Remarkable Polymorphism in Gels of New Azobenzene Bis-urea Gelators

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Azobenzenes substituted with two urea groups, and especially the 2,2′-disubstituted azobenzenes, form thermoreversible gels with a wide range of organic solvents at concentrations which are in some cases even as low as 0.2 mM. Most remarkably, the 2,2′-disubstituted azobenzene gelator can form two different morphs, which is governed by the properties of the solvent and kinetic factors.

Introduction

The self-assembly of small functional molecules into supramolecular structures comprises a powerful approach toward the development of new materials and devices of nanoscale dimensions, and the control of these organizational processes by chemical or physical elements is a major challenge. A promising approach toward such responsive or smart materials is the integration of an addressable function, e.g., photochromic moieties, into the supramolecular building blocks, which would offer the possibility to alter the self-assembly process of the individual molecules or change the properties of the supramolecular arrays by means of light. A number of photosensitive host–guest systems and receptors have been reported, but studies of self-assembling photoswitchable systems, in which the macroscopic properties are affected by light, are limited to a few examples. Switchable organogels have been reported by Shinkai et al. almost a decade ago, and more recently by Pozzo et al., whereas the photoreversible self-assembly of peptide tubules has been reported by Ghadiri et al. Recently our group showed that the extension of dithienylcyclopentene photochromic molecules or change the properties of the supramolecular building blocks, which would offer the possibility to alter the self-assembly process of the individual molecules or change the properties of the supramolecular arrays by means of light.

Results and Discussion

The 4,4′-disubstituted azobenzene 1 and 2,2′-disubstituted azobenzene 2 represent two structurally relatively simple bis-urea azobenzenes (Chart 1). These compounds have, however, all the primary prerequisites for a gelling agent, i.e., two strongly interacting self-complementary groups along a common axis, thus favoring the formation switches with strongly interacting groups such as amides gave highly viscous solutions with apolar solvents due to extensive aggregation of the compounds. Most remarkably, the degree of aggregation and hence the viscosity can reversibly be changed by light.

In recent years there has been significant progress in the rational design of new gelling agents, and from successful designs it has emerged that the presence of strong self-complementarity and unidirectional interactions are essential features for a good gelling agent. Urea moieties fulfill these requirements, and especially compounds that contain two urea groups have been reported to be very potent and versatile gelling agents for a wide range of organic solvents. It has been shown that the conformational properties of the linking group between the urea moieties strongly influence the gelation ability and properties. The replacement of a static linking group by a functional molecule whose properties respond to some external stimulus might thus well lead to the formation of responsive gels. Here we report on new azobenzene bis-urea gelling agents, in which the azobenzene group has been used to link the two urea groups, and a first study of their gelation behavior by microscopic and spectroscopic techniques.
of infinite quasi-1D aggregates. Compounds 1 and 2 are easily synthesized by an addition reaction of the corresponding bis-aminoazobenzenes with an isocyanate. Usually this reaction proceeds rapidly at room temperature, but in this case the reaction proceeded relatively slowly due to the decreased nucleophilicity of the aniline-type amine groups, and reflux in toluene was found to be necessary to obtain 1 and 2 in a reasonable yield of 83% and 40%, respectively. The relatively low yield of 2 is most likely caused by its efficient gelation of the reaction mixture which begins even at low conversions, thereby preventing stirring and slowing down mass transport.

Bis-urea azobenzenes 1 and 2 are almost insoluble in most organic solvents at room temperature, but upon heating they gradually dissolve. In apolar solvents such as hexane or cyclohexane compound 1 did not dissolve at all, even after prolonged heating at temperatures above the boiling point of the solvent. Upon cooling to room temperature, 1 precipitates from most solvents. Only with aromatic solvents gels were formed (Table 1). These gels had a turbid appearance and were easily and irreversibly disrupted by mechanical agitation like shaking or vortexing, indicating that aggregates of macroscopic dimensions have been formed. Light microscopy revealed that toluene gels of 1 consist of thin elongated fibers of macroscopic dimensions, with diameters up to 5 µm (Figure 1a). The fibers are strongly birefringent, indicating a well-defined molecular arrangement within the fibers. The formation of similar fibers has been commonly observed for other bis-urea compounds in which the two urea groups are connected by a linear linker.\(^{11a}\)

Azobenzene bis-urea 2 behaves much differently. It dissolves at considerably lower temperatures and to higher maximum concentrations than 1 in all solvents investigated including hexane and cyclohexane. Moreover, upon cooling of hot solutions gels are formed with all solvents investigated, except for cyclohexanone and polar solvents such as DMSO and water (not shown) (Table 1). In all cases the minimum gelation concentrations are less than 8 mM, and in toluene and n-hexane very fragile gels are even formed at concentrations as low as 0.2 mM, which is comparable to those of the recently reported "super-gelators".\(^{13}\) Gels can be formed up to concentrations of at least 30 mM, and these exhibit excellent thermal stability with melting temperatures exceeding 100 °C at higher concentrations for the n-butyl acetate gels (Figure 2).

Furthermore, gels of 2 are optically transparent, and optical microscopy did not reveal any structural features. The morphology of a toluene gel of 2 was further studied by cryo electron microscopy. Because the melting point of

Table 1. Gelation of Organic Solvents by Azobenzene Bis-ureas\(^a\)

<table>
<thead>
<tr>
<th>solvent</th>
<th>1</th>
<th>2</th>
<th>solvent</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>p</td>
<td>8</td>
<td>cyclohexanone</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>DMSO</td>
<td>p</td>
<td>p</td>
<td>cyclohexane</td>
<td>i</td>
<td>1.5</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>p</td>
<td>1.5</td>
<td>p-xylene</td>
<td>8</td>
<td>1.5</td>
</tr>
<tr>
<td>2-propanol</td>
<td>p</td>
<td>3</td>
<td>1,2-dichloroethane</td>
<td>p</td>
<td>3</td>
</tr>
<tr>
<td>toluene</td>
<td>8</td>
<td>0.8</td>
<td>n-butyl acetate</td>
<td>p</td>
<td>8</td>
</tr>
<tr>
<td>hexane</td>
<td>i</td>
<td>0.2</td>
<td>tetralin</td>
<td>8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^a\) Minimum gelation concentrations in mM: p = precipitation; i = insoluble; s = soluble.
The minimum gelation concentration is shown in Figure 3. The gels have an orange color. The electronic absorption and cyclohexane the color change is less pronounced and in the gel state. However, in apolar solvents such as toluene it is readily observed that gelation is accompanied by a blue shift. This blue shift can be attributed to exciton coupling like ethanol, ethyl acetate, and 1,2-dichloroethane, respectively. The absorptions obey Beer's law, which indicates that under these conditions azobenzene chromophores within the aggregates. According to Kasha's exciton coupling theory the blue shift points to the formation of face-to-face type of aggregates. On the other hand, in apolar solvent like cyclohexane gelation causes a shift of the ππ* transition to longer wavelengths together with the appearance of a vibronic structure with maximum intensity at 433 nm. The appearance of this vibronic structure, however, complicates the interpretation of spectral changes in relation to the supramolecular structure of the aggregates by a simple model as Kasha's exciton coupling theory. Nevertheless, from the distinct changes in the absorption spectra going from solution to the gel phase, it is evident that different types of aggregates are formed in more polar and in apolar solvents, from hereon referred to as type I and type II aggregates, respectively.

The structure of the gels was further investigated by infrared spectroscopy and small-angle X-ray scattering (SAXS). Type I gels of 2 in CHCl₃ show two almost overlapping NH vibrations at 3353 and 3310 cm⁻¹, and two sharp bands at 1640 and 1554 cm⁻¹, which can be assigned to the amide I and amide II band, respectively. The positions of these bands are only slightly different from the positions in the solid state at 3324, 1634, and 1557 cm⁻¹ for the NH, amide I and II bands, and clearly show that the urea groups participate in a hydrogen-bonded network. Type II gels of 2 in cyclohexane show a different pattern. The NH vibrations are slightly broadened and shifted to 3344 and 3320 cm⁻¹, and the amide I band is shifted to 1646 cm⁻¹. Most remarkably, the amide II band is split into two bands with maxima at 1563 and 1524 cm⁻¹. Although the position of the amide I vibration clearly indicates that both the urea groups of 2 are still involved in hydrogen bonding, the splitting of the amide II bands reveals that they are no longer equivalent. Apparently, the hydrogen bonding network of type I and type II gels of 2 formed in chloroform and cyclohexane, respectively, is different. To further support the formation of different morphs by bisurea azobenzene, SAXS experiments have been carried out. For type I gels of 2 in ethanol a clear Bragg peak was observed at a Q value of 0.26 Å⁻¹, corresponding to a spacing of 24 Å, but for type II gels of azobenzene 2 in cyclohexane, no Bragg reflections were observed at all. These results indicate that azobenzene 2 adopt a different molecular arrangement in type I and type II gels, but the actual arrangements within the gels remain unclear because of the absence of higher order reflections.

The distinct spectroscopic changes accompanying gel formation offer an excellent tool to investigate the mechanism of gelation by spectroscopic methods. A surprising result has been found for the gelation of toluene by 2. Cooling of a toluene solution of 2 from above the gel-to-solid phase transition temperature to room temperature causes in the first few minutes a red shift and increase of the intensity of the ππ* transition together with the appearance of a vibronic structure (Figure 4). As shown above, this spectral change is typical for the formation of type II aggregates such as is observed in gels of 2 cyclohexane. Most likely, the initially formed aggregate in toluene has a similar structure. Within 10–60 min, depending on the concentration, the intensity of this band at 433 nm decreases and transforms slowly to a spectrum with a maximum at 391 nm which is typical for type I aggregates such as the gels of 2 in more polar solvents.

![Figure 3](image-url) Absorption spectra of a solution of 2 in 1,2-dichloroethane (0.1 mM, —) and of a gel in 1,2-dichloroethane (1.85 mM, ——) and in cyclohexane (2.37 mM, ---) at 25 °C.
in toluene compound 2 first assembles into the kinetically favored type II aggregates, which over time slowly transform into the thermodynamically favored type I aggregates. The time traces and concentration dependencies showed that the kinetics of these processes are very complex. Preliminary experiments revealed that the rate of transformation of type II into type I aggregates is slowed at lower temperatures and at 0 °C the type II aggregates are stable for several hours. Most remarkably, the rate of transformation of type II into type I aggregates is also slowed with increasing concentration of 2, a result which is contrary to that expected for classical first- or second-order processes and which can only be explained by including the state of aggregation into the kinetic model.

In conclusion, whereas the 4,4'-disubstituted azobenzene bis-urea 1 is a rather poor gelator and resembles in this regard other “linear” types of bis-urea gelling agents, the 2,2'-disubstituted derivative 2 is an excellent gelator for a wide range of solvents, even at very low concentrations. Most remarkably, the electronic and infrared spectroscopic investigations of the gels clearly indicate that 2 can form two types of supramolecular aggregates depending on the polarity of the solvent, which differ in the stacking of the chromophore moieties as well as the hydrogen bonding pattern. Although polymorphism is well-known phenomena in molecular crystallography, this is probably one of the first examples in the field of organogels. The preliminary results of gelation of toluene indicate that two morphs have different thermodynamic stabilities, but their formation is determined by kinetics. Although the supramolecular arrangement within the different morphs is not yet clear, the azobenzene bis-urea gelling agent forms in this regard an ideal model system for mechanistic investigations of polymorph formation because of the distinct spectroscopic changes which accompany formation of the two morphs. Another intriguing aspect, especially in relation to the polymorphism, is the photochromism of the bis-urea azobenzenes which is currently under investigation.

Experimental Section

Materials and Methods. 4,4'-Diaminoazobenzene2 and 2,2'-diaminoazobenzene2 were prepared according to literature procedures. All other compounds are commercially available.

24 h. The SAXS measurements were performed at 25 °C, using a NanoStar device (Bruker AXS and Anton Paar) and Cu Kα radiation.23

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