Physicochemical Properties of New Gelators Based on a Chromen-2-one Core

Fusheng Zhang, Yuki Morita, Kosuke Kawabe, Takeyasu Tasaka, Hiroaki Okamoto,
Shunsuke Takenaka,* and Hidetoshi Kita
Department of Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,
*Tokiwadai 2557, Ube, Yamaguchi 755-8611*

Homologous series of 2-oxochromen-6-yl 4-alkoxyben-zoates (**1**-*n*, *n* = 2–10) and 4-alkoxybiphenyl-4′-carboxylates (**2**-*n*, *n* = 5–8) can gelate various organic solvents, where the gel–sol transition temperatures are ca. 60 and 90 °C, respectively.

Gelation is fundamentally a self-assembly of molecules, followed by formation of a three-dimensional network in solvents, so that intermolecular interactions such as hydrogen bonding, ionic and π–π ones, and van der Waals force are considered to be important, as well as the solvophobic effect.[1] In fact, many gelators hitherto reported consist of two parts, that is, one is protic functional groups such as hydroxyl, amino, and carboxyl groups, and the other is bulk aromatic core and/or long hydrocarbon chain. Even in aprotic gelators, a bulk or a long hydrocarbon moiety appears to be necessary for gelation.[2]

A dipole–dipole interaction may be enumerated as a non-bonding interaction enhancing the self-assembly. Lactones, cyclic esters, are known to induce a large dipole moment comparing with cyano and nitro groups. 2-Oxochromen-6-yl 4-alkoxy-benzoates (**1**-*n*) and the related compounds reveal liquid crystal properties and induce a large dielectric anisotropy in LC mixture.[3,4] In this connection, we are interested in the polar effect of the chromen-2-one skeleton on gelling ability.

This paper describes physicochemical properties of novel low mass gelators, 2-oxochromen-6-yl 4-alkoxybenzoates (**1**-*n*) and 4-alkoxybiphenyl-4′-carboxylates (**2**-*n*), as shown in Figure 1. The molecular characteristics are that both incorporate neither protic function nor long hydrocarbon chain. As a result, the chemical structure is simple, and molecular weight is low compared with gelators hitherto reported. Furthermore, chemical modification is so easy.
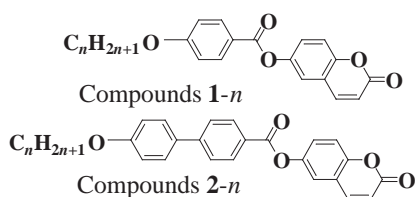
Gel samples were prepared according to the following procedure. A sample (ca. 20 mg) was dissolved in a solvent (1.0 mL) by heating, and the resulting solution was stood for 30 min at room temperature and then 30 min in a refrigerator, in order to complete gelation. Then, gelation was checked visually. If a test tube containing the solution was inverted and no liquid was observed running down the wall of the tube, it was judged to be a gel. When the samples caused gelation, the gelation ability was evaluated quantitatively by critical gel concentration (cgc), which was the minimum concentration of gelling materials necessary for gelation at room temperature. For preparation of SEM samples, **1**-5 and **2**-7 were dissolved in cyclohexane or ethanol at the cgc in sample tube and a piece of thin glass was soaked in the solution. Then, the solvent was removed off by pumping in vacuo for 12 h and the gels were loaded on a piece of thin glass. The SEM pictures were taken using Nihon-denshi JSM 6335F NT. All homologues of **1**-*n* (*n* = 2–10) and **2**-*n* (*n* = 5–8) could gelate various solvents. **1**-2 gel (the gel state of **1**-2) frequently crystallized within 1–2 h by standing at room temperature, and the other gels were stable for long time. **1**-*n* gels and **2**-*n* gels experienced a gel to sol transition at ca. 60 and 90 °C in 1-octanol (5 wt %) on heating, respectively.

The critical gel concentrations (cgc, wt %) for organic solvents are summarized in Table 1.
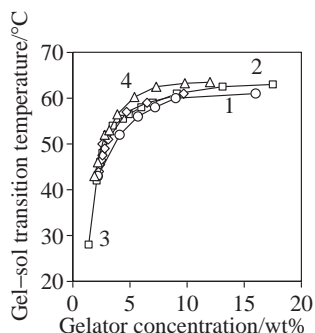
Table 1. Critical gel concentrations (cgc, wt %) of **1**-*n* and **2**-*n* in organic solvents

| Solvents	**1**-*n*		**2**-*n*	
	n = 3	*n* = 8	*n* = 5	*n* = 8
Methanol	4	5	insoluble[a]	insoluble[a]
1-Octanol	2	2	0.3	0.4
n-Octane	1	2	insoluble[a]	insoluble[a]
Cyclohexane	1	2	0.4	1
Toluene	15	30	3	3
Acetonitrile	23	6	1	1
DMF	37	10	12	7
Chloroform	22	37	16	30
Diglyme			7	5

[a]Less than 0.3 wt %.

1-*n* and **2**-*n* have high solubility for low mass ether solvents such as dimethyl ether, diethyl ether, and THF, so that gelation could not be observed visually. Both compounds dissolve well (>30 wt %) in ethyl acetate, giving a viscous solution. Both also can gelate many alcoholic solvents such as ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, in addition to methanol and 1-octanol. In Table 1, interestingly, cgc values are insensitive to the hydrocarbon chain length incorporated in both gelators and solvents. In order to examine the trend in more detail, the effect of the hydrocarbon chain on the gel to sol transition temperatures was examined, and the results are shown in Figure 2. Certainly, both cgc values and the gel–sol transition temperatures are almost independent of the chemical modification of the hydrocarbon chain in alcohols.

In Table 1, both compounds can gelate not only hydrocarbon and aromatic solvents but also polar solvents such as chloroform,

$C_nH_{2n+1}O$ —〈benzene ring〉— C(=O)O —〈chromen-2-one〉

Compounds **1**-*n*

$C_nH_{2n+1}O$ —〈biphenyl〉— C(=O)O —〈chromen-2-one〉

Compounds **2**-*n*

Figure 1. Chemical structures of **1**-*n* and **2**-*n*.

Figure 2. Plots of gel–sol transition temperatures of **1**-8 vs concentration (wt %). (1) Ethanol, (2) 1-butanol, (3) 2-butanol, and (4) 1-octanol.
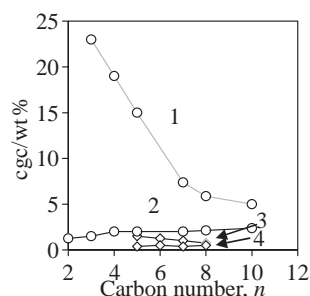

Figure 3. Plots of cgc values vs carbon number n. (1) **1**-n in acetonitrile, (2) **1**-n in 1-octanol, (3) **2**-n in acetonitrile, (4) **2**-n in 1-octanol.

acetonitrile, DMF, and diglyme, while the cgc values are much higher than those of hydrocarbon solvents. Interestingly, the cgc values for acetonitrile, DMF, and diglyme increase with increasing n, inversely to the other solvents. In order to confirm the difference quantitatively, the cgc values in acetonitrile and 1-octanol solvents were examined, and the results are shown in Figure 3.

We can assume from the figure that the octyl moiety of 1-octanol has low affinity with the aromatic cores of **1**-n and **2**-n, since the cgc values are almost independent of n and low. On the other hand, acetonitrile is easy to solvate the 2-oxochromen-6-yl benzoate portion and then steeply difficult with increasing n. Considering thus, the solvophobic effect and intermolecular interactions around aromatic cores, that is, dipole–dipole and π–π interactions should be responsible for the broad gelling ability.

The gelation was also confirmed by SEM examination, and the results are shown in Figure 4. It is apparent from the figure that **1**-n and **2**-n gels consist of un-uniform fibers, where the diameter is in the range between 10 and 500 nm.

Conclusively, intermolecular interactions around lactone moiety having a broad shape and a large dipole moment play important roles for the broad gelling ability. Present results should
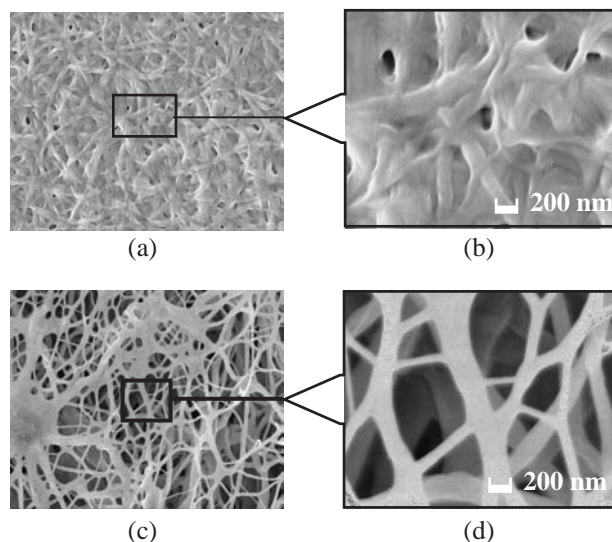
Figure 4. SEM pictures of freeze-dried **1**-5 gel prepared from cyclohexane (surface of gel mass). (a) 1×10^4, and (b) 5×10^4, and **2**-7 gel prepared from cyclohexane (interior of gel mass), (c) 1×10^4, and (d) 5×10^4 (apparatus: JEOL JSM-6335F).

provide new and important information for the gelation phenomena, and the easy chemical modification will bring about vast development of novel low mass gelators and extension of their applications.

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