

Binary organogelators which show light and temperature responsiveness

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Received 22nd April 2003, Accepted 16th June 2003

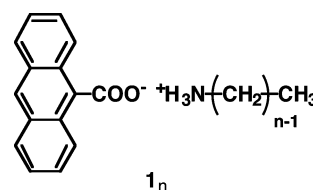
First published as an Advance Article on the web 30th June 2003

The gelation ability of 10 alkylammonium ($C_nH_{2n+1}NH_3^+$ where $n = 4-11, 12$ and 16) anthracene-9-carboxylates ($\mathbf{1}_n$) has been evaluated. In cyclohexane, $\mathbf{1}_4$, $\mathbf{1}_5$, $\mathbf{1}_6$ and $\mathbf{1}_7$ only provided precipitates whereas $\mathbf{1}_{11}$, $\mathbf{1}_{12}$ and $\mathbf{1}_{16}$ provided very viscous solutions. In contrast, $\mathbf{1}_8$, $\mathbf{1}_9$ and $\mathbf{1}_{10}$ resulted in gels. The critical gelation concentration of $\mathbf{1}_{10}$ was very low ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$). SEM observations showed that in the gel phase the morphology changes from straight fibrils to frizzy fibrils with the increase in n , whereas in the sol phase the formation of the sheet-like, two-dimensional aggregate is recognized. When the cyclohexane $\mathbf{1}_{10}$ gel was photoirradiated ($\lambda > 300 \text{ nm}$), the UV-VIS absorption bands assignable to monomeric anthracene were decreased and the gel was changed into the sol. It was confirmed by dark-field optical microscopy that the fibrillar bundles supporting the gel formation gradually disappear with photoirradiation time. When this sol was warmed at 30°C in the dark, the gel was *not* regenerated but the precipitation of $\mathbf{1}_{10}$ resulted. When this sol was heated once at the bp of cyclohexane and cooled to 15°C , the solution was changed into the gel again. This finding indicates that the fibrillar structure required for the gel formation is not reconstructed at 30°C but obtained only when the hot cyclohexane solution is cooled.

Introduction

n-Dodecylammonium propionate (DAP) is a representative surfactant for the preparation of reversed micelles in organic solvents and has been utilized as a reaction media for various organic, enzymatic, inorganic sol–gel systems, *etc.*¹ It occurred to us that although the micellar aggregates constructed from DAP are relatively ‘soft’, they may be ‘hardened’ by replacing propionate with some appropriate aromatic carboxylate and the resultant binary composites may behave as organogelators. Such an idea of *binary organogelators* has been reported by Huc’s group, and are composed of cationic gemini surfactants acting as a structure-forming component and tartaric acid acting as a chirality-generating component.² Meanwhile, we previously designed new gelators consisting of azobenzene–sugar conjugates, some of which could act as hydrogelators.³ One of the research purposes was to obtain a new photo-responsive gelator useful in an aqueous system. In the gel phases, however, the photo-induced *trans*-to-*cis* isomerization scarcely proceeded, presumably because the *trans*-azobenzene moieties are tightly packed in the fibrous gel superstructures. In fact, such a tight packing aggregation mode has been found in several aromatic-ring-containing organogelators.⁴ In addition, the difficulty in the photo-induced isomerization has also been recognized in azobenzene-containing micellar and monolayer systems, in which the azobenzene moieties exist in a face-to-face aggregation mode.^{5,6} In contrast, the azobenzene skeleton appended to cholesterol-based gelators is amenable to the photo-induced *trans*-to-*cis* isomerization.⁷ Presumably, there is sufficient room for the isomerization around the azobenzene moiety in the cholesterol-based gelators. Thus, the survey of these past references stimulated us to design a new photo-responsive gelator on the basis of the concept of binary gelators, because if the photoresponsive component is ‘*not*’ covalently-linked to the structure-forming component, it should be able to acquire the more space necessary for the isomerization. We thus chose anthracene-9-carboxylic acid as an aromatic carboxylic acid, because (1) the molecular symmetry is high, (2) there are a few precedents in which the anthracene skeleton plays an important role in the stabilization

of organogels^{8,9} and (3) one can expect photoresponsiveness (based on the monomer–dimer interconversion), successful examples of which are still very limited.^{7,10} With these ideas in mind, we designed binary organogelators $\mathbf{1}_n$ (Scheme 1: $n =$



Scheme 1 Anthracene-containing binary gelators.

4–11, 12 and 16) composed of alkylammonium and anthracene-9-carboxylate. One may expect that the carboxylate moiety in $\mathbf{1}_n$ has more room for the structural change necessitated for photoisomerization. We have found that (1) with increasing methylene number (n) the cyclohexane solutions of $\mathbf{1}_n$ change from precipitates to viscous solutions *via* gels, (2) photoirradiation ($\lambda > 300 \text{ nm}$) at 15°C does induce dimerization of anthracene-9-carboxylates and the gels are changed into sols and (3) warming the sols interconverts the dimer to the monomer and the gels are regenerated.

Results and discussion

Solvent dependence and influence of the alkyl chain length

Compounds $\mathbf{1}_n$ were prepared from equimolar amounts of anthracene-9-carboxylic acid and the corresponding alkylamine in THF. The IR spectra (KBr disk) of the resultant white powders showed a strong $\nu_{C=O}$ band at 1552 cm^{-1} , indicating that the carboxylic acid group is dissociated into the carboxylate anionic group. We consider that the carboxylate group and the ammonium group are strongly associated with hydrogen-bonding and electrostatic interactions.

Firstly, we tested the gelation ability of $\mathbf{1}_{10}$ for 10 typical organic solvents with $[\mathbf{1}_{10}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$. It was insoluble in hexane and MeCN but soluble in chloroform,

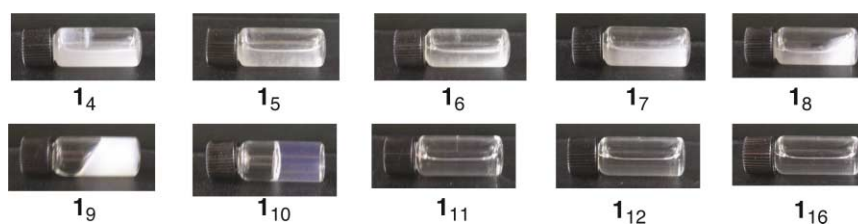


Fig. 1 Pictures of 1_n ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) solubilized in boiling cyclohexane and then cooled to 20°C .

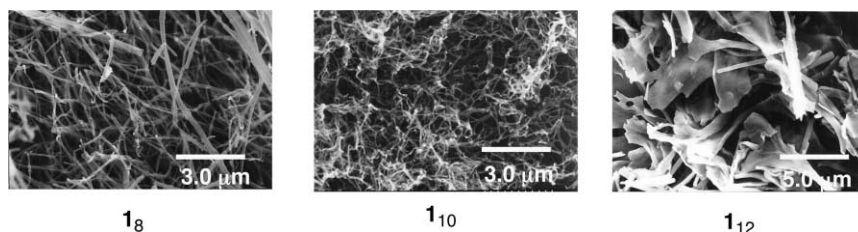


Fig. 2 SEM images of the dried samples prepared from cyclohexane mixtures with 1_8 , 1_{10} and 1_{12} .

dichloromethane, benzene, toluene, THF, methanol and ethanol. We found, however, that it is capable of gelating in cyclohexane. The critical gelation concentration, the minimum concentration where the gelation is induced, was $5.0 \times 10^{-3} \text{ mol dm}^{-3}$. The results show that 1_{10} is a specific and powerful gelator for cyclohexane.

Secondly, we evaluated the gel formation capability of 10 ion-paired compounds ($[1_n] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$) in cyclohexane. The visual images are shown in Fig. 1. Compounds 1_4 , 1_5 , 1_6 and 1_7 could be solubilized into cyclohexane at bp, but when they were cooled to 20°C , they precipitated. On the other hand, when the cyclohexane solutions of 1_8 , 1_9 and 1_{10} were cooled to 20°C , they resulted in gels. It is seen from Fig. 1 that 1_8 , 1_9 and 1_{10} give a partial gel, a turbid gel and a translucent gel, respectively. Compounds 1_{11} , 1_{12} and 1_{16} gave transparent, very viscous solutions. This change in the physical properties implies that the gel lies between the precipitate and the viscous solution and in 1_8 , 1_9 and 1_{10} the precipitation force arising from the anthracene-9-carboxylate moiety and the solubilization force arising from the alkylammonium moiety are well balanced.

SEM observation

To obtain a visual image of the aggregation mode in the gel phase and the viscous solution phase, we took the pictures of the xerogels with a scanning electron micrograph (SEM). As shown in Fig. 2, the SEM pictures obtained from the cyclohexane gels of 1_8 and 1_{10} show a network structure consisting of fibrils. Furthermore, the SEM picture of 1_8 having the shortest alkyl chain among the three gelators is filled with more or less straight fibrils whereas that of 1_{10} is filled with frizzy fibrils. We consider, therefore, that 1_n having an alkyl chain shorter than 1_8 tend to aggregate into the one-dimensional direction, but cannot cross-link the straight fibrils. On the other hand, the frizzy fibrils are advantageous for entangling each other and eventually to construct the network, by which the solvent fluidity is suppressed and the precipitation of gelator molecules is suppressed. On the other hand, the xerogel of 1_{12} affording a viscous solution results in a sheet-like structure. We consider, therefore, that 1_n having an alkyl chain longer than 1_{10} tend to aggregate into the two-dimensional direction and partially suppress the solvent fluidity.

Photoresponsive functions

The cyclohexane gel containing 1_{10} ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) was subjected to photoirradiation with a 200 W high-pressure Hg-lamp at 15°C . As shown in Fig. 3, the UV-VIS absorption bands characteristic of anthracene-9-carboxylate disappeared with the photoirradiation time and the physical state changed

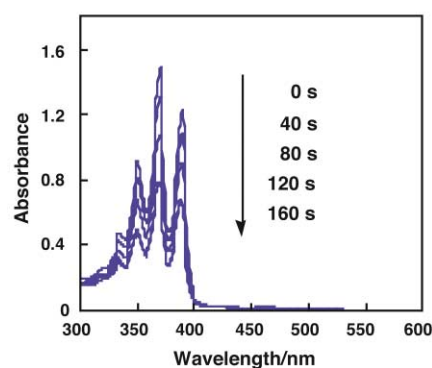


Fig. 3 The UV spectral change in the 1_{10} cyclohexane gel induced by photoirradiation ($>300 \text{ nm}$): $[1_{10}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, 15°C .

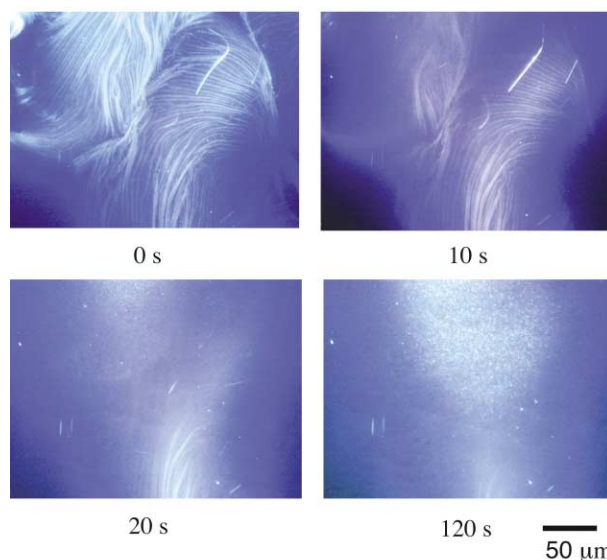
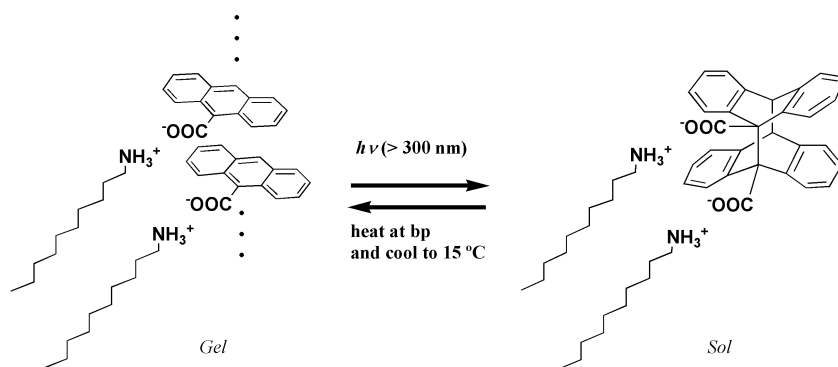


Fig. 4 Morphological change in the cyclohexane gel containing 1_{10} monitored by dark-field optical microscopy with the photoirradiation time.

from the gel to the sol at 120 s. As the gel-to-sol phase-transition temperature for the cyclohexane gel of 1_{10} ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) was 41°C , the phase transition induced at 15°C is ascribed to a photo-induced structural change (photodimerization) in the anthracene-9-carboxylate moieties.¹¹ The photo-induced morphological change was monitored by dark-field optical microscopy (Fig. 4). In the initial gel phase (at 0 s) one



Scheme 2 Photo- and thermo-responsive phase changes in $\mathbf{1}_{10}$.

can recognize the fibrillar bundles. With the photoirradiation time they gradually disappear, and such a structure cannot be detected in the screen after 120 s when the gel is changed to the sol.

When the sol solution was warmed at 30 °C in the dark, the UV–VIS absorption bands ascribable to the monomeric anthracene were gradually regenerated (Fig. 5). Strangely, the UV–VIS absorption bands decreased after 100 min. We found that this is due to the precipitation of $\mathbf{1}_{10}$ reproduced by thermal isomerization. In other words, the gel phase could not be regenerated ‘directly’ from the sol phase. When this mixture was once heated at bp and then cooled to 15 °C, the gel was in fact regenerated. The absorbance after leaving the sample for 3 days was 92.6% of that before photoirradiation. The slight loss of the absorbance (7.4%) is probably due to the photo-induced decomposition of $\mathbf{1}_{10}$. We consider, therefore, that the network structure as shown in Fig. 2 can be constructed only when $\mathbf{1}_{10}$ is cooled from the hot cyclohexane solution (Scheme 2).¹¹ Once this structure is destroyed, it cannot be reconstructed at 30 °C.

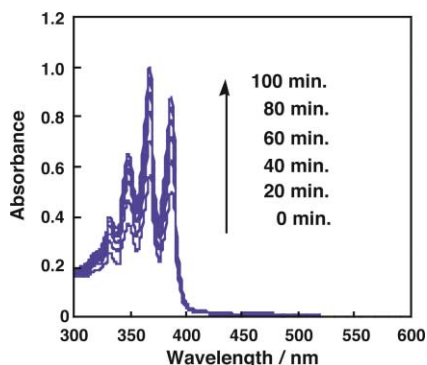


Fig. 5 The UV spectral change in the cyclohexane sol containing photodimerized $\mathbf{1}_{10}$ at 30 °C.

Lastly, we considered why the photo-induced structural change that is fairly difficult in the gel system can be easily attained in the present system. As shown by the influence of the alkyl chain length on the phase changes (Fig. 1) and the fibril morphology (Fig. 2), the aggregation mode seems to be mainly governed by the alkylammonium moiety and only partly by the anthracene-9-carboxylate moiety. This implies that in the binary organogel system the anthracene-9-carboxylates are not so well-ordered and not so tightly packed: they are just assembled as ‘counteranions’ of the ordered alkylammonium assemblies. Thus, the structural change is not so strongly suppressed as that in other systems. The photo-induced monomer-to-dimer structural change eventually destroys the network superstructure (Fig. 4): presumably, the alignment of the alkylammonium moieties is not so stable as to suppress this structural change, because they are not linked by a covalent bond but just assembled by the weak van der Waals interaction.

Conclusion

In conclusion, the present study showed that photoresponsive organogelators, the molecular design of which has been very difficult,^{7,10} can be readily obtained from a binary system composed of anthracene-9-carboxylate acting as a photoresponsive site and alkylammonium groups acting as a structure forming site. As expected, the phase changes among gel, sol and precipitate can be controlled by light and temperature. We expect that this molecular design concept can be extended to the exploitation of new photoresponsive low molecular-weight hydrogelators and that the photoresponsive nature attained herein can be applied to the control of various reaction rates in organic solvents, the introduction of the concept of phase transition into molecular assemblies, the development of photoresponsive reversed micelles, *etc.*

Experimental

Preparation of $\mathbf{1}_n$

An equimolar amount of anthracene-9-carboxylic acid and the corresponding amine was dissolved in THF at 60 °C. The solution was concentrated *in vacuo*, the resultant white solid being dissolved in chloroform. The product was purified by reprecipitation pouring the chloroform solution into hexane. The spectral analyses gave similar data, so that we here record typical data for $\mathbf{1}_{10}$: $^1\text{H NMR}$ (600 MHz; CDCl_3 ; Me_4Si) δ = 0.68–1.28 (m, *n*-decyl except NH_2CH_2 , 19H), 2.43 (t, NH_2CH_2 , 2H), 7.35 (t, Ar-*H*, 2H), 7.41 (t, Ar-*H*, 2H), 7.97 (d, Ar-*H*, 2H), 8.26 (d, Ar-*H*, 2H), 8.37 (s, Ar-*H*, 1H); IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1552 (CO), 1387 (CO), 2920 (CH).

Gelation test and photoirradiation

The general procedure for the gelation test was described previously.^{3,4,7} For the photoirradiation, a 200 W high-pressure Hg-lamp (USH-200MB) was used. The sample gel adjusted to 15 °C was photoirradiated by an Hg-lamp from 15 cm distance through a glass filter (Toshiba UV-29; $\lambda > 300$ nm). The sample was subjected to UV–VIS spectral measurements at an appropriate interval (Fig. 3).

Equipment

SEM pictures (Fig. 2) were taken using a Hitachi S-5000 Scanning Electron Microscope. The dark-field optical microscope used for the observation of the photo-induced gel collapse was an Olympus BHF-342.

Acknowledgements

We are indebted to Mr. Takuya Nakashima for the dark-field optical microscopy measurements. This paper is dedicated to Emeritus Professor Soich Misumi on the occasion of his 77th birthday.

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- 11 Photodimerization of anthracene-9-carboxylate results in both *syn*- and *anti*-isomers. We expect that the sol phase, and the gel phase should give different isomer ratios, but this problem has not yet been examined.