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A Favorable, Narrow, δ_h Hansen-Parameter Domain for Gelation of Low-Molecular-Weight Amino Acid Derivatives

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Abstract: In recent years, the design of new low-molecular-weight gelators (LMWGs) has attracted considerable attention because of the interesting supramolecular architectures as well as industrial applications. In this context, the role of the organic solvent in determining the organogelation behavior is a central question. Herein we report the results of a systematic study of the organogelation behavior of amino acid derivatives in a wide range of solvents to establish a relationship between the nature of the solvent and the formation of the gel. We highlight that the majority of the gelified solvents are aromatic, except for carbon tetrachloride and tetrachloroethylene. In addition, different parameters related to the nature of the solvent were considered and their influence on the physical properties of gelation was evaluated. The hydrogen-bonding Hansen parameter (δ_h) allows us to draw a narrow favorable δ_h domain for gelation in the range of 0.2–1.4 $(cal\,cm^{-3})^{1/2}$. Furthermore, a general increase of the Hildebrand parameter (δ) leads to the formation of poor gels (small gelation numbers, GNs) in aromatic solvents. Scanning electron microscopy (SEM) revealed that the gels prepared from (L)-phenylalanine and (L)-leucine derivatives in different solvents are composed of an entangled 3D fibrillar network, the diameter of which is only slightly influenced by the nature of the solvent.

Keywords: amino acids · fibrillar networks · gels · Hansen parameters · solvent effects

Introduction

Gels represent an interesting colloidal state of matter that is present in many important consumables: cosmetics,[1] plastic surgery,[2] contact lenses,[3] nanoscale electronics,[4] biomedical materials[5] and so forth. Generally, the solidlike phase of gels is the result of solvent immobilization in 3D fibrillar networks, which are, in many cases, made from polymeric matrices.[6]

An alternative class of gels derives from self-assembly of organic low-molecular-weight gelator molecules (LMWG molecules: molecular mass usually $<2000\,g\,mol^{-1}$) at very low concentration.[6] These small molecules are able to gelify a wide range of liquids, either organic (organogels) or aqueous solvents, and even pure water (hydrogels).[7] Furthermore, the existence of so-called ambidextrous LMWGs, which are derived from vitamin C and amino acids and are able to immobilize both organic and aqueous solvents, has also been reported.[8]

If 3D self-assembly of organogelators takes place through noncovalent interactions (hydrogen bonds, π–π stacking, van der Waals interactions, etc), the gels obtained are designated as supramolecular or physical gels.[6,7f]

Over the past ten years, this kind of organogels has attracted much attention among scientists, as witnessed by the exponential number of papers published in various journals.[6] This trend is justified by the fact that the intriguing properties of gels allow the use of these supramolecular materials in various areas of chemistry and biology, such as sensors,[9] drug-delivery agents,[10] biomimetics,[11] and in the field of catalysis.[12] They can also be used to improve mechanical properties of soft solids.[13] A preliminary analysis shows that the structures of LMWGs can be of different natures.

Well-known organogelators include cholesterol derivatives,[14] porphyrins,[15] carbohydrates,[16] urea/bisurea compounds,[17] and oligoamides.[18] Moreover, several examples of small amino acid derivatives have been reported in the literature.[19] These molecules have the interesting ability to self-assemble through highly specific noncovalent interactions into long fibrous structures, which in turn form an intertwined 3D network that is able to immobilize the solvent.[6] This characteristic has allowed significant progress in the understanding of gel-formation mechanisms, even though many aspects of these phenomena, such as the influence of chemical structure of the gelator or the precise role of the solvent in the organogelation, still remain unknown.[20] It appears that the nature of the solvent has a fundamental importance in the delicate equilibrium that leads to the formation of gel; that is why some attention has been recently focused on the study of solvent–gelator interactions.[21] Different parameters that characterize solvent

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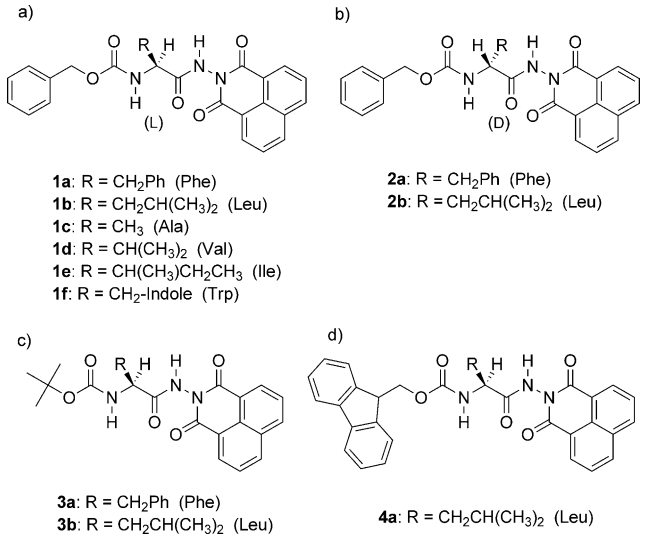
nature, such as solubility (Hildebrand, δ), polarity ($E_T(30)$),[22] and the dielectric constant (ε), were taken into account and their influences on the physical properties of gelation were highlighted. Very recently, Smith and co-workers reported a study that promotes better understanding of the role of the solvent in the gelation process.[23] They considered the solvent effect in terms of Kamlet–Taft parameters.[24] They were able to establish, for their own class of gels, based on a self-assembly process through hydrogen bonding of the gelator molecules, that the α parameter of the solvent (hydrogen-bond donor ability) had primary importance in the control of the formation of hydrogen-bond networks.

During the last few years, our research group has studied a family of new L-amino-acid-type gelators with carboxybenzyl (Z) as the amine-protecting group and a naphthalimide moiety as the fluorescent chromophore.[25a] Different spectroscopic techniques, such as NMR, FT-IR, and fluorescence spectroscopy as well as circular dichroism (CD) have been used to elucidate the detailed structures of supramolecular gels obtained with (L)-phenylalanine (**1a**, Scheme 1a) and (L)-leucine (**1b**, Scheme 1a) derivatives in aromatic solvents,



Scheme 1. Structures of the amino acid derivatives, for which the synthesis is described herein.

such as toluene.[25b,c] These compounds are highly versatile as they contain a lateral chain, a chiral center, and protecting groups and allow the synthesis of a large number of analogs. Actually, Hildebrand (δ) and Hansen (δ_d, δ_p, and δ_h)[22] parameters have been used to analyze gelation strength. Herein, based on this new series of compounds we propose the use of Hildebrand and Hansen parameters, a valuable alternative to the Kamlet–Taft parameters, to predict gelation behavior.

Results and Discussion

Synthesis: It is difficult to predict the gelation ability of a molecule, and almost all small gelators were discovered by accident. In most cases, new compounds described in the literature[6,7] are the result of fine structural changes of a gelator lead molecules. Therefore, we decided to synthesize new potential organogelators inspired by those previously discovered by our research group.[25a] Thus, we have synthesized compounds derived from (L)-alanine, (L)-valine, and (L)-isoleucine (**1c**–**e** respectively, Scheme 1a), which can be seen as the result of small modifications of the aliphatic residue of the (L)-leucine-based gelator **1b**.

Subsequently, we hypothesized that replacing phenylalanine with a tryptophan residue (**1f**, Scheme 1a) would increase the aromatic part of lead-molecule **1a** and would increase the gelation ability through additional π–π stacking interactions.[26]

Compounds **2a** and **2b** (Scheme 1b), enantiomers of **1a** and **1b**, respectively, were also synthesized to check the influence of the α-CH chirality on the gelation properties in achiral solvents.

Finally, to extend the results (see the section on solvent-parameters analysis), we synthesized compounds **3a** and **3b** (Scheme 1c) with a *tert*-butyl carbamate group (Boc) and **4a** (Scheme 1d) with a 9-fluorenylmethyloxycarbonyl group (fmoc) instead of the carboxybenzyl (Z) amine protecting group.

Preliminary organogelation behavior: The new synthesized, potential gelators, listed in Scheme 1a and b, were screened for gelation ability in 33 selected solvents: 10 aromatic solvents, 2 linear and cyclic alkanes, 5 chlorinated solvents, 2 alcohols, 3 esters, 3 ethers, and 3 ketones. The class called "others" included 4 solvents, such as dimethyl sulfoxide and water, which do not match any other classes. The gelation behaviors are classified as: insoluble (I) if the gelator is completely insoluble in the solvent; precipitate (P) if the gelator is soluble in hot solution, but precipitates in cold solution; soluble (S) if the gelator is completely soluble in the solvent, and gel (G) if the gelator is able to gelify the solvent. The results obtained are listed in Table 1.

On first inspection of the data, it appears that only phenylalanine **1a** and leucine **1b** derivatives are able to gelify some of the tested solvents. (L)-Alanine **1c**, (L)-valine **1d**, (L)-isoleucine **1e**, and (L)-tryptophan **1f** derivatives are insoluble or precipitate under the same conditions (Table 1).

As expected, the D-enantiomers **2a** and **2b**, exhibit the same behavior as the corresponding L-gelators **1a** and **1b** in achiral solvents (Table 1). We performed circular-dichroism experiments, which showed an inversion of chirality from one enantiomer to the other (see the Supporting Information).

The second important observation concerns the nature of the solvent. We notice that most of the gelified solvents are aromatic; this might suggest a primary importance of the π–

Table 1. Gelation behavior for **1a–f** in different solvents[a].

Class of solvent	Solvents	(L)-Phe (**1a**)	(L)-Leu (**1b**)	(D)-Phe (**2a**)	(L)-Ala (**1c**)	(L)-Val (**1d**)	(L)-Ile (**1e**)	(L)-Trp (**1f**)
aromatic	benzene	G (0.16)	G (0.66)	G (0.66)	I	I	P	I
	toluene	G (0.17)	G (0.30)	G (0.30)	P	I	P	I
	p-xylene	G (0.18)	G (0.25)	G (0.25)	I	P	P	P
	ethylbenzene	G (0.18)	G (0.42)	G (0.42)	I	I	I	I
	p-diethylbenzene	G (0.12)	G (0.11)	G (0.11)	I	I	I	I
	o-diethylbenzene	G (0.30)	G (0.5)	G (0.5)	I	I	I	I
	chlorobenzene	G (0.6)	G (>2)	G (2)	P	P	P	S
	tetraline	G (0.18)	G (0.18)	G (0.18)	P	P	I	P
	1-methylnaphthalene	G (1.3)	S	S	P	P	P	P
	nitrobenzene	S	S	S	S	S	S	S
alkanes	*n*-nctane	I	I	I	I	I	I	I
	cyclohexane	I	I	I	I	I	I	I
chlorinated	carbon tetrachloride	I	G (0.2)	I	I	I	I	I
	tetrachloroethylene	G (0.06)	G (0.05)	G (0.06)	I	I	I	I
	1,2-dichloroethane	P	S	P	P	P	P	I
	dichloromethane	S	S	S	S	S	S	I
	chlorform	S	S	S	S	S	S	I
alcohols	methanol	S	S	S	S	S	S	S
	ethanol	S	S	S	S	S	S	S
esters	methyl acetate	S	S	S	S	S	S	S
	ethyl acetate	S	S	S	S	S	S	I
	ethyl propionate	S	S	S	S	S	S	I
ethers	diethyl ether	I	I	I	I	I	I	I
	diisopropyl ether	I	I	I	I	I	I	I
	tetrahydrofuran	S	S	S	S	S	S	S
ketones	acetone	S	S	S	S	S	S	S
	4-methyl-pentan-2-one	S	S	S	S	S	S	I
	cyclopentanone	S	S	S	S	S	S	S
others	dimethyl sulfoxide	S	S	S	S	S	S	S
	acetonitrile	S	S	S	S	S	S	P
	dimethylformamide	S	S	S	S	S	S	S
	water	I	I	I	I	I	I	I

[a] G(*x*): gel (critical gelation concentration (CGC) in wt%); S: soluble; I: insoluble; P: precipitate.

π stacking interactions between the gelator and the solvent. The only exceptions to this trend are carbon tetrachloride and tetrachloroethylene. Compound **1b** is able to gelify the first one, whereas gelator **1a** form gels in both. Finally, gelators **1a** and **1b** are soluble in all other solvents tested, except in diethyl ether, diisopropyl ether, and water, in which they precipitate.

To understand the solvent effects on gelation, we decided to consider the Hildebrand and Hansen parameters[22] for the different solvents.

Solvent parameters analysis: Before turning to this study, we analyzed the gelation behavior of our molecules as a function of most common solvent parameters, such as dielectric constant (ε), dipole moment (μ), boiling point (bp), and density (*d*). However, no relationship could be established between these parameters and the gelation behavior (see Table 1 in the Supporting Information). Then, following the recent work reported by Smith and co-workers,[23] we have tried to explain the organogelation behavior of **1a** and **1b** in various solvents by using the Kamlet–Taft parameters (see the Supporting Information). In their approach, the α parameter (hydrogen-bond donor ability, Table 2) appears to have primary importance and should ideally be zero for effective gelation.

We tried to apply this theory to our gels, but, unfortunately, we realized that the α parameter alone cannot explain the behavior of our compounds **1a** and **1b** towards the tested solvents. Indeed, as shown in Figure 1, many solvents with an α parameter of zero are not gelified by gelators **1a** and **1b**, which are soluble or insoluble in the considered solvents.

Contrary to the conclusions given by Smith and co-workers,[21b,23] we conclude that the consideration of the α parameter, which only represents the hydrogen-bond donor ability of a solvent, is not sufficient to understand the gelation phe-

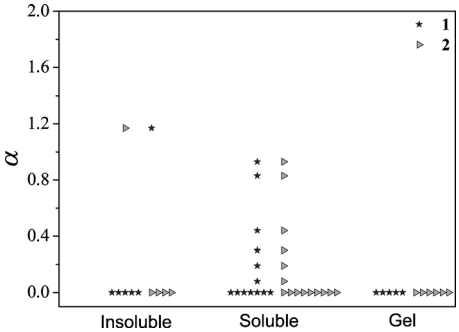


Figure 1. α-Depending behavior of gelators **1a** and **1b** in the studied solvents.

Table 2. Hydrogen-bond donor ability (α)[a] and Hildebrand (δ)[b] and Hansen (δ_d, δ_p, δ_h)[b] parameters of the solvents.

Class of solvent	Solvents	a	δ [(cal cm^{-3})$^{1/2}$]	δ_d [(cal cm^{-3})$^{1/2}$]	δ_p [(cal cm^{-3})$^{1/2}$]	δ_h [(cal cm^{-3})$^{1/2}$]
aromatic	benzene	0.00	9.1	9	0	1
	toluene	0.00	8.9	8.8	0.7	1
	p-xylene	0.00	8.8	N.A.[c]	N.A.	N.A.
	ethylbenzene	N.A.	8.7	8.7	0.3	0.7
	p-diethylbenzene	N.A.	8.8	8.8	0	0.3
	o-diethylbenzene	N.A.	N.A.	N.A.	N.A.	N.A.
	chlorobenzene	0.00	9.6	9.3	2.1	1
	tetraline	N.A.	9.8	9.6	1	1.4
	1-methylnaphthalene	N.A.	10	10	0.4	2.3
	nitrobenzene	0.00	10.9	9.8	4.2	2
alkanes	*n*-octane	0.00	7.6	7.6	0	0
	cyclohexane	0.00	8.2	8.2	0	0.1
	carbon tetrachloride	0.00	8.7	8.7	0	0.3
chlorinated	tetrachloroethylene	0.00	9.9	9.3	3.2	1.4
	1,2-dichloroethane	0.00	10.2	9.3	3.6	2
	dichloromethane	0.3	9.9	8.9	3.1	3
	chlorform	0.44	9.3	8.7	1.5	2.8
alcohols	methanol	0.93	14.5	7.4	6	10.9
	ethanol	0.83	13	7.7	4.3	9.5
esters	methyl acetate	0.00	9.2	7.6	3.5	3.7
	ethyl acetate	0.00	8.9	7.7	2.6	3.5
	ethyl propionate	0.00	8.4	N.A.	N.A.	N.A.
ethers	diethyl ether	0.00	7.7	7.1	1.4	2.5
	diisopropyl ether	0.00	6.9	N.A.	N.A.	N.A.
	tetrahydrofuran	0.00	9.5	8.2	2.8	3.9
ketones	acetone	0.08	9.8	7.6	5.1	3.4
	4-methyl-pentan-2-one	N.A.	N.A.	N.A.	N.A.	N.A.
	cyclopentanone	0.00	10.4	N.A.	N.A.	N.A.
others	dimethyl sulfoxide	0.00	13	9	8	5
	acetonitrile	0.19	12	7.5	8.8	3
	dimethylformamide	0.00	12.1	8.5	6.7	5.5
	water	1.17	23.4	7.6	7.8	20.7

[a] The data were extracted from Ref. [24]. [b] The data were extracted from Ref. [22]. [c] N.A.: not available.

nomena. The use of a parameter able to represent both abilities of a solvent—to accept or donate hydrogen bonds—would be more judicious.

The gelation phenomenon is a complex solubility–insolubility balance between the gelator and the solvent. By taking into account that the complete miscibility of a two-components system is expected if the Hildebrand parameters and the degree of hydrogen bonding (δ_h) are similar,[22] we decided to report the behavior of our gelators as a function of these solvent parameters.

Despite the lack of data concerning our molecules, solubility parameters are well referenced in literature for a wide range of solvents (Table 2). First we considered the Hildebrand parameter, which can be formulated as a function of the Hansen parameters (δ_d, δ_p, δ_h):

$$\delta^2 = {\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2$$

where δ_d accounts for the dispersive interactions, δ_p for the permanent dipole–dipole interactions, and δ_h for the hydrogen-bonding interactions.[22] Finally, δ represents the total solubility parameter.

Figure 2 shows the behavior of gelators **1a** and **1b** as a function of the value of δ. Only three classes of behavior (insoluble, soluble, and gel) have been indicated; the precipitate class is included in the insoluble one.

In a first approach, we can define a favorable δ domain for gelation between 8.5 and 10.5 (cal cm^{-3})$^{1/2}$ (Figure 2). However, this domain also includes solvents in which gelators **1a** and **1b** are soluble. Then, we decided to analyze separately the three components of δ, the results are shown in Figure 3.

The gelation behavior of **1a** and **1b** as a function of δ_d (Figure 3a) and δ_p interactions (Figure 3b) gives two gelation domains, which once more include solvents that dissolve gelators **1a** and **1b**. We then focused on δ_h, which evaluates the ability of the solvent to donate or to accept hydrogen bonds. The behavior of the two gelators **1a** and **1b** defines another narrow, favorable, δ_h domain for gelation between 0.2 and 1.4 (cal cm^{-3})$^{1/2}$ at which only "gel" behaviors are observed (Figure 3c).

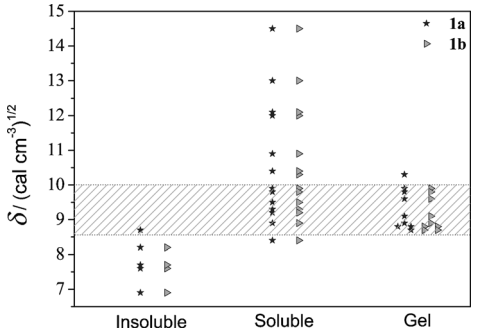


Figure 2. δ-Depending behavior of gelators **1a** and **1b** in the studied solvents.

In our series based on amino acid derivatives, the hydrogen-bond interactions seem to play a key role in 3D self-assembly of the organogelator molecules.[25c] In this context, the δ_h parameter is assumed to be of primary importance compared with the two other Hansen parameters (δ_d and δ_p), which represent weaker interactions. In the defined, narrow, favorable, δ_h domain the solvent–gelator interac-

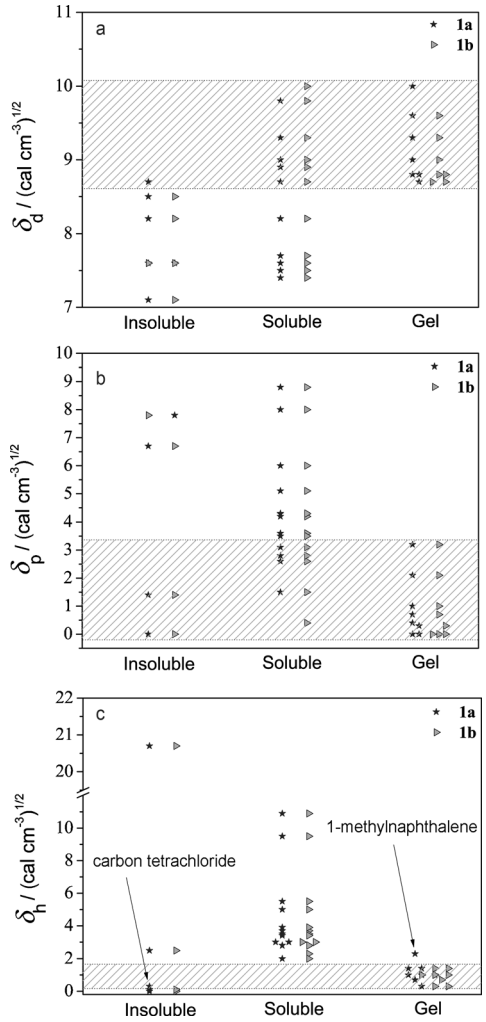


Figure 3. Hansen-parameter-depending behaviors of gelators **1a** and **1b** in the studied solvents: a) δ_d, b) δ_p, and c) δ_h.

tions have the right force to allow molecules **1a** or **1b** to interact through hydrogen bonds and form the fibrous network. Moreover, the fact that this favorable domain includes quite low values of δ_h means that the hydrogen-bonding interactions between solvent and gelator have to be sufficiently weak to not compromise the self-assembly of gelators.

Nevertheless, two exceptions can be noticed: In 1-methylnaphthalene, which is slightly outside the δ_h domain (Figure 3c), **1b** is soluble whereas **1a** forms a gel, but at higher concentrations than in other aromatic solvents (critical gelation concentration (CGC) = 1.3 wt%, Table 1). It can be assumed that the high δ_h value of this solvent ($\delta_h = 2.3$) destabilizes the formation of the 3D network based on hydrogen bonds. However, the gelation ability of **1a** could be explained by the presence of aromatic groups on the lateral chain; this could induce a self-assembly of gelator molecules by additional π–π stacking interactions. This condition is not satisfied for **1b**, which has a less aromatic character than **1a** due to the alkyl side chain. The organogelation behavior in carbon tetrachloride, in which **1b** forms a gel and **1a** is completely insoluble, although this solvent is inside the favorable δ_h domain ($\delta_h = 0.3$ (cal cm^{-3})$^{1/2}$, Figure 3c), is currently unexplained.

Moreover, above, we describe a favorable δ domain for gelation of **1a** and **1b** that also includes solvents in which the gelators are soluble (Figure 2). After the δ_h analysis, we concluded that these solvents have too many gelator–solvent hydrogen-bonding interactions (Table 2); this prevents the self-assembly of gelator molecules.

To complete this study, we decided to consider the behavior of the new molecules **3a–b** and **4a** in different classes of solvent. The results are shown in Table 3.

We can note that **3a–b** and **4a** have very similar gelation abilities to **1a** and **1b** in the same solvents. They are able to gelify most of the tested aromatic solvents and the chlorinated solvents, for example, tetrachloroethylene in the case of **3a** and **3b**. Derivatives **3a–b** and **4a** are soluble (S) or insoluble (I) in all other solvents tested (Table 3). The surprising exception to this trend concerns the behavior of gelator **4a** in tetrachloroethylene. Indeed, whereas **3a** and **3b** form a gel in this solvent at low concentration (CCG = 0.12 wt%/12.8 mM and 0.25 wt%/9.56 mM, respectively), gelator **4a** appears to be completely insoluble.

As described above for **1a** and **1b** (Figure 3c), we were able to establish a relationship between the δ_h parameter and the gelation ability of **3a–b** and **4a** (Figure 4). Therefore, also for these analogs, the δ_h values of the gelified solvents are located in a very narrow domain. In accordance with recent reports,[23] we demonstrated that the ability of a solvent to support self-assembly and that gelation of our class of molecules is dependent of the ability to form hydrogen bonds. However, in our case, both hydrogen-bonding acceptor and donor abilities have to be taken into account.

Table 3. Gelation behavior for **3a–b** and **4a** in different solvents[a].

Class of solvent	Solvents	(L)-Phe (**3a**)	(L)-Leu (**3b**)	(L)-Leu (**4a**)	δ_h[b] [(cal cm^{-3})$^{1/2}$]
	benzene	G (0.57)	G (1.63)	G (0.97)	1
	toluene	G (0.46)	G (1.43)	G (0.77)	1
	p-xylene	G (0.35)	G (0.63)	G (0.46)	N.A.
aromatic	chlorobenzene	G (0.81)	G (1.79)	G (1)	1
	tetraline	G (0.35)	G (1.04)	G (0.57)	1.4
	1-methylnaphthalene	S	S	S	2.3
	nitrobenzene	S	S	S	2
alkanes	cyclohexane	I	I	I	0.1
	carbon tetrachloride	P	P	I	0.3
chlorinated	tetrachloroethylene	G (0.12)	G (0.25)	I	1.4
	chlorform	S	S	S	2.8
alcohols	methanol	P	S	S	10.9
esters	ethyl acetate	S	S	S	3.5
ethers	diethyl ether	I	I	I	2.5
ketones	acetone	S	S	S	3.4
others	water	I	I	I	20.7

[a] G(*x*): gel (CGC in wt%); S: soluble, I: insoluble, P: precipitate, N.A.: not available. [b] H-bonding Hansen parameter; the data were extracted from Ref. [22].

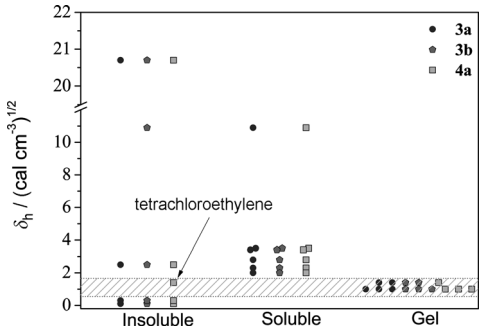


Figure 4. δ_h-Depending behavior of gelators **3a–b** and **4a** in the studied solvents.

As a result, we demonstrated that the capacity of a solvent to form a gel by our series of compounds can be predicted by the δ_h parameter representative of the ability to establish hydrogen bonds. However, we think that the complete description of the gelation phenomenon, even of more complex systems, necessitate other parameters, such as one describing π–π stacking interactions, to be taken into account.[6,7] Indeed, as observed herein and in another recent work of our group,[25c] these latter interactions are driving forces in the organogelation phenomenon.

Gelation-strength analysis: The CGC, defined as the minimum concentration at which a gel is formed, is one of the most common criterions to evaluate the strength of a gel as well as the sol–gel transition temperature (T_{gel}).[6] The values of CGC expressed in wt% depend on the density of the solvent, whereas the values of CGC expressed in mM depend on the molecular weight of the gelator. To eloquently describe the strength of the gel, we translated the CGC into gelation number (GN), which gives the number of solvent molecules gelified per molecule of gelator.[21d]

Following the analysis of the previous section, we first tried to correlate the GN with δ and then with δ_h (Figure 5).

Generally, an increase in the δ parameter represents a higher solvation of polar gelators; this prevents the H-bonding interactions responsible for gelation and consequently leads to a GN decrease. A similar behavior was been recently reported by Zhu and Dordick for thehalose-based gelator structures in different solvents.[21d] In the same way, Hirst and Smith reported that an increase of δ_a ($\delta_a^2=\delta_p^2+\delta_h^2$) leads to a gel-strength decrease (i.e., T_{gel} decrease).[21b]

Even though we can notice a similar trend for gelators **1a** and **1b** in aromatic solvents as far as δ is concerned (see arrow, Figure 5a), the data does not seem to correspond entirely to this assumption. Furthermore, we were not able to find any correlation between GN and δ_h; the GN of gelators **1a** and **1b** in the chosen solvents seem to be completely random (Figure 5b). Furthermore, gelators **1a** and **1b** show the highest GN in tetrachloroethylene, which does not have the lowest δ value compared with other gelified solvents (Figure 6).

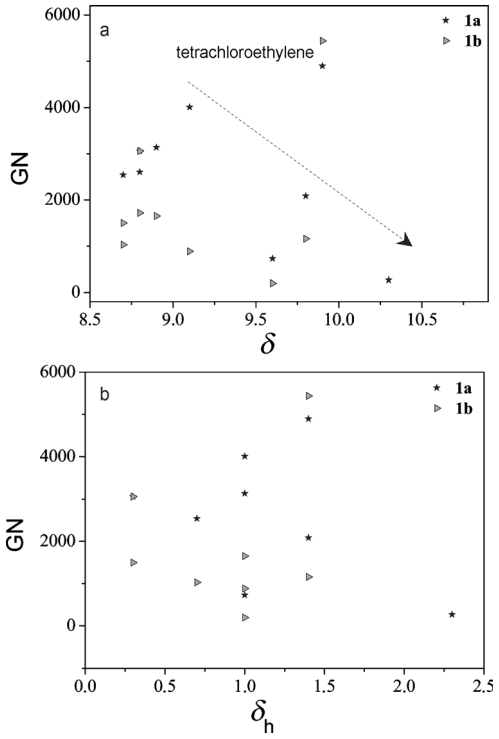


Figure 5. a) Effect of the δ on GN of gelators **1a** and **1b**. b) Effect of the δ_h on GN of gelators **1a** and **1b**.

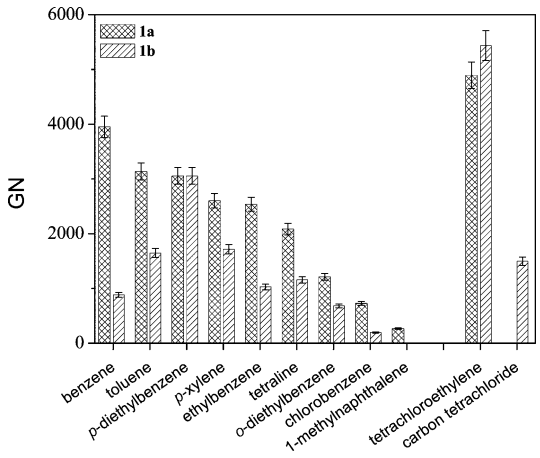


Figure 6. GN for gelators **1a** and **1b** in the studied solvents. The error bars represent 5% of the total value.

These latter results indicate that the variables involved in the gelation process are much more complicated than those described to date. Nevertheless, if we carefully analyze the evolution of GN for gelators **1a** and **1b** in aromatic solvents (Figure 6), we can still draw some general conclusions. The best result for gelator **1b** has been found with *p*-diethylbenzene as an aromatic solvent (GN = 3058 ± 153), whereas gelator **1a** presents the best value in benzene (GN = 3951 ± 198). Moreover for **1b**, GN is very low in benzene (GN = 884 ± 44), probably due to the lack of an aliphatic moiety in the solvent structure. However, for gelator **1a**, we note that

independent of the nature of the aliphatic moiety of the solvent, the GN value is always smaller than the one found for benzene (Figure 6). In this case, the presence of alkyl chains on the structure of the solvent seems to be a disturbing parameter for the gelation phenomenon. For chlorobenzene, the disturbing effect seems to be due to high polarity of this solvent; this contributes to the weakness of the hydrogen-bonding network of gelator molecules.[21b,d,e]

These last observations are in accordance with the results reported by Banerjee et al. concerning the gelation property of a family of tripeptides gelators.[19c] They found that changing the protecting group from *tert*-butyloxycarbonyl (Boc) to benzyloxycarbonyl (Z) improved the gel properties in various aromatic solvents. By taking these last conclusions into account, we could have expected that the best solvent for gelator **1a** would be 1-methylnaphthalene, because of the higher aromatic character than benzene. Actually, as discussed above, only poor gels were obtained in this solvent; the high value of δ_h for this aromatic solvent does not allow a good self-assembly of the gelator molecules.

Gel morphology: Scanning electron microscopy (SEM) is a good tool to analyze the influence of the nature of the solvent on gel morphology.[6] We have compared the pictures of xerogels (dried gels, Figure 7) obtained from organogels of compounds **1a** and **1b** in solvents with different solubility and polarity (Table 2). A xerogel is a shrunk gel for which the structure has collapsed because of the capillary forces upon solvent evaporation during the drying process.[27]

First of all, we notice that despite the shrinking of the structure, all xerogels are composed of a similar and highly entangled 3D fibrillar network (Figure 7). Indeed, we never observed a total loss of the 3D network due to solvent polarity (solvent–gelator interactions)[21d] or induced by the capillary forces.[28] The only observable difference is given by the gels obtained from gelator **1a** in toluene (Pictures F1 and F2, Figure 7), which seem to have less fibrillar density than other gels. This result would suggest that weaker capillary forces have been applied on the gel structure during the preparation of these xerogels. However, the same effect was not obtained with gelator **1b** in toluene (Picture L1, Figure 7), which presents the same compactness as other xerogels. Furthermore, the variation of the concentration of the gelator in the gel does not seem to have a significant effect on the size and shape of the fibers. As a result, no differences can be observed when comparing 0.23 and 1 wt% of gelator **1a** in toluene (Figure 7, pictures F1 and F2, respectively).

Nevertheless, a closer look at the SEM pictures reveals a small influence of the solvent on the gel morphology, especially on the fiber diameter. Figure 8 shows the average fiber diameters of the gels obtained in different solvents.

The fiber sizes of gelators **1a** and **1b** are slightly different in a given solvent. The most obvious cases are the gels prepared by using *p*-xylene as solvent. For gelator **1a**, the average diameter is approximately 75 nm, whereas for gelator **1b** the average diameter is approximately 195 nm with a wide distribution of fiber size (Figure 8). In tetrachloroethylene, for which we found the highest values of GN

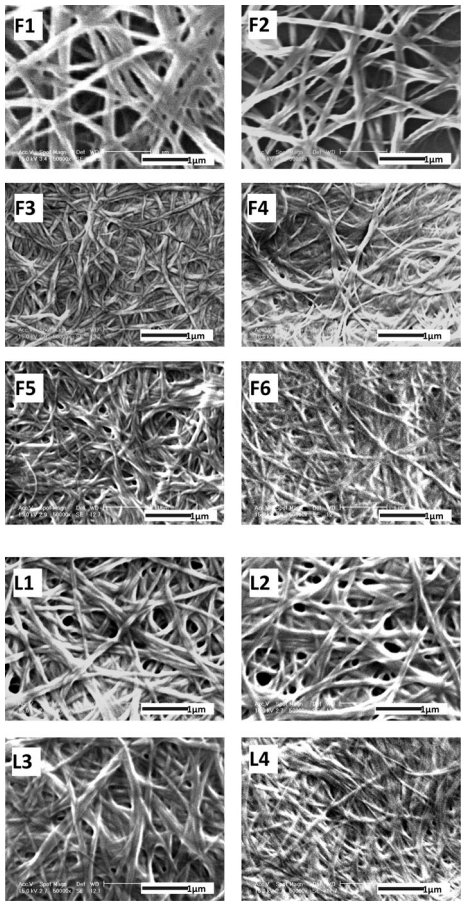


Figure 7. SEM pictures of dried gels (xerogel) in different solvents: F1) gelator **1a** in 0.23 wt% toluene; F2) gelator **1a** in 1.0 wt% toluene; F3) gelator **1a** in 0.07 wt% tetrachloroethylene; F4) gelator **1a** in 0.22 wt% *p*-xylene; F5) gelator **1a** in 0.72 wt% chlorobenzene; F6) gelator **1a** in 1.55 wt% 1-methylnaphthalene; L1) gelator **1b** in 0.36 wt% toluene; L2) gelator **1b** in 0.06 wt% tetrachloroethylene; L3) gelator **1b** in 0.28 wt% *p*-xylene; and L4) gelator **1b** in 3.4 wt% chlorobenzene.

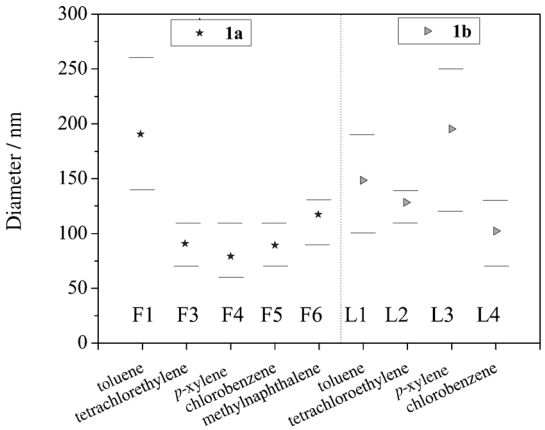


Figure 8. Average fiber diameters for the gels prepared from gelators **1a** and **1b** in different solvents. The horizontal black lines represent the maximum and minimum fiber diameter observed for each sample.

(Figure 6), the difference between the average diameters of the gels prepared from the two gelators is less marked.

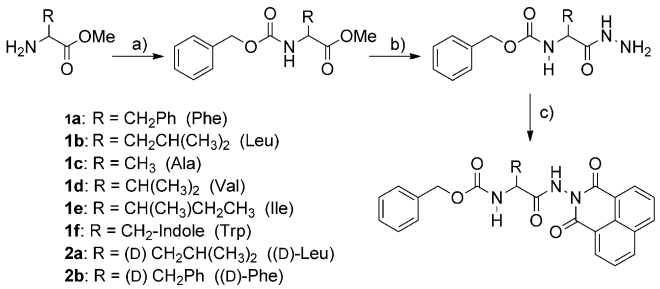
Thus, the solvent somehow affects the microscopic structure of the gel similarly to what has been reported previously.[21,28] For example, Zhu and Dordick reported that an increase of the solvent–gelator interactions favors the formation of fine nanofibres.[21d] Nevertheless, in the present work, no relationship could be found between the nature of the solvent and the size of the fibrillar network of the xerogels. Further SEM experiments on organogels are currently in progress to settle this question.

Conclusion

Herein we report the synthesis of several low-molecular-weight amino acid derivatives and their organogelation behavior in a large variety of solvents. We observed that small variations in the structure of the gelators can induce a drastic change in the gelation properties. Indeed, only leucine and phenylalanine derivatives are able to gelify different aromatic solvents, carbon tetrachloride, and tetrachloroethylene. The highest gelation number was found for the latter solvent for both gelators **1a** and **1b** (GN = 4894 ± 245 and 5437 ± 272, respectively). SEM pictures revealed that the obtained gels are composed of entangled 3D fibrillar networks, and that the fiber diameters are slightly influenced by the nature of the solvent. Importantly, we point out herein that δ_h appears to have primary importance in controlling whether hydrogen-bond networks of gelators can be established. This study led us to determine a narrow δ_h domain favorable to gelation. We think that this approach could be applied to other amino-acid-derivative gelation systems, as well as to other classes of gelators based on the self-assembly through hydrogen-bond interactions.

Experimental Section

Synthetic procedure: Compounds **1b–f** as well as **2a** and **2b** were prepared in three steps (Scheme 2) from L-amino-acid esters according to a general procedure described previously.[25]



Scheme 2. General procedure for the preparation of gelators **1b–f**, **2a** and **2b**: a) Benzyl chloroformate (Z-Cl), $NaHCO_3$ (saturated solution), RT, overnight; b) $NH_2NH_2{\cdot}H_2O$, MeOH, reflux, overnight; c) Naphthalic anhydride, toluene, reflux, 10 h.

Data for compound 1a: m.p. = 188–190 °C; $[\alpha]_D^{20} = -27.9°$ (c = 0.067 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO, RT): δ = 11.07 (s, 1H), 8.58–8.52 (m, 4H), 7.96–7.90 (m, 2H), 7.74 (d, 1H, J = 9.0 Hz), 7.42–7.22 (m, 10H), 4.97 (d, 2H, J = 3.8 Hz), 4.70–4.63 (m, 1H), 3.32–3.28 (m, 1H), 2.95–2.87 ppm (m, 1H); ^{13}C NMR (75 MHz, [D$_6$]DMSO, RT): δ = 170.8, 161.7, 161.5, 155.8, 137.9, 137.0, 135.2, 131.54, 131.47, 129.3, 128.3, 128.1, 127.6, 127.44, 127.36, 127.2, 126.4, 121.8, 65.2, 64.8, 37.8 ppm; HRMS (ESI):
m/z: calcd for $C_{29}H_{23}N_3Na_1O_5$: 516.1535 [M+Na]$^+$; found: 516.1530.

Data for compound 1b: m.p. = 164–166 °C; $[\alpha]_D^{20} = -17.7°$ (c = 0.067 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO, RT): δ = 10.89 (s, 1H), 8.55–8.50 (m, 4H), 7.93–7.88 (m, 2H), 7.62 (d, 1H, J = 8.9 Hz), 7.44–7.29 (m, 5H), 5.08 (d, 1H, J = 1.9 Hz), 4.51–4.43 (m, 1H), 1.84–1.59 (m, 3H), 0.97–0.94 ppm (m, 6H); ^{3}C NMR (75 MHz, [D$_6$]DMSO, rt): δ = 171.4, 161.6, 161.4, 165.9, 137.0, 135.1, 131.5, 131.4, 128.3, 127.8, 127.7, 127.4, 127.2, 121.7, 65.5, 51.6, 41.1, 24.2, 23.1, 21.5 ppm; HRMS (ESI): m/z: calcd for $C_{26}H_{25}N_3Na_1O_5$: 482.1692 [M+Na]$^+$; found: 482.1686.

Data for compound 1c: m.p. = 195–197 °C; $[\alpha]_D^{20} = -25.8°$ (c = 0.057 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO, RT): δ = 10.81 (s, 1H), 8.53–8.46 (m, 4H), 7.91–7.86 (m, 2H), 7.66 (d, 1H, J = 8.0 Hz), 7.38–7.28 (m, 5H), 5.12–5.02 (m, 2H), 4.50–4.45 (m, 1H), 1.45 ppm (d, 3H, J = 7.6 Hz); ^{13}C NMR (300 MHz, [D$_6$]DMSO, RT): δ = 171.6, 161.6, 161.4, 155.6, 137.0, 135.0, 131.5, 131.4, 128.3, 127.8, 127.4, 127.1, 121.7, 65.5, 48.7, 18.6 ppm; HRMS (ESI): m/z: calcd for $C_{23}H_{19}N_3Na_1O_5$: 440.1222 [M+Na]$^+$; found: 440.1217.

Data for compound 1d: m.p. = 229–231 °C; $[\alpha]_D^{20} = -17.4°$ (c = 0.067 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO,): δ = 10.88 (s, 1H), 8.56–8.52 (m, 4H), 7.95–7.90 (m, 2H), 7.48–7.32 (m, 5H), 5.10 (s, 2H), 4.31–4.26 (m, 1H), 2.19–2.12 (m, 1H), 1.07–0.98 ppm (m, 6H); ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 169.9, 161.5, 161.4, 156.1, 137.0, 135.1, 131.4, 128.3, 127.7, 127.6, 127.4, 127.2, 121.7, 65.4, 58.6, 30.8, 19.1, 17.9 ppm; HRMS (ESI): m/z: calcd for $C_{25}H_{23}N_3Na_1O_5$: 468.1535 [M+Na]$^+$; found: 468.1530.

Data for compound 1e: m.p. = 239–241 °C; $[\alpha]_D^{20} = -23.7°$ (c = 0.067 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.89 (s, 1H), 8.55–8.50 (m, 4H), 7.94–7.88 (m, 2H), 7.49 (d, 1H, J = 9.0 Hz), 7.42–7.30 (m, 5H), 5.10 (s, 2H), 4.34–4.28 (m, 1H), 1.94–1.85 (m, 1H), 1.63–1.56 (m, 1H), 1.32–1.17 (m, 1H), 1.06 (d, 3H, J = 6.8 Hz), 0.89 ppm (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 170.0, 161.5, 161.4, 156.0, 137.1, 135.1, 131,5, 131.44, 131.41, 128.3, 127.7, 127.6, 127.4, 127.2, 121.7, 65.4, 57.7, 36.9, 24.2, 15.2, 11.0 ppm; HRMS (ESI): m/z: calcd for $C_{26}H_{25}N_3Na_1O_5$: 482.1692 [M+Na]$^+$; found: 482.1686.

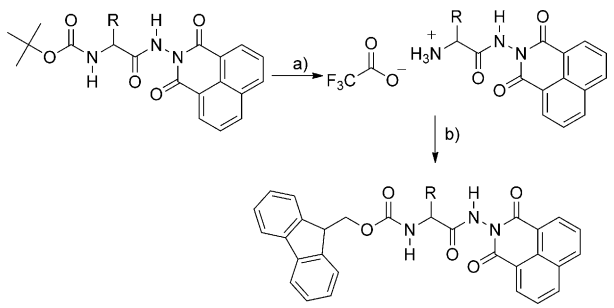
Data for compound 1f: m.p. = 184–186 °C; $[\alpha]_D^{20} = -42.3°$ (c = 0.067 g mL^{-1} in DMSO); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.11 (s, 1H), 10.86 (s, 1H), 8.59–8.53 (m, 4H), 7.96–7.91 (m, 2H), 7.78 (d, 1H, J = 7.7 Hz), 7.60 (d, 1H, J = 9.0 Hz), 7.39–7.24 (m, 6H), 7.10–7.02 (m, 3H), 4.97 (s, 2H), 4.72–4.67 (m, 1H), 3.44–3.39 (m, 1H), 3.12–3.04 ppm (m, 1H); ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 171.1, 161.6, 161.5, 155.8, 136.9, 136.1, 135.1, 131.5, 131.4, 128.2, 127.6, 127.4, 127.2, 124.0, 121.7, 120.8, 118.5, 118.2, 111.3, 109.9, 65.2, 54.1, 28.2 ppm; HRMS (ESI): m/z: calcd for $C_{31}H_{24}N_4Na_1O_5$: 555.1644 [M+Na]$^+$; found: 555.1639.

Compounds **3a** and **3b** were prepared according to the Scheme 2 by using the amino acids protected with a Boc group as starting material.[25]

Data for compound 3a: m.p. = 158–161 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (s, 1H,), 8.57 (br, 2H,), 8.22 (d, 2H, J = 8.2 Hz), 7.73 (br, 2H,), 7.37–7.22 (m, 5H), 5.22 (d, 2H, J = 7.6 Hz), 4.76 (br, 1H), 3.40–3.12 (m, 2H), 1.42 ppm (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.3, 162.6 (2C), 156.8, 137.2, 135.4, 132.7, 132.5, 130.3, 129.3, 128.8, 127.7 (2C), 123.0, 81.6, 55.0, 38.2, 28.9 ppm.

Data for compound 3b: m.p. = 181–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 8.65 (br, 2H), 8.24 (d, 2H, J = 9.0 Hz), 7.83–7.72 (m, 2H), 5.0 (d, 1H, J = 8.5 Hz), 4.48 (br, 1H), 1.93–1.85 (m, 2H), 1.68–1.51 (m, 10H), 1.04–0.99 ppm (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.8, 162.1, 162.0, 156.4, 135.5, 134.7, 133.5, 131.9, 131.8, 128.1, 127.6, 127.0, 122.4, 118.9, 80.6, 51.4, 40.5, 28.5, 24.8, 23.2, 22.2 ppm.

Finally, compound **4a** was prepared in two steps from Boc-protected amino-acid **3b** according to the procedure described in the Scheme 3.



Scheme 3. General procedure for the preparation of gelator **4a**: a) CF_3COOH, CH_2Cl_2, RT, 2 h; b) FmocCl, $NaHCO_3$, 50% dioxane/H_2O.

Data for compound 4a: m.p. = 186–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63–8.56 (m, 3H), 8.24 (d, 2H, J = 8.1 Hz), 7.76 (d, 4H, J = 7.3 Hz), 7.67–7.61 (m, 2H), 7.41–7.29 (m, 4H), 5.28 (d, 1H, J = 7.7 Hz), 4.58–4.53 (m, 2H), 4.45–4.40 (m, 1H), 4.31–4.26 (m, 1H), 1.90–1.68 (m, 3H), 1.04–0.99 ppm (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.5, 161.9, 156.9, 144.1, 143.7, 141.4, 134.8, 132.1, 131.8, 128.1, 127.7, 127.2, 127.0, 125.4, 125.3, 122.3, 120.0, 67.4, 52.0, 47.2, 40.8, 24.8, 23.1, 22.2 ppm.

Gelation test: A given amount of potential organogelator (ca. 5 mg) in 1 mL of organic solvent was placed in a flask fitted with a reflux condenser and heated until complete dissolution of the solid. Compounds that did not dissolve under these conditions were classified as insoluble (I). When cooled down to RT (ca. 30 min.), the solution was transferred into a closed glass vial and cooled at 4 °C for 24 h. The gelation was simply confirmed by turning the glass vial upside down. For the CGC measurements, the gels were repeatedly diluted, heated, and then cooled at 4 °C until no further formation of gel was observed or until a viscous liquid was obtained by inverting the glass vial.

SEM observations: SEM was performed with a Philips XL30-ESM instrument. The accelerating voltage of the microscope was 30 kV. The dry samples (xerogels), prepared by evaporation of the solvent under vacuum at RT, were coated with gold (15 Å) during 4 min through physical vapor deposition.

Acknowledgements

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[1] a) V. Jenning, A. Gysler, M. Schäfer-Korting, S. H. Gohla, *Eur. J. Pharm. Biopharm.* **2000**, *49*, 211–218; b) A. Wynne, M. Whitefield, A. J. Dixon, S. Anderson, *J. Dermatol. Treat.* **2002**, *13*, 61–66.

[2] C. Bergeret-Galley, X. Latouche, Y.-G. Illouz, *Aesthetic Plastic Surgery* **2001**, *25*, 249–255.

[3] L. Alvord, J. Court, T. Davis, C. F. Morgan, K. Schindhelm, J. Vogt, L. Winterton, *Optometry & Vision Science* **1998**, *75*, 30–36; Vision Science **1998**, 75, 30–36.

[4] a) T. Kato, *Science* **2002**, *295*, 2414–2418; b) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, S. J. George, *Angew. Chem.* **2007**, *119*, 6376–6381; *Angew. Chem. Int. Ed.* **2007**, *46*, 6260–6265; c) J. Puigmartí-Luis, V. Laukhin, A. P. del Pino, J. Vidal-Gancedo, C. Rovira, E. Laukhina, D. B. Amabilino, *Angew. Chem.* **2007**, *119*, 242–245; *Angew. Chem. Int. Ed.* **2007**, *46*, 238–241.

[5] a) K. Y. Lee, D. J. Mooney, *Chem. Rev.* **2001**, *101*, 1869–1880; b) Z. Yang, G. Liang, L. Wang, B. Xu, *J. Am. Chem. Soc.* **2006**, *128*, 3038–3043; c) G. Bastiat, F. Plourde, A. Motulsky, A. Furtos, Y. Dumont, R. Quirion, G. Fuhrmann, J.-C. Leroux, *Biomaterials* **2010**, *31*, 6031–6038.

[6] P. Terech, R. G. Weiss, *Molecular Gels: Materials with Self-Assembled Fibrillar networks*, Springer, Dordrecht, **2006**.

[7] a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3160; b) D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237–1247; c) O. Gronwald, E. Snip, S. Shinkai, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 148–156; d) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836; e) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489–497; f) P. Dastidar, *Chem. Soc. Rev.* **2008**, *37*, 2699–2715.

[8] a) J. Makarević, M. Jokić, B. Perić, V. Tomišić, B. Kojić-Prodić, M. Žinić, *Chem. Eur. J.* **2001**, *7*, 3328–3341; b) P. Kumar Vemula, U. Aslam, V. Ajay Mallia, G. John, *Chem. Mater.* **2007**, *19*, 138–140.

[9] a) K. Murata, M. Aoki, T. Nishi, A. Ikeda, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1991**, 1715–1718; b) M. Ayabe, T. Kishida, N. Fujita, K. Sada, S. Shinkai, *Org. Biomol. Chem.* **2003**, *1*, 2744–2747; c) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, *304*, 278–281.

[10] a) G. Bastiat, J.-C. Leroux, *J. Mater. Chem.* **2009**, *19*, 3867–3877; b) G. Liang, Z. Yang, R. Zhang, L. Li, Y. Fan, Y. Kuang, Y. Gao, T. Wang, W. W. Lu, B. Xu, *Langmuir* **2009**, *25*, 8419–8422.

[11] a) R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters, R. J. M. Nolte, *Chem. Commun.* **1997**, 545–546; b) E. Pouget, E. Dujardin, A. Cavalier, A. Moreac, C. Valéry, V. Marchi-Artzner, W. Weiss, A. Renault, M. Paternostre, A. Franck, *Nat. Mater.* **2007**, *6*, 434–439.

[12] a) G. Bühler, M. C. Feiters, R. J. M. Nolte, K. H. Dötz, *Angew. Chem.* **2003**, *115*, 2599–2602; *Angew. Chem. Int. Ed.* **2003**, *42*, 2494–2497; b) M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.

[13] a) B. Isare, L. Petit, E. Bugnet, R. Vincent, L. Lapalu, P. Sautet, L. Bouteiller, *Langmuir* **2009**, *25*, 8400–8403; b) M. Fahrländer, K. Fuchs, R. Mülhaupt, C. Friedrich, *Macromolecules* **2003**, *36*, 3749–3757.

[14] a) Y. C. Lin, R. G. Weiss, *Macromolecules* **1987**, *20*, 414–417; b) M. Žinić, F. Vogtle, F. Fagos in *Topics in Current Chemistry Vol. 256: Low Molecular Mass Gelator*, Springer-Verlag, Berlin Heidelberg **2005**, pp. 39–76; c) X. Huang, S. R. Raghavan, P. Terech, R. G. Weiss, *J. Am. Chem. Soc.* **2006**, *128*, 15341–15352; d) S. Malik, S.-i. Kawano, N. Fujita, S. Shinkai, *Tetrahedron* **2007**, *63*, 7326–7333.

[15] a) P. Terech, G. Gebel, R. Ramasseul, *Langmuir* **1996**, *12*, 4321–4323; b) T. Kishida, N. Fujita, K. Sada, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 7298–7299.

[16] a) K. Yoza, N. Amanokura, Y. Ono, T. Akao, H. Shinmori, M. Takeuchi, S. Shinkai, D. N. Reinhoudt, *Chem. Eur. J.* **1999**, *5*, 2722–2729; b) G. John, G. Zhu, J. Li, J. S. Dordick, *Angew. Chem.* **2006**, *118*, 4890–4893; *Angew. Chem. Int. Ed.* **2006**, *45*, 4772–4775; c) W. Cai, G.-T. Wang, P. Du, R.-X. Wang, X.-K. Jiang, Z.-T. Li, *J. Am. Chem. Soc.* **2008**, *130*, 13450–13459.

[17] a) K. Hanabusa, K. Shimura, K. Hirose, M. Kimura, H. Shirai, *Chem. Lett.* **1996**, *25*, 885–886; b) F. Fages, F. Vögtle, M. Žinić in *Topics in Current Chemistry Vol. 256: Low Molecular Mass Gelator*, Springer-Verlag, Berlin Heidelberg, **2005**, pp. 77–131; c) O. J. Dautel, M. Robitzer, J.-P. Lère-Porte, F. Serein-Spirau, J. J. E. Moreau, *J. Am. Chem. Soc.* **2006**, *128*, 16213–16223; d) N. Zweep, A. Hopkinson, A. Meetsma, W. R. Browne, B. L. Feringa, J. H. van Esch, *Langmuir* **2009**, *25*, 8802–8809.

[18] R. Schmidt, M. Schmutz, A. Mathis, G. Decher, M. Rawiso, P. J. Mésini, *Langmuir* **2002**, *18*, 7167–7173.

[19] a) K. Hanabusa, K. Okui, K. Karaki, M. Kimura, H. Shirai, *J. Colloid Interface Sci.* **1997**, *195*, 86–93; b) J. Makarević, M. Jokić, L. Frkanec, D. Katalenić, M. Žinić, *Chem. Commun.* **2002**, 2238–2239; c) A. K. Das, P. P. Bose, M. G. B. Drew, A. Banerjee, *Tetrahedron* **2007**, *63*, 7432–7442; d) A. Pal, Y. K. Ghosh, S. Bhattacharya, *Tetrahedron* **2007**, *63*, 7334–7348; e) D. Bardelang, F. Camerel, J. C. Margeson, D. M. Leek, M. Schmutz, M. B. Zaman, K. Yu, D. V. Soldatov, R. Ziessel, C. I. Ratcliffe, J. A. Ripmeester, *J. Am. Chem. Soc.* **2008**, *130*, 3313–3315; f) S. Debnath, A. Shome, S. Dutta, P. Das, *Chem. Eur. J.* **2008**, *14*, 6870–6881; g) M. Suzuki, H. Saito, K. Hanabusa, *Langmuir* **2009**, *25*, 8579–8585.

[20] J. H. van Esch, *Langmuir* **2009**, *25*, 8392–8394.

[21] a) R. Wang, C. Geiger, L. Chen, B. Swanson, D. G. Whitten, *J. Am. Chem. Soc.* **2000**, *122*, 2399–2400; b) A. R. Hirst, D. K. Smith, *Lang-*

muir **2004**, *20*, 10851–10857; c) Y. Jeong, K. Hanabusa, H. Masunaga, I. Akiba, K. Miyoshi, S. Sakurai, K. Sakurai, *Langmuir* **2005**, *21*, 586–594; d) G. Zhu, J. S. Dordick, *Chem. Mater.* **2006**, *18*, 5988–5995; e) M. Bielejewski, A. Lapiński, R. Luboradzki, J. Tritt-Goc, *Langmuir* **2009**, *25*, 8274–8279; f) P. Zhu, X. Yan, Y. Su, Y. Yang, J. Le, *Chem. Eur. J.* **2010**, *16*, 3176–3183; g) V. Čaplar, L. Frkanec, N. Š. Vujičić, M. Žinić, *Chem. Eur. J.* **2010**, *16*, 3066–3082; h) T. Pinault, B. Isare, L. Bouteiller, *ChemPhysChem* **2006**, *7*, 816–819; i) A. Aggeli, M. Bell, N. Boden, J. N. Keen, P. F. Knowles, T. C. B. McLeish, M. Pitkeathly, S. E. Radford, *Nature* **1997**, *386*, 259–262.

[22] J. Branderup, E. H. Immergut, E. A. Grulke, *Polymer Handbook*, 4th ed, John Wiley & Sons, New York, **1999**.

[23] W. Edwards, C. A. Lagadec, D. K. Smith, *Soft Matter* **2011**, *7*, 110–117.

[24] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.

[25] a) N. Brosse, D. Barth, B. Jamart-Grégoire, *Tetrahedron Lett.* **2004**, *45*, 9521–9524; b) Q. N. Pham, N. Brosse, C. Frochot, D. Dumas, A. Hocquet, B. Jamart-Gregoire, *New J. Chem.* **2008**, *32*, 1131–1139; c) F. Allix, P. Curcio, Q. N. Pham, G. Pickaert, B. Jamart-Grégoire, *Langmuir* **2010**, *26*, 16818–16827.

[26] H.-F. Chow, J. Zhang, C.-M. Lo, S.-Y. Cheung, K.-W. Wong, *Tetrahedron* **2007**, *63*, 363–373.

[27] N. Hüsing, U. Schubert, *Angew. Chem.* **1998**, *110*, 22–47; *Angew. Chem. Int. Ed.* **1998**, *37*, 22–45.

[28] a) M. Kölbel, F. M. Menger, *Chem. Commun.* **2001**, 275–276; b) M. Kölbel, F. M. Menger, *Adv. Mater.* **2001**, *13*, 1115–1119; c) G. John, J. H. Jung, M. Masuda, T. Shimizu, *Langmuir* **2004**, *20*, 2060–2065.

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