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Hydrophobic and oleophobic surface modification using gelling agents derived from amino acids

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ABSTRACT

A series of fluorinated and non-fluorinated organogelators containing urea and amide functionalities was synthesized from readily available amino acid building blocks. These derivatives showed excellent gelation behavior in a variety of organic solvents at low concentrations ranging from 0.5–4 wt%. Gelation in the presence of a fibrous substrate led to a gel-coated surface, which upon drying provided a composite with a porous microstructure morphology impregnated on the surface. The composites obtained via the impregnation of gelators provided surfaces with excellent hydrophobic properties. The superior hydrophobic behaviors observed in these composites were ascribed to a combination of increased surface roughness created by the xerogel and the presence of hydrophobic functionalities present in the gelator backbone. The composites obtained via the impregnation of gelators bearing long-chain perfluoroalkyl group on non-woven substrates also showed excellent oleophobic behavior.

1. Introduction

Organogelation is a much-studied but still poorly understood subject, which involves the interplay of inter- and intramolecular forces between small molecules in solution that ultimately change the macroscopic properties of the system. Low molecular-weight organogelators have attracted considerable interest and have potential applications towards the design of new soft materials [1–6]. The process of self-assembly of small organic molecules into supramolecular structures is complex and varies based on the functionalities present in the molecule as well as external factors such as solvent, temperature, pH, etc. 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 solute molecules [3]. In general, the non-covalent forces are weak compared to covalent bonds, which makes them reversible, and it requires several of them to be combined to form a strong association. 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 [3,7]. Evaporation of the solvent leads to a dried gel (xerogel) with a microstructure morphology. Thus surface morphology of a surface could be altered via a gel-impregnation and drying process and the method could be employed for designing the low surface energies desired for fabricating surfaces that behave superhydrophobic in nature [8–11]. Surfaces on which the contact angle of water exceeds 150°, and show low contact angle hysteresis, are described as superhydrophobic or ultrahydrophobic [12–14]. 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 [15–17]. The self-cleaning ability of these surfaces is essentially due to the two-tier micro and nano roughness present on the surface. The microscale morphologies created by organogelator impregnation could be further controlled by suitable gelling solvents, as well as concentration and temperature effects. In addition, incorporation of low surface energy functionalities like fluorinated groups in the gelator frame work could further lower the surface energy and bring oleophobic properties to the treated surfaces.

Recently, we demonstrated the above concept by fabricating extremely low surface energy surfaces via the surface modification

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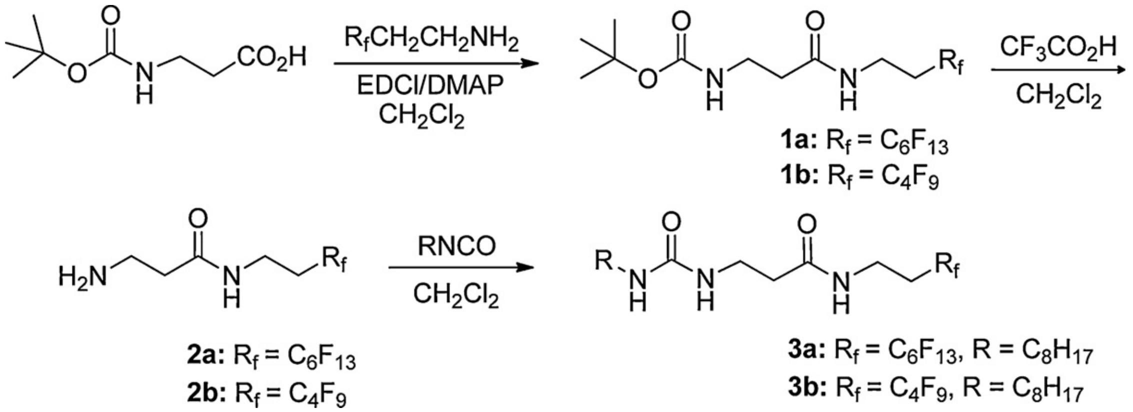
of the nonwoven substrates using simple fluorinated bis urea and bis amide gelators [11]. Gelation in the presence of a nonwoven substrate led to a gel-impregnated surface, which upon drying produced a composite with porous microstructure morphology on the surface. The resulting composite showed high water and hexadecane contact angles indicative of excellent hydrophobic and oleophobic properties. The superior hydrophobic and oleophobic behaviors observed in these composites are attributed to a combination of increased surface roughness and the presence of perfluoroalkyl functionality in the gelator backbone. Herein, we discuss the design and synthesis of novel fluorinated and non-fluorinated organogelators derived from amino acids, a detailed investigation of their gelling behavior, and the effect of structural changes on repellency behavior on treated non-woven substrates.

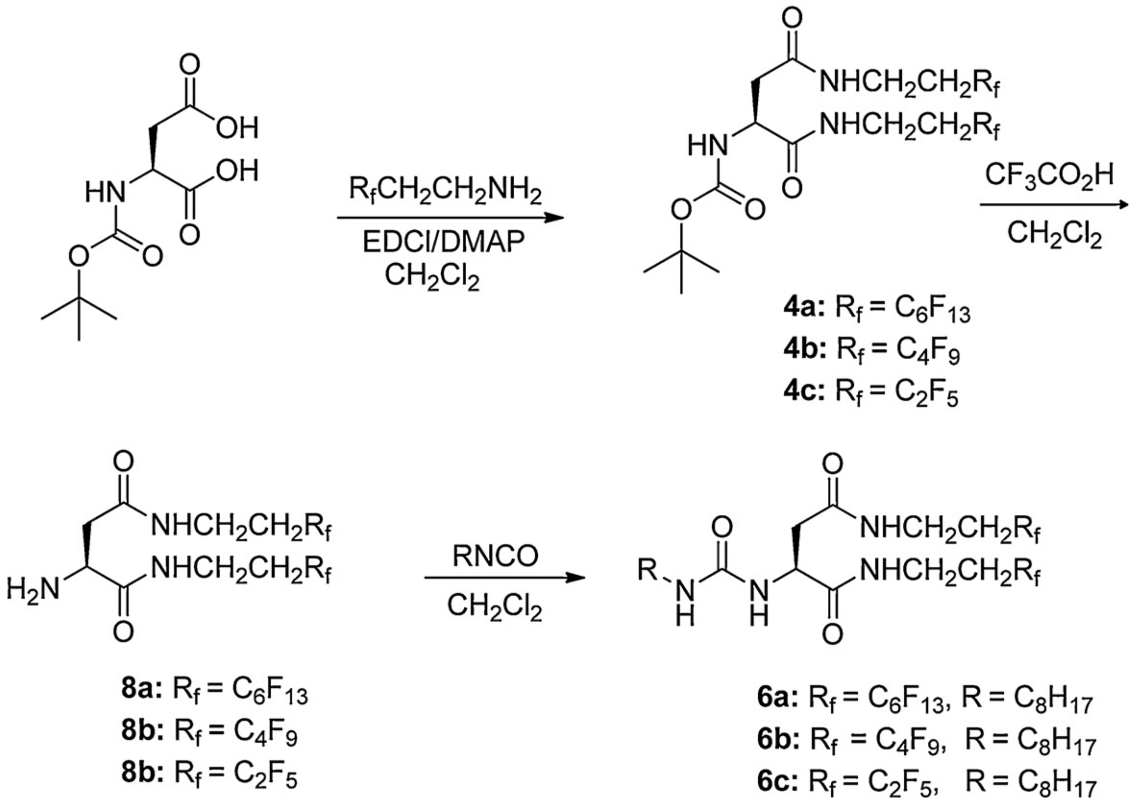
2. Results and discussion

2.1. Organogelators: design and synthesis

Urea and amide 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. We designed a series of fluorinated organogelators by careful manipulation of hydrogen bonding (urea and amide) and hydrophobic functionalities (fluorocarbon and hydrocarbon) in the same molecule from readily available amino acids. Boc-protected amino acids, *N*-Boc-β-alanine and *N*-Boc-aspartic acid were chosen as the building blocks. Thus *N*-Boc-β-alanine was transformed to the corresponding *N*-Boc-protected fluorinated amides (**1a** and **1b**) by reacting with fluorinated amines (Scheme



Scheme 1. Preparation of fluorinated urea and amide gelators from *N*-Boc-β-alanine.



Scheme 2. Preparation of perfluoroalkyl urea–amide gelators from *N*-Boc-L-aspartic acid.

1). The resulting amides were deprotected to obtain the corresponding free amines (**2a** and **2b**) which upon reaction with commercially available isocyanates provided the fluorinated urea–amide derivatives suitable as gelling agents (**3a** and **3b**). All the urea–amide derivatives were white crystalline solids and showed gelation properties in methylene chloride during their isolation.

In order to investigate the effect of structural changes on gelation behavior and repellency, we designed similar urea–amide-based gelator system which incorporates a bis-fluoroalkyl chain. Thus fluorinated bis-amide–urea derivatives (**6a**–**6c**) were synthesized by the reaction of *N*-Boc-L-aspartic acid with 2 equiv. of fluorinated amine followed by deprotection and reaction with *n*-octyl isocyanate as shown in Scheme 2.

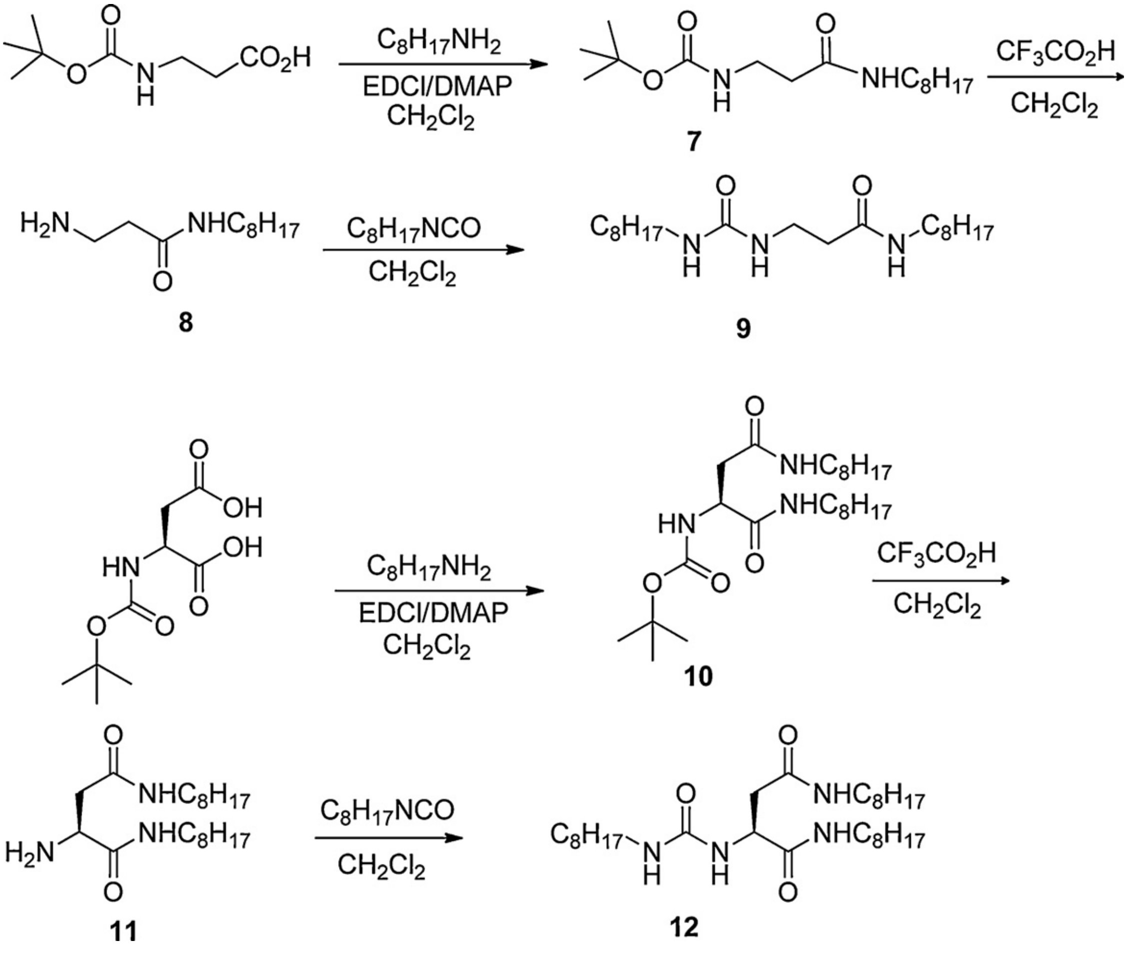
In order to compare the effect of structural changes (fluorocarbon vs hydrocarbon) on gelation behavior and repellency, we also synthesized the corresponding non-fluorinated urea amide derivatives **9** and **12** via the reaction of *N*-Boc-β-alanine or *N*-Boc-L-aspartic acid with *n*-octylamine followed by deprotection and reaction with *n*-octyl isocyanate (Scheme 3).

2.2. Gelation in organic solvents

We examined the gelation behavior of fluorinated and non-fluorinated urea–amide derivatives in various organic solvents and determined the minimum gelation concentration for each 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, 0.5–4 wt% slurries of the organogelators in various organic solvents were prepared and heated with stirring at a temperature 3–5 °C below the boiling point of the solvent to induce dissolution. Gelation occurred upon cooling, as was evident by significant increase in viscosity and/or the formation of a translucent-to-opaque appearance without the formation of crystals or precipitate. We found that the fluorinated and non-fluorinated urea–amide derivatives underwent gelation in many organic solvents at remarkably low concentrations ranging from 0.5 to 4 wt%. The gels formed were stable for several weeks at room temperature. Some of the gelation attempts and best conditions where stable gels were obtained at a minimum concentration of the gelator are summarized in Table 1.

The fluorinated urea–amide derivatives **3a** and **3b** formed stable gels in acetone at 1–2 wt% concentration. **3a** also provided a hazy gel in *n*-butanol at 2 wt% concentration. Compounds **6a** and **6b** formed very stable gels in *n*-butanol at 3.5 and 4 wt% respectively. Attempted gelation of **6c** in *n*-butanol led to a clear solution at 1–4 wt% concentration, but provided a stable gel in toluene at 2 wt% concentration. The fluorinated urea amide compounds described above could be useful as gelators for supercritical CO_2 [8,11]. The non-fluorinated urea–amide derivatives **9** and **12** provided stable gels in a variety of solvents at 0.5–2 wt% concentration.



Scheme 3. Preparation of alkyl urea–amide gelators from *N*-Boc-β-alanine and *N*-Boc-L-aspartic acid.

Table 1
Gelation characteristics for compounds **3a**, **3b**, **6a**–**6c** and **9** and **12**.

Compound	Gelation conditions		Appearance[b]
	Wt% gelator	Solvent	
3a	1	Hexane	Insoluble
	1,2,3	Toluene	Solution/precipitate
	0.5,1,2	Tetrahydrofuran	Soluble/precipitate
	0.5,1[a],2	Acetone	Transparent gel
	2[a],3	*n*-Butanol	Hazy gel
3b	1,2,3	Toluene	Solution/precipitate
	1,2,3	Tetrahydrofuran	Solution/precipitate
	1,2[a],3	Acetone	Thick gel
	1,2,3	*n*-Butanol	Partial gel/precipitate
6a	1,2,3	Toluene	Insoluble
	1,2,3,4	Acetonitrile	Partial gel/precipitate
	1,2,3,4	Tetrahydrofuran	Solution/precipitate
	3,3.5[a],4	*n*-Butanol	Opaque gel
6b	1,2,3	Hexane	Partial gel
	1,2	Toluene	Soluble
	1,2,3,4	Acetonitrile	Soluble
	4[a]	*n*-Butanol	Transparent gel
6c	2	Hexane	Partial gel
	2[a]	Toluene	Hazy gel
	2,3	Acetone	Solution
	1,2,3,4	*n*-Butanol	Solution
9	1[a],2	Toluene	Transparent gel
	1[a],2	Cyclohexane	Hazy gel
	2	Acetone	Opaque gel
	2	Methylene chloride	Transperent gel
	1,2	*n*-Butanol	Partial gel
12	0.5[a],1	Cyclohexane	Transparent gel
	1	Toluene	Transparent gel
	2	*n*-Butanol	Transparent gel
	2[a],3	Acetonitrile	Hazy gel

[a] Minimum gel concentration for stable gel formation.

[b] Hazy, solid gel partially transparent; transparent, solid gel completely transparent; opaque, solid gel not transparent; partial, solid gel with partial movement in the liquid.

2.3. 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 fibrous or solid 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 thermally reversible organogelators 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 of the gelator, 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 such as a hand operated Thin Layer Chromatography (TLC) plate coater to a uniform thickness. Drying (i.e. removal of the solvent) the treated substrate leaves behind a microstructured xerogel on the solid or fibrous support. For fibrous and smaller sized substrates the gel impregnation in presence of solvent was the preferred method.

The urea–amide gelators were gel-impregnated on commercially available nonwoven supports (Tyvek® polyethylene nonwoven fabric and Kolon® polyester fabric) in a suitable organic solvent. These samples were dried in a vacuum oven at room temperature to produce a composite of xerogel coated on the substrate. The amount of dried gel coated per unit area of the support was estimated to be 0.0005–0.0035 g/cm^2 and was dependent on gelation conditions and the support used for surface modification. The surfaces of the composites were characterized by scanning electron microscopy (SEM) and showed a porous xerogel comprised of fibrous structures ranging from 50 nm to about 500 nm in effective average fiber diameter. The average fiber diameter observed was different from the fiber diameter observed for untreated Tyvek® polyethylene (5–20 μM) or Kolon® polyester fabric (15–30 μM). This indicates that the self-assembly of molecular entities can be transferred from the liquid–gel phase to surfaces, giving a changed surface morphology. The surface modified composites were stable to mild physical stress such as bending and rubbing, however not stable for more rigorous abrasive treatment. Urea–amide gelator **3a** was impregnated on Tyvek® and Kolon® fabric in acetone, and dried composites were analyzed by SEM. Fig. 1 shows SEMs at 10,000× magnification of the composite network structures of the Tyvek® and Kolon® fabric surfaces with an average fiber diameter of 140 nm treated with gelator **3a**. The rest of the fluorinated urea–amide gelators (**3b**, **6a**, **6b** and **6c**) were similarly impregnated on nonwovens from a solution of acetone (**3b**), *n*-butanol (**6a** and **6b**) or toluene (**6c**) and dried to obtain the treated composites similar to **3a**. Fig. 2 shows

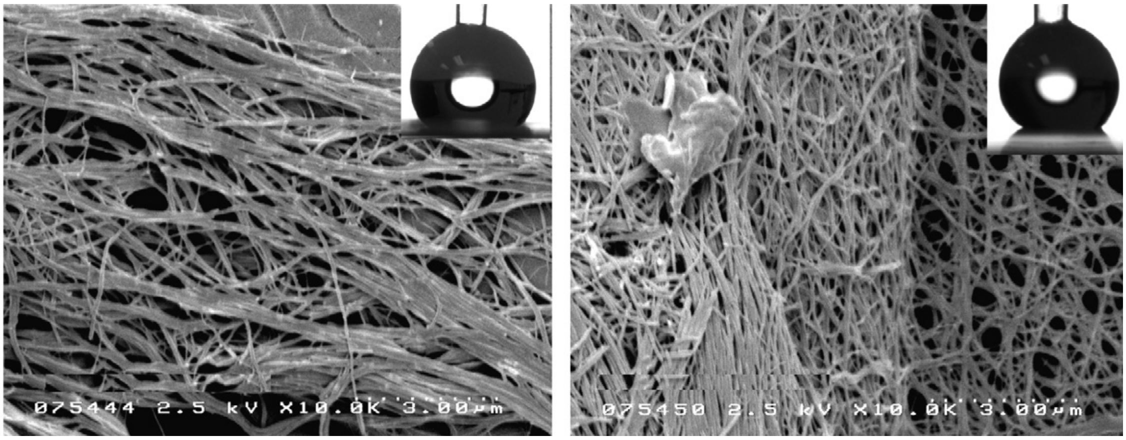


Fig. 1. SEMs of composite prepared by impregnation of gelator **3a** on Tyvek® (left) and Kolon® (right) fabric at 10,000× magnification.

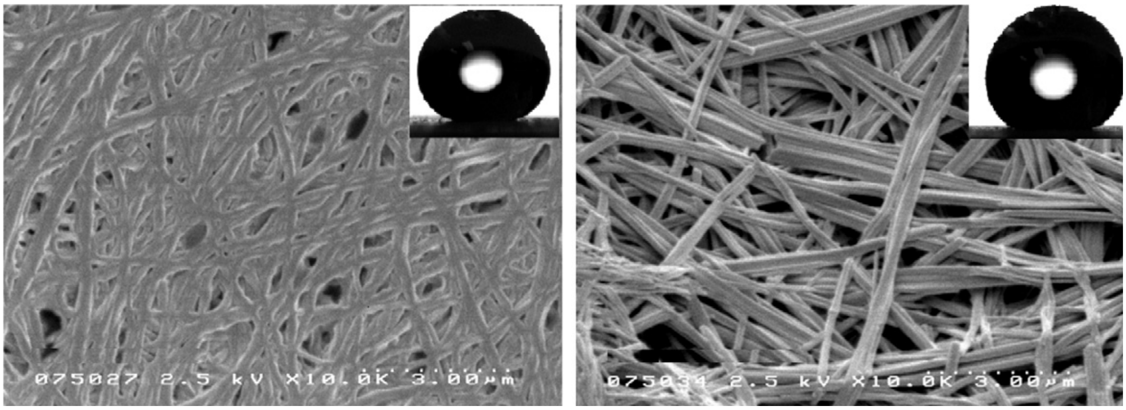


Fig. 2. SEMs of composite prepared by impregnation of gelator **6a** on Tyvek® (left) and Kolon® (right) fabric at 10,000× magnification.

SEMs at 10,000× magnification of the composite network structures of the Tyvek® and Kolon® fabric surfaces with an average fiber diameter of 130 nm treated with fluorinated urea–amide gelator **6a**

The composites produced by the gel-impregnation of fluorinated organogelators were evaluated for water/oil repellency by measuring the dynamic contact angles for water and hexadecane. Table 2 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 fluorinated gelators **3a**, **3b**, **6a**, **6b** and **6c** exhibit significantly higher water advancing contact angles than the untreated controls. Interestingly, the urea–amides with shorter fluoroalkyl chains (**3b**, **6b** and **6c**) also showed high water advancing angles similar to **3a** or **6a** indicating that high water repellency is independent of the length and number of fluoroalkyl moieties in the molecule.

The water advancing and receding contact angles observed for all the gelator treated surfaces were higher than the untreated controls. The advancing contact angle observed for these composites were much higher than highest possible water contact angle achievable for a perfectly smooth surface with a hexagonally packed array of CF_3 groups [18]. This reiterates the fact that the surface created has a higher surface area resulting from the increased surface roughness due to gelator incorporation. A combination of surface roughness along with hydrophobic fluorocarbon or hydrocarbon tails present in the gelator backbone, essentially leads to the increased water repellency of the treated composite. Insets in Figs. 1 and 2 show water droplets sitting on the nonwoven surfaces treated with gelator **3a** and **6a** with advancing contact angles above 150°. The effect of surface structure created by gel-impregnation is particularly important as clear solutions (no gel with solvents chosen) of fluorinated (**3a** and **6a**) or non-fluorinated (**9** and **12**) gelators dip-coated on nonwoven substrates showed relatively inferior performance (water Adv. CA < 115°). The treated composites derived from gelators **3a** and **6a** also showed a high advancing contact angle for hexadecane, whereas the corresponding composites **3b** and **6b** showed slightly reduced advancing contact angles for hexadecane. This observation was not surprising, as compounds **3b** and **6b** are comprised of short fluoroalkyl groups ($R_f = C_4$) and are expected to show reduced oil repellency compared to a longer chain ($R_f = C_6$ or higher) perfluoroalkyl containing gelator [19]. Although **6b** was composed of twin fluoroalkyl chains ($R_f = C_4$) in the same molecule, it also still lacked enough oil repellency underscoring the importance of longer chain fluoroalkyl group for oil repellency. We then looked at the oil repellency behavior of composite created by the gel-impregnation compound **6c**, which comprises of a two carbon fluoroalkyl chain ($R_f = C_2$) and showed no oil repellency. Hexadecane sank into the composite that was gel-impregnated with compound **6c**. This further confirms that longer fluoroalkyl chains ($R_f = C_6$ or higher) need to be incorporated in the gelator backbone

Table 2
Water and hexadecane contact angles of treated nonwoven composites prepared via gelation in organic solvents.

Composite	Amount of gel impregnated per unit area (g/cm^2)	Contact angle[a]			
		Water		Hexadecane	
		Adv CA	Rec CA	Adv CA	Rec CA
3a on Tyvek®	0.0009	149 ± 1	141 ± 3	104 ± 2	71 ± 4
3a on Kolon®	0.0022	159 ± 2	148 ± 3	127 ± 1	89 ± 3
3b on Tyvek®	0.0009	144 ± 4	134 ± 2	71 ± 3	41 ± 1
3b on Kolon®	0.0021	150 ± 3	136 ± 1	57 ± 2	39 ± 3
6a on Tyvek®	0.0011	154 ± 2	153 ± 6	155 ± 2	133 ± 0
6a on Kolon®	0.0026	152 ± 4	135 ± 2	126 ± 2	84 ± 2
6b on Tyvek®	0.0010	149 ± 2	135 ± 5	92 ± 1	61 ± 3
6b on Kolon®	0.0026	152 ± 1	132 ± 4	84 ± 3	56 ± 5
6c on Tyvek®	0.0007	128 ± 4	105 ± 4	28 ± 3	12 ± 3
6c on Kolon®	0.0024	138 ± 3	114 ± 2	Absorbed in 40 s	
9 on Tyvek®	–	132 ± 4	115 ± 3	Absorbed upon contact	
9 on Kolon®	0.0030	147 ± 2	130 ± 3	Absorbed upon contact	
12 on Tyvek®	0.0012	133 ± 4	109 ± 4	Absorbed upon contact	
12 on Kolon®	0.0028	151 ± 4	136 ± 2	Absorbed upon contact	
Untreated Tyvek®	–	108 ± 1	78 ± 1	Absorbed upon contact	
Untreated Kolon®	–	115 ± 4	85 ± 4	Absorbed upon contact	

[a] Average of 3 runs at different positions on each sample.

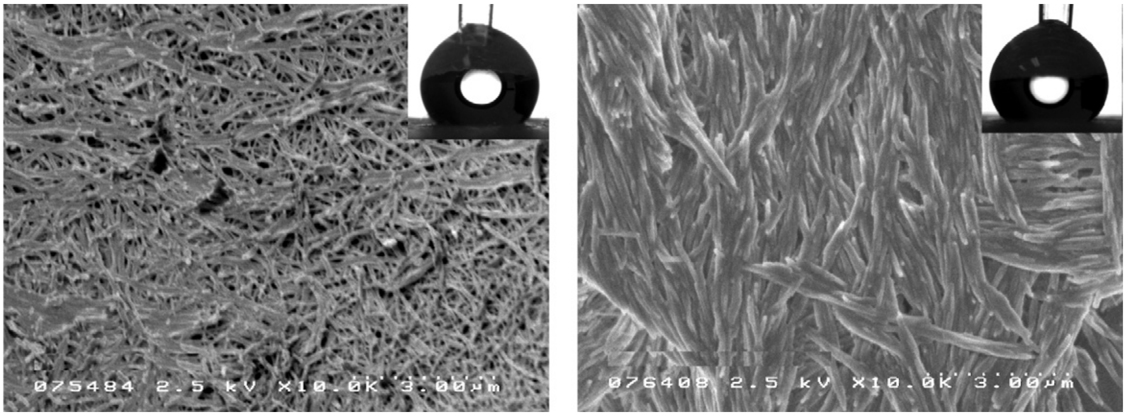


Fig. 3. SEMs at 10,000× magnification of composites prepared by impregnation of non-fluorinated gelator **9** (left) and **12** (right) on Tyvek® fabric.

in addition to the roughness (created by the xerogel) to obtain good oil repellency on the treated composites.

In order to understand whether changes to the surface topology in the absence of fluorine could result in water/oil repellency, we attempted the gel-impregnation of non-fluorinated ($R = C_8H_{17}$) organogelators **9** and **12** on Tyvek® and Kolon® fabrics in toluene and obtained the corresponding treated composites. Fig. 3 shows SEMs at 10,000× magnifications of the composite network structures of the Tyvek® and Kolon® fabric surfaces with an average fiber diameter of 120 nm treated with fluorinated urea–amide gelator **9**.

Surprisingly, the non-fluorinated gelators **9** and **12** also provided high advancing contact angles for water similar to **3a** or **6a**, indicating that high water repellency could be achieved just by using urea–amide derivatives containing hydrocarbon tails. Fluorocarbon functionalities are not essential in achieving high water repellency on these composites. The combination of microporous structure created by the gelator and hydrocarbon functionalities in the gelator backbone helps to provide very good hydrophobic behavior. However, composites derived from non-fluorinated gelators **9** and **12** did not show any hexadecane repellency, and hexadecane was absorbed completely into the substrate upon contact with the surface. The results of the contact angle measurements of organogelators **3a** and **3b**, **6a**–**6c**, **9** and **12** are summarized in Table 2.

A comparison of water/hexadecane contact angles of urea–amides with bis fluoroalkyl chains, **6a** ($R_f = C_6$), **6b** ($R_f = C_4$), **6c** ($R_f = C_2$) and corresponding non fluorinated (hydrocarbon) urea–amide **12**, gel-impregnated on Tyvek® and Kolon® fabrics is shown in Figs. 4 and 5 respectively. The contact angles indicate a clear trend in the reduction of hexadecane advancing and receding contact angles as the perfluoroalkyl chain length of the treated gelator is altered from $R_f = C_6$ (**6a**) to non-fluorinated (**12**) in both Tyvek® and Kolon® fabrics [19].

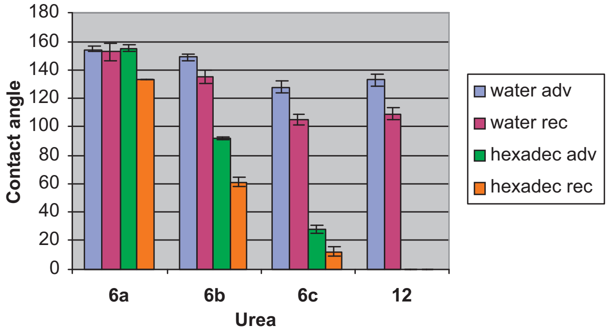


Fig. 4. Water/oil repellency of **6a** ($R_f = C_6$), **6b** ($R_f = C_4$), **6c** ($R_f = C_2$) and corresponding non fluorinated urea–amides (**12**) impregnated on Tyvek® fabric.

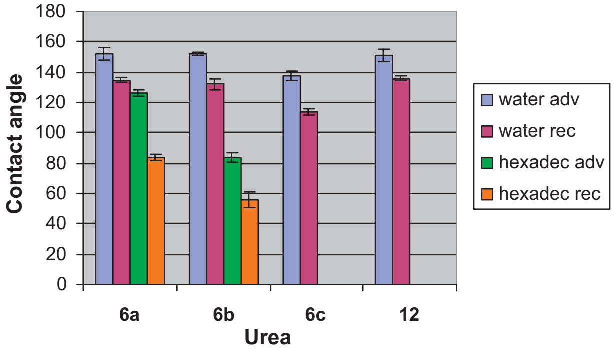


Fig. 5. Water/oil repellency of **6a** ($R_f = C_6$), **6b** ($R_f = C_4$), **6c** ($R_f = C_2$) and corresponding non fluorinated urea–amides (**12**) impregnated on Kolon® fabric.

3. Conclusions

A series of fluorinated and non-fluorinated organogelators bearing urea and amide functionalities were synthesized from readily available amino acid building blocks. These derivatives showed excellent gelation properties in a variety of organic solvents at concentrations ranging from 0.5 to 4 wt%. Gelation in the presence of a nonwoven substrate led to a gel-coated surface, which upon drying provided a composite with porous microstructure morphology impregnated on the surface. The composites obtained via the impregnation of gelators provided surfaces with excellent hydrophobic properties. The superior hydrophobic behavior shown by these composites were attributed to a combination of microsurface morphology created by the xerogel and the presence of hydrophobic functionalities present in the gelator backbone. The composites obtained via the impregnation of gelators bearing long chain perfluoroalkyl group on non-woven substrates also showed excellent oleophobic behavior. Analogous gelators bearing short fluoroalkyl chains or non-fluorinated organogelators showed poor or no oleophobicity.

4. Experimental

4.1. General

All solvents and reagents, unless otherwise indicated, were purchased from commercial sources and used directly as supplied.

1H,1H,2H,2H-perfluorobutylamine, 1H,1H,2H,2H-perfluorohexylamine and 1H,1H,2H,2H-perfluorooctylamine were synthesized from corresponding commercially available iodides via the azide followed by reduction using Raney Ni as described in the literature [20]. Tyvek® polyethylene nonwoven fabric was obtained from E.I. du Pont de Nemours and Company, 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 3a

A mixture of dichloromethane (250 mL), *N*-Boc-β-alanine (5.67 g, 30.0 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCl) (5.75 g, 30.0 mmol) and 4-(dimethylamino)pyridine (3.66 g, 30.0 mmol) was stirred for 10 min at room temperature (RT) followed by addition of 1H,1H,2H,2H-perfluorooctylamine (11.2 g, 31.0 mmol) via an addition funnel. The mixture was stirred for 12 h at RT. The mixture was washed with 2% HCl (2 × 60 mL), saturated $NaHCO_3$ solution (1 × 50 mL) and brine (1 × 50 mL). The resulting organic layer was dried ($MgSO_4$) and concentrated to provide compound **1a** (15.1 g, 28.4 mmol, 94%) as a white crystalline solid. Mp 107–108 °C; ^{1}H NMR (acetone-*d6*): δ 6.25 (bs, 1H), 5.09 (bs, 1H), 3.61 (q, *J* = 6.8 Hz, 2H), 3.42 (q, *J* = 5.8 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.37 (m, 2H), 1.45 (s, 9H); ^{19}F NMR (acetone-*d6*): δ −81.2 (m, 3F), −114.3 (m, 2F), −122.2 (s, 2F), −123.2 (s, 2F), −124.0 (s, 2F), −126.5 (m, 2F).

A suspension of compound **1a** (14.5 g, 27.1 mmol) in dichloromethane (50 mL) was stirred with trifluoroacetic acid (TFA) (24.7 g, 217.2 mmol) at RT for 3 h. Chloroform (50 mL) was added and the bulk of the solvents and TFA were evaporated under vacuum. The resulting trifluoroacetate salt was stirred with saturated $NaHCO_3$ solution (200 mL) and the solid formed was filtered. The residue was washed with cold water and dried under vacuum to provide compound **2a** (9.1 g, 20.9 mmol, 77%) as a white crystalline solid. Mp 115–117 °C; ^{1}H NMR (acetone-*d6*): δ 7.62 (bs, 1H), 3.57 (q, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.0 Hz, 1H), 2.51 (m, 2H), 2.41 (t, *J* = 6.8 Hz, 2H), 1.95–1.77 (bs, 2H); ^{19}F NMR (acetone-*d6*): δ −81.1 (m, 3F), −114.9 (m, 2F), −122.8 (s, 2F), −123.8 (s, 2F), −124.0 (s, 2F), −126.5 (m, 2F).

To a mixture of compound **2a** (4.34 g, 10.0 mmol), dichloromethane (50 mL) and triethylamine (0.05 g, 0.5 mmol) under a N_2 purge was added *n*-octyl isocyanate (1.55 g, 10.0 mmol) and the mixture was stirred for 5 h at RT. The solid product was filtered and washed with cold hexanes (2 × 5 mL) to provide compound **3a** (5.29 g, 9.0 mmol, 90%) as a white crystalline solid. Mp 149–151 °C; ^{1}H NMR (acetone-*d6* @ 50 °C): δ 7.27 (bs, 1H), 5.33 (bs, 2H), 3.40 (q, *J* = 6.0 Hz, 2H), 3.23 (q, *J* = 6.4 Hz, 2H), 2.96 (q, *J* = 6.0 Hz, 2H), 2.36 (m, 2H), 2.20 (t, *J* = 6.4 Hz, 2H), 1.30 (m, 2H), 1.16 (m, 10H), 0.74 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (acetone-*d6* @ 50 °C): δ −82.1 (m, 3F), −114.7 (m, 2F), −122.6 (s, 2F), −123.6 (s, 2F), −124.4 (s, 2F), −126.9 (m, 2F). Elemental analysis: calculated C, 40.75; H, 4.79; N, 7.13; found: C, 40.40; H, 4.83; N, 7.55.

4.3. Synthesis of gelator 3b

Using a similar procedure as described for the synthesis of gelator **3a**, reaction of 1H,1H,2H,2H-perfluorohexylamine (11.8 g, 45.0 mmol) with *N*-Boc-β-alanine (8.5 g, 45.0 mmol) provided **1b** (16.9 g, 38.9 mmol, 87%) as a crystalline solid. Mp 135–137 °C; ^{1}H NMR (acetone-*d6*): δ 7.25 (bs, 1H), 5.76 (bs, 1H), 3.41 (q, *J* = 6.8 Hz, 2H), 3.16 (q, *J* = 6.4 Hz, 2H), 2.32 (m, 2H), 1.42.24 (t, *J* = 7.2 Hz, 2H), 1.26 (s, 9H); ^{19}F NMR (acetone-*d6*): δ −82.4 (m, 3F), −115.2 (m, 2F), −125.5 (m, 2F), −127.1 (m, 2F).

Deprotection of **1b** (16.9 g, 38.9 mmol) using trifluoroacetic acid at RT followed by treatment with saturated $NaHCO_3$ provided compound **2b** (11.9 g, 35.6 mmol, 97%) as a crystalline solid. Mp 90–92 °C; ^{1}H NMR (acetone-*d6*): δ 7.46 (bs, 1H), 3.40 (q, *J* = 4.8 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 1H), 2.34 (m, 2H), 2.25 (t, *J* = 4.8 Hz, 2H), 1.78–1.65 (bs, 2H); ^{19}F NMR (acetone-*d6*): δ −82.4 (m, 3F), −115.2 (m, 2F), −125.5 (m, 2F), −127.1 (m, 2F).

Reaction of **2b** (3.0 g, 8.98 mmol) with *n*-octyl isocyanate (1.39 g, 8.98 mmol) provided compound **3b** (3.68 g, 7.5 mmol, 84%) as a white solid. Mp 135–136.5 °C; ^{1}H NMR (acetone-*d6*): δ 3.39 (q, *J* = 7.2 Hz, 2H), 3.22 (q, *J* = 6.4 Hz, 2H), 2.97 (q, *J* = 6.8 Hz, 2H), 2.33 (m, 2H), 2.22 (t, *J* = 6.4 Hz, 2H), 1.32 (m, 2H), 1.19 (m, 10H), 0.77 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (acetone-*d6*): δ −82.4 (m, 3F), −115.3 (m, 2F), −125.5 (m, 2F), −127.1 (m, 2F). Elemental analysis: C, 44.17; H, 5.77; N, 8.59; found: C, 44.53; H, 5.94; N, 8.66.

4.4. Synthesis of gelator 6a

N-Boc-L-aspartic acid (13.9 g, 60.0 mmol) was condensed with 1H,1H,2H,2H-perfluorooctylamine (43.6 g, 120.0 mmol) and provided compound **4a** (50.8 g, 55.0 mmol, 92%) as a white crystalline solid. Mp 162.5–164 °C; ^{1}H NMR (acetone-*d6*): δ 7.68 (bs, 2H), 6.30 (bs, 1H), 4.35 (bs, 1H), 3.54 (bm, 4H), 3.03–2.65 (bm, 2H), 2.28 (bm, 4H), 1.37 (s, 9H); ^{19}F NMR (acetone-*d6*): δ −81.6 (m, 6F), −114.3 (m, 4F), −122.5 (s, 4F), −123.5 (s, 4F), −124.2 (s, 4F), −126.8 (m, 4F).

Deprotection of **4a** (49.0 g, 53.1 mmol) using trifluoroacetic acid at RT followed by treatment with saturated $NaHCO_3$ provided compound **5a** (36.2 g, 43.9 mmol, 83%) as a white crystalline solid. Mp 108 °C; ^{1}H NMR (acetone-*d6*): δ 4.37 (q, *J* = 4.5 Hz, 2H), 3.61–3.48 (m, 4H), 2.65 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.55–2.38 (m, 5H); ^{19}F NMR (acetone-*d6*): δ −82.2 (m, 6F), −115.0 (m, 4F), −122.8 (s, 4F), −123.8 (s, 4F), −124.6 (s, 4F), −127.2 (m, 4F).

Reaction of **4a** (8.23 g, 10.0 mmol) with *n*-octyl isocyanate (1.55 g, 10.0 mmol) provided compound **6a** (9.4 g, 9.6 mmol, 96%) as a white crystalline solid. Mp 183–185 °C; ^{1}H NMR (acetone-*d6*): δ 7.78 (t, *J* = 5.2 Hz, 1H), 7.68 (bs, 1H), 6.09, (bs, 1H), 5.90 (bs, 1H)], 4.62 (t, *J* = 5.6 Hz, 1 H), 3.57 (m, 4H), 3.18 (m, 2H), 2.80 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.66 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.47 (m, 4H), 1.51 (m, 2H), 1.31 (m, 10H), 0.89 (t, *J* = 6.1 Hz, 3H); ^{19}F NMR (acetone-*d6*): δ −82.1 (m, 6F), −115.1 (m, 4F), −122.8 (s, 4F), −123.8 (s, 4F), −124.5 (s, 4F), −127.1 (m, 4F). Elemental analysis: C, 35.59; H, 3.30; N, 5.73; found: C, 35.82; H, 3.39; N, 5.75.

4.5. Synthesis of gelator 6b

Using a similar procedure as described for the synthesis of gelator **6a**, reaction of 1H,1H,2H,2H-perfluorohexylamine (14.2 g, 54.0 mmol) with *N*-Boc-L-aspartic acid (5.8 g, 25.0 mmol) provided **4b** (15.6 g, 21.6 mmol, 86%) as a white crystalline solid. Mp 155–156 °C; ^{1}H NMR (acetone-*d6*): δ 7.57 (bs, 2H), 6.32 (bs, 1H) 4.38 (q, *J* = 7 Hz, 1 H), 3.55 (m, 4H), 2.69 (dd, *J* = 16, 6 Hz, 1H), 2.64 (dd, *J* = 16, 4 Hz, 1H), 2.45 (m, 4H), 1.4 (s, 9H); ^{19}F NMR (acetone-*d6*): δ −82.4 (m, 6F), −115.3 (m, 4F), −125.6 (s, 4F), −127.1 (m, 4F).

Deprotection of **4b** (14.8 g, 20.4 mmol) using trifluoroacetic acid at RT, followed by treatment with saturated $NaHCO_3$ provided **5b** (12.2 g, 19.58 mmol, 96%) as a white solid. Mp 81–82 °C; ^{1}H NMR ($CDCl_3$): δ 7.73 (bs, 1H), 6.40 (bs, 1H), 3.58 (dd, 6.4, 4.8 Hz, 1H), 3.52 (m, 4H), 2.60–2.50 (m, 2H), 2.33–2.20 (m, 5H); ^{19}F NMR ($CDCl_3$): δ −81.5 (m, 6F), −114.6 (m, 4F), −125.0 (s, 4F), −126.4 (m, 4F).

Reaction of **5b** (6.0 g, 9.6 mmol) with *n*-octyl isocyanate (1.49 g, 9.6 mmol) provided compound **6b** (7.25 g, 9.3 mmol, 97%) as a white crystalline solid. Mp 172 °C; ^{1}H NMR (acetone-*d6*): δ 7.72 (bs, 1H), 7.58 (bs, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.93 (bs, 1H), 4.58 (q, *J* = 5.8 Hz, 1 H), 3.55 (m, 4H), 3.15 (m, 2H), 2.74 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.55 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.47 (m, 4H), 1.48 (m, 2H), 1.30 (m, 10H), 0.90 (t, *J* = 6.1 Hz, 3H); ^{19}F NMR (acetone-*d6*): δ −82.4 (m, 6F), −115.3 (m, 4F), −125.5 (t, *J* = 8.6 Hz, 4F), −127.1 (m, 4F). Elemental analysis: C, 38.57; H, 4.14; N, 7.20; found: C, 38.51; H, 4.21; N, 7.22.

4.6. Synthesis of gelator 6c

Using a similar procedure as described for the synthesis of gelator **6a**, reaction of 1H,1H,2H,2H-perfluorobutylamine (2.23 g, 12.27 mmol) with *N*-BOC-L-aspartic acid (1.43 g, 6.13 mmol) provided **4c** (2.06 g, 5.06 mmol, 83%) as a white crystalline solid. ^{1}H NMR (CDCl$_3$): δ 7.29 (bs, 1H), 6.26 (bs, 1H), 6.11 (bs, 1H), 4.35 (q, *J* = 4.0 Hz, 1H), 3.57 (m, 4H), 2.83 (dd, *J* = 15.2, 4.4 Hz, 1H), 2.56 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.32 (m, 4H), 1.47 (s, 9H); ^{19}F NMR (CDCl$_3$): δ −86.2 (d, *J* = 26 Hz,6F), −118.4 (dq, *J* = 18.4, 7.8 Hz, 4F).

Deprotection of **4c** (1.94 g, 4.77 mmol) using trifluoroacetic acid at RT, followed by treatment with saturated NaHCO$_3$ provided **5c** (1.5 g, 3.54 mmol, 74%) as a white solid. ^{1}H NMR (CDCl$_3$): δ 7.83 (bs, 2H), 6.33 (bs, 1H), 6.10 (bs, 1H), 4.32 (bs, 1H), 3.57 (m, 4H), 2.64 (m, 2H), 2.30 (m, 4H); ^{19}F NMR (CDCl$_3$): δ −86.2 (d, *J* = 26 Hz,6F), −118.3 (dq, *J* = 18.4, 7.8 Hz, 4F).

Reaction of **5c** (0.5 g, 1.18 mmol) with *n*-octyl isocyanate (0.183 g, 1.18 mmol) provided compound **6c** (0.56 g, 0.963 mmol, 82%) as a white crystalline solid. ^{1}H NMR (acetone-*d6*): δ 7.78 (t, *J* = 5.2 Hz, 1H), 7.68 (bs, 1H), 7.58 (bs, 1H), 5.92 (bs, 1H), 5.54 (bs, 1H), 4.41 (bs, 1H), 3.53 (m, 4H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.80 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.66 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.41 (m, 4H), 1.47 (m, 2H), 1.31 (m, 10H), 0.90 (t, distorted, 3H); ^{19}F NMR (CDCl$_3$): δ −86.2 (d, *J* = 26 Hz,6F), −118.3 (dq, *J* = 18.4, 7.8 Hz, 4F). Elemental analysis: C, 43.60; H, 5.58; N, 9.69; found: C, 44.2; H, 5.87; N, 9.5.

4.7. Synthesis of gelator 9

Using a similar procedure as described in the synthesis of gelator **3a**, reaction of *n*-octylamine (5.71 g, 45.0 mmol) with *N*-Boc-β-alanine (8.50 g, 45.0 mmol) provided **7** (11.6 g, 38.6 mmol, 86%) as a white crystalline solid. Mp 67.5–68.4 °C. Deprotection of **7** (10.5 g, 35.0 mmol) with trifluoroacetic acid at RT provided **8** (6.5 g, 32.5 mmol, 93%) as a white solid. Mp 142–143.5 °C. Reaction of **8** (1.5 g, 7.5 mmol) with *n*-octyl isocyanate (1.16 g, 7.5 mmol) provided compound **9** (2.41 g, 6.78 mmol, 91%) as a white solid. Mp 176.5–177.5 °C; ^{1}H NMR (methanol-*d4*): δ 3.38 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 1.49 (m, 4H), 1.33 (bs, 20H), 0.92 (t, distorted, 6H).

4.8. Synthesis of gelator 12

Using a similar procedure as described in the synthesis of **6a**, reaction of *N*-Boc-L-aspartic acid (10.0 g, 43.1 mmol) with *n*-octylamine (11.1 g, 86.2 mmol) provided *N*-Boc-L-Asp-dioctylamide **10** (18.8 g, 41.3 mmol 92%) as a white solid. Mp 112–113 °C. Compound **10** (18.6 g, 41.0 mmol) was deprotected using trifluoroacetic acid to obtain **11** (13.4 g, 37.7 mmol, 96%) as a white solid. Mp 120.5–122 °C. Reaction of **10** (1.78 g, 5.0 mmol) with *n*-octyl isocyanate (0.776 g, 5.0 mmol) provided compound **12** (2.53 g, 4.96 mmol, 99%) as a white crystalline solid. Mp 169.6–171.4 °C; ^{1}H NMR (DMF-*d7*): δ 7.38 (bs, 2H), 6.06 (d, *J* = 8.0 Hz, 1H), 6.01 (t, *J* = 5.2 Hz, 1H), 4.52 (g, *J* = 6.4 Hz, 1H), 3.13 (m, 6H), 2.59 and 2.55 (2 merged dd, *J* = 15.0, 6.5 Hz, 2H), 1.48 (m, 6H), 1.31 (bs, 30H), 0.89 (t, distorted, *J* = 6.8 Hz, 9H). Elemental analysis: C, 68.19; H, 11.44; N, 10.97; found: C, 68.28; H, 11.62; N, 10.87.

4.9. Gelation in organic solvents

Generally, 1–4 wt % of a gelator in an organic solvent in a closed vial was heated in a reactor block equipped to heat multiple vials to 5 °C below the boiling point of the solvent until a clear solution was obtained. The vials were allowed to cool to RT either 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. Stability of the gel was tested by inverting the vial, and gel samples for which the whole mass remains a single phase (no phase separation between solid and liquid phase) are considered stable.

4.10. 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 to 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 at RT 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.

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