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Novel Odd/Even Effect of Alkylene Chain Length on the Photopolymerizability of Organogelators

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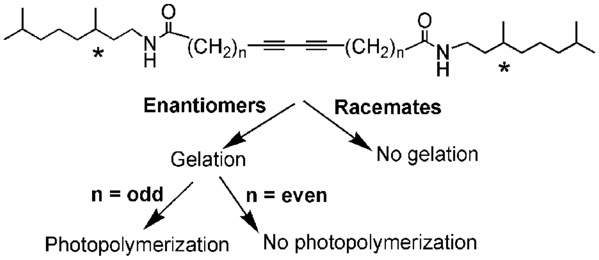
ABSTRACT



Starting from diactylene diacarboxylic acids, we have synthesized a series of photopolymerizable organogelators that possess simple amide structures, different alkylene chain lengths, and either optically active or racemic 3,7-dimethyl-1-octylamine units. The alkylene chain length of these compounds exhibits a prominent odd/even effect with respect to the photopolymerization in the gel state and is accompanied by a stereostructural effect on the gelation ability.

Organogelation by low-molecular-weight molecules is attributed to the encapsulation of environmental organic solvents into fibrous networks formed through intermolecular interactions such as hydrogen bonds and van der Waals interactions.[1] Recently, diacetylene-containing organogelators have attracted much interest because their noncovalently organized fibrous networks can be photopolymerized through 1,4-addition reactions among the diyne groups,[2] which leads to stable, covalently linked polydiacetylene networks. To date, however, only a few papers describing diacetylene gelators have been reported,[3−5] including rather-complicated compounds prepared from cholesteryl ester,[3] glucosamide,[4] and lipid[5a−c] derivatives. In this paper, we describe novel diacetylene-type organogelators that possess extremely simplified structures (Figure 1) to investigate the relationships between their chemical structures and their behavior during gelation and subsequent photopolymerization. We describe here the first example of a remarkable odd/even effect that the alkylene spacer length (n) has on the photopolymerization of these gels.

We prepared a series of diacetylene derivatives (**3R**−**8R**, **3S**, **8S**, **3rac**, and **8rac**; Figure 1) through condensation reactions between (R)-, (S)-, and *rac*-3,7-dimethyl-1-octylamine[6] and diacetylenedicarboxylic acids[7] in dichlo-

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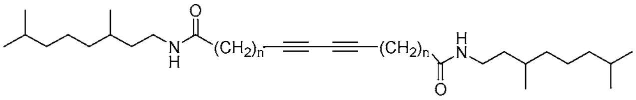

3R, **3S**, **3rac**: n=3
4R: n=4
5R: n=5
6R: n=6
7R: n=7
8R, **8S**, **8rac**: n=8

Figure 1. The diacetylene gelators we used in this study.

romethane. All of the enantiomerically pure compounds in the series **3R**−**8R** have different alkylene chain lengths (*n*) and gelated cyclohexane at concentrations >0.2−0.3% (w/w) to give translucent or turbid organogels; each of these samples exhibits a sol−gel phase transition temperature (T_{gel}) in the range from 57 to 70 °C at a concentration of 1 wt %. An SEM image of the freeze-dried cyclohexane gel of **3R** displays fibrous assemblages that have minimum diameters of ca. 100 nm (Figure 2a). The corresponding *S*-form compounds **3S** and **8S** exhibit quite similar behavior, but the racemic compounds **3rac** and **8rac** failed to gelate any of the organic solvents we studied here. Table 1 summarizes the gelation abilities of these compounds in various solvents. Our results indicate that the introduction of the optically active group plays an important role in the formation of the stable gels.[1,8]

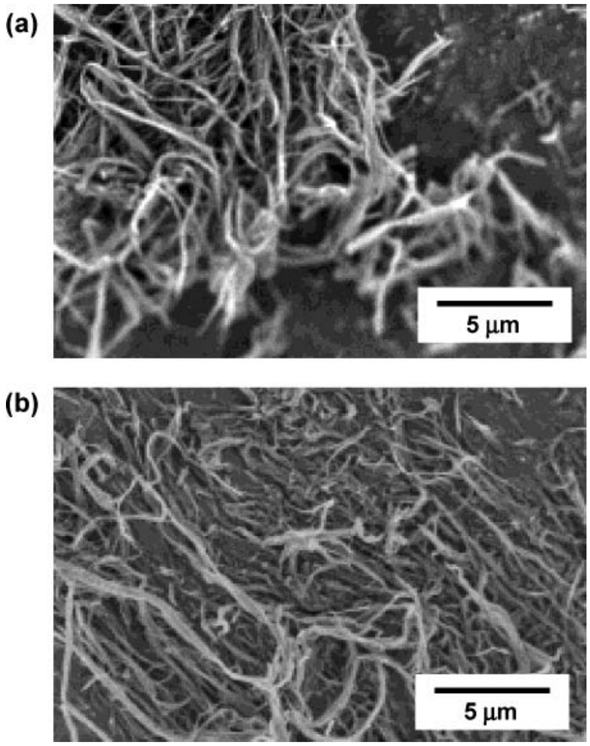

Figure 2. SEM images of the xerogels of **3R** formed in cyclohexane at a concentration of 0.3% (w/w) (a) before and (b) after photoirradiation for 5 min.

Table 1. Gelation Ability of Compounds 3R-8r, 3S, 8S, 3Rac, and 8Rac at a Concentration of 1 wt %[a]

	3R	**3S**	**3 rac**	**4R**	**5R**	**6R**	**7R**	**7S**	**7 rac**	**8R**	**8S**	**8 rac**
n-Hexane	D	D	D	G*	D	D	D	D	D	G*	G*	D
Cyclohexane	G*	G*	D	G*	G*	G*	G*	G*	D	G*	G*	D
Benzene	D	D	D	D	D	S	D	D	D	G	G	D
Toluene	V	V	D	G*	V	G	V	V	D	G	G	D
Acetonitrile	D	D	D	D	D	D	D	D	D	D	D	D
Ethyl acetate	D	D	D	−	−	−	−	−	−	D	D	D
Acetone	D	D	D	−	−	−	−	−	−	D	D	D
Dioxane	D	D	D	S	D	D	D	D	D	G*	G*	D
CCl_4	G	G	D	D	D	G	G*	G	D	G	G	D

[a] G = Gel; G*= translucent/turbid gel; V = viscous liquid; D = deposition; S = solution; S* = dissolved without heating; − = not measured.

Photoirradiation[9] of the cyclohexane gels of **3R**, **5R**, and **7R**, which have odd spacers, led to remarkable color changes to either orange (**3R**) or blue-violet (**5R** and **7R**), accompanied by the appearance of absorption bands in the visible region at ca. 400−550 nm for **3R** (Figure 3) and 400−650 nm for **5R** and **7R**. These results reflect the formation of polydiacetylenes as the result of 1,4-addition reactions of the diyne groups.[2] We observed no significant changes in the geometric shapes of the fibrous networks after photoirradiation, as exemplified by Figure 2a,b. We estimated the ultimate yields of the polydiacetylenes of **3R** and **3S** after photoirradiation for 5 min to be 15−16%, irrespective of their difference in the optical activities, by measuring the weight of the insoluble fractions obtained upon diluting with

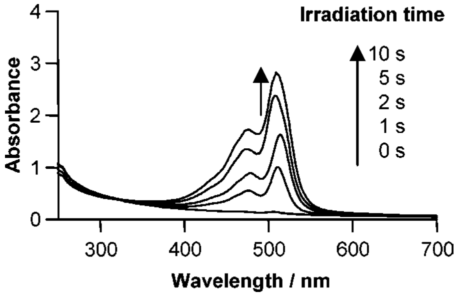

Figure 3. UV−Vis spectral changes of a cyclohexane gel of **3R** at a concentration of 0.3% (w/w) upon irradiation with light.

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(9) Photoirradiation to the gels [0.3% (w/w) in a quartz cell: 1-mm path length] was performed using a high-pressure Hg lamp without any filters.

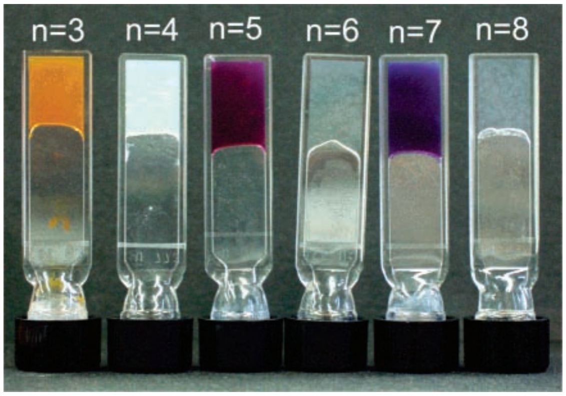

Figure 4. A photographic image of the photoirradiated cyclohexane gels of compounds **nR**.

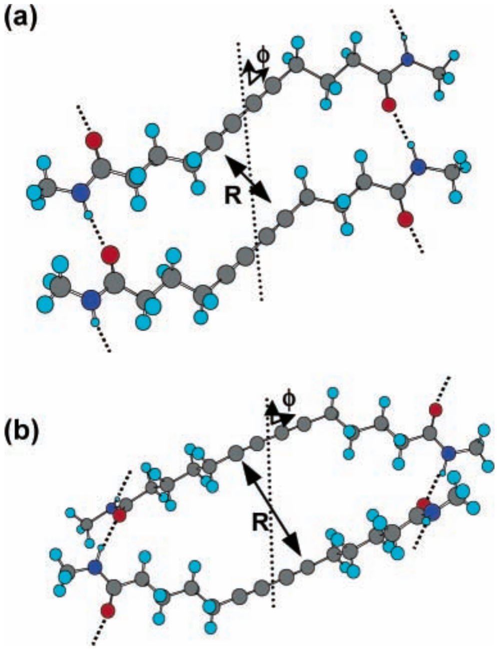

Figure 5. Schematic representation of the results obtained from the calculations of the theoretical structures: (a) $n = 3$ and (b) $n = 4$.

dichloromethane and passing the solution through a 0.2-μm filter. In contrast, the gels formed from diynes having an even number of methylene units (**4R**, **6R**, and **8R**) did not undergo photopolymerization (Figure 4). That is to say, the organogelators having odd-numbered methylene-unit spacers engaged selectively in photopolymerization in the gel state. The photopolymerized gels possessed higher thermal stabilities; when we heated such a gel up to the boiling point of cyclohexane, the color changed to orange and the size contracted as a result of the release of some solvent, but the shape was maintained without the dissolution of the polymer.

We were extremely interested to discover how and why such distinct parity effects emerged. The FTIR spectra of the series of gelators **3R**−**8R** recorded from their cyclohexane gels [0.3% (w/w)] exhibited the characteristic ν_{NH}, $\nu_{C=O}$ (amide I), and ν_{NH} (amide II) absorption bands at ca. 3315−3325, 1640−1641, and 1539−1545 cm^{-1}, respectively, which reveal the formation of intermolecular hydrogen bonds between the secondary amide moieties. This situation leads us to propose a simple organization model in which the secondary amide units at both sides of neighboring molecules become fixed through the formation of intermolecular hydrogen bonds.[10] Under this assumption, we computed the optimal packing modes in the dimer through ab initio quantum chemical calculations using the HF/6-21G method[11] and optimizing the geometries fully. The results of the calculations predict significant differences between the odd- ($n = 3$) and even-numbered derivatives ($n = 4$): we estimate the intermolecular distances (R) between diyne groups and the inclination angles (ϕ) of diyne groups against the packing axis to be 0.46 nm and 55° for $n = 3$ and 0.66 nm and 72° for $n = 4$ (Figure 5a and b, respectively). These geometric differences at the molecular level may have a crucial effect

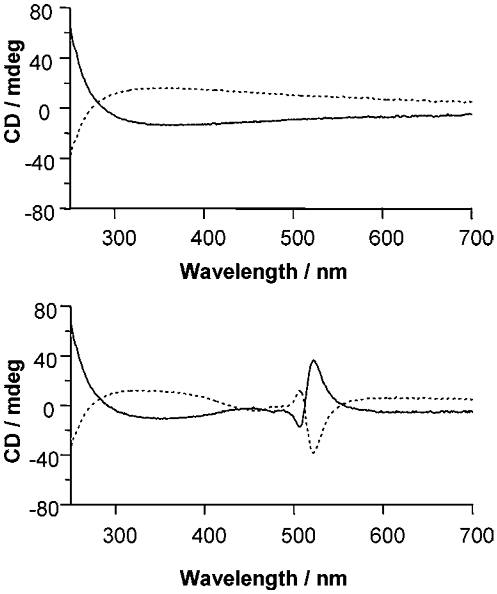

Figure 6. Circular dichroism spectra recorded from the cyclohexane gels of compounds **3S** (solid line) and **3R** (dotted line) before (top) and after irradiation for 2 s (bottom).

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on the bulk photopolymerization properties because it is known that the polymerization of diyne groups is controlled strictly by the molecular packing mode. The solid-state polymerization of diacetylenes requires packing states in which R falls in the range 0.35−0.40 nm and ϕ is ca. 45°;[2] these values are approximately in agreement with our calculated structure of the photopolymerizable gel formed from an odd-numbered methylene-unit gelator ($n = 3$). Related studies of odd/even effects for the polymerization of diacetylene compounds have been reported by Evans and co-workers[12] for monolayer systems and by Tachibana et al.[13] for solid-state systems, but to the best of our knowledge, this paper provides the first observation of such a phenomenon occurring in a gel state. We believe that the results of this study will lead us to the creation of more stable organogels that have even higher photopolymerizability.

We note that chirality transfer occurred from the chiral 3,7-dimethyl-1-octylamino groups to the obtained polydiacetylene main chains. Figure 6 displays the circular dichroism spectra of the cyclohexane gels of compounds **3R** and **3S** before and after their photopolymerization. After irradiation, the gel of **3S** displays a positive Cotton effect with $\lambda_{\max}$ at 522 nm and $\lambda_{\theta=0}$ at 512 nm, which correspond to the peak wavelengths for the exciton absorption band of polydiacetylene. We obtained perfect mirror images of these CD spectra when analyzing the gel prepared from **3R**.

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Supporting Information Available: Detailed descriptions of synthetic procedures and the characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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