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Preparation and photoreaction of organogels based on benzophenone

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Abstract

In this paper, first photoreactive low-molecular weight organogels are described. Benzophenone derivatives functionalised with two long alkylamides **1a–c** were designed and synthesized as photoreactive gelator molecules. The compounds formed organogels in several hydrogen donor solvents, e.g. 2-propanol and 1,3,5-triisopropylbenzene. Microstructures of the gels by scanning electron microscopy (SEM) revealed a 3D fibrous network and spherical aggregation. Compound **4** based on isopropylbenzene having an octadecylamide, which was designed as a photochemical hydrogen donor molecule, occurred gelation in a variety of organic solvents. In the case of a 1:1 mixture of **1c** and **4** in several solvents, each component independently caused gelation to give a simple mixture of different gels. Irradiation of the gel of **1a** in 2-propanol decomposed gradually the gel into solution to give pinacol as a main product. Similarly, photoreaction of the 1:1 two-component gel of **1c** and **4** in benzene afforded corresponding pinacol.

Keywords: Organogels; Photoreaction; Microstructures; Benzophenone; Hydrogen abstraction; Pinacolization

1. Introduction

Organogels of low-molecular weight organic compounds are the subject of increasing attention [1–3]. Gelator molecules imprison solvent molecules to aggregate into 3D microstructures through self-assembly. The well-refined molecular arrangements within the microstructures may offer unique photochemical reaction fields. Crystal is an ultimate organized system in which molecules are arranged in 3D regularity. The crystalline state causes specific and highly selective photoreactions due to the restricted molecular motion in the crystal lattice [4–6]. However, it is sometimes accompanied with no occurrence of reaction and slow reaction speed due to too tight molecular packing in crystal lattice. Hence, slightly more flexible medium than crystal is desired to lead us to study gel state photoreaction. Recent papers with low-molecular weight organogels revealed that the driving forces for molecular aggregation of gelators are hydrogen bonding and non-hydrogen bonding such as π–π interaction. Typical examples of the former group are aliphatic amide derivatives [7–13], aliphatic urea derivatives [14–17], and sugar-based compounds [18–22], and of the latter group, cholesterol derivatives [23–27]. Two-component gels are also reported which are formed through hydrogen bondings between the two different molecules [28,29]. Some gels have photofunctional properties, e.g. photochromism [30], and *cis–trans* photoisomerization of azobenzene group [24]. However, photochemical reaction in gel state has never been studied. Benzophenone is the most typical compound to cause photochemical pinacolization in solution as well as in solid state [31]. Herein, we designed benzophenone derivatives functionalised with long alkylamides as photoreactive gelator molecules (**1a–c**, **2a–c**). Further, gelator molecules (**3**,**4**) based on isopropylbenzene were synthesized as hydrogen donors in photochemical process (Scheme 1(a)). The gelation properties including solvent dependence and microstructure were investigated in not only single component but also in two components. Finally, photochemical reactions were performed in the gel state.

2. Experimental details

2.1. General procedures

^{1}H NMR spectra were measured on a JEOL JNM-GSX270 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-300E spectrophotometer. Melting points (mp) were not corrected. Elemental analysis was carried out with a Yanaco CHN Corder MT-5. The solvents for gelation experiments were of analytical grade. All the solvents and

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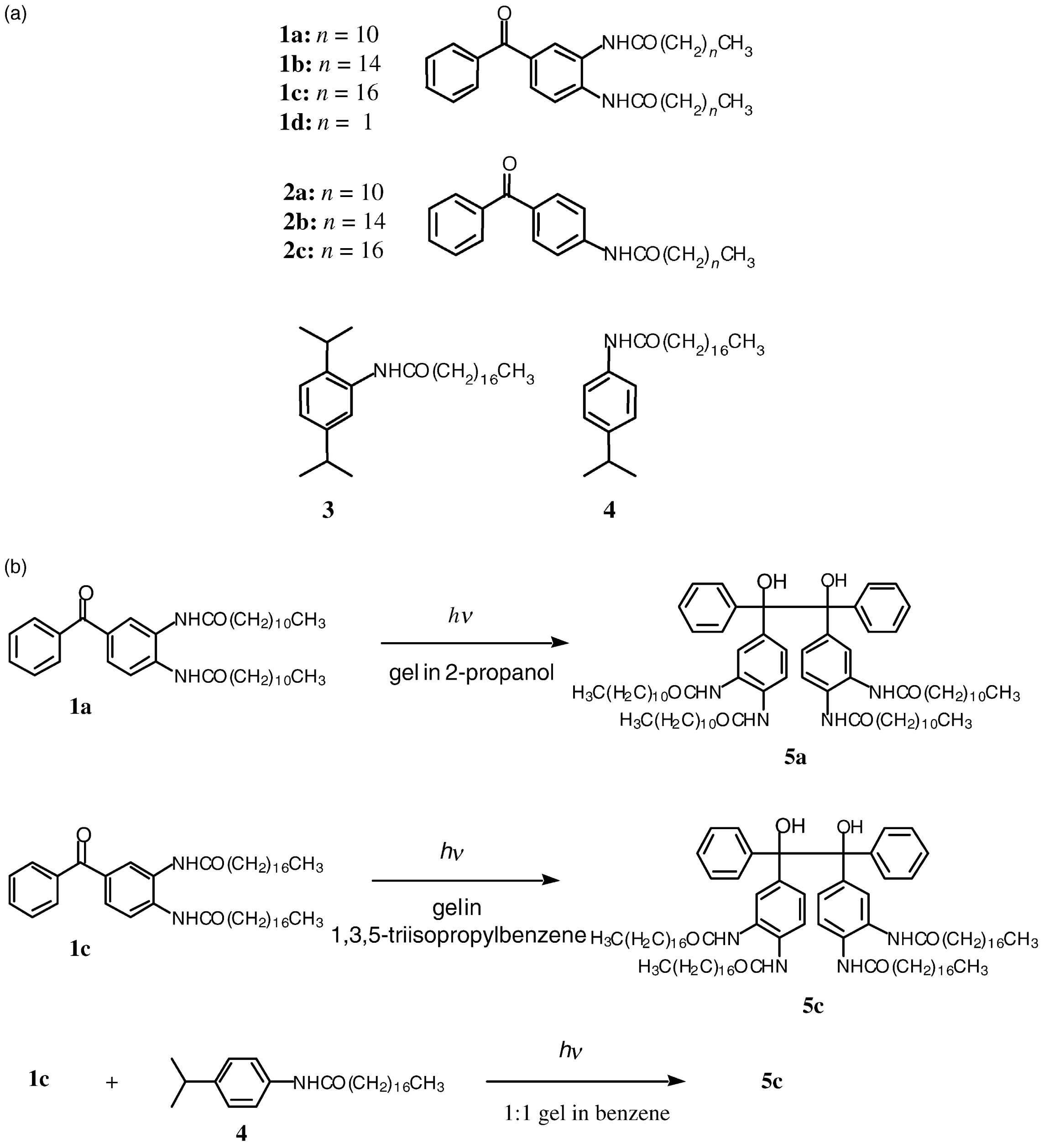

Scheme 1. (a) Gelator components. (b) Photoreaction of benzophenone-based gels.

reagents were commercially available and used as received.

2.2. Synthesis of gel components

A series of gel components were prepared by condensation of corresponding amino compounds and long alkanoyl chlorides of three different lengths **a–c** ($CH_3(CH_2)_nCOCl$, $n = 10, 14, 16$) in THF in the presence of triethylamine for several hours at room temperature. The amino compounds used are 3,4-diaminobenzophenone, 4-aminobenzophenone, 2,6-diisopropylaniline, and 4-isopropylaniline for **1–4**, respectively (Scheme 1(a)). The reaction mixtures were filtered off and washed with water. The residues were dried and recrystallized from methanol.

1a: Yield 92%; mp 111.2–111.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.54 (s, 1H, NH), 8.08 (s, 1H, NH), 7.79–7.46 (m, 8H, Ph), 2.42–2.36 (m, 4H, CH_2), 1.74–1.66 (m, 4H, CH_2), 1.26 (s, 32H, CH_2), 0.88 (t, 6H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3245 (NH), 1655 (C=O). Analytically calculated for $C_{33}H_{48}N_2O_3$: C, 77.04; H, 9.78; N, 4.86. Found: C, 76.66; H, 9.67; N, 4.96.

1b: Yield 89%; mp 104.2–105.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.48 (s, 1H, NH), 7.95 (s, 1H, NH), 7.80–7.46 (m, 8H, Ph), 2.43–2.37 (m, 4H, CH_2), 1.72–1.70 (m, 4H, CH_2), 1.26 (s, 48H, CH_2), 0.88 (t, 6H, $J = 6.6$ Hz, CH_3); IR (KBr)

cm^{-1}, 3256 (NH), 1656 (C=O). Analytically calculated for $C_{41}H_{64}N_2O_3$: C, 78.44; H, 10.53; N, 4.07. Found: C, 78.17; H, 10.39; N, 4.09.

1c: Yield 87%; mp 105.2–107.0 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 8.46 (s, 1H, NH), 7.91 (s, 1H, NH), 7.80–7.46(m, 8H, Ph), 2.44–2.37 (m, 4H, CH_2), 1.72–1.70 (m, 4H, CH_2), 1.26 (s, 56H, CH_2), 0.88 (t, 6H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3295 (NH), 1656 (C=O). Analytically calculated for $C_{45}H_{72}N_2O_3$: C, 78.98; H, 10.82; N, 3.76. Found: C, 78.73; H, 10.61; N, 3.83.

1d: Yield 93%; mp 159.0–160.6 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 8.66 (s, 1H, NH), 8.35 (s, 1H, NH), 7.77–7.46 (m, 8H, Ph), 2.41 (q, 4H, $J = 7.5$ Hz, CH_2), 1.24–1.19 (m, 6H, CH_3); IR (KBr) cm^{-1}, 3279 (NH), 1654 (C=O). Analytically calculated for $C_{21}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.40; H, 6.29; N, 8.60.

2a: Yield 77%; mp 100.4–100.8 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 7.84–7.46 (m, 9H, Ph), 7.37 (s, 1H, NH), 2.40 (t, 2H, $J = 7.5$, CH_2), 1.74 (m, 2H, CH_2), 1.26 (s, 16H, CH_2), 0.88 (t, 3H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3298 (NH), 1663 (C=O). Analytically calculated for $C_{23}H_{28}NO_2$: C, 79.11; H, 8.76; N, 3.69. Found: C, 78.99; H, 8.66; N, 3.82.

2b: Yield 93%; mp 111.0–111.6 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 7.84–7.46 (m, 9H, Ph), 7.35 (s, 1H, NH), 2.40 (t, 2H, $J = 7.5$ Hz, CH_2), 1.75 (m, 2H, CH_2), 1.25 (s, 24H, CH_2), 0.88 (t, 3H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3301 (NH), 1663 (C=O). Analytically calculated for $C_{27}H_{36}NO_2$: C, 79.95; H, 9.49; N, 3.22. Found: C, 80.03; H, 9.51; N, 3.05.

2c: Yield 84%; mp 114.9–115.4 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 7.83–7.45 (m, 9H, Ph), 7.40 (s, 1H, NH), 2.40 (t, 2H, $J = 7.5$ Hz, CH_2), 1.74 (m, 2H, CH_2), 1.25 (s, 28H, CH_2), 0.88 (t, 3H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3301 (NH), 1663 (C=O). Analytically calculated for $C_{29}H_{40}NO_2$: C, 80.30; H, 9.87; N, 3.02. Found: C, 80.16; H, 9.74; N, 3.02.

3: Yield 72%; mp 78.0–79.5 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 7.26 (s, 1H, Ph), 7.18 (t, 2H, $J = 7.5$ Hz, Ph), 7.61 (s, 1H, NH), 3.20–3.02 (m, 2H, CH_2), 2.43 (t, 2H, $J = 7.5$, CH_2), 1.77 (m, 2H, CH_2), 1.44–1.12 (m, 40H, CH_2), 0.88 (t, 3H, $J = 7.5$ Hz, CH_3); IR (KBr) cm^{-1}, 3258 (NH), 1650 (C=O). Analytically calculated for $C_{28}H_{49}NO$: C, 81.20; H, 12.04; N, 3.16. Found: C, 81.36; H, 11.91; N, 3.11.

4: Yield 83%; mp 77.4–79.6 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 7.42 (d, 2H, $J = 8.5$, Ph), 7.18 (t, 2H, $J = 7.5$ Hz, Ph), 7.06 (s, 1H, NH), 3.14–3.05 (m, 4H, CH_2), 2.87 (m, 1H, CH), 2.33 (t, 2H, $J = 7.5$ Hz, CH_2), 1.72 (m, 2H, CH_2), 1.42 (t, 6H, $J = 7.5$, CH_3), 1.25(s, 24H, CH_2), 0.88 (t, 3H, $J = 7.5$ Hz, CH_3); IR (KBr) cm^{-1}, 3309 (NH), 1654 (C=O). FAB(M^+) = 443.8 (calculated = 443.8).

2.3. Preparation of gels

In a typical gelation test, a weighed amount of gel compound and 1 ml of solvent were placed in a vial, covered and dissolved by gentle heating. The solution was allowed to cool to room temperature. Gelation was considered to have occurred when a homogeneous substance was obtained, which exhibited no gravitational flow.

2.4. Photoreaction of gels

Gel prepared in a Pyrex test tube was irradiated with a 400 W high-pressure mercury lamp at 15 °C by using a merry-go-round apparatus. After the reaction, the solvent of reaction mixture was evaporated and products were separated by silica gel column chromatography using toluene and ethyl acetate.

Irradiation of gel of **1a** (0.352 g) in 2-propanol (5 ml) for 55 h gave pinacol **5a** in 20% yield at 31% recovery of **1a**. Compound **5a**, mp 174.2–175.3 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 8.22 (s, 4H, NH), 7.61–7.22 (m, 16H, ph), 2.30 (t, 8H, $J = 7.3$ Hz, CH_2), 1.64 (s, 2H, OH), 1.26 (s, 64H, CH_2), 0.88 (t, 12H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3551 (OH), 3327 (NH), 1645 (C=O); FAB (M^+) = 1155.9 (calculated = 1155.7).

Irradiation of gel of **1c** (0.167 g) in 1,3,5-triisopropylbenzene (10 ml) for 232 h afforded **5c** in 40% yield at 23% recovery of **1c**. Compound **5c**, mp 104.5–106.3 °C; ^1H NMR (300 MHz, $CDCl_3$), δ 8.44 (s, 4H, NH), 7.80–7.47 (m, 16H, ph), 2.40 (q, 8H, $J = 7.0$ Hz, CH_2), 1.72 (m, 8H, CH_2), 1.72 (s, 2H, OH), 1.26 (8s, 112H, CH_2), 0.88 (t, 12H, $J = 6.6$ Hz, CH_3); IR (KBr) cm^{-1}, 3450 (OH), 3271 (NH), 1655 (C=O); FAB(M^+) = 1492.4 (calculated = 1492.4).

Irradiation of 1:1 of **1c** (0.303 g, 0.525 mmol) and **4** (0.211 g, 0.525 mmol) in benzene (5 ml) for 151 h gave **5c** in 8% yield at 35% and 39% recovery of **1c** and **4**, respectively.

2.5. Electron microscopy

A piece of gel was placed on a scanning electron microscope (SEM) stub with carbon tape, dried, coated with Au, and observed on the stage of a JEOL JSM-5300 scanning electron microscope (SEM) using a 15–20 kV accelerating voltage.

2.6. X-ray diffraction

For X-ray diffraction measurements, gel prepared in a vessel was dried and mounted on a glass plate. X-ray diffractograms (PXD) were taken on a Rigaku RINT2000 powder diffractometer using Cu Kα1/Kα2 radiation (1.54060 Å and 1.54439 Å).

*2.7. Crystal structure determination of **1d***

X-ray data were collected on a Rigaku RAXIS RAPID imaging plate with Cu Kα radiation to a maximum 2θ of 136.5°. A total of $30 \times 5.00^\circ$ oscillation images were collected, each being exposed for 15 min. The reflection data were corrected for Lorentz-polarization effects and secondary extinction. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were not refined. The final cycle of full-matrix least-squares refinement was based on all reflections ($2\theta < 136.5^\circ$) and variable parameters and converged with unweighted and weighted agreement factors of: $R = \sum \| F_o | - | F_c \| / \sum |F_o|$ for $I > 2.0\sigma(I)$ and $R_w = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$. All calculations were performed by using teXsan crystallographic software. **1d**: $C_{19}H_{20}N_2O_3$, $M_w = 324.37$, colorless, needle shaped crystal (0.10 mm × 0.48 mm × 0.23 mm), monoclinic, space group $P2_1/a$ with $a = 8.3655(9)$, $b = 16.000(2)$, $c = 12.507(1)$ Å, $\beta = 92.218(6)^\circ$, $V = 1672.8(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.288\,\mathrm{g\,cm^{-3}}$, $F(0\,0\,0) = 688.00$, $\mu = 7.14\,\mathrm{cm^{-1}}$. A total of 17898 reflections were measured, 3041 independent. Final $R = 0.072$, $R_w = 0.242$, GOF = 1.87 for 218 parameters. A final Fourier showed no residual density outside 0.44 and $-0.34\,\mathrm{e\,Å^{-3}}$.

3. Results and discussion

3.1. Preparation and microstructures of gels

Benzophenone derivatives **1a–c** and **2a–c** linked with two and one long alkylamides of three different lengths ($n = 10$, 12 and 16) were designed and synthesized as photoreactive gelator molecules. Di and monoisopropylbenzene derivatives **3** and **4** having a long alkylamide ($n = 16$) were prepared as hydrogen donor gelators in photochemical process. Results of the gelation test of **1–4** using a variety of solvents were summarized in Table 1. Benzophenone-based gelator **1a** with shortest two alkyl chains ($n = 10$) formed opaque gel in 1,3,5-triisopropylbenzene. Some gels of **1a** in 2-propanol and methanol were once formed but not very stable; gradually decomposed on standing and changed to viscous fluid after a few days. The unstable gel is termed as UG in Table 1. The other solvents gave precipitates. Introducing longer alkyl chains in the molecules of **1b** and **1c** shifted to the occurrence of gelation in lower polar solvents. For instance, **1c** formed gels or unstable gels in hexane and benzene, but not in 2-propanol and methanol. However, high polar solvent dimethylsulfoxide occurred gelation with **1a–c**. Herein, 1,3,5-triisopropylbenzene is a best solvent for the gelation of **1a–c**.

On the other hand, benzophenone derivatives **2a–c** having an alkyl chain in each molecule apparently formed semi-transparent or opaque gels in all the solvents, because the vessels could be inverted without changing the shape of the gels. The results alone of **2c** are shown in Table 1. However, they were not real gels but aggregates of fine needle or plate crystals, which were confirmed by the SEM photographs and the appearance of a number of sharp peaks by powder X-ray diffraction, termed as crystalline gel (CG) in Table 1. Namely, the difference between two and one alkyl chain numbers in the molecules of **1a–c** and **2a–c** induce the quite different gelation behavior.

Diisopropylbenzene-based compound **3** apparently formed gels with various solvents. However, most of them were not real gels but aggregates of very fine needle or plate crystals, similar to those of **2a–c**. Monoisopropylbenzene-based **4** gave real gels in various solvents at lower concentrations than **3**.

Two-component gels of **1c** with **3** and **4** were also prepared in order to examine gel state photoreactivity (Table 2). A 1:1 mixture of **1c** and **3** formed two-component gels in four solvents such as 1,3,5-triisopropylbenzene and acetone, and unstable gel in acetonitrile. In the case of a 1:1 mixture of **1c** and **4**, two-component gels were obtained by using 1,3,5-triisopropylbenzene and acetonitrile, unstable gels in four solvents, e.g. benzene and toluene. The gelation behavior is approximately similar to that of **1c** alone, indicating that the occurrence of gelation in the two-component system is controlled by **1c**.

Microstructures of several dried gels were examined by SEM. The benzophenone-based gel of **1a** in 2-propanol revealed a 3D fibrous network to form globular structure of around 100 μm diameter (Fig. 1a). In the case of gel of

Table 1
Minimum concentrations of components **1–4** for the formation of gels in a variety of solvents[a]

Solvent	**1a**	(g/l)	**1b**	(g/l)	**1c**	(g/l)	**2c**	(g/l)	**3**	(g/l)	**4**	(g/l)
Hexane	P	–	UG	5	UG	11	CG	18	P	–	G	4
Benzene	P	–	G	55	UG	41	CG	36	G	332	G	43
Toluene	P	–	P	–	G	45	CG	29	CG	322	G	31
1,3,5-Triisopropylbenzenes	G	8	G	10	G	15	CG	15	G	36	G	7
Chlorobenzene	P	–	UG	69	G	51	CG	37	CG	363	G	64
Ethyl acetate	P	–	P	–	P	–	CG	31	CG	88	P	–
Tetrahydrofurane	P	–	P	–	P	–	CG	241	P	–	P	–
2-Propanol	UG	70	UG	20	P	–	CG	22	G	133	G	67
Acetone	P	–	P	–	P	–	CG	31	CG	116	G	70
Ethanol	P	–	P	–	P	–	CG	15	CG	146	G	46
Methanol	UG	15	P	–	P	–	CG	17	CG	88	G	26
Acetonitrile	P	–	P	–	P	–	CG	5	CG	26	G	8
Dimethylsulfoxide	UG	76	G	23	G	21	CG	9	G	40	G	9

[a] G: gel; UG: unstable gel; CG: crystalline gel; P: precipitation.

Table 2
Minimum concentrations of sum of both the components for the formation of 1:1 two-component gels in a variety of solvents[a]

Solvent	**1c** + **3**	(g/l)	**1c** + **4**	(g/l)
Hexane	P	–	P	–
Benzene	P	–	UG	79
Toluene	P	–	UG	99
1,3,5-Triisopropylbenzene	G	66	G	17
Chlorobenzene	G	109	UG	97
Ethyl acetate	P	–	P	–
Tetrahydrofurane	P	–	P	–
2-Propanol	P	–	P	–
Acetone	G	47	P	–
Ethanol	P	–	P	–
Methanol	P	–	P	–
Acetonitrile	UG	30	G	50
Dimethylsulfoxide	G	21	UG	27

[a] G: gel; UG: unstable gel; P: precipitation.

1c in 1,3,5-triisopropylbenzene, thin plates like scales of about 0.1 μm thickness aggregate in a radial manner to form spherical microstructures of several tens μm diameter (Fig. 1b). Dense aggregation of linear fibers of several tens nm diameter is observed in the gel of **4** in acetonitrile (Fig. 1d).

The 1:1 two-component gel of **1c** and **4** in benzene contains three different microstructures (Fig. 1e). They are wrinkled spheres of around 10 μm diameter, thin sticks of several μm width and very fine fibers. In order to confirm whether the two-component gel is real physical gel aggregated between both components on the molecular level, or simple mixture of the independent gels formed from each component, the gels of **1c**, **4** and **1c** + **4** were characterized by the measurements of X-ray diffraction, IR spectra, and gelation temperature. Powder X-ray diffraction peaks of the three dried gels are very broad (Fig. 2), different from sharp peaks of crystalline substances. The diffraction pattern of the 1:1 gel (Fig. 2c) is coincident with the sum of them of the components of **1c** (Fig. 2a) and **4** (Fig. 2b), indicating a simple mixture of the independent gels of each component. IR absorption bands of the 1:1 gel in benzene appear at 3246 (broad) and 1651 cm^{-1}, which correspond to hydrogen bonding of amides and C=O stretching vibrations of benzophenone and amides, respectively. The IR bands are almost similar to 3311 (broad) and 1657 cm^{-1} of the gel of **1c** and 3285 (broad) and 1647 cm^{-1} of the gel of **4**. Gelation points of the single component gels of **1c** and **4** measured by differential scanning calorimeter (DSC) are 47 and 36 °C, respectively. While the 1:1 gel has two

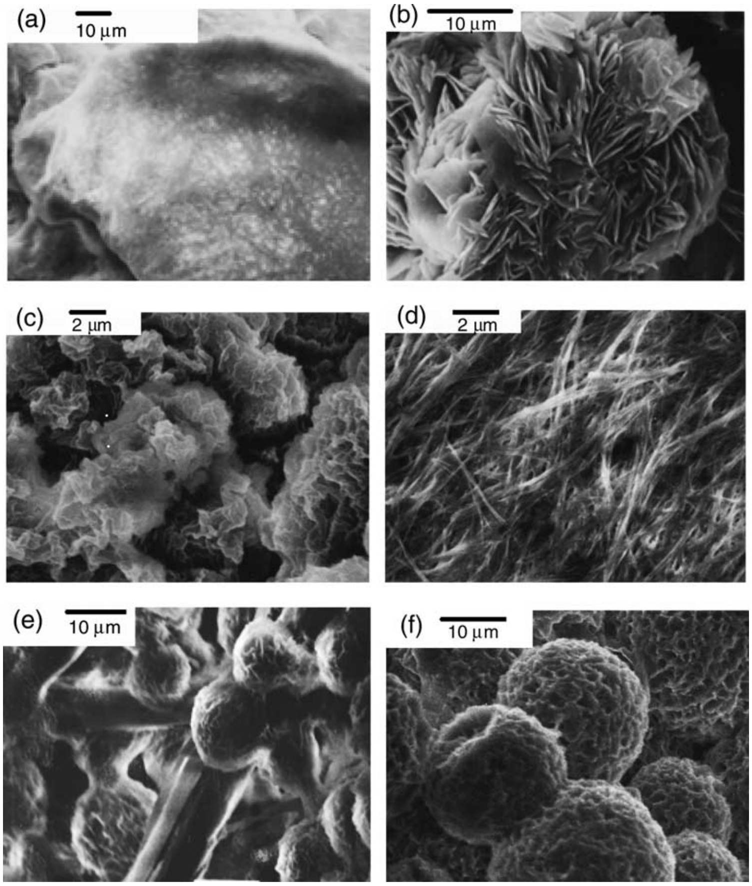

Fig. 1. SEM pictures of gels of: (a) **1a** in 2-propanol; (b) **1c** in 1,3,5-triisopropylbenzene; (c) after irradiation of (b); (d) **4** in acetonitrile; (e) two-component gel of **1c** and **4** in benzene; and (f) after irradiation of (e).

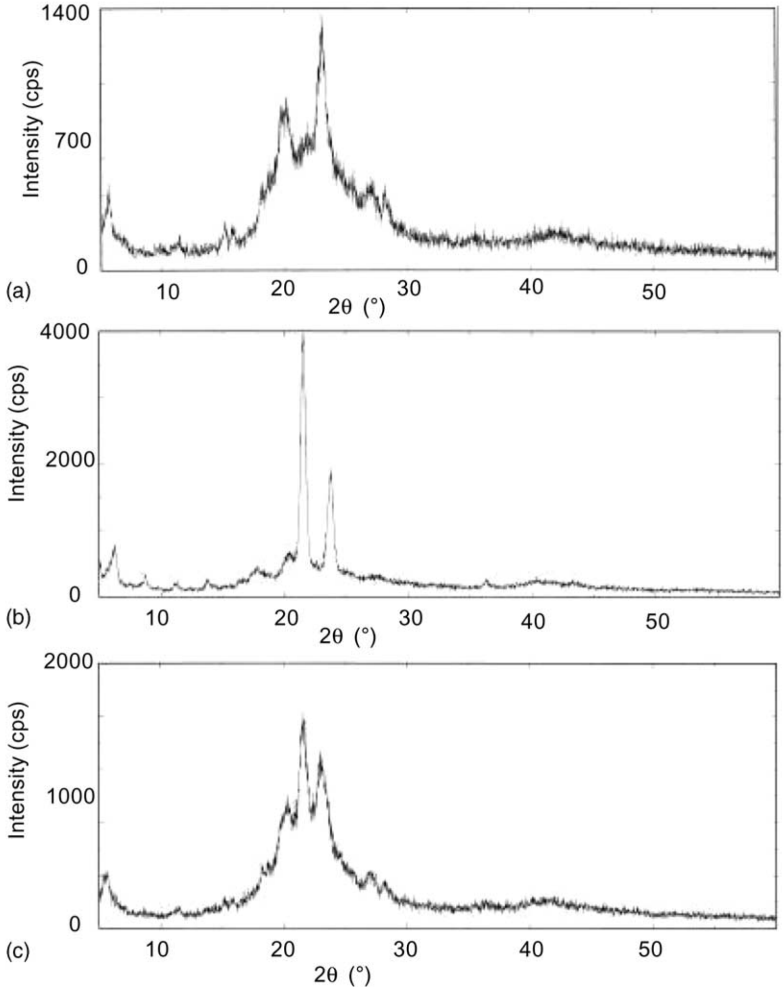

Fig. 2. X-ray diffraction patterns of gels of: (a) **1c**, (b) **4**, and (c) 1:1 two-component gel of **1c** and **4** in benzene.

gelation points at 44 and 25 °C, showing simple gelation temperature decrease of each component. These results by IR and DSC measurements also support that the 1:1 gel is a simple mixture of each component gel.

For the purpose of elucidation of gelation mechanism, X-ray crystal structure of **1d** having two short alkyl chains ($n = 1$) was performed, because single crystals of **1a–c** were not obtained despite much effort. Ortep drawing shows that the molecule of **1d** is in a conformation with the amido groups in a parallel orientation (Fig. 3a). The two phenyl planes of benzophenone unit has some torsional conformation; the O(1)–C(7)–C(1)–C(C2) and O(1)–C(7)–C(8)–C(9) torsion angles are 34.3° and 18.4°, respectively.

The main packing motif is 1D chain of molecules, running parallel to the *a*-axis (Fig. 3b). N–H· · · O=C hydrogen bonds link two adjacent molecules, which are related by a crystallographic glide operation. The donor–acceptor distances are 2.17 and 2.43 Å; the N–H· · · O angles are 168.8° and 155.0°, respectively. Furthermore, the phenyl groups with alkylamides stack in almost parallel; the plane-to-plane distance is 3.5 Å to induce π–π interaction. The molecular arrangement projected on the *bc* face (Fig. 3c) suggests that if more longer alkyl chains are introduced in the molecule, the cavities formed by the alkyl groups become larger to make possible to include solvent molecules in the cavities (Fig. 3c). Finally, the initial packing arrangement cannot be maintained to decompose the crystal structure. Nevertheless, the initial 1D hydrogen bond chains and other intermolecular interactions remain in some extent to aggregate into gel state. In fact, the X-ray diffraction pattern of the gel of **1c** in benzene reveals a broad band in the range of $2\theta = 15$–30° ($d = 5.9$–3.0 Å) and two large peaks at around $2\theta = 20$ and 23° ($d = 4.4$ and 3.9 Å; Fig. 2a). The crystal of **1d** also has a number of sharp diffraction peaks in the same range of $2\theta = 15$–30°, suggesting the formation of some similar ordered structures in the gels.

3.2. Gel state photoreaction

The gel of **1a** in 2-propanol was irradiated in a Pyrex test tube. With the proceeding of photoreaction, the gel gradually dissolved from the outside to inside. After irradiation for 55 h, the gel completely changed to a mixture of yellow solution and some precipitates. Pinacol **5a** was obtained in 20% yield as a main product (Scheme 1(b)). HPLC analysis of **5a** using C_{18} column was confirmed to be a 1:1 diastereomeric mixture of enantiomers of *R*,*R* and *S*,*S* and meso forms of *R*,*S* and *S*,*R*, showing that the gel photoreaction is not stereospecific. Other minor products could not be identified due to the small quantities. The reaction speed seems to be considerably slow in comparison with solution phase reaction. As irradiation of solution of a short alkyl chain compound **1d** in 2-propanol under the same conditions completed the reaction after only 2 h and gave the corresponding pinacol **5d** in 59% yield at 100% conversion of **1d**. The slow reaction speed in the gel may be due to the diffused reflection on the opaque gel surfaces as well as smaller molecular mobility in the gel than that in the solution.

The gel of **1c** in 1,3,5-triisopropylbenzene proceeded the photoreaction more slowly than that of the gel of **1a** in 2-propanol. Even irradiation for 232 h did not complete the reaction, giving pinacol **5c** in 40% yield at 77% conversion of **1c** (Scheme 1(b)). The initial gel remained at the core part in the test tube and the outside was decomposed to viscose and opaque solution. SEM photographs reveal that the spherical aggregates of scale-like plates before irradiation (Fig. 1b) were changed to shapeless aggregates in the dried opaque solution after irradiation (Fig. 1c).

Finally, the 1:1 gel of **1c** and **4** in benzene was submitted to irradiation. With the proceeding of photoreaction, the gel gradually dissolved to a mixture of yellow solution and some precipitates after 151 h. Separation of the reaction mixture afforded **5c** in 8% yield as a 1:1 diastereomeric mixture (Scheme 1(b)). Others were minor products and mostly polymerized substances. In this reaction, the isopropylbenzene-based compound **4** should act as a hydrogen donor, of which methine hydrogen of isopropyl group is abstracted by the benzophenone carbonyl group of **1c**. It is understood from the changing of microstructures observed by SEM that the fine fibers and the thin sticks derived from **4** before irradiation (Fig. 1e) disappeared in the precipitates after irradiation (Fig. 1f). However, it is not clear at present, whether the reaction directly occurs between the independent gel microstructures of **1c** and **4**, or the gels are once dissolved in the solvent and then the reaction proceeds in solution phase.

In summary, the gel state photoreactions cause the same pinacolization as solution phase but the reaction speeds are considerably slow.

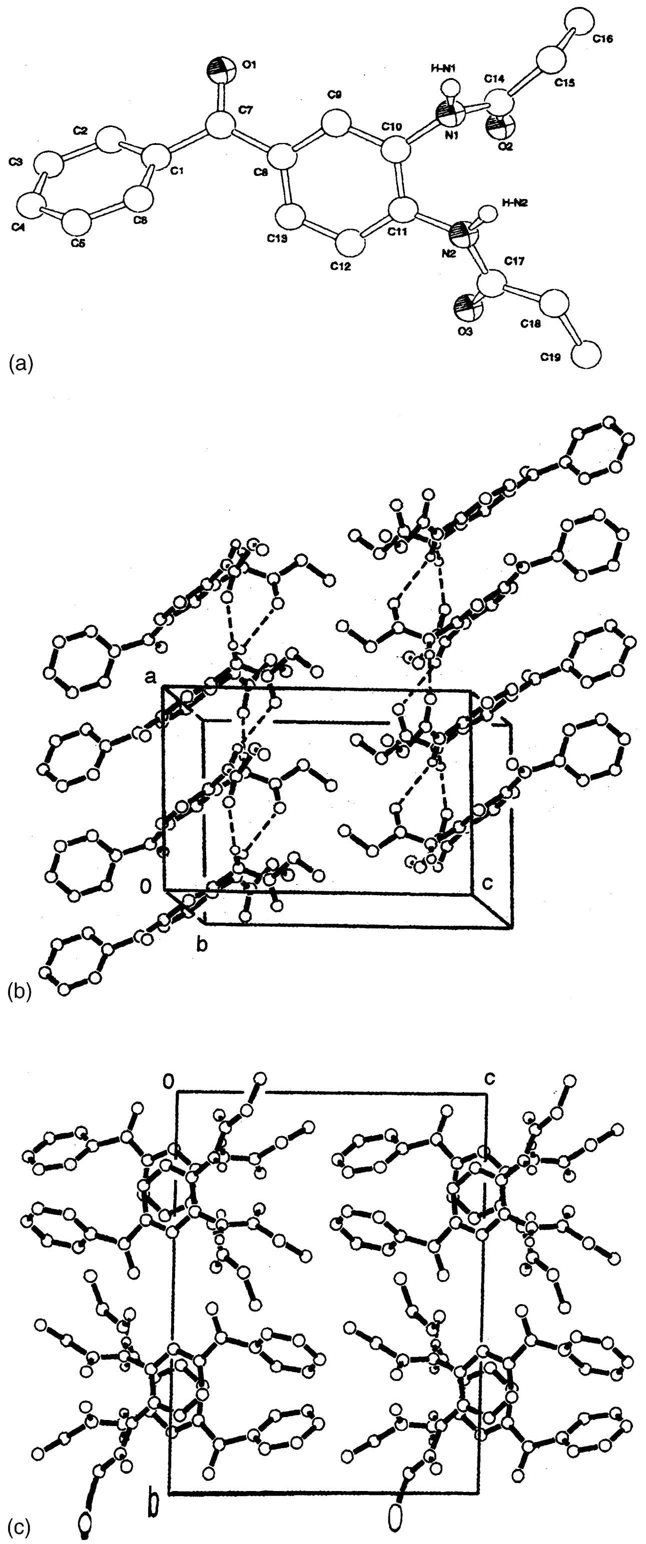

Fig. 3. (a) Ortep drawing of the molecular structure of **1d** obtained from X-ray crystal structure determination, and the molecular arrangements (b) along the *a*-axis and (c) on the *bc* face. Hydrogen atoms except amide hydrogen have been omitted for clarity.

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