer (DAB), the PEI contains not only tertiary amine branching units and primary amine ends of branches but also secondary amine linear units. By coupling of carbonyldiimidazol (CDI)-activated carboxylic acids, the  $\text{CO}_2$ -philic moieties were introduced selectively at the primary amine groups (Scheme 1).<sup>8,24</sup>  $^{13}\text{C}$  NMR spectroscopy clearly showed complete amidation of primary amine end groups and the absence of unreacted acid derivatives ( $\text{CH}_2\text{CH}_2\text{NH}_2$  of PEI and acid carbonyl signals were absent; amide carbonyl resonance peak appeared).<sup>8</sup>

In addition to the PEI-amide with the aforementioned perfluoroalkyl (1) and perfluorooligoether moieties (2), polysiloxane (3), non-fluorinated alkyl (4), and oligoethylene glycol (5) peripheries were prepared. For comparison, the perfluoroalkyl-modified DAB dendrimer (6) analogue of 1 was prepared. The DAB-32-Am used as a core ( $M$  3514  $\text{g mol}^{-1}$ ) possesses 32 primary amine branch ends, which is similar to the average 35 primary amine branch ends of the PEI.

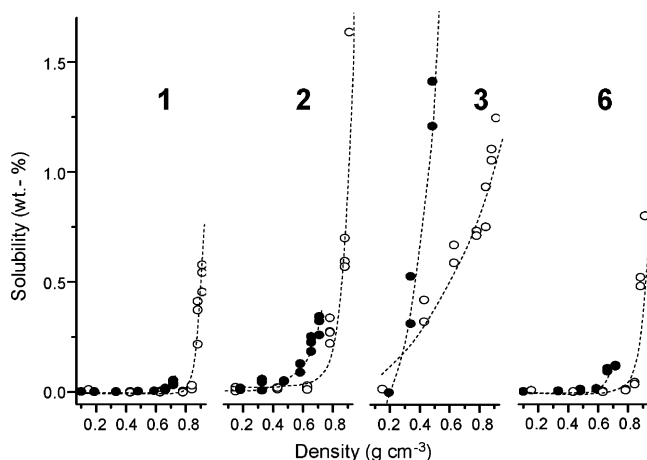
For a comparison and interpretation of the solubility properties of 1–6, the  $\text{CO}_2$ -philic/ $\text{CO}_2$ -phobic balance  $B$ ,<sup>25</sup> that is, the mass ratio of shell/core, is a useful parameter (Table 1). Note that the aforementioned dendrimers DAB-32-NHCOC<sub>19</sub>O<sub>5</sub>F<sub>41</sub> and

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**Figure 1.** Evolution of the solubility with the density at 40 °C (○) and 100 °C (●).

DAB-16-NHCOC<sub>7</sub>F<sub>15</sub> previously reported to be CO<sub>2</sub>-soluble<sup>14,16</sup> possess high *B* values (9.5 and 13, respectively).

Infrared spectroscopy was employed for quantitative solubility determination (cf. Supporting Information).<sup>26</sup> The molar extinction coefficients ( $\epsilon$ ) of characteristic vibration bands (at least two) were calculated from FT-IR spectra collected at high CO<sub>2</sub> density with a small amount of the compounds studied. Then the solubility was measured at several pressures along two isotherms (40 and 100 °C) by integration of the vibration bands from FT-IR data. This assumes  $\epsilon$  to be independent of pressure and temperature, which is reasonable as no significant band shift was noticed. Figure 1 depicts the solubility vs CO<sub>2</sub> density for **1**, **2**, **3**, and **6**. Solubilities at 40 °C and  $\rho = 0.88 \text{ g cm}^{-3}$  are also given in Table 1. Two general trends emerge: solubility increases with the density, and at a given density, solubility increases with temperature. Even at high CO<sub>2</sub> density, the alkyl-substituted **4** and the oligoethylene oxide-substituted **5** were insoluble.<sup>27</sup>

Comparing **1** and **2**, the perfluorooligoether shell results in a higher solubility than the perfluoroalkyl shell at a similar *B*. The polysiloxane-substituted compound **3** possesses a similar solubility as the fluorinated **1** and **2** at high CO<sub>2</sub> density. Remarkably, it also displays a substantial solubility at low carbon dioxide densities and pressures.

Comparing **1** with a hyperbranched PEI core with the corresponding dendrimer **6**, very similar total solubilities and also dependence of solubilities on CO<sub>2</sub> density are observed.

In summary, perfluoroalkyl-, perfluorooligoether-, and polysiloxane-substituted hyperbranched PEIs possess a significant solubility in compressed CO<sub>2</sub>. The latter is of particular interest, as the high cost of fluorinated compounds is an obstacle to broader applications of CO<sub>2</sub> as a solvent, and also polysiloxanes are harmless to the environment. The polymer topology of the dendritic core, hyperbranched or dendrimer, does not affect the solubility behavior. These findings are of interest for the development of easily accessible, economical, and environmentally benign unimolecular micelle carriers in CO<sub>2</sub> as a solvent.

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**Supporting Information Available:** Experimental procedures, characterization data, and solubility measurements details. This material is available free of charge via Internet at <http://pubs.acs.org>.

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