Journal of Fluorine Chemistry 130 (2009) 410–417

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

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

Anilkumar Raghavanpillai *, Stefan Reinartz, Keith W. Hutchenson

DuPont Central Research & Development, Experimental Station, Wilmington, DE 19880, United States

ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 20 January 2009
Accepted 21 January 2009
Available online 31 January 2009

Keywords:
Fluorinated amine
Fluorinated bis-urea
Fluorinated bis-amide
Organogelator
Xerogel
Nonwoven
Supercritical CO_2
Superhydrophobic
Oleophobic

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.

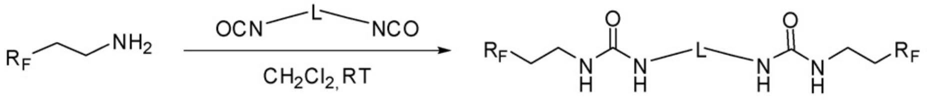
In general, each molecule of an organogelator can establish several types of physical interaction with a neighboring molecule. The intermolecular hydrogen bonds or π–π interactions usually facilitate the growth of linear, elongated aggregates in gels, leading to microscale morphologies consisting of 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

---

* Corresponding author. Tel.: +1 302 695 6846; fax: +1 302 695 2112.
E-mail address: anilkumar.raghavanpillai@usa.dupont.com (A. Raghavanpillai).

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2009.01.006



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.

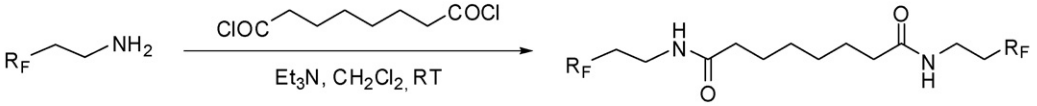
We also considered investigating the corresponding fluorinated bis-amide derivatives, which were expected to show gelation behavior in organic solvents via directional hydrogen bonds. Four fluorinated bis-amides were synthesized as white crystalline solids by the reaction of suberoyl chloride with fluorinated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

Table 1
Gelation characteristics for bis-ureas gelators **1**, **7** and **8**.

Solvent	Gelator (wt%)		
	1	**7**	**8**
Toluene	Hazy (1)	Hazy (2)	Hazy (2)
Xylene	Hazy (1)	Hazy (1.5)	Hazy (2)
Chloroform	Hazy (3)	Precipitate (2)	Partial (2)
THF	Transparent (1)	Hazy (2)	Opaque (2.5)
Acetone	Transparent (1)	Opaque (2)	Opaque (3)
Acetonitrile	Hazy (1)	Opaque (2)	Opaque (2)
Ethyl acetate	Transparent (1)	Partial (2)	Hazy (3)
DMF	Transparent (1)	Transparent (1)	Transparent (2)
DMSO	Opaque (1)	Transparent (1)	Transparent (2)
Dimethyl acetamide	Transparent (2)	Transparent (1)	Partial (2)
N-methylpyrolidone	Hazy (1)	Partial (1.5)	Clear Solution (2)
Pyridine	Hazy (1)	Partial (1.5)	Hazy (2)
n-Butanol	Transparent (1)	Transparent (1.5)	Hazy (2)
Isopropanol	Transparent (1)	Transparent (1.5)	Hazy (2)
Methanol	Hazy (1)	Opaque (1.5)	Transparent (4)
Ethanol	Transparent (2)	Hazy (1.5)	Hazy (3)

[†] Number in parenthesis indicates minimum gel concentration (wt%). Hazy: solid gel partially transparent; transparent: solid gel completely transparent; opaque: solid gel, not transparent; partial: solid or semi-moving gel that has some free flowing liquid in it; precipitate: more like a precipitate than a gel.

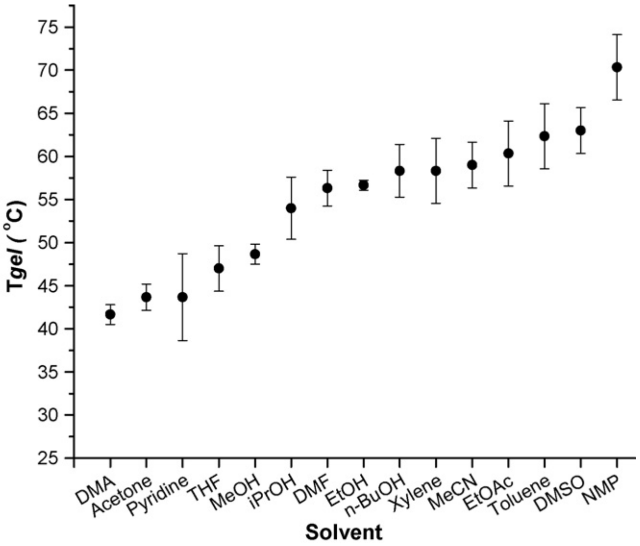


Fig. 1. Melting temperature (T_{gel}) of bis-urea gelator **1** in gelling solvents.

The gels obtained by gelation of bis-ureas and bis-amides were stable at room temperature for many days. We determined the melting temperature (T_{gel}) of gels obtained from bis-urea gelator **1** in different solvents (entries in the Table 1) by a method similar to the dropping ball method described in the literature [18–19]. Fig. 1 plots the melting temperature of the gels vs. the corresponding gelling solvents. All gels of **1** showed excellent thermal stability up to 40 °C. The majority of gels of **1** were stable up to the 55–60 °C range. The gel of **1** from NMP showed the highest observed thermal stability (71 °C), whereas the corresponding gel from DMA was the least thermally stable (42 °C).

2.3. Gelation in $scCO_2$

The success of these fluorinated bis-ureas to gel a large number of organic solvents prompted us to attempt their gelation ability in $scCO_2$. Carbon dioxide is a potentially attractive solvent for chemical processes because it is readily abundant, environmentally benign, nontoxic, nonflammable, inexpensive, and it is suitable for use as a supercritical fluid solvent at relatively moderate temperatures [20]. Carbon dioxide is considered a green alternative to common organic solvents in a variety of industrial chemical processes such as extractions [21], polymerizations [22–25], and organic reactions and catalysis [20]. A particular advantage of CO_2 gelation is that the solvent can be readily removed after gel formation by slowly venting the carbon dioxide [23,26]. In addition, $scCO_2$ is an attractive medium for preparing composites from organogelators because the solvent and transport properties of the supercritical fluid solution (e.g., the solution density) can be varied appreciably and continuously with relatively minor changes in temperature or pressure. Thus, the solvent environment can be optimized for a specific gelation application by tuning the various density-dependent fluid properties.

Table 2
Gelation characteristics for bis-urea and bis-amide gelators.

Compound	Gelation conditions		Appearance[†]
	wt% gelator	Solvent	
2	2–3	Methanol, n-butanol	Partial/precipitate
	1–2	Toluene, THF, acetone, DMF, DMSO	Clear solution
3	2	DMSO	Partial
4	2.5	Acetonitrile	Partial
	1–2	Ethanol, acetone, DMF, DMSO, THF, ethyl acetate	Clear solution
5	2	Acetonitrile	Transparent
	2	Toluene	Hazy
6	2	DMSO	Partial
	2	Toluene, ethanol, acetone, acetonitrile, THF, ethyl acetate	Cloudy solution
9	1–2	DMF	Transparent
	2	DMSO	Opaque
10	2	CH_2Cl_2	Opaque
11	1	DMSO	Opaque
	2	DMF	Hazy
12	3	CH_2Cl_2	Partial

[†] Same meaning as described for Table 1.

Compounds that form self-assembled structures could be useful for surface modifications as described previously for gelators in organic solvents [15–16] and fluorinated dendrons in CO_2 [27]. In addition, such compounds could be useful as viscosity modifiers for CO_2. For example, CO_2 is used extensively as a flooding agent for enhanced oil recovery from underground formations [28,29]. Various additives have been used to increase the viscosity of CO_2 in an attempt to improve oil recovery efficiency and production rates by more closely aligning the mobilities of the CO_2 and oil in the reservoir [30]. There are many reports on new gelators for CO_2, and one primary criterion for their design is incorporation of CO_2-philic functional moieties such as long chain fluoroalkyl groups in the molecular design [31–32]. The fluorinated bis-urea and bis-amide compounds described above could be advantageous as CO_2 gelators since they comprise shorter chain fluoroalkyl functionalities and are relatively easy to synthesize.

We examined the gelation of compounds **1**, **5**, **7**, **8**, **9**, and **10** in $scCO_2$ with a gelator concentration of 0.3–0.7 wt% at moderate temperatures (70–100 °C) and elevated pressures (260–350 bar). The best gelation conditions of these various bis-urea and bis-amide gelators in CO_2 are summarized in Table 3.

2.4. Surface modification of nonwoven supports in organic solvents

We next explored whether the gelators described above could be used for creating particular surface effects on porous or solid

Table 3
Gelation conditions for bis-ureas and bis-amides in $scCO_2$.

Compound	Gelation conditions in $scCO_2$		
	wt% gelator[†]	Temperature (°C)	Pressure, bar (MPa)
1	0.44	69	346 (34.6)
5	0.48	68	274 (27.4)
7	0.73	103	307 (30.7)
8	0.49	100	351 (35.1)
9	0.37	68	257 (25.7)
10	0.32	68	259 (25.9)

[†] Overall gelator concentration in CO_2 in the view cell. The actual gelator solubility in CO_2 was generally less than this concentration at the indicated conditions.

substrates. The gelators self-assemble into fiber-like morphologies in solution, which grow sufficiently long and become entangled with one another to form a gel with their solvent medium. In the presence of a solid or fibrous substrate, the gelation occurs on the surface of the substrate, creating a composite with an altered surface topology. Removal of the solvent from the gel composite leaves behind a network of assembled gelator fibers on the substrate, thus producing a composite surface with high surface area and roughness which are desired for superior hydrophobic/oleophobic behavior.

The preparation of a thermally reversible organogelator on solid supports (nonwovens) was accomplished by different methods. In one of the methods (gel-impregnation in the presence of substrate), the gelator in a preferred solvent was pre-heated in the presence of a porous support to provide a homogeneous solution, which was then cooled to room temperature. In another method (treatment of pre-formed gel on a substrate), a gel obtained by cooling a gelator solution in a preferred solvent was spread on a substrate by a mechanical device. Drying (i.e., removing the solvent) the treated substrate leaves behind a microstructured xerogel on the solid or fibrous support.

Bis-urea gelators that showed excellent gelation properties (**1**, **7** and **8**) were chosen and gel-impregnated on commercially available nonwoven supports (Tyvek® polyethylene nonwoven fabric and Kolon® polyester fabric) in organic solvents. These samples were dried in a vacuum oven at room temperature to produce a composite of xerogel on the substrate. The surfaces of the composites were characterized by scanning electron microscopy and showed a porous xerogel comprised of fibrous structures ranging from 50 nm to about 500 nm in effective average fiber diameters as determined with electron microscopy. Bis-urea gelator **1** was impregnated on Tyvek® and Kolon® fabric in acetone, and dried composites were analyzed by SEM. Fig. 2 shows SEMs of the composite network structures of the Tyvek® fabric surface treated with gelator **1** at 2000× and 10,000× magnifications with an average fiber diameter of 140 nm. The larger fibers in Fig. 2 are the nonwoven support, and the smaller fibers are representative of the xerogel network. Gelators **7** and **8** were similarly impregnated on nonwovens from a solution of methanol or n-butanol and dried to obtain the treated composites. Fig. 3 shows SEMs of the composite network structures of the Kolon® fabric surface treated with gelator **7** at 2000× and 5000× magnifications with an average fiber diameter of 120 nm.

Table 4
Water and hexadecane contact angles of treated nonwoven composites prepared via gelation in organic solvents.

Example	Contact angle[a]			
	Water		Hexadecane	
	Adv CA	Rec CA	Adv CA	Rec CA
Untreated Tyvek®	108 ± 1	78 ± 1	abs	abs
Untreated Kolon®	115 ± 4	85 ± 4	abs	abs
1 on Tyvek®	152 ± 5	122 ± 5	89 ± 4	50 ± 5
1 on Kolon®	155 ± 2	132 ± 3	103 ± 4	54 ± 4
7 on Tyvek®	136 ± 4	100 ± 5	99 ± 3	53 ± 3
7 on Kolon®	149 ± 4	106 ± 3	110 ± 4	58 ± 3
8 on Tyvek®	127 ± 3	84 ± 3	76 ± 4	42 ± 3
8 on Kolon®	130 ± 4	110 ± 4	48 ± 3	16 ± 2

[a] Average of 3 runs at different positions on each sample; abs = completely absorbed into the fabric.

The treated surfaces were evaluated for water/oil repellency by measuring dynamic contact angles for water and hexadecane. Table 4 summarizes the results of contact angle measurements for the composites and that for untreated controls (Tyvek® and Kolon® fabrics). The results indicate that the composite materials produced by the gel-impregnation of gelators **1**, **7** and **8** exhibit significantly higher advancing contact angles for water than the untreated controls. Insets in Figs. 2 and 3 show water droplets sitting on the nonwoven surfaces treated with gelators **1** and **7** showing advancing contact angles above 150°. The treated composites also showed a high advancing contact angle for hexadecane; whereas the untreated controls rapidly absorb hexadecane upon contact. The high water and oil repellency exhibited by composite surfaces are attributed to a combination of fluoroalkyl functionalities present in the gelator and the increased surface roughness created by the fibrous xerogel network. The effect of surface structure created by gel-impregnation is particularly important as clear solutions (no gel with solvents chosen) of fluorinated bis-ureas dip-coated on nonwoven substrates showed relatively inferior performance (water Adv. CA < 118°).

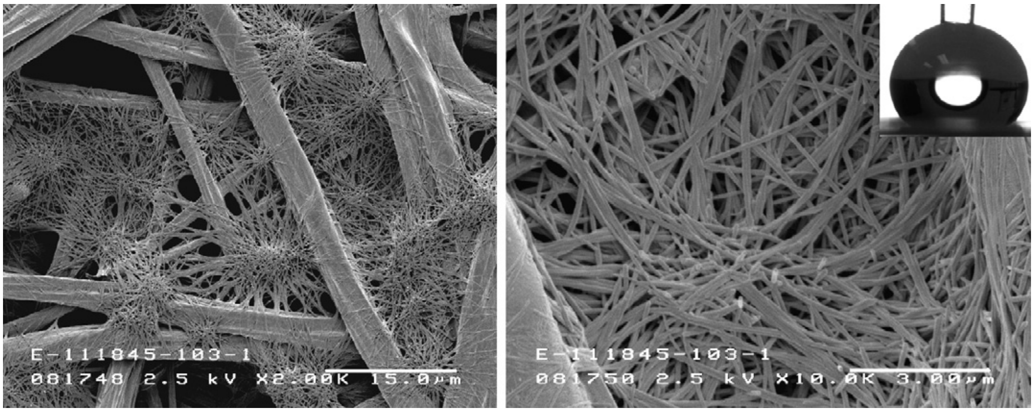


Fig. 2. SEMs of composite prepared by impregnation of gelator **1** on Tyvek® fabric at 2000× and 10000× magnifications.

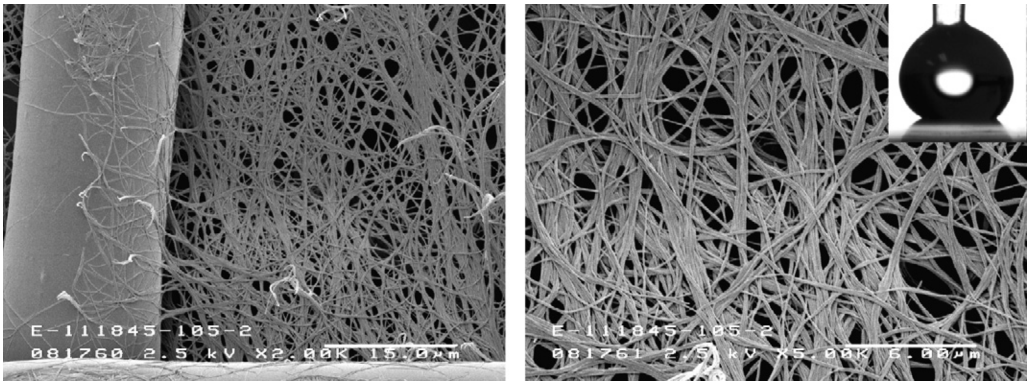


Fig. 3. SEMs of composite prepared by impregnation of gelator **7** on Kolon® fabric at 2000× and 5000× magnifications.

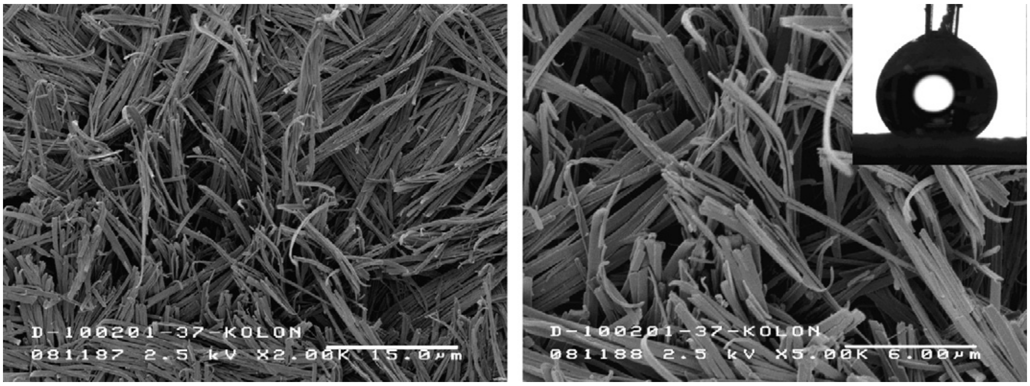


Fig. 4. SEMs of composite prepared by impregnation of gelator **9** on Kolon® fabric at 2000× and 5000× magnifications.

2.5. Surface modification of nonwoven supports in scCO$_2$

Gelators **8**, **9**, **11** and **12** were also gel-impregnated on commercially available nonwoven supports (Tyvek® fabric, Kolon® fabric) in scCO$_2$ using a high-pressure variable volume view cell. After the gelation process, the CO$_2$ was slowly vented from the view cell, and the resulting composite materials were removed and imaged by scanning electron microscopy. Fig. 4 shows SEMs of the composite network structures of the Kolon® fabric surface treated with gelator **9** at 2000× and 10,000× magnifications showing long fibrillar structures with an average fiber diameter of 340 nm. The treated surfaces were evaluated for water/oil repellency, and Table 5 summarizes the results of these contact angle measurements for the composites and that for untreated controls. These results indicate that the composite materials produced by the gel-impregnation of gelators **8**, **9**, **11** and **12** in scCO$_2$ exhibit significantly higher advancing contact angle with water than the untreated controls. They also showed high advancing contact angle with hexadecane; whereas the untreated controls rapidly absorb hexadecane. In many cases, we observed water contact angles of >150° with low contact angle hysteresis indicative of superhydrophobic behavior. The inset in Fig. 4 shows a water droplet sitting on the nonwoven surface treated with gelator **9** from scCO$_2$. The high water and oil repellency exhibited by the gelator-impregnated surfaces were attributed to a combination of xerogel microstructures and the fluoroalkyl functionalities present in the gelator.

Table 5
Water and hexadecane contact angles of treated nonwoven composites prepared via gelation in scCO$_2$.

Example	Contact angle[a]			
	Water		Hexadecane	
	Adv CA	Rec CA	Adv CA	Rec CA
Untreated Tyvek®	108 ± 1	78 ± 1	abs	abs
Untreated Kolon®	115 ± 4	85 ± 4	abs	abs
8 on Tyvek®	143 ± 4	122 ± 3	70 ± 1	28 ± 3
8 on Kolon®	160 ± 2	141 ± 3	30 ± 5	abs
9 on Tyvek®	147 ± 4	131 ± 3	66 ± 5	24 ± 4
9 on Kolon®	157 ± 4	149 ± 2	94 ± 4	39 ± 4
11 on Kolon®	159 ± 2	146 ± 2	81 ± 3	34 ± 3
12 on Kolon®	154 ± 3	129 ± 3	68 ± 4	29 ± 3

[a] Average of 3 runs at different positions on each sample; abs = slowly absorbed into the fabric.

3. Conclusions

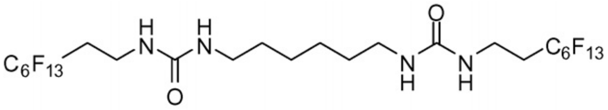
In conclusion, a series of fluorinated bis-urea and bis-amide derivatives were explored as surface modifiers for nonwoven substrates. The majority of the new derivatives showed excellent gelation behavior in both organic solvents and scCO$_2$. Gelation in the presence of a nonwoven substrate led to a gel-impregnated surface which upon drying, created a composite with a microstructure morphology on the surface. The composites thus produced showed excellent hydrophobic and oleophobic behavior as evidenced by the high water and hexadecane contact angles. The high water and oil repellency exhibited by the gelator-impregnated surfaces were attributed to the increased surface roughness created by the xerogel microstructures and the presence of fluoroalkyl functionalities in the gelator backbone. The composite materials can be used to produce superior water/oil repellent surfaces suitable for various applications. We are currently exploring polymerizable fluorinated organogelators to impart robustness to the treated surfaces.

4. Experimental

4.1. General

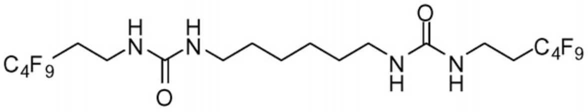
All solvents and reagents, unless otherwise indicated, were purchased from commercial sources and used directly as supplied. 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine and 1*H*,1*H*,2*H*,2*H*-perfluorooctylamine were synthesized from corresponding commercially-available iodides via the azide followed by reduction using Raney Ni/$N_2H_4.H_2O$ as described in the literature procedure [33]. 2-(1*H*,1*H*,2*H*,2*H*-perfluoroalkylthio)ethylamine was prepared by the reaction of 1*H*,1*H*,2*H*,2*H*-perfluoralkyl iodides with 2-aminoethanethiol as disclosed in the literature procedure [34]. Tyvek® polyethylene nonwoven fabric was obtained from E.I. du Pont de Nemours, Wilmington DE, and Kolon® gsm70 spun bound polyester fabric was obtained from Korea Vilene Inc. ^{1}H, $\{^{1}H\}$ ^{13}C and ^{19}F NMR spectra were recorded on a Brucker DRX 400 or 500 Spectrometer. Chemical shifts have been reported in ppm relative to an internal reference ($CDCl_3$, $CFCl_3$ or TMS). All melting points reported were uncorrected. Contact angle (CA) measurements for both water and hexadecane on a surface were performed according to procedures in the manufacturer's manual using a Ramé-Hart Standard Automated Goniometer Model 200 employing DROP image standard software and equipped with an automated dispensing system with a 250 μL syringe and an illuminated specimen stage assembly.

4.2. Synthesis of gelator 1



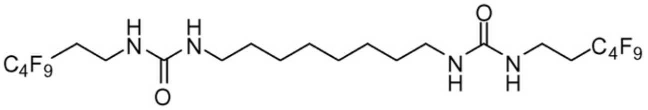
To a mixture of 1*H*,1*H*,2*H*,2*H*-perfluorooctylamine (1.81 g, 5.0 mmol) and triethylamine (0.02 g, 0.2 mmol) in dry methylene chloride (15 mL), under nitrogen atmosphere and cooled to 0 °C, was added dropwise 1,6-diisocyanatohexane (0.420 g, 2.5 mmol). The mixture was slowly warmed to RT, and stirred for 3 h. The precipitated urea was filtered and washed repeatedly with cold methylene chloride. The resulting solid was dried to provide compound **1** as a white solid (2.0 g): mp 156.8–158.5 °C; ^{1}H NMR (methanol-d4): δ 3.41 (t, *J* = 6.8 Hz, 4H) 3.06 (t, *J* = 6.8 Hz, 4H), 2.34 (m, 4H), 1.46 (m, 4H,), 1.34 (m, 4H); ^{19}F NMR (methanol-d4): δ −81.4 (m, 6F), −114.2 (m, 4F), −121.8 (s, 4F), −122.8 (s, 4F), −123.7 (s, 4F), −126.3 (m, 4F). Elemental analysis: $C_{24}H_{24}F_{26}N_4O_2$, calc. C 32.23, H 2.70, N 6.26; found C 32.37, H 2.77, N 6.35.

4.3. Synthesis of gelator 2



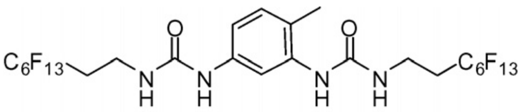
Using a similar procedure as described in the synthesis of gelator **1**, reaction of 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine (2.10 g) with of 1,6-diisocyanatohexane (0.672 g) provided compound **2** as a white solid (2.18 g): mp 130–131.8 °C; ^{1}H NMR (methanol-d4): δ 3.45 (t, *J* = 6.8 Hz, 4H) 3.10 (t, *J* = 6.8 Hz, 4H), 2.35 (m, 4H), 1.48 (m, 4H), 1.35 (m, 4H); ^{19}F NMR (methanol-d4): δ −81.7 (m, 6F), −114.4 (m, 4F), −124.7 (m, 4F), −126.2 (m, 4F). Elemental analysis: $C_{20}H_{24}F_{18}N_4O_2$, calc. C 34.59, H 3.48, N 8.07; found C 34.59, H 3.30, N 7.93.

4.4. Synthesis of gelator 3



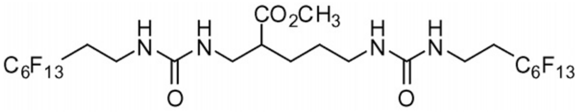
To a solution of 1,8-diisocyanatooctane (1.4 g, 6.9 mmol) in dry chloroform (25 mL), cooled to −5 °C, was added and 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine (3.6 g, 13.8 mmol) dropwise under nitrogen atmosphere, maintaining temperature below 0 °C. The reaction was slowly warmed to RT and stirred overnight. The resulting precipitate was isolated by filtration, rinsed with diethyl ether and dried to provide compound **3** as a white solid (5.0 g). ^{1}H NMR (TFA-d): δ 3.81 (4H), 3.30 (br, 4H), 2.52 (br, 4H), 1.70 (br, 4H), 1.40 (br, 8H); ^{19}F NMR (TFA-d): δ −89.4 (6F), −122.1 (4F), −132.3 (4F), −133.7 (4F).

4.5. Synthesis of gelator 4



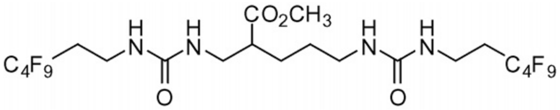
To a solution of 2,4-tolylene diisocyanate (0.435 g) in dry methylene chloride (15 mL) was added and 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine (2.0 g) dropwise under nitrogen atmosphere at RT. The mixture stirred for 10 h at RT, and the solid formed was filtered, washed with cold DCM and dried to obtain compound **4** as an off-white solid (2.1 g): ^{1}H NMR (Acetone d6) δ 7.79 (s, 2H), 7.67 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.1 (bs, 2H), 3.44 (q, *J* = 6.8 Hz, 4H), 2.39 (m, 4H), 1.99 (s, 3H); ^{19}F NMR (Acetone d6) δ −82.1 (tt, *J* = 10, 2 Hz, 6F), −114.8 (m, 4F), −122.6 (m, 4F), −123.8 (m, 4F), −124.6 (m, 4F), −127.1 (m, 4F).

4.6. Synthesis of gelator 5



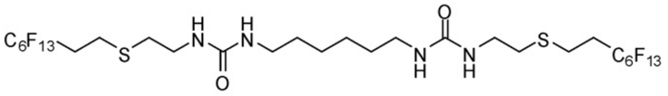
Using a similar procedure as described in the synthesis of gelator **3**, reaction of lysine diisocyanate (1.1 g) with 1*H*,1*H*,2*H*,2*H*-perfluorooctylamine (3.9 g) provided compound **5** as a white solid (5.05 g): ^{1}H NMR (TFA-d): δ 4.58 (m, 1H), 3.90 (s, 3H), 3.76, 3.70, 3.33 (t, 2H each, *J* = 6.4 Hz), 2.55–2.37 (m, 4H), 1.83, 1.74 (m, 1H each), 1.71, 1.54 (m, 2H each); ^{19}F NMR (TFA-d): δ −89.9 (6F), −112.5 (4F) −129.6 (4F), −131.0 (4F), −132.0 (4F), −134.6 (4F); ^{13}C NMR (TFA-d): δ 178.1, 162.3, 161.8, 56.5, 55.6 43.7, 36.4, 35.8, 33.7, 32.9 (t), 32.6 (t), 29.7, 24.6.

4.7. Synthesis of gelator 6



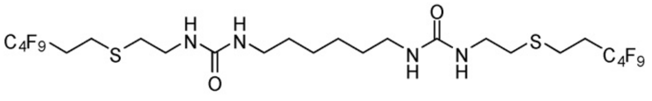
Using a similar procedure as described in the synthesis of gelator **3**, reaction of lysine diisocyanate (1.4 g) with 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine (3.6 g) provided compound **6** as a white solid (5.05 g): ^{1}H NMR (TFA-d): δ 4.57 (br, 1H), 3.91 (s, 3H), 3.77, 3.71, 3.34 (m, 2H), 2.46 (br, 4H), 2.00, 1.83 (br, 1H each), 1.72, 1.53 (br, 2H each); ^{19}F NMR (TFA-d): δ −89.4 (6F), −122.0 (4F), −132.2 (4F), −133.6 (4F); ^{13}C NMR (TFA-d): 178.1, 162.4, 161.8, 56.5, 55.7, 43.7, 36.4, 35.8, 33.7, 32.8, 32.6, 29.8, 24.6.

4.8. Synthesis of gelator 7



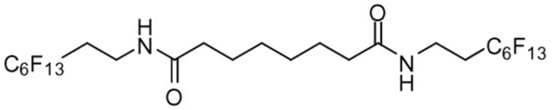
Using a similar procedure as described in the synthesis of gelator **1**, reaction of 2-(1*H*,1*H*,2*H*,2*H*-perfluorooctylthio)ethylamine (4.23 g) with 1,6-diisocyanatohexane (0.84 g) provided compound **7** as a white solid (4.3 g): mp 176.8–177.5 °C; ^{1}H NMR (DMF-d7 100 °C): δ 5.84 (bs, 2H), 5.73 (bs, 2H), 3.38 (q, *J* = 6.4 Hz, 4H), 3.15 (q, *J* = 6.8 Hz, 4H), 2.83 (t, *J* = 6.4 Hz, 4H), 2.73 (t, *J* = 6.8 Hz, 4H), 2.57 (m, 4H), 1.56 (m, 4H), 1.35 (m, 4H,); ^{19}F NMR (DMF-d7 100 °C): δ −81.4 (m, 6F), −113.4 (m, 4F), −121.7 (m, 4F), −122.7 (m, 4F), −123.2 (s, 4F), −126.0 (m, 4F). Elemental analysis: $C_{28}H_{32}F_{26}N_4SO_2$, calc. C 33.14, H 3.17, N 5.52; found C 33.18, H 3.18, N 5.53.

4.9. Synthesis of gelator 8



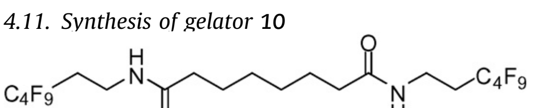
Using a similar procedure as described in the synthesis of gelator **1**, reaction of 2-(1*H*,1*H*,2*H*,2*H*-perfluorohexylthio)ethylamine (1.94 g) with 1,6-diisocyanatohexane (0.504 g) provided compound **8** as a white solid (1.97 g): mp 160–162 °C; ^{1}H NMR (DMF-d7 100 °C): δ 5.85 (bs, 2H), 5.74 (bs, 2H), 3.39 (q, *J* = 6.4 Hz, 4H), 3.13 (q, *J* = 6.8 Hz, 4H), 2.84 (t, *J* = 6.4 Hz, 4H), 2.72 (t, *J* = 6.8 Hz, 4H), 2.58 (m, 4H), 1.55 (m, 4H), 1.35 (m, 4H); ^{19}F NMR (DMF-d7 100 °C): δ −81.6 (m, 6F), −113.5 (m, 4F), −124.2 (m, 4F), −125.8 (m, 4F). Elemental analysis: $C_{24}H_{32}F_{18}N_4SO_2$, calc. C 35.38, H 3.96, N 6.88; found C 35.56, H 3.92, N 6.84.

4.10. Synthesis of gelator 9



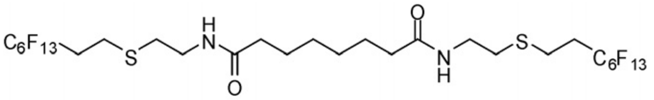
To a mixture of 1*H*,1*H*,2*H*,2*H*-perfluorooctylamine (3.6 g, 9.9 mmol), methylene chloride (30 mL) and triethylamine (0.999 g, 9.9 mmol) under a N_2 purge was added suberoyl chloride (0.949 g, 4.5 mmol), and the mixture was stirred for 12 h at RT. The reaction mixture was concentrated to half its volume and filtered. The solid product was washed with cold methylene chloride (5 mL) followed by 1% HCl (2 × 5 mL), water (2 × 5 mL) and finally hexanes (2 × 5 mL). The resulting solid was recrystallized from methanol to provide compound **9** as a white solid (4.0 g): mp 133.5–134.6 °C; ^{1}H NMR (methanol-d4): δ 3.48 (t, *J* = 6.8 Hz, 4H), 2.39 (m, 4H), 2.18 (t, *J* = 7.6 Hz, 4H), 1.59 (m, 4H), 1.34 (m, 4H); ^{19}F NMR (methanol-d4): δ −84.3 (m, 6F), −117.1 (m, 4F), −124.6 (m, 4F), −125.9 (m, 4F), −126.6 (m, 4F), −128.9 (m, 4F). Elemental analysis: $C_{24}H_{22}F_{26}N_2O_2$, calc. C 33.35, H 2.57, N 3.24; found C 33.37, H 2.58, N 3.31.

4.11. Synthesis of gelator 10



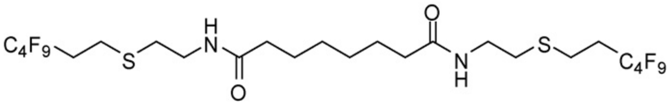
Using a similar procedure as described in the synthesis of gelator **9**, reaction of 1*H*,1*H*,2*H*,2*H*-perfluorohexylamine (2.6 g) with suberoyl chloride (0.949 g) provided compound **10** as a white solid (3.2 g): mp 114.1–115.2 °C; ^{1}H NMR (methanol-d4): δ 3.51 (t, *J* = 6.8 Hz, 4H), 2.41 (m, 4H), 2.20 (t, *J* = 7.6 Hz, 4H), 1.63 (m, 4H), 1.36 (m, 4H); ^{19}F NMR (methanol-d4): δ −83.1 (m, 6F), −116.0 (m, 4F), −126.1 (m, 4F), −127.6 (m, 4F). Elemental analysis: $C_{20}H_{22}F_{18}N_2O_2$, calc. C 36.16, H 3.34, N 4.22; found C 36.10, H 3.22, N 4.31.

4.12. Synthesis of gelator 11



Using a similar procedure as described in the synthesis of gelator **9**, reaction of 2-(1*H*,1*H*,2*H*,2*H*-perfluorooctylthio)ethylamine (2.09 g) with suberoyl chloride (0.475 g) provided compound **11** as a white solid (3.2 g): mp 144.8–146.2 °C: ^{1}H NMR (acetone-d6): δ 7.22 (bs, 2H), 3.42 (q, *J* = 6.0 Hz, 4H), 2.86 (t, *J* = 6.4 Hz, 4H), 2.75 (t, *J* = 6.8 Hz, 4H), 2.57 (m, 4H), 2.16 (t, *J* = 7.2 Hz, 4H), 1.59 (m, 4H), 1.35 (m, 4H); ^{19}F NMR (acetone-d6): δ −82.1 (m, 6F), −115.0 (m, 4F), −122.8 (m, 4F), −123.8 (m, 4F), −124.2 (s, 4F), −126.2 (m, 4F). Elemental analysis: $C_{28}H_{30}F_2N_2S_2O_2$, calc. C 34.15, H 3.07, N 2.85; found C 34.05, H 3.12, N 2.94.

4.13. Synthesis of gelator 12



Using a similar procedure as described in the synthesis of gelator **9**, reaction of 2-(1*H*,1*H*,2*H*,2*H*-perfluorohexylthio)ethylamine (1.59 g) with suberoyl chloride (0.475 g) provided compound **12** as a white solid (1.4 g): mp 122–123.5 °C; ^{1}H NMR (acetone-d6): δ 7.22 (bs, 2H), 3.40 (q, *J* = 6.0 Hz, 4H), 2.85 (t, *J* = 6.4 Hz, 4H), 2.75 (t, *J* = 6.8 Hz, 4H), 2.55 (m, 4H), 2.15 (t, *J* = 7.2 Hz, 4H), 1.56 (m, 4H), 1.37 (m, 4H); ^{19}F NMR (acetone-d6): δ −82.4 (m, 6F), −116.2 (m, 4F), −126.2 (m, 4F), −127.7 (m, 4F). Elemental analysis: $C_{24}H_{30}F_{18}N_2S_2O_2$, calc. C 36.74, H 3.85, N 3.57; found C 36.61, H 3.83, N 3.65.

4.14. Gelation in organic solvents

Generally 0.5–3 wt% of a gelator in an organic solvent in a closed vial was heated to 5–10 °C below the boiling point of the solvent until a clear solution was obtained in a reactor block equipped to heat multiple vials. The vials were allowed to cool to RT either by a slow cool by switching off the heat or by transferring the vials to a constant temperature water bath kept at 25 °C. The state of the solution was evaluated after 2–12 h. Stable gel formation was tested by inverting the vial. Compounds **1**, **7** and **8** gelled a variety of the organic solvents with various polarities, whereas compounds **2**–**6** and **9**–**12** gelled more selectively.

4.15. Gelation in $scCO_2$

A gelator was charged to a high-pressure variable volume view cell equipped with a TEFLON® polymer-coated stir bar and an electrical heating jacket. The cell was sealed and then charged volumetrically with liquid CO_2 dispensed by an Isco syringe pump (Isco Model 260D) to give a final overall gelator concentration of 0.3–0.7 wt%. The cell was then heated to about 70–100 °C and pressurized to about 260–350 bar (26.0–35.0 MPa) with agitation to solubilize a significant portion of the gelator. Agitation was then suspended, and the cell was slowly cooled to room temperature over several hours at constant pressure to allow gel formation within the cell volume. The CO_2 was then slowly vented from the view cell, and the gelled sample was removed from the cell and imaged by scanning electron microscopy, revealing ‘xerogel’ microstructure.

4.16. *T_{gel} of bis-urea gelator* 1

A procedure similar to that described in the literature [18–19] was used to measure the melting temperature of the gel. A steel ball (260 mg, diameter ~4.5 mm) was gently placed on the top of the gel (4 g) in a glass vial. The closed vial was placed firmly in a water bath initially at 25 °C which was then heated progressively at a rate of 2 °C per minute. The sample temperature was determined by a sensor dipped in a separate vial next to the heating gel which was filled with the same solvent used for gelation. The T_{gel} was defined as the temperature at which the ball touched the bottom of the vial. The experiment was repeated multiple times to produce consistent results.

4.17. Gel-impregnation on nonwoven supports in organic solvents

Nonwoven fabrics: Tyvek® polyethylene nonwoven fabric and Kolon® spun bound polyester fabric (about 3.0 cm × 3.0 cm) were immersed in a suspension of a gelator in organic solvent kept in closed reaction flask equipped with a stir bar and temperature controller. The mixtures were heated 5 °C below the boiling point of the solvent for 1–2 h until clear solutions formed. The flasks were then either rapidly cooled to RT by removing the oil bath or slowly cooled to RT by switching off the heat. Gel formation was usually observed in about 0.5–6 h, and the gels were allowed to age for an additional 6 h. The gelator-impregnated samples were removed and dried in a vacuum oven at RT overnight. The dried samples were weighed and used for contact angle measurements.

4.18. Gel-impregnation on nonwoven supports in $scCO_2$

Samples of Tyvek® and Kolon® nonwoven fabrics identical to those of Section 4.17 were mounted in a high-pressure variable volume view cell which had been charged with gelator and equipped with a TEFLON®-coated stir bar and an electrical heating jacket. The cell was sealed and then charged with liquid CO_2 to give a final overall gelator concentration of 0.2–0.5 wt%. The cell was then heated to about 70 °C and pressurized to about 210 bar (21.0 MPa) with agitation to solubilize a significant portion of the gelator. Agitation was then suspended, and the cell was slowly cooled to room temperature over several hours at constant pressure to allow gel formation within and upon the nonwoven fabric samples. The CO_2 was then slowly vented from the view cell, and the gelator-impregnated samples were removed, imaged by scanning electron microscopy, and utilized for contact angle measurements.

Acknowledgements

We gratefully acknowledge Walter Meredith, Janice Hytrek and Gregg Sunshine of DuPont CR&D for their assistance with the experiments, and Liang Liang of DuPont Corporate Center for Analytical Sciences (CCAS) for SEMs.

References

[1] P. Terech, R.G. Weiss, Chem. Rev. 97 (1997) 3133–3160.
[2] J. Van Esch, B.L. Feringa, Angew. Chem. Int. Ed. 39 (2000) 2263–2266.
[3] J. Van Esch, F. Schoonbeek, M.D. Loos, E.M. Veen, R.M. Kellog, B.L. Feringa, in: R. Ungaro, E. Dalcanale (Eds.), Supramolecular Science, Where it is Going, Kluwer Academic Publishers, Netherlands, 1999, pp. 233–259.
[4] L.A. Estroff, A.D. Hamilton, Chem. Rev. 101 (2001) 1869–1879.
[5] K. Hanabusa, Springer Ser. Mater. Sci. 78 (2004) 118–137.
[6] H. Ihara Hirotaka, M. Takafuji, T. Sakurai, Encyclopedia of Nanoscience and Nanotechnology, vol. 9, 2004, pp. 473–495.
[7] E.J. Acosta, A. Raghavanpillai, S. Peng, S. Reinartz, S. Moudgil, U.S. Pat. 7473658 B2 (2009).
[8] E.J. Acosta, A. Raghavanpillai, S. Peng, S. Reinartz, U.S. Pat. Appl. Publ. 2008113172 A1.
[9] A. Nakajima, K. Hashimoto, T. Watanabe, Monateshefte. Fur Chemie 132 (2001) 31–41.
[10] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, S. Yanlin, B. Liu, L. Jiang, D. Zhu, Adv. Mater. 14 (2002) 1857–1864.
[11] W. Chen, A.Y. Fadeev, M. Che Hsieh, D. Oner, J. Youngblood, T. McCarthy, Langmuir 15 (1999) 3395–3399.
[12] W. Barthlott, C. Neinhuis, Planta 202 (1997) 1–8.
[13] E. Nun, M. Oles, B. Schleich, Macromol. Symp. 187 (2002) 677–682.
[14] P. Gold, Mater. Today 6 (2003) 44–48.
[15] Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang, C. Huyang, Chem. Mater. 18 (2006) 2974–2981.
[16] M. Yamanaka, K. Sada, M. Miyata, K. Hanabusa, K. Nakano, Chem. Commun. (2006) 2248–2250.
[17] F.S. Schoonbeek, J.H. Van Esch, R. Hulst, R.M. Kellogg, B.L. Feringa, Chem. Eur. J. 6 (2000) 2633–2643.
[18] A. Takahashi, M. Sasaki, T. Kato, T. Polym. J. 12 (1980) 335–341.
[19] K. Yabuchi, E. Mafro-Owesu, T. Kato, Org. Biomol. Chem. 1 (2003) 3464–3469.
[20] K.W. Hutchenson, in: Y.-P. Sun (Ed.), Organic Chemical Reactions and Catalysis in Supercritical Fluid Media, in Supercritical Fluid Technology in Materials Science and Engineering: Syntheses, Properties, and Applications, Marcel Dekker, New York, 2002, pp. 87–187.
[21] M.A. McHugh, V.J. Krukonis, Supercritical Fluid Extraction: Principles and Practice, 2nd ed., Butterworth-Heinemann, Boston, 1994.
[22] J.M. DeSimone, Z. Guan, C.S. Elsbernd, Science 257 (1992) 945–947.
[23] C. Lepilleur, E.J. Beckman, Macromolecules 30 (1997) 745–756.
[24] A.J. Mesiano, E.J. Beckman, A.J. Russell, Chem. Rev. 99 (1999) 623–633.
[25] M. Kemmere, T. Meyer (Eds.), Supercritical Carbon Dioxide: in Polymer Reaction Engineering, Wiley-VCH Verlag GmbH & Co, 2005.
[26] M. George, R.G. Weiss, J. Am. Chem. Soc. 123 (2001) 10393–10394.
[27] C.K. Luscombe, S. Proemmel, W.T.S. Huck, A.B. Holmes, H. Fukushima, J. Org. Chem. 72 (2007) 5505–5513.
[28] M.R. Todd, G.W. Grand, Energy Convers. Manage. 34 (1993) 1157–1171.
[29] S. Thomas, Oil Gas Sci. Technol. 63 (2008) 9–19.
[30] C. Shi, Z. Huang, E.J. Beckman, R.M. Enick, S.-Y. Kim, D.P. Curran, Ind. Eng. Chem. Res. 40 (2001) 908–913.
[31] C. Shi, Z. Huang, S. Kilic, J. Xu, R.M. Enick, E.J. Beckman, A.J. Carr, R.E. Melendez, A.D. Hamilton, Science 286 (1999) 1540–1543.
[32] Z. Huang, C. Shi, R. Enick, E.J. Beckman, Chem. Mater. 14 (2002) 4273–4280.
[33] H. Trabelsi, F. Szoenyi, N. Michelangeli, A. Cambon, J. Fluorine Chem. 69 (1994) 115–117.
[34] C.S. Rondestvedt Jr., G.L. Thayer Jr., J. Org. Chem. 42 (1977) 2680–2683.