Synthesis and Self-Assembling Properties of Polymerizable Organogelators

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Abstract: In this paper we report the development of a family of polymerizable urea derivatives that are gelators for organic solvents. The design involves amino-acid-based urea derivatives containing methacrylate functional groups. Several of the bis-ureas show excellent gelation properties in a variety of organic solvents at very low concentrations (1.5 mM). The self-assembling properties of these compounds were studied by X-ray powder diffraction, optical microscopy, and electronic microscopy. The molecules self-assemble into fibrous aggregates as indicated by scanning electron microscopy. Depending on the nature of the monomeric unit, the structure of the aggregates ranges from small to large fibers and planar sheets. In polar solvents, the molecules exhibit multilamellar packing modes. The organogels can be polymerized by photoirradiation leading to significant increases in stability as indicated by changes in phase-transition temperature. The morphology of the aggregates was seen to maintain a similar structure both before and after irradiation. This method provides a novel type of polymer with designed self-assembling architecture and also affords to a route to stabilized polymer gels.

Keywords: organogels · polymerization · self-assembly · supramolecular chemistry · synthesis

Introduction

There has been a growing interest in the gelation of organic solvents by low molecular-weight organic compounds.[1] This activity is fueled by the potential application of the gels as novel and functional materials with a level of order imposed by the interactions of the molecular gelator. Gels are thought to form through the initial assembly of the gelator molecules into fibrous nanostructures which then further organize into a three dimensional lattice, trapping the solvent within the voids of the network. The gels formed by small organic molecules in organic solvents are often called physical gels or organogels. In these systems, the three-dimensional network is held together by noncovalent forces such as hydrogen bonding, $\pi-\pi$ stacking, and van der Waals interactions. The attraction of self-assembled gel matrices as materials lies in their ease of formation, their potential for functionalization, and the presence of large pores throughout the network. In particular, the self-assembled nanostructures formed by organogelators may find use as sensor matrices[2] or as templates for the synthesis of novel or smart materials.[3, 4]

Despite the advances made in supramolecular chemistry, the prediction of gelation properties for different compound classes remains difficult. An attractive strategy for imposing a predictable interaction within the gel is to incorporate complementary hydrogen-bonding groups into the monomer unit. Ureas are good candidates for this purpose. The hydrogen-bonding properties of the urea group have been extensively studied and exploited in various molecular recognition systems.[5] For example, urea derivatives have been shown to form extended linear hydrogen-bonding arrays in the solid state as shown in Figure 1. When combined with other

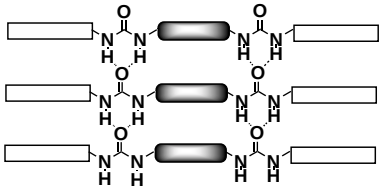

Figure 1. Schematic representation of hydrogen bonding array formed by bis-ureas.

structural features, this type of hydrogen-bonded self-recognition can lead to good gelation properties for ureas in organic or aqueous solvents.[6, 7]

Organogels generally suffer from a structural instability that leads to collapse of the network within the aerogels when the solvent is removed. In some cases mixtures of supercritical (sc) CO_2 and organic solvents have been used as the environment for gel formation.[8] Removal of the solvent under conditions of low pressure and temperature can lead to the formation of low-density materials (aerogels) that are highly porous with extensive cavities throughout the supramolecular network.[9] We have recently reported a family of fluorinated

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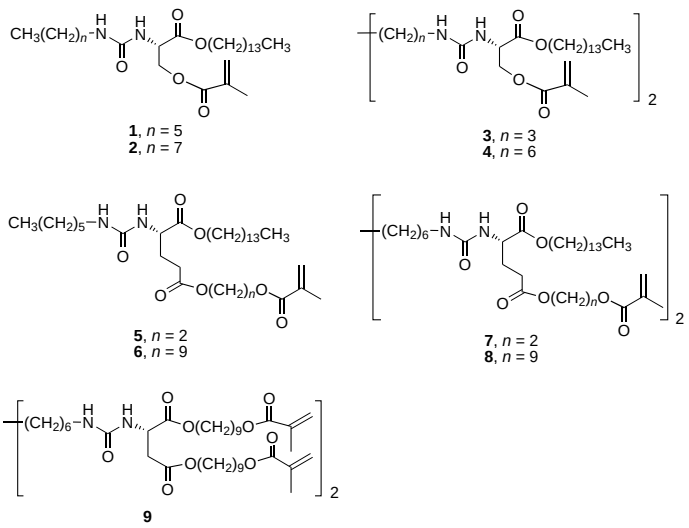
bis-ureas that gel sc CO_2 without the need for co-solvents.[8] The high vapor pressure of sc CO_2 leads to its facile evaporation as temperature and pressure approach ambient, leaving the gel matrix unperturbed. The resulting solid has a density of approximately 0.004 g mL^{-1} and a well-defined short fibrous network. However, like most aerogels derived from organogelators, the fluorinated bis-urea foam is fragile and crumbles on contact. This fragility is almost certainly due to the weak noncovalent interactions that are the primary stabilizing forces for the aerogel network. In contrast, aerogels from polymer gelators are generally more stable because of their covalent framework.[10] However, this strategy lacks the flexibility of application and subunit structure that comes from the self-assembly of small molecule subunits.

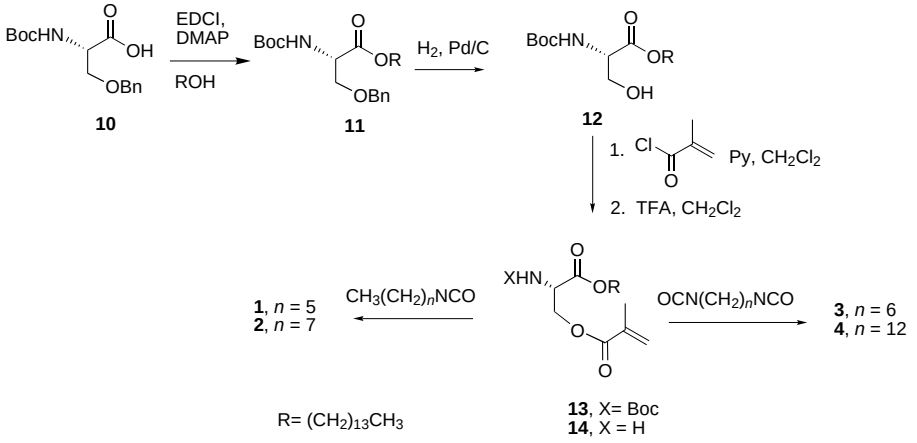
An ideal approach to stable aerogels might involve combining the advantages of self-assembling organogels with those of polymer gels.[10] This could be achieved by first allowing the gel to self-assemble through noncovalent interactions and then stabilizing the system by polymerization of latent functional groups within the monomer. The reactive groups must be positioned so that they are close enough to cross-link in the self-assembled network and not cause a disruption in the matrix. If these criteria are met, polymerization of the gel should lead to a material with much improved stability and mechanical strength.[11] Despite much effort in the field, there are few readily accessible polymerizable organogelators.[12–14]

Our approach to this problem involved the design of chiral polymerizable derivatives that could gel a range of organic solvents. The polymerizable subunits are based on an amino acid and bis-urea platform incorporating methacrylate functional groups. We had earlier shown that bis-urea derivatives could function either as molecular hosts for dicarboxylic guests[5a] or as organogelators,[7a] depending on the nature of the backbone. In this paper, we describe the preparation of a series of derivatives based on this strategy, and show that they are versatile gelators for organic solvents at very low concentration and the gels are significantly stabilized by polymerization.



linking chain in bis-ureas, size of the alkyl esters, and positioning of the methacrylate groups, we prepared a series of mono- and bis-urea derivatives **1**–**9**. Compounds **1** and **2** contain a single urea linked to a serine alkyl ester, **3** and **4** are bis-urea/serine derivatives, **5** and **6** link a glutamate ester to a mono-urea, **7** and **8** are bis-glutamate ester/bis-urea derivatives, and **9** is an aspartic acid derivative with methcrylates at the end of both chains. All compounds except **9** have mixed alkyl and methacrylate-containing esters.

The syntheses of compounds **1**–**9** are shown in Schemes 1–3. The serine derivatives **1**–**4** were synthesized

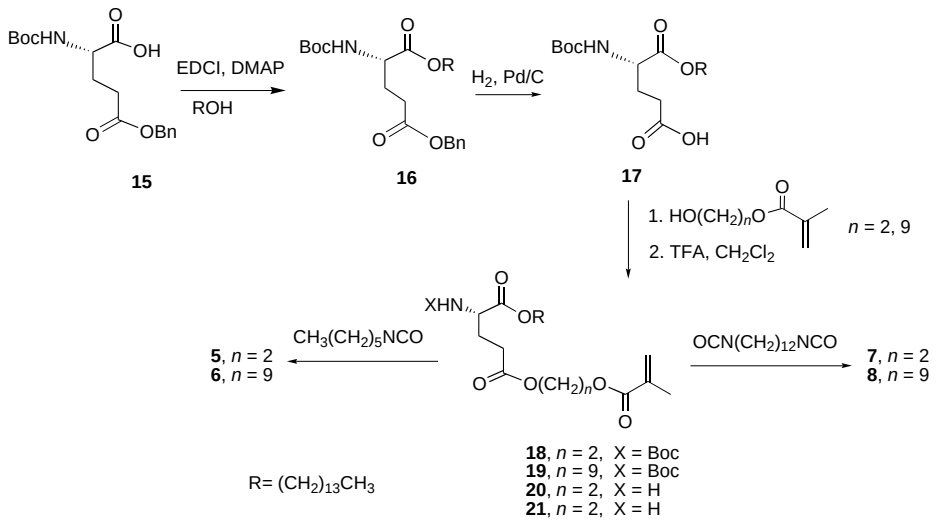


Scheme 1. Synthesis of serine derivatives **1**–**4**.

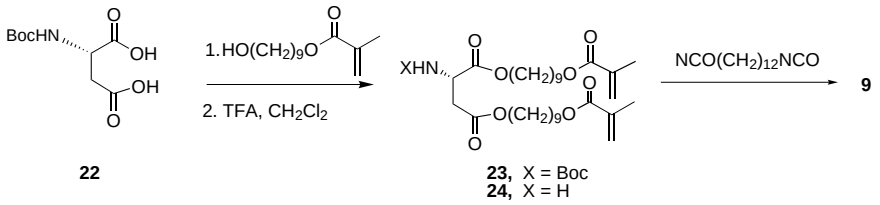
Results and Discussion

Synthesis: Three key features were incorporated into the polymerizable organogelator design: the urea hydrogen bonding motif, one or more alkyl chains, and the methacrylate groups. Ureas tend to be highly crystalline, which is an unsuitable property for gel formation. However, introduction of long chain alkyl ester and/or methacrylate groups should increase the solubility of the molecule in nonpolar solvents. To test the relative importance of number of ureas, length of the linking chain in bis-ureas, size of the alkyl esters, and positioning of the methacrylate groups, we prepared a series of mono- and bis-urea derivatives **1**–**9**. Compounds **1** and **2** contain a single urea linked to a serine alkyl ester, **3** and **4** are bis-urea/serine derivatives, **5** and **6** link a glutamate ester to a mono-urea, **7** and **8** are bis-glutamate ester/bis-urea derivatives, and **9** is an aspartic acid derivative with methcrylates at the end of both chains. All compounds except **9** have mixed alkyl and methacrylate-containing esters.

The syntheses of compounds **1**–**9** are shown in Schemes 1–3. The serine derivatives **1**–**4** were synthesized from the *t*Boc, benzyl-protected amino acid by esterification with tetradecanol and debenzylation by hydrogenation. The hydroxyl group was re-esterified using methacryloyl chloride to give the *t*Boc protected derivatives. Deprotection and reaction of the free amine with the corresponding isocyanate gave the desired urea derivatives. Formation of the urea as the last step in the synthetic route avoided the problems of poorly soluble intermediates. Similar routes were used to prepare the glutamate and aspartate derivatives.



Scheme 2. Synthesis of glutamic acid derivatives **5**–**8**.



Scheme 3. Synthesis of aspartic acid derivative **9**.

Gelation properties: The gelation properties of compounds **1**–**9** were tested in a range of solvents, and the results are collected in Table 1. In general, the bis-ureas were found to be more effective organogelators than the corresponding mono-urea derivatives. This was true for a variety of organic solvents, including alkanes, esters, alcohols, and acetone. The gelation usually occurred at room temperature at concentrations of urea derivative as low as 0.2% wt. The bis-ureas have lower solubility compared to the mono-ureas and in some cases heating was required to fully dissolve them. The glutamic acid derivatives form more stable gels than the serine derivatives. Compound **9**, with methacrylate groups at the end of both long chain alkyl esters, showed greater solubility than the other bis-ureas. This is consistent with the branched methacrylate group influencing hydrocarbon packing and increasing chain randomness. However, the presence of two identical hydrocarbon tails and the overall symmetry of **9** appear to make it a poorer gelator compared to the compounds containing two different alkyl ester chains.

Table 1. Gelation properties of compounds **1**–**9** in organic solvents at room temperature.[a]

	Hexane	Ethyl acetate	Chloroform	Acetone	EtOH	Ethylene glycol
1	S	S	S	S	S	G (2.5)/C
2	S	S	S	S	S	I/C
3	G (3)	G (5)	S	G (10)	G (10)/P	I
4	G (10)	G (8)	S	G (10)	G (4)	I/C
5	S	S	S	S	S	I/C
6	S	S	S	S	S	I/C
7	G (2.5)	G (2.5)	S	G (2.5)	G (2.5)	I
8	G (2)	G (2)	S	G (2.5)	G (2)	I
9	I	S	S	S	S	I

[a] G: gel, S: soluble ($> 20\,mg\,mL^{-1}$), I: insoluble upon heating, P: precipitation, C: crystallization. The value given in parentheses is the minimum concentration in $mg\,mL^{-1}$ to achieve gelation at room temperature.

Stabilization of the gel on polymerization: The effect of light-induced polymerization on the gels and their thermal stability was assessed at 0.5% and 1% wt concentrations in ethyl acetate. The melting point of the gels was measured before and after polymerization by using the dropping ball method (Table 2).[5a] Polymerization was carried out with a 500 W Hg lamp, and the extent of cross-linking was monitored by observing the disappearance of the alkene ^1H NMR resonances at $\delta \sim 6.0$ and 5.5 ppm. Interestingly, the ease with which the ureas underwent polymerization varied with their structures. Compounds **7** and **8** were fully polymerized after 2–4 hours of irradiation, whilst **4** required approximately 6–8 hours for complete reaction. Compound **3** only forms a gel in ethanol with fast cooling or by sonication. The gel was not stable to the addition of the radical initiator or to mechanical shaking, with the compound precipitating out of the solution. This effect is presumably related to the relative structural flexibility of the compounds. Glutamic acid represents a more flexible linker, relative to serine, and the glutamate/ureas may be better able to conformationally accommodate intrasubunit cross-linking. The serine derivatives are more rigid and this may decrease the ability of the methacrylate groups to adopt an optimal position for reaction.

Table 2. Thermal stability of the ethyl acetate gels before and after polymerization by melting point measurement.

	7 [5 mg mL^{-1}]	**7** [10 mg mL^{-1}]	**8** [5 mg mL^{-1}]	**8** [10 mg mL^{-1}]
before [°C]	34	40	36	39
after [°C]	>110	>110	>110	>110

With compound **7** the melting point of the gel in ethyl acetate after polymerization was $>110\,^{\circ}C$ at concentrations of $5\,mg\,mL^{-1}$ and $10\,mg\,mL^{-1}$;

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this temperature is significantly above the boiling point of ethyl acetate (77 °C). Heating to 110 °C caused little change in the appearance of the gel with no shrinkage or loss of solvent. The melting point of the gels after polymerization seems to be somewhat independent of concentration perhaps due to the strength of covalent bonding compensating for the concentration effect. A similar increase in stability has recently been reported for a gelator based on (1*R*,2*R*)-*trans*-1,2-bis(ureido)cyclohexane. In that case polymerization gave a thermostability change at a concentration of 10 mg mL^{-1} in butyl acetate from 80 °C to 135 °C, an increase of 55 °C.[13a]

Morphology studies: Scanning electron and optical microscopy were used to investigate the morphologies of the aggregates. The various urea derivatives in this investigation gave rise to gels of widely differing morphologies, from sheets to ribbons and fibers. However, the morphology of the gels did not change significantly after polymerization. Clusters of ribbonlike structures are formed by compound **8** in ethyl acetate (Figure 2a) that after polymerization (Figure 2b)

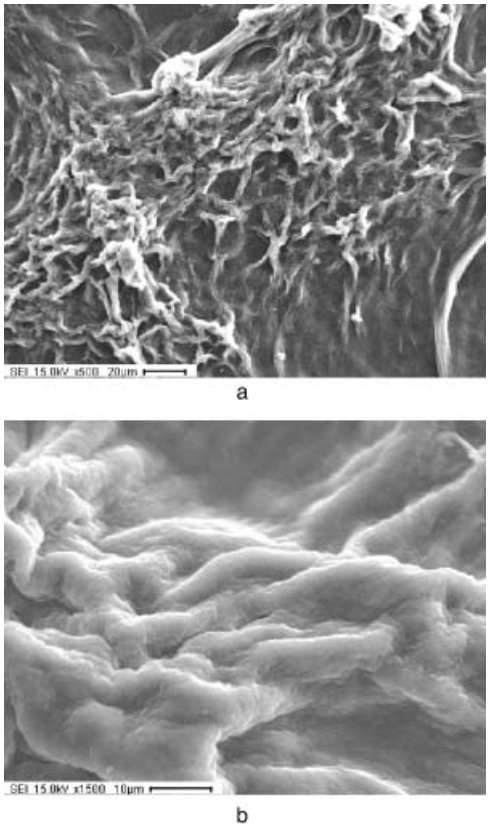

Figure 2. SEM images of the dried gels formed by compound **8** in ethanol: a) before polymerization, b) after polymerization. The scale bar represents 20 μm in a) and 10 μm in b).

retain essentially the same morphology with somewhat smoother surfaces. Similarly, compound **7** in ethyl acetate forms a material composed of bundled ribbons that are little affected by polymerization (Figure 3a,c). At high magnification (× 10000) the individual bundles are seen to be composed of aggregated fibers (Figure 3b,d). The morphologies of the areogels formed by compound **3** in ethanol correspond to long intertwined fibers (Figure 4a,b), with an individual diameter

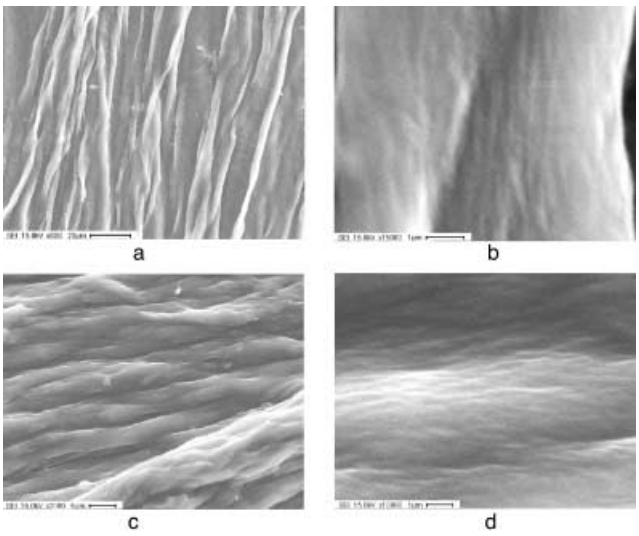

Figure 3. SEM images of the dried gels formed by compound **7** in ethyl acetate: a) and b) are before polymerization, c) and d) are after polymerization. The scale bar represents 20 μm in a), 1 μm in b), 5 μm in c), and 1 μm in d).

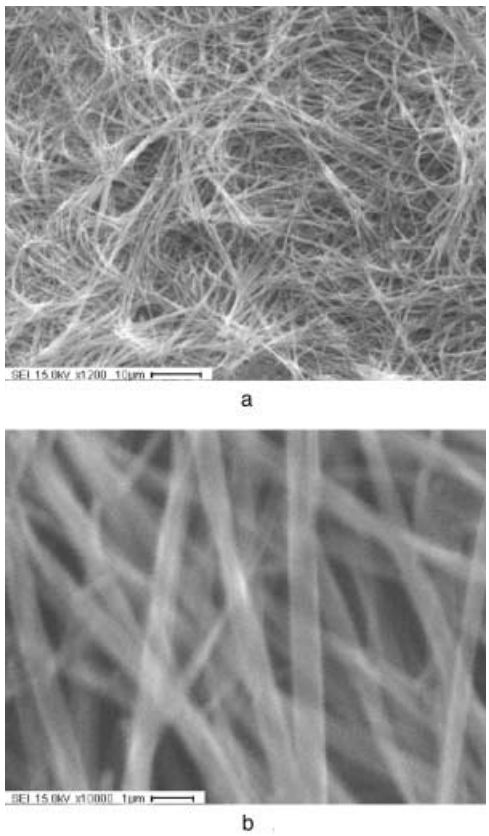

Figure 4. SEM images of the dried gels formed by compound **3** in ethanol: a) at low magnification, b) at high magnification. The scale bar represents 10 μm in a) and 1 μm in b).

of about 0.5 μm and length of approximately 200 μm. When dissolved in ethylene glycol, serine mono-urea **2** formed unstable gels which crystallize on standing. An optical microscopy study of these aggregates indicated typical lamellar packing structures (Figure 5). Monoureas **1**, **2**, and **5**, with a shorter link between the methacrylate and the amino acid backbone, formed highly birefringent images under polarized

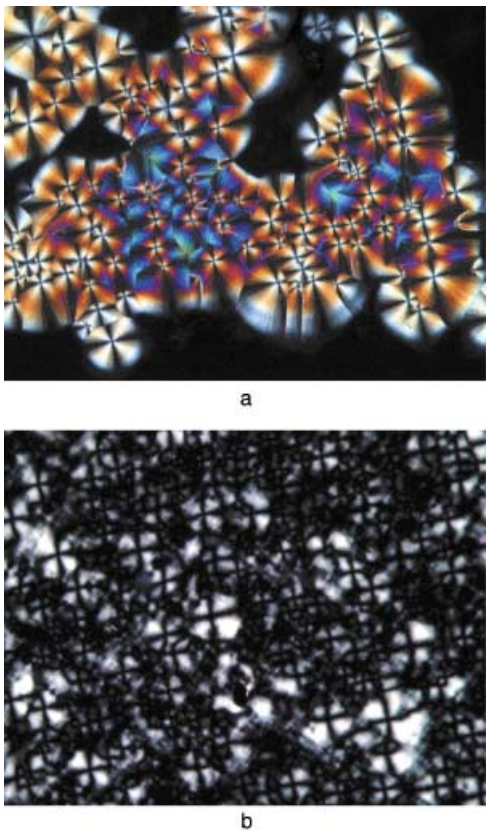

Figure 5. Optical micrographs of the mono-ureas by polarized light: a) compound **1** in ethylene glycol, b) compound **6** from ethanol/water (10%).

light (Figure 5a), indicating an ordered, crystalline arrangement. Analysis of the samples by SEM showed them to contain fibrous ribbons and sheets. The spherulite structures formed by these compounds are dependent on the chirality of the self-assembling molecules, as is typical for many chiral liquid crystalline phases.[15] In contrast, the mono-ureas with a longer link between the methacrylate and amino acid (compounds **6** and **8**) show the characteristic Maltese cross formed by structures that pack in a lamellar arrangement (Figure 5 b). Generally, polar solvents were necessary to observe these structures.

Structure determination by X-ray diffraction (XRD): The molecular packing of the gelators prior to polymerization was studied by wide-angle X-ray powder diffraction. Good diffraction patterns were obtained for the mono-ureas and the major peaks observed are collected in Table 3. In particular, distinct interchain distances of 3–5 Å were observed. In the case of certain bis-ureas, however, only reflections corresponding to the layer separation could be seen. This suggests a low crystallinity (high fluidity) among the hydrocarbon chains as compared to the mono-ureas. For mono-ureas, such as **1**, **2**, **5**, and **6**, relatively high crystallinity is observed, with the components packing more tightly than the corresponding bis-urea. These properties mirror the gelation properties of the molecules, again indicating that the gel state is intermediate between liquid and crystal phases. When the crystallinity of the system is high, as with the mono-urea, solvent encapsulation is low, leading to poorer gelation properties. When the hydrocarbon chains are more flexible, subunit packing is less dense and as a result more solvent molecules can be entrapped within the intranetwork cavities leading to better gelation properties.

Table 3. Major peaks in the XRD pattern for compounds **1**–**9**.

	d-spacing [Å]
1	solid: 31.32, 18.48, 15.66, 12.38, 10.35, 5.17, 4.44, 4.05, 3.91; gel: 31.40, 15.72
2	solid: 32.71, 16.18, 9.51, 4.52, 4.10, 3.94, 3.63
3	solid: 32.97, 19.99, 16.48, 13.27, 11.02, 9.93, 8.25, 7.95, 6.61, 5.48, 4.07, 3.96
4	solid: 20.1; gel: 20.2
5	solid: 19.2, 12.9, 9.84, 8.79, 6.61, 4.96, 4.49, 4.28, 3.84, 3.58
6	solid: 33.5, 16.4, 12.5, 10.8, 6.64, 4.12, 3.90, 3.73
7	solid: 28.3, gel: 23.9
8	solid: 34.2, gel: 31.3, 25.8
9	none observed

In a mixture of water and ethanol, mono-ureas **1**, **2**, **5**, and **6** can self-assemble into well-organized planar sheets, ribbons, and fibers. The optical micrographs reveal that the molecules adopt ordered lamellar structures, in agreement with the XRD data. An effort was made to determine the X-ray diffraction pattern of the gel state, and a distance corresponding to the layer length could be observed. As shown in Table 3, the general trend was that the gels give fewer reflections than solids, consistent with the decreased order within the gel. In this study, compound **8** showed the best gelation property among all of the mono- and bis-urea derivatives. The morphology of the areogel is somewhat different from a fibrous-type aggregate, instead adopting a smooth planar sheet or ribbon structure. There appears to be an important requirement for two urea functional groups attached to long alkyl chains for effective gelation. The mono-ureas have higher crystallinity and show liquid crystalline properties, but are not good gelators. Possibly, the smaller size and greater rigidity of the mono-ureas inhibit them from forming three-dimensional networks. The bis-urea glutamate derivatives contain one long chain and one shorter chain and show better gelation properties than the corresponding serine derivatives perhaps due to the increased rigidity of the latter.

Conclusion

We have designed and synthesized a family of polymerizable organogelators. The bis-ureas synthesized were found to be excellent organogelators with optimal properties being shown by the glutamic acid bis-urea derivatives. These molecules form gels at concentrations as low as 0.2% wt in a variety of solvents. Furthermore, irradiation with UV light leads to polymerization and stabilization of the gels. The self-assembled structure and morphologies of these compounds were studied by using electronic and optical microscopy and X-ray powder diffraction. The SEM of the areogels showed fibrous and sheetlike morphologies depending on the structure of the gelators, the solvent, and the concentration. In more polar solvents and at lower concentrations, the fibrous structures are well resolved. At higher concentrations, only flat sheetlike ribbons or bundles are observed. The X-ray powder diffrac-

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tion data are consistent with the gelation properties, with higher crystallinity indicating poorer gelation. The presence of a long alkyl chain is essential for effective gelation. In general, incorporation of branched methacrylate groups leads to disruption of the packing of the hydrocarbon tail and an increase in solubility. Upon polymerization, the bis-ureas show increased thermal stability at temperatures above the boiling point of the solvent. The mono-ureas showed interesting liquid crystalline phases observed by optical microscopy under crossed polarizers.

Experimental Section

Gelation: A weighed amount of each compound was mixed with a measured volume of selected solvents. Generally, low heating or sonicating are necessary to dissolve the sample, after which it was cooled to room temperature for 30 minutes. Gelation was determined by the absence of flow of the solvent when the vial was inverted.

Electron microscopy: A small piece of gel was deposited onto a cleaned glass slide, which was then dried in the air under vacuum. The slides were coated with carbon and imaged using a JEOL JXA-8600 electron microprobe with an accelerating voltage of 15 kV and an emission current of 100–500 pA.

Synthesis: The compounds in this study were synthesized by similar procedures. Details are given for the first example of each class. Particular caution was taken to avoid the decomposition of the methacrylate containing compounds.

Tetradecyl (2*S*)-3-(benzyloxy)-2-[(*tert*-butoxycarbonyl)amino]propanoate (11): *N*-*t*Boc-*O*-Benzyl-L-serine **10** (2.95 g, 0.01 mol), 1-tetradecanol (2.40 g, 0.011 mol), and dimethylamino pyridine (0.12 g, 0.001 mol) were added to dry dichloromethane (50 mL). The mixture was cooled in an ice bath and protected from moisture by using a calcium chloride drying tube. 1,[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI) (2.10 g, 0.011 mol) was added to the cooled mixture, and the reaction was stirred for 6–8 h, after which time the esterification was complete as indicated by TLC. The reaction mixture was concentrated to dryness, taken up in ethyl acetate, and washed with water three times. The organic layer was dried over sodium sulfate, and the solvent was removed to yield a white solid (5.00 g). The crude mixture was purified by flash chromatography (hexane/acetate 9:1) to give pure product as a white crystalline solid (4.82 g, 98%). M.p. 34.5–35.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$), $\delta = 7.34$–7.24 (m, 5H), 5.38 (d, $J = 8.51$ Hz), 4.49 (m, 2H), 4.40 (m, 1H), 4.12 (m, 2H), 3.86 (m, 1H), 3.67 (m, 1H), 1.58 (m, 2H), 1.43 (s, 9H), 1.23 (br s, 24H), 0.83 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.7$, 155.4, 137.6, 128.3, 127.7, 127.5, 79.8, 73.2, 70.1, 65.6, 54.0, 31.9, 29.6, 29.5,29.5, 29.3, 29.2, 28.5, 29.3, 25.8, 22.6, 14.1; HRMS (FAB) calcd for $C_{29}H_{50}NO_5$ [M^++H]: 492.3689; found: 492.3689.

Tetradecyl (2S)-2-[(*tert*-butoxycarbonyl)amino]-3-hydroxypropanoate (12): Pd/C catalyst (0.25 g) was added to compound **11** (2.46 g, 5.0 mmol) in ethanol (100 mL), and the mixture was stirred under one atmosphere of hydrogen for 24 h. The catalyst was removed by filtration through celite. The solution was concentrated, and the sample was further dried under vacuum for 12 h to give a colorless crystalline material (2.00 g, 99%). M.p. 32.5–33.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.44$ (s, 1H), 4.34 (s, 1H), 4.14 (t, $J = 6.62$ Hz, 2H), 3.91 (m, 2H), 2.38 (s, 1H; OH), 1.62 (m, 2H), 1.43 (s, 9H), 1.23 (s, 24H), 0.85 (t, $J = 7.25$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.8$, 155.8, 80.3, 67.0, 63.8, 55.8, 31.9, 29.7, 29.6, 29.5, 29.5, 29.3, 29.2, 28.5, 28.3, 25.8, 22.7, 14.1; HRMS (FAB) calcd for $C_{22}H_{44}NO_5$ [M^++H]: 402.3219; found: 402.3221.

(2*S*)-2-[(*tert*-Butoxycarbonyl)amino]-3-oxo-3(tetradecyloxy)propyl 2-methylacrylate (13): Compound **11** (2.0 g, 5.0 mmol) was dissolved in pyridine (1 mL) and dry dichloromethane (50 mL), and the mixture was cooled to 0 °C in an ice bath. Methacryloyl chloride (0.53 mL, 5.5 mmol) was added to the mixture under dry nitrogen. The reaction mixture was stirred under N_2 for 6 h. The mixture was poured into ice (20 g) and extracted with dichloromethane three times. The combined organic phase was dried over sodium sulfate, and the solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (hexane/acetate 12:1) to give the product as a white solid (2.10 g, 90%). M.p. 59.0–60.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.07$ (s, 1H), 5.57 (s, 1H), 5.28 (s, 1H), 4.60 (s, 1H), 4.42 (m, 2H), 4.15 (m, 2H), 1.90 (s, 3H), 1.60 (m, 2H), 1.43 (s, 9H), 1.23 (br s, 24H), 0.86 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 169.8$, 166.6, 155.1, 135.6, 126.2, 80.2, 66.0, 64.8, 53.0, 31.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.4, 28.2, 25.7, 22.6, 18.1, 14.0; HRMS (FAB) calcd for $C_{21}H_{40}NO_4$ [M^++H − Boc]: 370.2957; found: 370.2955.

(2*S*)-2-Amino-3-oxo-3-(tetradecyloxy)propyl 2-methylacrylate (14): The free amine of the serine derivative was not stable. It was generally not isolated before the next step. The *t*Boc-protected compound was deprotected with TFA in dichloromethane at 0–10 °C, the solvent was removed, and the residue was dried using a vacuum pump for 24 h before coupling with the bis-isocyanate. The spectroscopic data of the TFA salt of **14**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.10$ (s, 1H), 5.60 (s, 1H), 4.63 (m, 2H), 4.40 (s, 1H), 4.18 (m, 2H), 1.86 (s, 3H), 1.61 (m, 2H), 1.23 (s, 24H), 0.85 (t, $J = 7.25$ Hz, 3H); ^{13}C NMR(125 MHz, $CDCl_3$): $\delta = 166.8$, 166.7, 134.8, 127.6, 67.6, 61.8, 52.8, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.1, 28.2, 25.6, 22.7, 17.8, 14.0.

(2S)-2-{[(Hexylamino)carbonyl]amino}-3-oxo-3-(tetradecyloxy)propyl 2-methylacrylate (1): Compound **13** (0.18 g, 0.38 mmol) was deprotected by the same procedure as above. Triethylamine (0.08 mL, 0.7 mmol) and hexylisocynate (0.049 g, 0.38mmol) were added to amine **14** in dichloromethane at 0 °C. The reaction was stirred in an ice bath under nitrogen for 24 h. Then the mixture was concentrated, and the residue was taken up in dichloromethane and washed with water three times. The organic layer was dried over sodium sulfate, and the solvent was removed to give the crude product. This was purified by flash chromatography (hexane/acetate 4:1) to give a white crystalline material (0.17 g, 89%). M.p. 59.5–60.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.05$ (s, 1H), 5.55 (m, 1H), 5.15 (s, 1H), 4.79 (s, 1H), 4.48 (dd, $J = 3.79$, 11.37 Hz, 1H), 4.40 (dd, $J = 3.28$, 11.37 Hz, 1H) 4.12 (m, 2H), 3.14 (t, $J = 7.07$ Hz, 2H), 1.89 (s, 3H), 1.60 (m, 2H), 1.46 (m, 2H), 1.30–1.21 (m, 28H), 0.86 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.9$, 166.8, 157.2, 135.7, 126.1, 65.96, 65.2, 52.3, 40.6, 31.9, 31.5, 30.0, 29.6 (m), 29.5, 29.4, 29.3, 29.2, 28.5, 26.5, 25.7, 22.6, 22.5, 18.1, 14.1, 14.0; HRMS (FAB) cacld for $C_{28}H_{53}N_2O_5$ [M^++H]: 497.3954; found: 497.3953.

(2S)-2-{[(Octylamino)carbonyl]amino}-3-oxo-3-(tetradecyloxy)propyl 2-methylacrylate (2): The product was obtained as a white crystalline solid (96% from **13**) after purification by flash chromatography (hexane/ethyl acetate 3:1). M.p. 63.0–63.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.05$ (s, 1H), 5.54 (s, 1H), 5.28 (d, $J = 7.88$ Hz, 1H), 4.80 (m, 2H), 4.69 (s, 1H), 4.80 (m, 1H), 4.69 (m, 1H), 4.47 (dd, $J = 4.10$, 11.35 Hz, 1H), 4.38 (dd, $J = 3.47$, 11.35 Hz, 1H), 4.12 (m, 2H), 3.12 (m, 2H), 1.88 (s, 3H), 1.59 (m, 2H), 1.45 (m, 2H), 1.40–1.20 (m, 28H), 0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.8$, 166.8, 157.1, 135.7, 126.2, 66.0, 65.2, 52.65, 40.7, 31.9, 31.8, 30.0, 29.6(4), 29.5, 29.3, 29.3, 29.2, 28.5, 26.8, 25.8, 22.7, 22.6, 18.2, 14.1, 14.0; HRMS (FAB) calcd for $C_{30}H_{57}N_2O_5$ [M^++H]: 525.4267; found: 525.4270.

Ditetradecyl (2S,15S)-2,15-bis[(methacryloyloxy)methyl]-4,13-dioxo-3,5,12,14-tetraazahexadecane-1,16-dioate (3): The product was obtained as a white crystalline solid (93% from **13**) after purification by flash chromatography (hexane/acetone/dichloromethane 8:3:9). M.p. 100.5–101.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.05$ (s, 2H), 5.60 (m, 2H), 5.54 (m, 2H), 5.06 (m, 2H), 4.82 (m, 2H), 4.48 (m, 2H), 4.38 (m, 2H), 4.12 (m, 4H), 3.14 (m, 4H), 1.88 (br s, 6H), 1.60 (m, 4H), 1.45 (m, 4H), 1.23 (s, 48H), 0.88 (t, $J = 6.44$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.2$, 166.8, 157.7, 135.7, 126.1, 65.92, 65.36, 52.47, 39.71, 31.87, 29.65, 29.63, 29.61, 29.57, 29.52, 29.47, 29.32, 29.21, 28.48, 25.80, 25.77, 22.64, 18.14, 14.06; HRMS (FAB) cacld for $C_{50}H_{91}N_4O_{10}$ [M^++H]: 907.6735; found: 907.6734.

Ditetradecyl (2S,21S)-2,21-bis[(methacryloyloxy)methyl]-4,19-dioxo-3,5,18,20-tetraazadocosane-1,22-dioate (4): The product was obtained in 89% yield from **13** as a white solid after purification by flash chromatography (hexane/acetone/dichloromethane 4:1:5). M.p. 84.5–85.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.04$ (m, 2H), 5.53 (m, 2H), 5.46 (d, $J = 7.25$ Hz, 2H), 4.92 (s, 2H), 4.80 (m, 2H), 4.46 (dd, $J = 3.94$, 11.03 Hz, 2H), 4.37 (dd, $J = 3.47$, 11.03 Hz, 2H), 4.10 (m, 4H), 3.11 (t, $J = 6.31$, 4H), 1.87 (s, 6H), 1.58 (m, 4H), 1.44 (m, 4H), 1.22 (m, 60H), 0.85 (t, $J = 6.94$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.9$, 166.8, 157.3, 135.7, 126.1, 65.9, 65.3, 52.6, 40.6, 31.9, 30.0, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.5, 26.8, 25.8, 22.6, 18.1, 14.1; HRMS (FAB) cacld for $C_{56}H_{103}N_4O_{10}$ [M^++H]: 991.7674; found: 991.7675.

5-Benzyl 1-tetradecyl (2*S*)-2-[(*tert*-butoxycarbonyl)amino]pentanedioate (16): *N*-*t*Boc-L-Glutamic γ-benzyl ester **15** (3.37 g, 0.010 mol), tetradecanol (2.35 g, 0.011 mol), and DMAP (0.20 g, 1.6 mmol) were dissolved in 50 mL

of dichloromethane. The mixture was cooled in an ice bath to 0 °C, EDCI (2.10 g, 0.011 mol) was added, and the reaction mixture was stirred for 6 h in the ice bath. The work up was similar as before. The solution was concentrated to dryness, and the residue was taken up in ethyl acetate and washed with water three times. The organic phase was dried over sodium sulfate, and the solvent was removed to give the product as a white crystalline solid (5.20 g, 98 %) after purification by flash chromatography (hexane/ethyl acetate 6:1). M.p. 47.0 – 48.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.24 - 7.40$ (m, 5H), 5.17(d, $J = 7.57$ Hz, 1H), 5.08 (s, 2H), 4.30 (s, 1H), 4.08 (t, $J = 6.78$ Hz, 2H), 2.42 (m, 2H), 2.17 (m, 1H), 1.94 (m, 1H), 1.59 (m, 2H), 1.40 (s, 9H), 1.23 (s, 22H), 0.85 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 172.3, 172.1, 155.2, 135.7, 128.4, 128.1, 79.7, 66.3, 65.5, 52.8, 31.8, 30.2, 29.5, 29.4, 29.3, 29.2, 29.1, 28.4, 28.1, 27.7, 25.7, 22.5, 14.0; HRMS (FAB) calcd for $C_{31}H_{52}NO_6$ [M^++H]: 534.3795; found: 534.3795.

(4*S*)-4-[(*tert*-Butoxycarbonyl)amino]-5-oxo-5-(tetradecyloxy)pentanoic acid (17): Compound **16** (3.00 g, 0.056 mol) was dissolved in ethanol (100 mL), Pd/C (0.25 g) catalyst was added to the solution, and the mixture was stirred under one atmosphere of hydrogen for 24 h. The catalyst was removed by filtration through celite. The filtrate was concentrated to dryness, and the sample was further dried under vacuum for 12 h to give a colorless crystalline solid (2.42 g, 97 %). M.p. 49.0 – 50.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.16$ (s, 1H), 4.32 (s, 1H), 4.11 (t, $J = 6.78$ Hz, 2H), 2.45 (m, 2H), 2.29 (m, 1H), 1.82 (m, 1H), 1.62 (m, 2H), 1.42 (m, 9H), 1.24 (m, 22H), 0.86 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 177.8$, 172.2, 155.5, 80.1, 65.8, 52.8, 31.9, 30.1, 29.6, 29.5, 29.4, 29.2, 28.5, 28.2, 27.8, 25.8, 22.6, 14.1; HRMS (FAB) calcd for $C_{24}H_{46}NO_6$ [M^++H]: 444.3325; found: 444.3326.

Hydroxynonyl methacrylate was synthesized from the 1,9-nonane diol with methacryloyl chloride, and was purified by flash column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.07$ (s, 1H), 5.52 (m, 1H), 4.11 (t, $J =$ 6.78 Hz, 2H), 3.62 (t, $J = 6.78$ Hz, 2H), 1.92 (s, 3H), 1.64 (m, 2H), 1.54 (m, 2H), 1.28 – 1.38 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 167.5$, 136.5, 125, 1, 64.7, 62.9, 29.4, 29.2, 29.1, 28.5, 25.9, 25.6, 18.2.

5-[2-(Methacryloyloxy)ethyl] 1-tetradecyl (2*S*)-2-[(*tert*-butoxycarbonyl)-amino]pentanedioate (18): Compound **17** (0.88 g, 2.0 mmol), hydroxyethyl methacrylate (0.30 g, 2.3 mmol), and DMAP (0.02 g, 0.16 mmol) were dissolved in dry dichloromethane (20 mL). The mixture was cooled to 0 °C in an ice bath, and then EDCI (0.48 g, 2.5 mmol) was added. The mixture was stirred in the ice bath, protected from light and moisture, for 6 h. The work up was the same as before. Purification by chromatography (hexane/acetate 6:1) gave a white solid (1.05 g, 95 %). M.p.36.0 – 36.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.06$ (s, 1H), 5.53 (m, 1H), 5.13 (d, $J = 8.08$ Hz, 1H), 4.22 – 4.32 (m, 5H), 4.06 (t, $J = 6.82$ Hz, 2H), 2.36 (m, 2H), 2.14 (m, 2H), 1.88 (m, 4H), 1.57 (m, 2H), 1.37 (s, 9H), 1.19 (s, 22H), 0.81 (t, $J = 7.07$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.4$, 172.1, 166.9, 155.2, 135.7, 126.0, 79.8, 65.6, 62.2, 52.7, 31.8, 30.0, 29.5, 29.4, 29.4, 29.2, 29.1, 28.4, 28.1, 27.6, 25.7, 22.6, 18.1, 14.0; HRMS (FAB) calcd for $C_{25}H_{46}NO_6$ [M^++H – Boc]: 456.3325; found: 456.3325.

5-[9-(Methacryloyloxy)nonyl] 1-tetradecyl (2*S*)-2-[(*tert*-butoxycarbonyl)-amino]pentanedioate (19): The product was obtained as white crystals (97 % from **17**) after flash chromatography (hexane/acetate 7:1). M.p. 39.0 – 40.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.04$ (m, 1H), 5.49 (m, 1H), 5.10 (d, $J = 8.20$ Hz, 1H), 4.25 (m, 1H), 4.08 (t, $J = 6.63$ Hz, 2H), 4.07 (t, $J =$ 6.62 Hz, 2H), 4.01 (t, $J = 6.78$ Hz, 2H), 2.34 (m, 2H), 2.11 (m, 1H), 1.89 (m, 4H), 1.50 – 1.65 (m, 6H), 1.38 (s, 9H), 1.26 (s, 10H), 1.20 (s, 22H), 0.82 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.7$, 172.2, 167.4, 155.3, 136.5, 125.0, 79.7, 65.6, 64.7, 52.9, 31.8, 30.3, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 29.1, 28.5, 28.4, 28.2, 27.8, 25.9, 25.8, 25.7, 22.6, 18.2, 14.0; HRMS (FAB) calcd for $C_{32}H_{60}NO_6$ [M^++H – Boc]: 554.4421; found: 554.4420.

5-[2-(Methacryloyloxy)ethyl] 1-tetradecyl (2*S*)-2-aminopentanedioate (20): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.06$ (m, 1H), 5.51 (m, 1H), 4.14 (t, $J = 6.78$ Hz, 2H), 4.10 (t, $J = 6.78$ Hz, 2H), 4.02 (td, $J = 2.21$, 6.78 Hz, 2H), 2.54 (t, $J = 6.94$ Hz, 2H), 2.23 (m, 2H), 1.9 (s, 3H), 1.54 – 1.66 (m, 6H), 1.20 – 1.40 (m, 32H), 0.84 (t, $J = 6.94$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.1$, 169.1, 167.7, 136.4, 125.2, 67.2, 65.5, 64.8, 52.5, 31.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 29.1, 28.5, 28.3, 28.2, 25.9, 25.7, 25.6, 25.1, 22.6, 18.2, 14.0.

5-[9-(Methacryloyloxy)nonyl] 1-tetradecyl (2*S*)-2-aminopentanedioate (21): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.11$ (s, 1H), 5.60 (s, 1H), 4.28 – 4.32 (m, 4H), 4.14 – 4.24 (m, 3H), 2.62 (m, 2H), 2.27 (m, 2H), 1.9 (s, 3H), 1.63 (m, 2H), 1.20 – 1.30 (m, 22H), 0.85 (t, $J = 6.78$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.6$, 168.8, 167.9, 135.6, 126.8, 67.7, 63.4, 62.1, 53.0, 31.9, 29.9, 29.6, 29.5, 29.4, 29.3, 29.1, 28.2, 25.6, 24.8, 22.6, 18.0, 14.0.

5-[2-(Methacryloyloxy)ethyl] 1-tetradecyl (2*S*)-2-{[(hexylamino)carbonyl]-amino}pentanedioate (5): The product was obtained as white crystals (90 % from **18**) after flash chromatography (hexane/acetate 3:1). M.p. 45.0 – 46.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.10$ (m, 1H), 5.57 (q, $J =$ 1.58 Hz, 1H), 5.07 (d, $J = 7.88$ Hz, 1H), 4.63 (s, 1H), 4.47 (m, 1H), 4.25 – 4.35 (m, 2H), 3.12 (t, $J = 7.25$ Hz, 2H), 2.42 (m, 2H), 2.15 (m, 1H), 1.92 (m, 4H), 1.60 (m, 2H), 1.45 (m, 2H), 1.20 – 1.34 (m, 28H), 0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.1$, 172.9, 157.5, 135.9, 126.1, 65.7, 62.3, 52.5, 40.6, 31.9, 31.5, 30.2, 30.1, 29.6, 29.6, 29.5, 29.3, 29.2, 28.5, 28.0, 26.5, 25.8, 22.7, 22.5, 18.2, 14.1, 14.0; HRMS (FAB) calcd for $C_{32}H_{59}N_2O_7$ [M^++H]: 583.4322; found: 583.4324.

5-[9-(Methacryloyloxy)nonyl] 1-tetradecyl (2*S*)-2-{[(hexylamino)carbonyl]-amino}pentanedioate (6): The product was obtained as white crystals (92 % from **19**) after flash chromatography (hexane/acetate 5:1). M.p. 37.5 – 38.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.06$ (m, 1H), 5.51 (q, $J =$ 1.58 Hz, 1H), 5.22 (d, $J = 5.99$ Hz, 1H), 4.78 (brs, 1H), 4.45 (brs, 1H), 4.10 (t, $J = 6.78$ Hz, 2H), 4.09 (t, $J = 6.78$ Hz, 2H), 4.01 (t, $J = 6.78$ Hz, 2H), 3.10 (t, $J = 7.25$ Hz, 2H), 2.37 (m, 2H), 2.11 (m, 1H), 1.90 (m, 4H), 1.54 – 1.67 (m, 6H), 1.44 (m, 2H), 1.18 – 1.34 (m, 38H), 0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.3$, 173.2, 167.5, 157.6, 136.5, 125.1, 65.6, 64.7, 52.5, 40.6, 31.9, 31.5, 30.4, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.5(3), 28.1, 26.5, 25.9, 25.8, 22.6, 22.5, 18.25, 14.0, 13.9; HRMS (FAB) calcd for $C_{39}H_{73}N_2O_7$ [M^++H]: 681.5418; found: 681.5420.

1,24-Bis[2-(methacryloyloxy)ethyl] 3,22-ditetradecyl (3*S*,22*S*)-5,20-dioxo-4,6,19,21-tetraazatetracosane-1,3,22,24-tetracarboxylate (7): The product was obtained as a white solid (90 % from **18**) after flash chromatography (hexane/dichloromethane/acetone 6:3:1). M.p. 86.0 – 87.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.11$ (brs, 2H), 5.58 (brs, 2H), 5.05 (d, $J =$ 7.88 Hz, 2H), 4.61 (s, 2H), 4.49 (m, 2H), 4.26 – 4.36 (m, 8H), 4.09 (t, $J =$ 6.62 Hz, 4H), 3.12 (m, 4H), 2.43 (m, 4H), 2.15 (m, 2H), 1.93 (m, 8H), 1.61 (m, 4H), 1.46 (m, 4H), 1.20 – 1.34 (m, 60H), 0.86 (t, $J = 6.94$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.3$, 172.7, 157.8, 135.8, 126.0, 65.5, 62.3, 62.2, 52.3, 40.4, 31.8, 30.2, 30.1, 29.6,29.5, 29.5, 29.4, 29.3, 29.2, 29.15, 28.4, 28.0, 26.8, 25.7, 22.6, 18.1, 14.0; HRMS (FAB) calcd for $C_{64}H_{115}N_4O_{14}$ [M^++H]: 1163.8410; found: 1163.8411.

1,24-Bis[9-(methacryloyloxy)nonyl] 3,22-ditetradecyl (3*S*,22*S*)-5,20-dioxo-4,6,19,21-tetraazatetracosane-1,3,22,24-tetracarboxylate (8): The product was obtained as a white solid (94 % from **19**). M.p. 88.0 – 89.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.06$ (m, 2H), 5.51 (m, 2H), 5.21 (m, 2H), 4.77 (m, 2H), 4.45 (m, 2H), 4.09 (m, 8H), 4.01 (t, $J = 6.78$ Hz, 4H), 3.10(q, $J =$ 6.62 Hz, 4H), 2.39 (m, 4H), 2.11 (m, 2H), 1.91 (m, 8H), 1.54 – 1.68 (m, 8H), 1.44 (m, 4H), 1.20 – 1.34 (m, 2s, 48H), 0.85 (t, $J = 6.94$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 173.3$, 173.2, 167.5, 157.6, 136.5, 125.1, 65.6, 64.7, 52.5, 40.5, 31.9, 30.4, 30.1, 29.6, 29.5, 29.5, 29.3, 29.2, 29.2, 29.1, 28.1, 26.8, 25.9, 25.8, 22.6, 18.3, 14.1; HRMS (FAB) calcd for $C_{78}H_{143}N_4O_{14}$ [M^++H]: 1360.0601; found: 1360.0601.

Bis[9-(methacryloyloxy)nonyl] (2*S*)-2-[(*tert*-butoxycarbonyl)amino]butanedioate (23): ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.04$ (m, 2H), 5.49 (m, 2H), 5.38 (d, $J = 8.51$ Hz, 1H), 4.49 (m, 1H), 4.08 (t, $J = 6.62$ Hz, 4H), 4.02 (m, 2H), 2.93 (dd, $J = 17.02$, 4.41 Hz, 1H), 2.75 (dd, $J = 16.71$, 4.73 Hz, 1H), 1.89 (m, 6H), 1.61 (m, 2H), 1.56 (m, 2H), 1.39 (s, 9H), 1.25 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.0$, 170.9, 167.4, 155.3, 136.5, 125.0, 79.9, 65.7, 65.0, 64.6, 50.0, 36.7, 29.3, 29.1, 29.0, 29.0, 28.5, 28.2, 25.9, 25.7, 18.2; HRMS (FAB) calcd for $C_{30}H_{52}NO_8$ [M^++H – Boc]: 554.3693; found: 554.3695.

Tetrakis[9-(methacryloyloxy)nonyl] (2*S*,21*S*)-4,19-dioxo-3,5,18,20-tetraazadocosane-1,2,21,22-tetracarboxylate (9): The product was obtained as a colorless solid (90 % from **23**). M.p.56.0 – 57.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.03$ (m, 4H), 5.58 (d, $J = 8.12$ Hz, 2H), 5.48 (q, $J = 1.58$ Hz, 4H), 5.02 (t, $J = 5.20$ Hz, 2H), 4.70 (m, 2H), 4.07 (t, $J = 6.62$ Hz, 8H), 4.04 (m, 4H), 3.97 (t, $J = 6.80$ Hz, 4H), 3.08 (q, $J = 6.50$ Hz, 4H), 2.77 (dd, $J =$ 16.71, 4.73 Hz, 2H), 2.91 (dd, $J = 16.71$, 5.04 Hz, 2H), 1.87 (m, 12H), 1.60 (m, 8H), 1.53 (m, 8H), 1.43 (m, 4H), 1.15 – 1.30 (m, 56H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.0$, 171.3, 167.4, 157.5, 136.4, 125.0, 65.5, 64.8, 64.6, 49.4, 40.4, 37.1, 30.0, 29.3, 29.2, 29.2, 29.0, 29.0, 28.5, 28.4, 28.3, 26.8, 25.8, 25.7, 25.6, 18.2; HRMS (FAB) calcd for $C_{74}H_{127}N_4O_{18}$ [M^++H]: 1359.9145; found: 1359.9151.

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