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Organogelation Properties of a Series of Oligoamides

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The monodisperse oligoamides **1**, **2**, **3**, and **4** have been tested as organic gelators. It was found that gelation occurs only above a critical degree of oligomerization of **2**, that is, for the trimer **3** and the tetramer **4**, and in aromatic solvents. Thermotropic and rheological properties of the trimer and the tetramer gels are reported. The tetramer gels have an elastic shear modulus 1 order of magnitude lower than that of the trimer gels. A structural study of the gels has been conducted by transmission electron microscopy.

Introduction

Organogelators are a growing class of materials that display the ability to form gels at low concentrations with organic solvents.[1] Typically, the microscopic structure of those gels consists of supramolecular aggregates which form long fibrous structures, which in turn assemble in an entangled network. Those structures entrap the solvent molecules and are responsible for the rheological properties of the binary system, including a large viscosity increase and the ability to form soft solid systems. These materials have applications in various fields such as lubricating greases,[2] biomedical applications,[3] and oil spill recovery.[4] An important group of gelators uses H-bonds as the driving force to self-assemble. These molecules can be depicted as two-part systems, where one part secures interactions between molecules by H-bonds and the other part promotes the solubility of the molecule and the unidirectionality of the crystallization. This rough view applies to structures such as amides,[5] ureas,[6] peptide derivatives,[7] pepsipeptide[8] or peptidomimetic structures,[9] sugars,[10] and alcohols.[11] Many other gelators without H-bond donors assemble through weaker interactions such as dipole interactions, van der Waals forces, or solvophobic

forces. For example, steroids,[12] aromatic derivatives,[13,14] and very simple molecules such as alkanes[15] or semifluorinated alkanes[16] fall into this category. Due to the wide structural variety of potential gelators, their properties cannot be easily predicted. Very subtle variations or derivatizations from a given gelator structure can result in a drastic change of the gel stability or suppress the gelation properties completely.

Amides constitute an important class of organogelators, since all peptide gelators can be included in this category. In the course of our studies, we synthesized a series of oligoamides shown in Chart 1.

In this paper, we report the gelation properties versus the degree of oligomerization of the species, especially the critical degree of oligomerization above which the gelation can be observed. The thermotropic and rheological properties of those gels have been investigated. A preliminary structural analysis of the gels has been carried out by electron microscopy.

Experimental Section

Materials. The synthesis of the monomer **1**, dimer **2**, and tetramer **4** has been described elsewhere.[17] Oligomers obtained by the classical polymerization/separation method are usually

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Chart 1. Structure of the Series of Oligomers 1, 2, 3, and 4 (n = 1, 2, 3, and 4, Respectively)
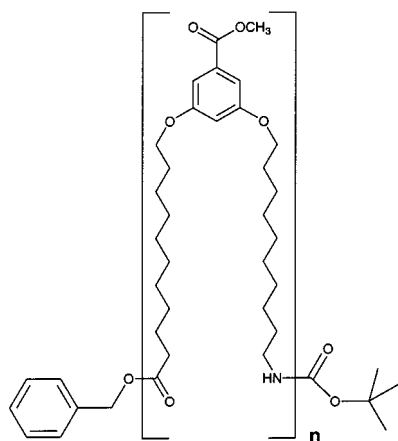
Scheme 1. Synthesis of the Trimer 3[a]

2: R = ^{t}BOC   **1b**

a

2a: R = H,HCl
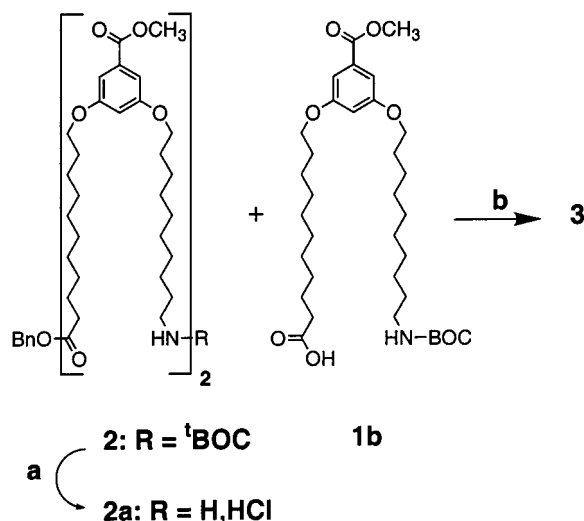
[a] (a) HCl 4 M in EtOAc. (b) EDCI, 2 equiv; HOBt, 1 equiv; Na$_2$CO$_3$, 1 equiv; 76% overall yield.

polydisperse. As the oligomers described here are obtained by a multistep synthesis, they are monodisperse. The same synthetic approach, using a set of two protecting groups, *tert*-butyl carbamate (BOC) and benzyl ester, was implemented to the trimer synthesis and is illustrated in Scheme 1. The dimer **2** was deprotected by acid treatment (4 M HCl in EtOAc) which resulted in the quantitative hydrolysis of the BOC group. The crude ammonium salt was not purified but subsequently condensed with the acid monomer **1b**[17] (EDCI, 2 equiv; HOBt, 1 equiv; Na$_2$-CO$_3$, 1 equiv) to afford the trimer **3** in fair yield (76%).

Synthesis of the Trimer 3. Compound **2** was dissolved in a HCl solution in EtOAc (4 M, 3 mL), and the mixture was stirred at 25 °C for 1 h and then evaporated under vacuum. The solid residue was dissolved in DMF (3 mL), and the mixture was treated with **1b** (102 mg, 0.17 mmol, 1.8 equiv), Na$_2$CO$_3$ (10 mg, 0.09 mmol, 1 equiv), and HOBt (13 mg, 0.09 mmol, 1 equiv). The reaction medium was cooled to 0 °C, and EDCI (36 mg, 0.18 mmol, 2 equiv) was added. The solution was stirred for 1 h at 0 °C and for 12 h at 25 °C, mixed with water (20 mL), and extracted with CHCl$_3$ (4 × 10 mL). The organic phases were combined, dried (Na$_2$SO$_4$), and concentrated under vacuum. The residue was purified by chromatography (SiO$_2$, 2-propanol/CH$_2$Cl$_2$ 5/95) to yield **3** as a white solid (123 mg, 76%): mp 83−86 °C.

^{1}H NMR (200 MHz, CDCl$_3$): δ (ppm) 7.34 (m, 5H, C$_6$**H**$_5$), 7.15−7.14 (m, 6H, C2-**H** and C6-**H**), 6.62 (t, 3H, J = 2.4 Hz, C4-**H**), 5.45 (s large, 2H, N**H**COCH$_2$), 5.10 (s, 2H, ArOC**H$_2$**C$_6$H$_5$), 4.50 (s large,

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1H, N**H**Boc), 3.95 (t, 12H, J = 6.5 Hz, ArOC**H$_2$**), 3.88 (s, 9H, COO**Me**), 3.22 (q, 4H, J = 6.5 Hz, C**H$_2$**NHCO), 3.09 (q, 2H, J = 6.4 Hz, C**H$_2$**NHBoc), 2.34 (t, 2H, J = 7.5 Hz, C**H$_2$**COOBn), 2.14 (t, 4H, J = 7.6 Hz, C**H$_2$**CH$_2$CONH), 1.76 (p, 6H, J = 6.8 Hz, C**H$_2$**CH$_2$NH), 1.43 (s, 9H, C(C**H$_3$**)$_3$), 1.28 (m, 90H).

^{13}C NMR (50 MHz, CDCl$_3$): δ (ppm) 173.6, 173.1, 166.9, 160.1, 131.7, 128.4, 128.0, 107.5, 106.5, 65.9, 52.1, 40.5, 39.4, 36.8, 34.2, 30.0, 29.6, 29.4, 29.2, 29.1, 28.3, 26.8, 26.7, 25.9, 25.8, 24.8.

IR (KBr): ν_{max} 3314, 2923, 2852, 1708, 1637, 1600, 1357, 1302, 1238, 1183 cm^{-1}.

Elemental Anal. Calcd for C$_{99}$H$_{157}$N$_3$O$_{18}$: C, 70.89; H, 9.43; N, 2.51. Found: C, 70.58; H, 9.56; N, 2.55.

MS (Fab+) m/z calcd for C$_{99}$H$_{157}$N$_3$O$_{18}$: 1676.2. Found: 1677.2 (M + H$^+$).

Gelation Tests. The synthesized compounds are solid at room temperature. Small amounts were heated in the appropriate volume of solvent in a sealed vial until complete dissolution of the compound. This solution was then cooled to test for gelation. Depending on the solvent and the substrate, different situations might occur upon cooling: a gel forms (G), the compound is soluble (S), the compound precipitates (P), or the compound is not soluble in boiling solvents (I).

Gel Melting Temperatures. The gel-to-sol transition temperatures were determined by the "dropping ball method": the gels at different concentrations were prepared (volume ~1 mL) in sealed vials (10 mm diameter), and 1 mm diameter glass beads (13 mg) were put on top of the gels. The samples were immersed in a temperature-regulated bath, and the position of the ball was observed while the temperature was increased at 0.5 °C min^{-1}. The gel-to-sol transition temperature T_{GS} was recorded as the temperature at which the ball sinks and reaches the bottom of the vial. The transition temperatures were measured at least twice, and the results were reproducible within a mean error of 0.5 °C.

Rheology. The experiments were conducted with a Haake RS 100 rheometer. Cone−plate geometry was used (25 mm, 1°, 0.058 mm gap), and the measurement area was equipped with a sealed Teflon hood to limit solvent evaporation.

IR spectra were recorded with a BoMem MB 155 or with a Cary 500 Scan in thermoregulated cells with a 0.1 mm path length. The temperature was monitored by a thermocouple.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC 4 with heating and cooling rates of 5 K min^{-1}.

Transmission electron microscopy (TEM) was performed with a Philips CM12 microscope operating at 120 kV. The first set of experiments was done on freeze-fractured samples: the gel samples were placed between two copper holders and rapidly frozen in liquid nitrogen. The sample was kept frozen and transferred into a freeze-fracture apparatus (developed by J.-C. Homo) where the sample was cleaved. The sample was warmed for a few seconds to −90 °C under vacuum to etch the sample by evaporation of small amounts of toluene. Pt was evaporated onto the sample under a 45° angle, and then carbon under a 90° angle respective to the surface. The sample was warmed to room temperature, and the replica was rinsed with chloroform and deposited on 400 mesh grids. Another set of experiments consisted of the simple deposition and air-drying of subcritical concentration solutions (i.e., below the minimal gel concentration) of the trimer **3** and the tetramer **4**. A droplet of the solution was deposited on a 400 mesh grid coated with a carbon film. After a few seconds of adsorption, the excess solvent was removed with a small piece of Whatman paper (no. 4 or 5). The grid was put in an evaporator, and a thin layer of Pt was evaporated under a 10° angle with rotation of the grid holder.

Results and Discussion

The monomer **1** and dimer **2** do not form gels with any of the tested solvents (Table 1). Gelation occurs for the trimer **3** and tetramer **4** in aromatic solvents. Gelation is observed above a critical oligomerization degree of 2.

This threshold has to be compared with the number of amide groups in the molecule. The compounds **1**, **2**, **3**, and **4** include 0, 1, 2, and 3 amide groups, respectively. Among the organogelators that possess H-bonding groups, it is

Table 1. Gelation Tests[a]

solvent	monomer	dimer	trimer	tetramer
toluene	S	S	17	11
benzene	S	S	30	38
o-xylene	S	S	32	35
THF	S	S	G*	G*
MeOH	S	S	I	I
EtOH	S	S	P	P
hexane	I	I	I	I

[a] Values for the minimum gel concentration (g L^{-1}) at 25 °C; S, soluble; P, precipitates upon cooling; I, insoluble; G*, gel stable only for $T < 10$ °C.
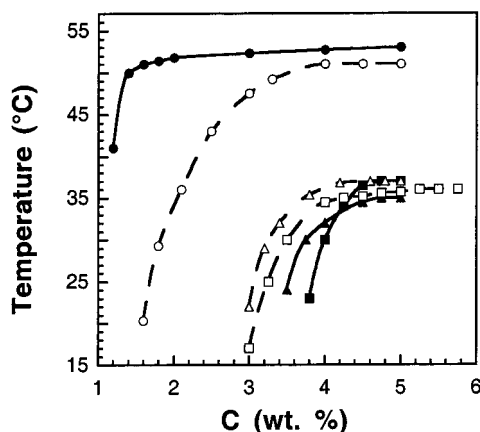

Figure 1. Concentration−temperature phase diagrams: ●, tetramer/toluene; ■, tetramer/benzene; ▲, tetramer/o-xylene; ○, trimer/toluene; □, trimer/benzene; △, trimer/o-xylene.

often observed that gelation arises when the molecule bears at least two of these groups. The synthesized oligomers follow this trend which has been verified by structure/activity relationship studies for amide−alcohol gels.[18] Tetramer gels are more turbid than trimer gels, and turbidity increases with concentration for both. The gel formation appears to depend on both the final temperature after cooling and the cooling rate. Investigations in this direction are in progress. These oligomers form gels only with aromatic solvents. In most of the other organic solvents, the compounds precipitate from the hot solution.

All studied gels showed a sharp melting point, that is, a well-defined gel-to-sol transition. The dropping ball method was used to determine the gel-to-sol transitions for the trimer **3** and tetramer **4** in three different aromatic solvents. The resulting concentration−temperature phase diagram is reported in Figure 1. It shows that the gels in toluene are the most stable of the studied systems.

A rheological characterization of the trimer−toluene and tetramer−toluene gels has been conducted. Figure 2 displays a flow experiment on the gels at 3 wt %. A continuous stress σ is applied to the sample and is uniformly increased over time (dσ/d$t \approx 0.2$ Pa min^{-1}). During a certain range of stress, the angular displacement, proportional to the deformation, is linear with respect to the stress (not shown).

The tetramer gel starts to flow at very low stresses ($\sigma^* = 25$ Pa s^{-1}), whereas the trimer gel starts at $\sigma^* = 133$ Pa s^{-1}. When the gel is subjected to an oscillating stress in the linear regime of deformations, the amplitude of the response and the phase lag between the applied stress and the response allows the calculation of both the elastic response modulus G' and the loss modulus G''. The complex

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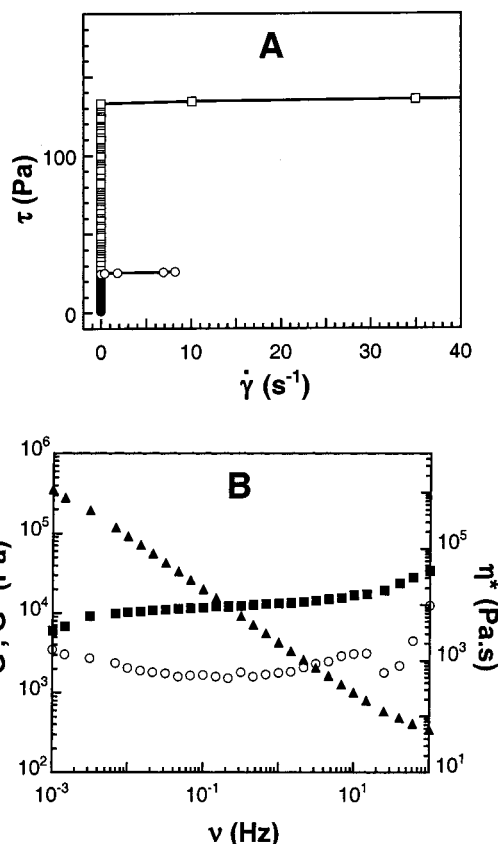

Figure 2. Rheology of the tetramer−toluene (○) and trimer−toluene (□) gel ($C = 3$ wt %). (a) Flow experiment: The gels were subjected to a linear stress increase (dσ/d$t = 0.2$ Pa min^{-1}) while the shear rate was measured. The gel starts to flow at $\sigma^* \approx 25$ Pa for the tetramer and $\sigma^* \approx 133$ Pa for the trimer. (b) Dynamic experiment with the trimer/toluene system: the gel slice is solicited by an oscillating stress ($\tau = 10$ Pa) with increasing frequencies $10^{-3} < \nu < 10^2$ at $T = 25$ °C. ■, Elastic modulus G'; ○, loss modulus G''; ▲, complex viscosity.

viscosity modulus is given by $\eta^* = [(G'^2 + G''^2)/(2\pi\nu)^2]^{1/2}$, where ν is the frequency of the imposed stress. The measurement was done in the frequency range from 10^{-3} to 10^2 Hz, with a logarithmic distribution. The elastic modulus increases very slowly as the frequency increases. From 3.16×10^{-3} to 61 Hz, the variation of log G' is linear with respect to log ν with a very weak slope: G' varies as $\nu^{0.06}$ for the trimer **3** and $\nu^{0.03}$ for the tetramer **4** (not shown). The value for G' at $\nu = 1$ Hz is 13 kPa for the trimer **3** and 4 Pa for the tetramer **4**. In the explored frequency range, the loss modulus is always 1 order of magnitude smaller than the elastic modulus (at $\nu = 1$ Hz, $G'' = 2.5$ kPa for **3** and $G'' = 0.14$ kPa for **4**). These observations show that the bonds between the particles of the network have a permanent character in the time scale of the experiment ($t > 1000$ s). The large differences between trimer and tetramer elastic shear moduli and between the yield stresses suggest differences in the gel structures.

Figure 3 shows a dynamic rheology experiment where an oscillating stress was applied to 3% gels at constant frequency and amplitude (trimer **3**, $\nu = 1$ Hz, $\sigma = 10$ Pa; tetramer **4**, $\nu = 1$ Hz, $\sigma = 3$ Pa), in the linear regime of deformations. G' was monitored as the temperature was increased. For a given temperature, the modulus dramatically drops to a lower limit that corresponds to the viscosity of the sol phase. This temperature is defined as the transition temperature T_{GS}. It is found to be 47.8 °C for the trimer **3** and 54.6 °C for the tetramer **4**. It differs from the value measured by the dropping ball method
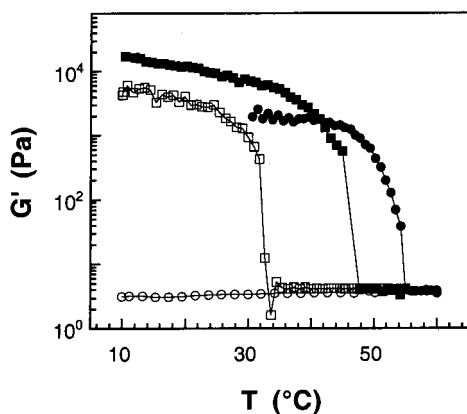
Figure 3. Temperature-dependent dynamic rheology experiment. The samples (3 wt % trimer−toluene, ■ and □; 3 wt % tetramer−toluene, ● and ○) are subjected to an oscillating stress (ν = 1 Hz) in the linear regime of deformations (tetramer, σ = 3 Pa; trimer, σ = 10 Pa) while the temperature is increased (black symbols, $dT/dt \approx 1$ K min^{-1}) and subsequently decreased (white symbols, $dT/dt \approx -1.5$ K min^{-1}).

(52.3 °C for the tetramer), but such differences have been well documented and explained by Terech et al.[19] When the trimer sample is subsequently cooled back at a rate of 1.5 K min^{-1}, the viscosity drastically increases. The singular point on the back curve is defined as T_{SG}, the sol-to-gel transition temperature, and its value is 32 °C. Hence, a gap is observed between T_{GS} and T_{SG}, which shows that for the trimer **3**, the cycle G → S → G is subject to a strong hysteresis. The tetramer **4** shows a similar behavior for the heating phase. However, we never succeeded in observing the sol-to-gel transition in the confined rheometer environment with the different cooling rates and temperatures allowed by the apparatus, although the thermoreversibility was currently observed under laboratory conditions.

IR spectroscopy in the near-IR area allows the observation of the NH stretch bands. The spectra of trimer and tetramer gels in toluene have been recorded at different temperatures. Both samples gave similar spectra, and the results for the tetramer gel shown in Figure 4 are representative of both.

The main peak that can be observed at room temperature (3314 cm^{-1}) is characteristic for the N−H stretching of H-bonded amides. Therefore, in the gel state, the majority of the amide groups are associated. As the temperature increases and passes T_{GS}, the intensity of the H-bonded amides decreases while another band at 3435 cm^{-1} (characteristic for the H-bond free N−H stretch) increases. The intensity of the peaks coarsely follows the gel-to-sol transition. At the transition temperature T_{GS}, only 17% of the H-bonds remain. The IR spectroscopic studies demonstrate that the H-bonds between amide groups disappear along with the gel-to-sol transition. This is strong evidence that the H-bonds are involved in the formation of the aggregates in the gel. The contribution of these bonds to the formation of the gel can be discussed in terms of energy. The heat exchange associated with the gel-to-sol transition was recorded by DSC and was found to be equal to 188 kJ/mol for the 3% tetramer gel in toluene. The tetramer **4** has three amide groups and potentially one carbamate that are susceptible to form H-bonds. However, the bond energy for an H-bond between two amide groups ranges from 5 to a maximum of 21 kJ/
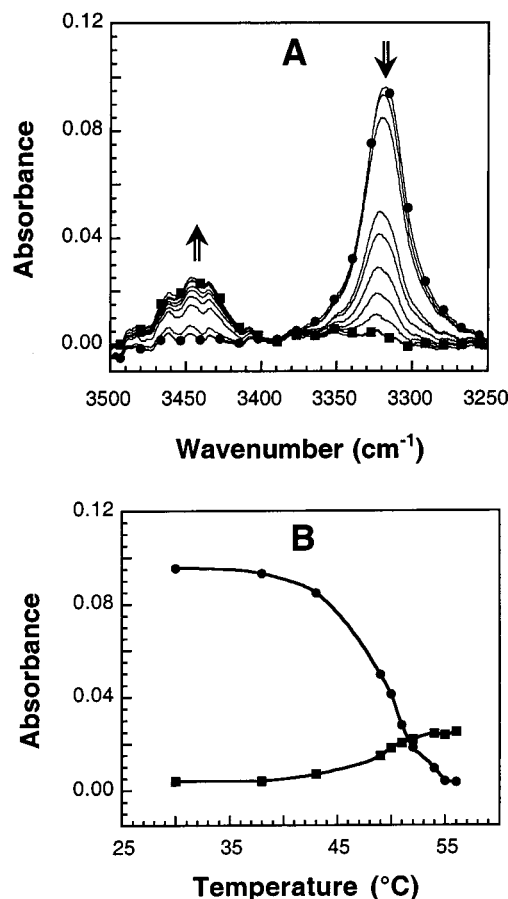

Figure 4. Variable temperature IR spectroscopy of the tetramer−toluene gel (2.8 wt %). (A) Spectrum in the N−H stretching region from 30 °C (●) to 56 °C (■). (B) Absorbance at 3320 cm^{-1} (●) and at 3446 cm^{-1} (■) vs temperature.
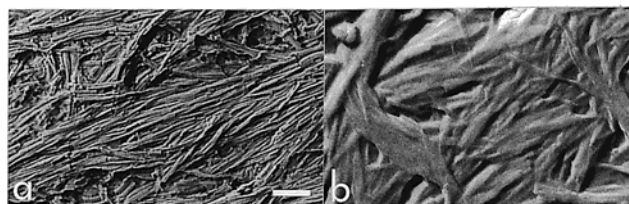

Figure 5. TEM observation of freeze-fractured gels. (a) The 3 wt % trimer gel in toluene observed after freeze-fracture and slight etching. Fibers tend to associate in parallel arrays to form larger strands. (b) The 3 wt % tetramer gel. The bar is 200 nm.

mol.[20] The value found by DSC is much bigger than 4 × 21 kJ/mol, thus showing the importance of other interactions in the gel. Interactions that are probably involved are van der Waals interactions and $\pi-\pi$ interactions between aromatics. This observation is quite common for organogelators and is largely supported by the fact that simple molecules bearing no H donors or acceptors can form gels. It should also be mentioned that the gelators developed by Pozzo et al.[14] share a structural feature with the oligoamides presented here (the meta-bis(alkoxy)-benzene group) but do not have any amide or alcohol groups.

Trimer and tetramer samples were freeze-fractured and observed by TEM (Figure 5). This technique allows checking the size of the aggregates in the native gel

(19) Terech, P.; Rossat, C.; Volino, F. *J. Colloid Interface Sci.* **2000**, *227*, 363−370.

(20) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Fransisco, 1960.

samples. The observation of both samples revealed the presence of fibrillar aggregates. Their lengths range from 0.1 to several μm. The aggregates show a trend to associate and to form parallel bundles. Only in a few samples is it possible to locate single fibers and to measure their thickness (about 10 nm). Characteristic differences can be observed for the bundle structure: for the trimer samples, the bundles look straight and parallel, whereas for the tetramer samples, the bundles seem to have more random orientations. Although the observations cannot be easily quantified, it is obvious that in the trimer samples, the persistence length of the fibers is longer than for the tetramer gels. Alternatively, the same fibrillar aggregates can be observed by TEM after evaporation of a subcritical solution directly deposited and dried on the TEM grid. Although the micrographs are not acquired from a gel, they reflect how the oligomers tend to self-associate. Under these experimental conditions, the trimer seldom exhibits isolated fiber structure. However, in some bundles (Figure 6A) it is possible to distinguish parallel striations. Those substructures are likely individual fibers that assemble into ordered strands. The tetramer **4** more often exhibits single structures (Figure 6B) than the trimer **3**. The widths of single fibers that can be measured are comparable for both experiments. The fibers look monodisperse throughout the samples, and their width is in the range of 8−16 nm. The inaccuracy of the measured thickness is due mainly to the metal particle coating. However, this estimation proved to be very good when compared with the X-ray and neutron scattering analysis, which will be published in a forthcoming paper.

In conclusion, in the series of synthesized oligoamides, gelation occurs only above a critical degree of oligomerization of 2. The trimer **3** and the tetramer **4** clearly behave
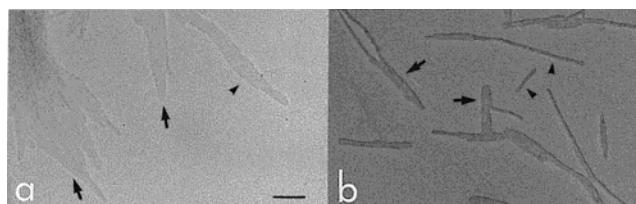

Figure 6. TEM observation of evaporated solutions. (a) The 0.8 wt % trimer solution in toluene. Large and thin aggregates are observed (arrowhead). Inside some aggregates, small individual fibers can be seen (arrows). (b) The 0.8 wt % tetramer solution in toluene. Single straight fibers (arrowhead) which can associate into larger aggregates (arrow) are shown. The bar is 100 nm.

as gelators for aromatic solvents and show all the characteristic properties of usual organic gelators in terms of thermotropic and rheological properties. The critical degree of oligomerization that is observed corresponds to two amide functional groups. Among organogelators, these compounds possess a rather high molecular mass, which puts them at the borderline between polymers and small gelators. However, the results from structural studies, especially the fiber morphology, show no difference when compared with the usually smaller gelators. The structures of these oligomer gels are currently under investigation using small-angle scattering techniques.