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Benzyl and *tert*-butyl carbamate derivatives of 1,ω-amino acids as simple yet efficient gelators

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Abstract—We report the synthesis and a study of the gelation properties of a series of *N*-protected long-chain amino acids. Especially, benzyl and *tert*-butyl carbamate derivatives of 11-aminoundecanoic acid in their deprotonated form can gelate polar organic solvents and water at very low concentration (less than 5 mM). This is explained by the contribution of multiple forces—H-bond, van der Waals and ionic interactions—in the gel aggregate formation and stabilization, which is confirmed by the experimental data. Among the series of compounds investigated, only a dimer of 11-aminoundecanoic acid is capable of gelating toluene, which stems from the increased number of hydrogen bonding sites in the main aliphatic chain.

1. Introduction

Molecular gels represent outstanding functional nanoscale materials with high potential in a wide range of advanced applications.[1] Their formation stems from the spontaneous but controlled self-assembly of low molecular mass compounds into fibrous architectures, which, in turn, form entangled three-dimensional networks entrapping solvent molecules.[1a,g] In contrast to the case of their polymeric counterparts, molecular gels involve discrete molecular components with well-defined chemical structures. It is therefore possible, by introducing subtle changes in the chemical composition of the gelator backbone, to fine-tune the morphology, chirality and size of the aggregates and, ultimately, the macroscopic properties of the gel.[1] Arguably this unique feature largely contributes to motivate the great deal of activity towards the synthesis of new gelator molecules. When considering the data available in the literature over the last 20 years, it is amazing to realize that both kinds of molecular systems, structurally sophisticated chemical entities and, on the other hand, simple compounds, can be found in the library of gelators. The former are generally multi-component molecular systems and they are appealing in that they give the opportunity to endow the aggregates and the gel materials with specific supramolecular functions, such as molecular recognition, photo- or electroactivity.[1,2] However, as they are usually available in small amounts because their synthesis needs numerous synthetic steps, they are not often suited for large-scale applications. Structurally simple compounds, that can be obtained in gram scale quantities from cheap precursors in a limited number of synthetic steps, are also of great interest because they allow the production of nanostructured materials with thermoreversible properties at very moderate costs.[1b,3] Such systems can find applications as host matrices or media for a variety of applications, including sensing and separation technologies, catalysis, (bio)mineralization, etc.

Recently, we reported in a preliminary communication the gelling behaviour of a series of *N*-acyl-1,ω-amino acid derivatives.[4] Within the series, amide compounds including the 11-aminoundecanoic acid (AUDA) motif were proven very effective and versatile gelators of water and/or organic solvents.[5,6] In this paper, we focus on a series of structurally simple carbamate derivatives of 1,ω-amino acids such as **CBZ-*n*-R** with different chain lengths (n=3, 5, 7, 10, 11, 12) and **Boc-10-R** (Scheme 1). The effects of the ionization state of the terminal carboxylic acid functionality (R=H or M^+), and of the nature of the alkali metal cation (M=Li, Na, K, Rb, Cs for n=10) are described. In line with our investigation on AUDA-based compounds,[5] the synthesis and gelation abilities of a new dimeric species of **CBZ-10-H**, **CBZ-10-10-H**, are also reported (Scheme 1).

Keywords: Self-assembly; Molecular gels; Amino acids; Hydrogen bonding; Ionic interactions.
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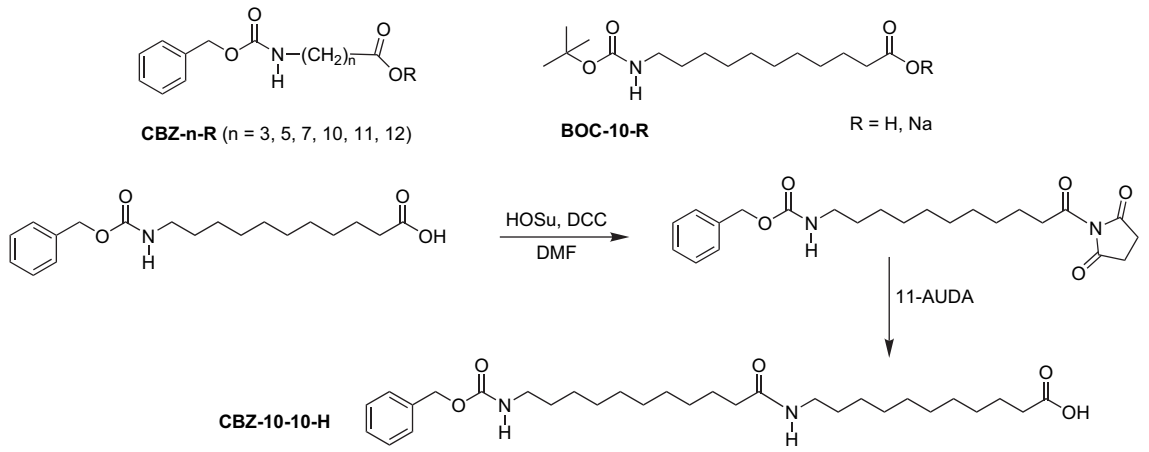


Scheme 1. Synthesis of the gelators.

2. Results and discussion

2.1. Synthesis

Compounds **CBZ-*n*-H** and **Boc-10-H** were obtained in good yields according to well-known synthetic procedures widely used for the protection of amino groups in oligopeptide synthesis (Scheme 1).[7] Especially, excellent gelators can be produced in large amounts from the commercially available and not expensive AUDA starting material, which is used industrially to produce Nylon-11®. The dimer species, **CBZ-10-10-H**, was prepared by a two-step procedure from **CBZ-10-H**. The latter was activated via DCC-mediated condensation with *N*-hydroxysuccinimide to give the corresponding ester **CBZ-10-OSu**. The latter was reacted with AUDA in DMF to afford the dimer. The sodium salt and, in the case of **CBZ-10-H**, the alkali metal salts of the *N*-protected-amino acid compounds were obtained upon treatment of the acid with 1 molar equiv of the corresponding metal hydroxide in solution.

2.2. Gelation experiments

The gelation ability of the compounds investigated was tested for 10 different solvents with 20 mM as a standard concentration. The results are summarized in Table 1. Only the sodium salts of the *N*-protected AUDA compounds, **CBZ-*n*-R** and **Boc-10-R** (R=H, Na), appeared to be gelators of polar organic solvents (DMF, DMSO) while they are insoluble in solvents of low polarity. Remarkably, these systems are also efficient gelators of concentrated aqueous NaOH (pH=14), which indicates an ambidextrous behaviour.[3b] The need for such a high pH value for self-aggregation to be observed has already been reported for fatty acids.[8] None of these compounds in their neutral carboxylic form are gelators in the solvents investigated. Instead, the protonated acids are highly soluble in the polar solvents. The only compound, which is able to gelate toluene, is the dimer **CBZ-10-10-H** as a result of a large number of hydrogen bonding sites, consistent with a trend previously reported for AUDA-containing amide derivatives.[5] At room temperature, the minimum gelation concentration (MGC) was about 7 mM in toluene, which is remarkably low, and the gel-to-solution phase transition temperature, T_{gel}, was observed to reach 82 °C at 20 mM. Within the series of compounds, **CBZ-10-Na** was found to gelate DMF at a concentration of ca. 5×10^{-3} M at room temperature, which represents less than 0.2 wt %, indicating that this substance has the character of a 'supergelator'.[9] The gels of **CBZ-10-Na** at such low concentration in DMF were transparent and thermoreversible over a period of more than 10 months. Transmission electron microscopy of a DMSO gel of **CBZ-10-Na** provided direct evidence of an entanglement of numerous, randomly orientated thin filaments, the diameter of the smallest ones being approximately 30 nm (Fig. 1). Rheology confirmed the occurrence of a rigid three-dimensional network in the gel samples. A DMF gel of **CBZ-10-Na** (20 mM) was subjected to a nondestructive

Table 1. Gelation ability of the gelators investigated in this study

R=	CBZ-5-R		CBZ-7-R		CBZ-10-R		CBZ-11-R		CBZ-12-R		Boc-10-R		CBZ-10-10-R	
	H	Na	H	Na	H	Na	H	Na	H	Na	H	Na	H	Na
Toluene	I	I	P	I	I	I	I	I	I	I	S	I	G (7)	I
EtOAc	P	I	P	I	I	I	I	I	I	I	S	I	P	I
THF	P	P	P	P	P	I	P	I	P	I	S	I	P	I
Dioxane	I	P	P	P	P	I	P	I	P	I	S	I	P	I
MeOH	P	P	P	P	P	I	P	I	P	I	P	P	I	P
DMF	S	G (17)	S	G (15)	S	G (4)	S	G (8)	S	G (4)	S	S	P	P
DMSO	S	G	S	G	S	G	S	G	S	G	S	G	S	P
Propylene carbonate	S	VS	S	G	S	G	S	G	S	G	S	G	VS	P
N,*N*-Dimethylacetamide	S	P	S	G	S	G	S	G	S	G	S	P	P	P
H_2O (pH=14)	S	S	S	G	G	G (5)	G	G	G	G	G	G (5)	P	P

Gelator concentration 20 mM (room temperature). G, gel; S, solution; VS, viscous solution; P, precipitate; I, insoluble when heated. Values in parentheses are MGC at 25 °C.

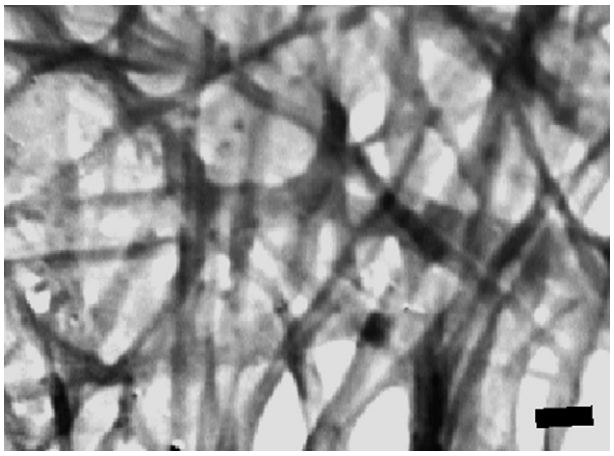


Figure 1. TEM image of xerogel prepared from a DMSO gel of **CBZ-10-Na** (4 mg/mL) (scale bar 100 nm).

frequency sweep experiment with a constant shear stress of 20 Pa at room temperature and the result is given in Figure 2. This shows that the G' and G'' parameters are independent of oscillation frequency over three decades and take the values 10,000 Pa and 1000 Pa, respectively, at 1 Hz. G' is thus one order of magnitude larger than G'', which reflects the dominant elastic character of this gel.[10]

2.3. Factors influencing the gelation ability

2.3.1. Influence of the counterion. From the data in Table 1, the presence of an ionized carboxylate function is required for gelation to be observed. The neutral form **CBZ-10-H** and a fortiori the ethyl ester derivative **CBZ-10-Et** did not show any gelation ability and only gave rise to solutions in DMF even at high concentration. To confirm the occurrence of an ionic interaction contributing to self-assembly, compound **CBZ-10-R** was investigated in which the nature of the alkali metal cation was varied (R=Li, Na, K, Rb). Indeed the gelation ability was found to be sensitive to the nature of the metal. Gels could be prepared with Na^+ and Rb^+ but not with Li^+ and K^+. In the case of Rb^+, a very weak gel at high concentration (70 mM) could only be observed at

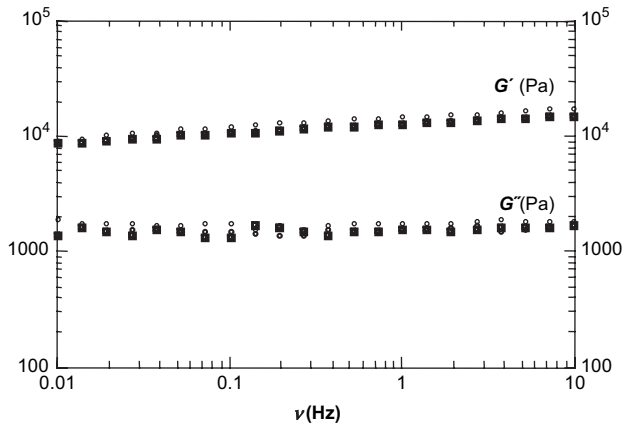


Figure 2. Frequency sweep experiments on a DMF gel of **CBZ-10-Na** (20 mM, 25 °C). Three different measurements of G' and G'' as a function of oscillation frequency (the gel was heated to yield the sol and reformed upon cooling between each measurements). The applied shear stress is 20 Pa and the experiment is performed in the linear regime.

0 °C. A similar trend has been observed for isophthalic acid derivatives forming long organic fibres.[11] Similarly, replacement of sodium ions by ammonium cations (NH_4^+, n-Bu_4N^+) led to the loss of gelation. When Kryptofix® [211] (a selective Na^+ binder) was introduced into a hot solution of **CBZ-10-Na**, gelation failed again, which points to the intimate participation of the sodium cation in the self-assembly and stabilization of the gel aggregate.

2.3.2. Hydrogen bond formation. The FTIR spectrum of a xerogel of **CBZ-10-Na** prepared from a DMF gel is characterized by bands attributed to hydrogen bonding and is similar to that of the solid obtained from evaporation of a methanol solution, which indicates the marked propensity of the compound to form hydrogen bonds. Bands at 3360 cm^{-1} and 1690 cm^{-1} were observed for N–H and C=O stretching vibrations, respectively. ^1H NMR spectra of **CBZ-10-Na** in DMSO-d_6 (12 mM) were recorded at different temperatures. At 25 °C, the spectrum of the gel showed resonance patterns close to those recorded for a methanol-d_4 solution. However, the signals of the gelator molecules in the gel network were observed to be shifted and considerably broadened. As compared to the solvent signal intensity, the peaks also displayed very low intensity in the gel state relative to the solution. Such features were already reported for other self-assembled gels and are typical of molecular systems with long correlation times as a result of aggregation.[12] When the temperature was increased, the ratio of the solvent signal (nondeuterated residue of DMSO-d_6) intensity to the urethane NH signal intensity significantly increased (Fig. 3a), which is consistent with the dissociation of the gel network leading to an increased gelator concentration in the solution. The plot in Figure 3 shows a gradual disassembly, which is complete by 50 °C, which is in agreement with the value of 48 °C for T_{gel} determined by the tube inversion method. Monitoring of the gelator's chemical shift changes as a function of temperature confirmed the occurrence of hydrogen bond formation (Fig. 3b). As the temperature increased, the NH proton of the urethane fragment was shifted upfield ($\Delta\delta$=0.26 ppm), while the phenyl and benzylic methylene protons were only very slightly shifted downfield ($\Delta\delta$<0.02 ppm).

2.3.3. Influence of the $(CH_2)_n$ spacer. As mentioned in Table 1, the MGC in DMF decreases with the length of the $(CH_2)_n$ spacer. The MGC values are around 15 mM for n=5, 7, and below 10 mM for n=10, 11, 12. The commercially available **CBZ-3-Na** was also able to gelate DMF, but only at high concentration (70 mM) and the gel was opaque and weak. This trend is due to the occurrence of solvophobic interactions during the gelation process; the longer the chain the larger the inter-chain interactions via van der Waals interactions. Such behaviour is well-known for self-assembling systems containing long alkyl chains.[13] It should be mentioned that the MGC value determined for **CBZ-11-Na** was found to be lower than that of **CBZ-10-Na** and **CBZ-12-Na**. In order to clarify this result, the T_{gel} values were plotted as a function of gelator concentration in DMF (Fig. 4). These curves clearly indicate that the melting temperature of the gels increases with concentration and tends to level off at higher concentrations. Noticeably, compounds with n=10 and 12 show a very similar behaviour, forming highly thermally stable gels (T_{gel} ca. 100 °C) above

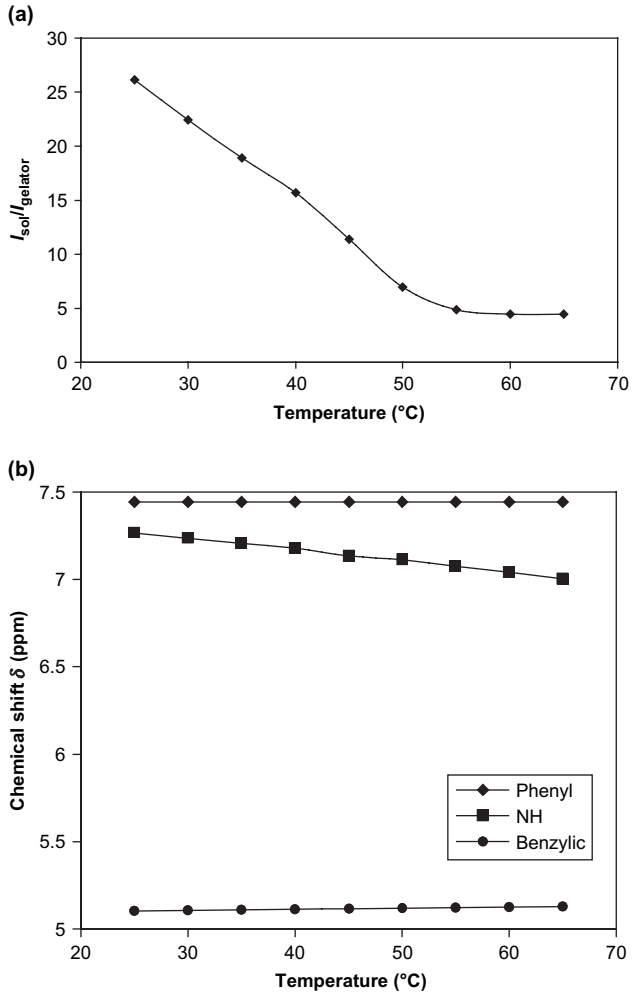
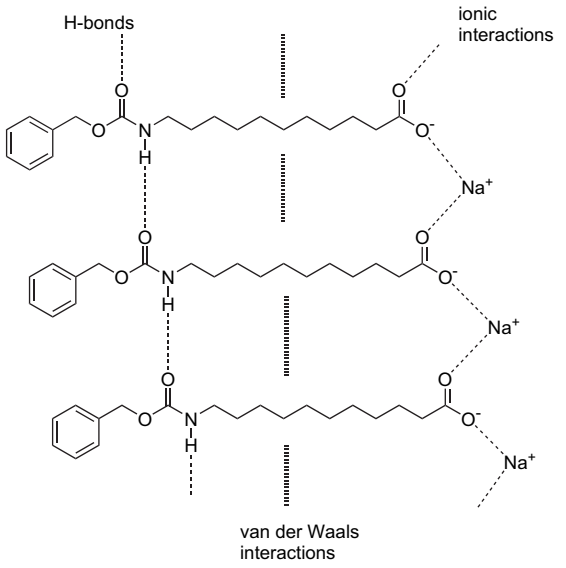


Figure 3. ^{1}H NMR experiments on a DMSO-d_6 gel of **CBZ-10-Na** (12 mM). (a) Changes of the solvent to gelator signal (N–H) intensity ratios ($I_{sol}/I_{gelator}$) and (b) changes of selected gelator chemical shifts (δ) versus temperature.

50 mM. Interestingly, the curve obtained for n=11 is below those of the two former compounds. This odd/even effect has already been observed for gelators containing long alkyl chains.[13] It is considered to be indicative of the presence of the molecules in the gel aggregate in their extended 'zig-zag' conformation, which controls the extent of H-bond and ionic interactions at the termini and, in turn, aggregate stability. All together, the results support a model of one-dimensional aggregation as sketched in Scheme 2, which is consistent with the literature data on fatty acids.[4,13]



Scheme 2. One-dimensional aggregate model of **CBZ-*n*-Na** in the gel phase.

2.3.4. CBZ versus Boc. The gelation properties of **CBZ-10-Na** and **Boc-10-Na** were compared in H_2O at pH=14. Both compounds have a MGC of about 5 mM (0.15 wt %) at 25 °C, which makes them also supergelators of water at highly basic pH. The gel-to-sol phase transition temperature was plotted against concentration (Fig. 5). The results show a higher thermal stability for the CBZ *N*-protected compound relative to the Boc derivative. Remarkably, the T_{gel} value for **CBZ-10-Na** at 25 mM is high (95 °C) and close to the boiling point of water, which reflects the remarkable stability of the self-assemblies in water. It is also worth

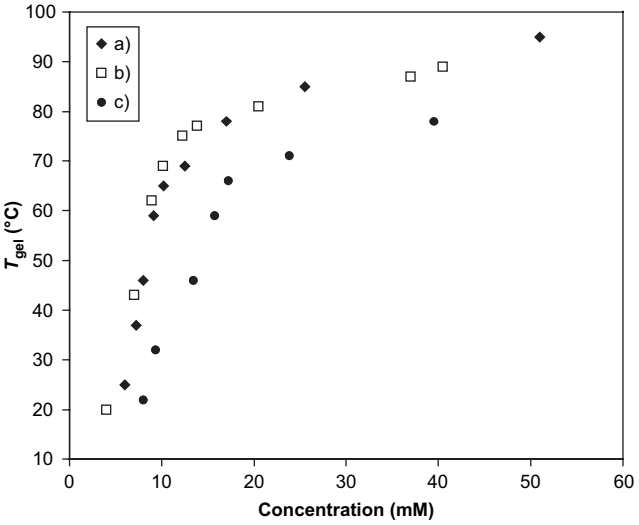


Figure 4. Plots of T_{gel} against gelator concentration in DMF: (a) **CBZ-10-Na**, (b) **CBZ-12-Na**, (c) **CBZ-11-Na**.

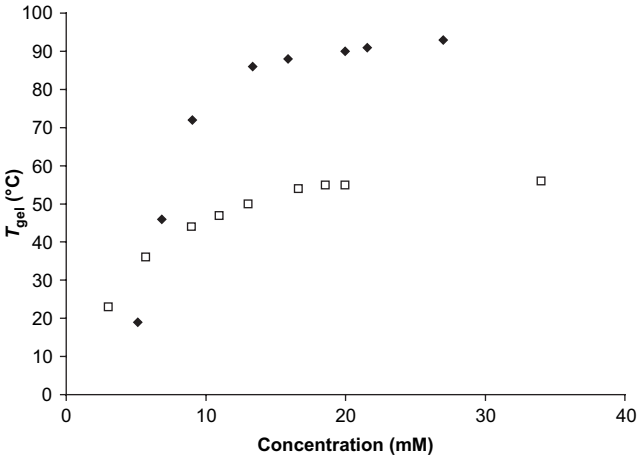


Figure 5. Plots of T_{gel} against gelator concentration in H_20 at pH=14: **CBZ-10-Na** (filled symbols), **Boc-10-Na** (empty symbols).

mentioning that gelation was complete in ca. 1 h with **Boc-10-Na** at 10 mM while the gelation time was only a few minutes with **CBZ-10-Na**. The discrepancy in thermal and kinetic features could arise from the occurrence of π-stacking interactions and a lower steric demand for the CBZ derivative as compared to the bulky *tert*-butyl-containing compound. Intriguingly, however, rheological experiments pointed to a higher mechanical rigidity of the **Boc-10-Na** network (30 mM). This system has G' and G'' parameters that are independent of the oscillation frequency, and the values obtained at 1 Hz are 1,70,000 Pa and 1200 Pa, respectively. These values are typical for a solid-like gel with a clear viscoelastic behaviour. Under the same conditions, the DMF gel of **CBZ-10-Na** has G' and G'' values of 19,000 Pa and 1200 Pa, respectively. Therefore, it is the best gelator with regard to gelation time and thermal stability but has lower rigidity. The origin of this disparity has not been the subject of further investigation and remains unclear at this point. In the literature, such behaviour has already been observed and kinetic effects have been proposed.[14]

3. Conclusion

The present study has demonstrated that very simple yet efficient gelators can be produced in large amounts from 1,ω-amino acids and classical reagents that form carbamate amino-protecting group. Especially, the compounds containing 10 methylene groups display remarkable gelation ability in polar solvents and also in highly basic water, acting as 'supergelators'. The results clearly indicate the contribution of multiple forces—H-bond, van der Waals and ionic interactions—in the gel aggregate formation and stabilization, which confirms the model of one-dimensional aggregation proposed previously (Scheme 2).[4] Gelation of nonpolar solvents, such as toluene, is possible by increasing the number of hydrogen bonding sites in the main aliphatic chain, as illustrated by the dimer compound **CBZ-10-10-H**. All together, the data allow us to delineate the influence of critical structural parameters and provide useful guidelines for producing gel materials with tailored characteristics. Moreover, the fact that some of the compounds are able to gelate highly concentrated alkaline solutions may be interesting for applications.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich and Merck, and were used as supplied. *N*-Carbobenzoxy-4-aminobutyric acid (**CBZ-3-H**) was obtained from TCI. The 12-membered amino acid was synthesized according to a published procedure.[15] ^{1}H and ^{13}C NMR spectroscopies were performed using a Bruker AM 400 apparatus operating at 400 MHz and 100.6 MHz, respectively. NMR spectra were obtained at 25 °C unless otherwise stated. Gelation tests and T_{gel} determinations were performed using the inverted-test tube method as published elsewhere.[16] Transmission electron microscopy was performed with a JEOL 2000 apparatus. The gels were deposited on copper grids coated with a carbon film and evaporated under vacuum. The rheological setup was described in a previous publication.[17]

4.2. Syntheses

4.2.1. General procedure for the synthesis of compounds CBZ-*n*-H (*n*=5, 7, 9, 10, 11, 12). Benzyloxycarbonyl chloride (11 mmol) was added dropwise to a solution of the corresponding 1,ω-amino acid (10 mmol) in aqueous NaOH (11 mmol) at 0 °C. The resulting suspension was stirred for 1 h. Concentrated HCl was then added under vigorous stirring until pH 2. The precipitated solid was filtered off and recrystallized twice from methanol. The desired products were obtained in good yields (75–85%). The sodium salts were obtained upon mixing the corresponding acid with the stoichiometric amount of NaOH in 1/1 (v/v) H_2O/MeOH and evaporation of the mixture to dryness. All compounds were obtained as white solids.

4.2.1.1. CBZ-5-H. FTIR (KBr) 3361, 2926, 2851, 1690, 1633, 1528 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO/CD_3OD$, 2/1, v/v) δ 7.40–7.20 (m, 5H), 5.03 (s, 2H), 3.05 (t, J=6.8 Hz, 2H), 2.15 (t, J=7 Hz, 2H), 1.30–1.20 (m, 6H). Elemental analysis calcd (%) for $C_{14}H_{19}NO_4$ (265): C 63.38, H 7.22, N 5.28; found: C 62.93, H 7.26, N 5.24.

4.2.1.2. CBZ-5-Na. FTIR (KBr) 3362, 2926, 2854, 1691, 1560, 1529 cm^{-1}.

4.2.1.3. CBZ-7-H. FTIR (KBr) 3363, 2922, 2852, 1690, 1634, 1528 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO/CD_3OD$, 2/1, v/v) δ 7.35–7.25 (m, 5H), 5.02 (s, 2H), 3.08 (t, J=6.8 Hz, 2H), 2.15 (t, J=6.9 Hz, 2H), 1.30–1.20 (m, 10H). Elemental analysis calcd (%) for $C_{16}H_{23}NO_4$ (293): C 65.51, H 7.90, N 4.77; found: C 65.13, H 7.86, N 5.04.

4.2.1.4. CBZ-7-Na. FTIR (KBr) 3359, 2922, 2861, 1688, 1560, 1530 cm^{-1}.

4.2.1.5. CBZ-10-H. FTIR (KBr) 3363, 2926, 2851, 1690, 1635, 1528 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO/CD_3OD$, 2/1, v/v) δ 7.38–7.25 (m, 5H), 5.14 (s, 2H), 3.04 (t, J=6.7 Hz, 2H), 2.15 (t, J=7.2 Hz, 2H), 1.35 (m, 16H); ^{13}C NMR δ 177.25, 158.2, 138.7, 129.5, 128.9, 128.8, 67.1, 35.2, 31.1, 30.7, 30.55, 30.4, 29.9, 29.3, 27.9, 26.1. Elemental analysis calcd (%) for $C_{19}H_{29}NO_4$ (335): C 68.03, H 8.71, N 4.18; found: C 68.43, H 9.03, N 4.24.

4.2.1.6. CBZ-10-Na. FTIR (KBr) 3362, 2926, 2854, 1690, 1560, 1529 cm^{-1}.

4.2.1.7. CBZ-11-H. FTIR (KBr) 3361, 2927, 2854, 1690, 1635, 1527 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO/CD_3OD$, 2/1, v/v) δ 7.36–7.25 (m, 5H), 4.95 (s, 2H), 3.04 (t, J=6.9 Hz, 2H), 2.15 (t, J=7.2 Hz, 2H), 1.35 (m, 18H). Elemental analysis calcd (%) for $C_{20}H_{31}NO_4$ (349): C 68.74, H 8.94, N 4.01; found: C 68.33, H 9.03, N 3.92.

4.2.1.8. CBZ-11-Na. FTIR (KBr) 3361, 2923, 2851, 1690, 1561, 1522 cm^{-1}.

4.2.1.9. CBZ-12-H. FTIR (KBr) 3362, 2927, 2854, 1690, 1634, 1529 cm^{-1}; ^{1}H NMR ($(CD_3)_2SO/CD_3OD$, 2/1, v/v) δ 7.50–7.35 (m, 5H), 5.05 (s, 2H), 3.14 (t, J=7.6 Hz, 2H), 2.15 (t, J=7.5 Hz, 2H), 1.10–1.50 (m, 20H). Elemental

analysis calcd (%) for $C_{21}H_{33}NO_4$ (363): C 69.39, H 9.15, N 3.85; found: C 69.03, H 9.13, N 4.04.

4.2.1.10. CBZ-12-Na. FTIR (KBr) 3363, 2927, 2854, 1690, 1559, 1529 cm^{-1}.

4.2.1.11. CBZ-10-Et. A mixture of compound **CBZ-10-H** (3.0 g, 8.94 mmol) and a catalytic amount of *p*-tolylsulfonic acid in 75 mL of ethanol and 75 mL of chloroform was refluxed for 6 h. The reaction mixture was extracted with water, the organic layer was dried over $MgSO_4$ and evaporated to dryness. Crystallization of the crude product from petroleum ether afforded the ethyl ester **CBZ-10-Et** (2.2 g, 68% yield) as a colourless solid. FTIR (KBr) 3289, 2926, 2853, 1742, 1690, 1534 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.25 (m, 5H), 5.05 (s, 2H), 4.05 (q, J=7.15 Hz, 2H), 3.05 (t, J=7.5 Hz, 2H), 2.25 (t, J=7.6 Hz, 2H), 1.2–1.5 (m, 18H). Elemental analysis calcd (%) for $C_{21}H_{33}NO_4$ (363): C 69.39, H 9.15, N 3.85; found: C 69.12, H 9.43, N 3.77.

4.2.1.12. Boc-10-H. Di-*tert*-butyl-dicarbonate (5.74 g, 26.3 mmol) was added portionwise to a solution of 11-aminoundecanoic acid (4.07 g, 20.2 mmol) in aqueous NaOH (0.3 M, 130 mL) at 5 °C for 3 h. The reaction mixture was stirred at room temperature for 3 h. The gelatinous precipitate was filtered off, washed with water and suspended in water and acidified with a few drops of concentrated HCl. The white precipitate was filtered off and dried under vacuum at 60 °C for 5 h. **Boc-10-H** was used without further purification (65% yield). FTIR (KBr) 3367, 2919, 2851, 1685, 1635, 1522, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.52 (br s, 1H), 3.09 (t, J=7 Hz, 2H), 2.35 (t, J=7.2 Hz, 2H), 1.70–1.60 (m, 2H), 1.50–1.40 (m, 11H), 1.35–1.20 (m, 12H). Elemental analysis calcd (%) for $C_{16}H_{31}NO_4$ (301): C 63.75, H 10.37, N 4.65; found: C 63.58, H 10.22, N 4.54.

4.2.1.13. Boc-10-Na. White solid; FTIR (KBr) 3289, 2919, 2852, 1686, 1560, 1522, 1470 cm^{-1}; ^1H NMR (CD_3OD) δ 3.01 (m, 2H), 2.24 (t, 2H), 1.70–1.55 (m, 2H), 1.55–1.40 (m, 2H), 1.45–1.35 (m, 11H), 1.31 (m, 12H).

4.2.1.14. CBZ-10-Su. A solution of **CBZ-10-H** (5.13 g, 15.3 mmol), *N*-hydroxysuccinimide (1.94 g, 16.8 mmol) and DCC (4.74 g, 23 mmol) in 45 mL DMF was stirred overnight at room temperature. After filtration, the solution was evaporated to dryness to give the succinimidyl ester in a quantitative yield (6.6 g) as a white solid. FTIR (KBr) 3327, 2925, 2851, 1816, 1786, 1739, 1684, 1634, 1532, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.35 (m, 5H), 5.31 (s, 2H), 3.25–3.17 (m, 2H), 2.90–2.80 (m, 4H), 2.61 (t, J=7.1 Hz, 2H), 1.20–2.00 (m, 16H).

4.2.1.15. CBZ-10-10-H. To a solution of **CBZ-10-OSu** (3.3 g, 7.6 mmol) in 70 mL DMF was added dropwise a solution of 11-aminoundecanoic acid (1.54 g, 7.6 mmol) and ethyl diisopropylamine (3.0 g, 23 mmol) in 20 mL DMF at 55 °C. Stirring was maintained for 6 h at 50–60 °C and then for 24 h at room temperature. After the reaction mixture was evaporated to dryness, the solid residue was taken up with dichloromethane and filtered off. The solid was washed several times with dichloromethane and then heated in refluxing methanol for 4 h. The white solid was filtered off, washed several times with pentane and dried under vacuum for 24 h. The compound was obtained as a white solid in 34.5% yield (2.74 g). FTIR (KBr) 3312, 3036, 2921, 2851, 1684, 1632, 1533, 1471 cm^{-1}; ^1H NMR ($(CD_3)_2SO$) δ 7.71 (m, 1H), 7.40–7.30 (m, 5H), 7.25–7.18 (m, 1H), 4.99 (s, 2H), 3.00–2.90 (m, 4H), 2.19 (t, J=7 Hz, 2H), 2.03 (t, J=7.1 Hz, 2H), 1.50–1.20 (m, 32H). Elemental analysis calcd (%) for $C_{30}H_{50}N_2O_5$ (518): C 69.46, H 9.72, N 5.40; found: C 68.98, H 9.83, N 5.24.

4.2.1.16. CBZ-10-10-Na. FTIR (KBr) 3314, 2921, 2851, 1685, 1641, 1558, 1533, 1471 cm^{-1}.

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