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Hydrophobic and oleophobic surface modification using fluorinated bis-urea and bis-amide gelators

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ABSTRACT

A series of fluorinated bis-urea and bis-amide derivatives were synthesized from fluorinated amines and explored as surface modifiers for nonwoven substrates. A majority of these derivatives showed excellent gelation properties both in organic solvents as well as in supercritical carbon dioxide ($scCO_2$) at concentrations ranging from 0.3 to 3 wt%. Gelation in the presence of a nonwoven substrate led to a gel-impregnated surface, which upon drying produced a composite with porous microstructure morphology on the surface. The composites thus produced showed high water and hexadecane contact angles, indicative of excellent hydrophobic and lyophobic properties. The superior hydrophobic and oleophobic behaviors observed in these composites are attributed to a combination of increased surface roughness and the presence of fluoroalkyl functionalities in the gelator backbone.

1. Introduction

Organogelation is a much-explored subject in the field of supramolecular chemistry, which involves the interplay of inter- and intramolecular forces between small molecules in solution that ultimately change the macroscopic properties of the system. The self-assembly of small functional moieties into supramolecular structures could be a powerful approach towards the design of new materials and nanoscale devices [1–6]. Various non-covalent interactions such as hydrogen bonding, π–π stacking, hydrophobic interactions, and metal coordination (or a combination thereof) are involved in the formation and stabilization of gelator self-assemblies. Gelation occurs by the encapsulation of solvents in the three dimensional network structures formed from the self-assembly of molecules [3]. In general, the non-covalent forces are reversible and weak compared to covalent bonds. For this reason, a greater number of such interactions are required to form strong associations. The establishment of these interactions may often be promoted by the architecture of the molecule, such as one or more heteroatom-hydrogen bonds, aromatic rings, unsaturation, bidentate metal coordination sites, and favorable packing geometries.

In general, each molecule of an organogelator can establish several types of physical interaction with a neighboring molecule. The intermolecular hydrogen bonds or π–π interactions usually facilitate the growth of linear, elongated aggregates in gels, leading to microscale morphologies consisting of fibers or web-like structures [3]. The microstructure morphology of the dried gel (xerogel) could be of interest in altering surface morphology and hence the low surface energies desired for fabricating surfaces that show superhydrophobic behavior [7–8]. Surfaces on which the contact angle of water exceeds 150°, and show low contact angle hysteresis, are described as superhydrophobic or ultrahydrophobic [9–11]. Such surfaces repel water like a lotus leaf and are also considered 'self-cleaning' since any surface contamination is removed by water as the droplets roll across the surface [12–14]. The self-cleaning ability of these surfaces is essentially attributed to the two-tier micro and nano roughness present on the surface.

Recent independent reports by Zhou et al. [15] and Yamanaka et al. [16] explored the ability of organogelators to form porous xerogels that show superhydrophobic behavior. The morphology is further controlled by suitable gelling solvents as well as concentration and temperature effects. Incorporation of low surface energy functionalities such as fluorinated groups in the gelator framework could further lower the surface energy and

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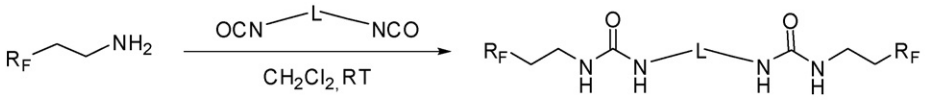


1) $R_F = C_6F_{13}$ L = $-(CH_2)_6-$

2) $R_F = C_4F_9$ L = $-(CH_2)_6-$

3) $R_F = C_6F_{13}$ L = $-(CH_2)_8-$

4) $R_F = C_6F_{13}$ L = 2,4-tolylene

5) $R_F = C_6F_{13}$ L = $-CH_2CH(CO_2CH_3)(CH_2)_3-$

6) $R_F = C_4F_9$ L = $-CH_2CH(CO_2CH_3)(CH_2)_3-$

7) $R_F = C_6F_{13}CH_2CH_2S$ L = $-(CH_2)_6-$

8) $R_F = C_4F_9CH_2CH_2S$ L = $-(CH_2)_6-$

Scheme 1. Preparation of fluorinated bis-urea gelators.

provide oleophobic properties. Herein, we discuss the design and synthesis of novel fluorinated gelators for organic solvents and supercritical carbon dioxide ($scCO_2$). Furthermore, we describe their potential use in fabricating low surface energy surfaces that show superior hydrophophobic and lyophobic properties.

2. Results and discussion

2.1. Fluorinated bis-ureas and bis-amides

Bis-urea derivatives are exceptionally well suited candidates for the design of low molecular weight gelators owing to their rigidity, strength and ability to form highly directional hydrogen bonds [17]. Zhou and co-workers demonstrated that a xerogel prepared from a novel tripodal gelator functionalized by three urea and three azobenzene moieties grafted with three long alkyl chains showed hydrophobic properties owing to the 'cabbage-like' surface morphology [15]. To create extremely low surface energy surfaces, we explored the surface modification of nonwoven substrates using low molecular weight and structurally simple fluorinated bis-urea gelators. Fluorinated bis-urea derivatives were synthesized by the reaction of various commercially available diisocyanates and fluorinated amines (compounds **1**–**8**, Scheme 1). The resulting bis-ureas were white crystalline solids and showed gelation properties in methylene chloride during their isolation.

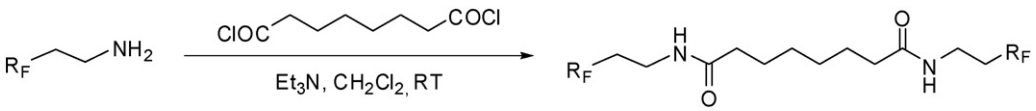
We also considered investigating the corresponding fluorinated bis-amide derivatives, which were expected to show gelation behavior in organic solvents via directional hydrogen bonds. Four fluorinated bis-amides were synthesized as white crystalline solids by the reaction of suberoyl chloride with fluorinated amines (compounds **9**–**12**, Scheme 2).

2.2. Gelation in organic solvents

We then examined fluorinated bis-urea and bis-amide derivatives for their gelation behavior in various organic solvents and determined the minimum gelation concentration for a given solvent. A methodology was developed for matching a solvent system with specific gelators to allow efficient gel formation. In general, a gelator that is too soluble will dissolve without forming a gel, even at high concentrations. If the gelator is not soluble enough, it may dissolve at high temperature, but precipitate again as the temperature is lowered. Ideally, the organogelators should dissolve in a solvent at a temperature close to its boiling point and assemble into a network upon cooling.

In a typical screening experiment, 1–4 wt% slurries of the organogelators in various solvents were prepared and heated with stirring at a temperature close to the boiling point of the solvent to induce dissolution. Gelation occurred upon cooling, as was evident by the formation of a translucent-to-opaque appearance without the formation of solid crystals and/or a significant increase in viscosity. We found that most of the new fluorinated bis-ureas and bis-amides gelled a wide spectrum of organic solvents in remarkably low concentrations ranging from 0.5 to 3 wt%.

Compounds **1**, **7** and **8** gelled a variety of the organic solvents (polar, non-polar, protic, and aprotic) and are aptly termed 'universal organogelators'. They produced stable gels at RT with typical gelator concentrations of 1–2 wt%. However, these gelators and the other bis-ureas and bis-amides were insoluble in aliphatic hydrocarbons even at concentrations <0.5 wt%. The results of gelation of compounds **1**, **7** and **8** are summarized in Table 1. Ureas **2**–**6** and amides **9**–**12** gelled rather more selectively in a few organic solvents. The results of gelation of these compounds are summarized in Table 2.



9) $R_F = C_6F_{13}$

10) $R_F = C_4F_9$

11) $R_F = C_6F_{13}CH_2CH_2S$

12) $R_F = C_4F_9CH_2CH_2S$

Scheme 2. Preparation of fluorinated bis-amide derivatives.