

Electronic Supplementary Information for

Role of solvophilic moieties of gelators in the thermal stability of organogels

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§S1. Backgrounds and detailed handling of Hansen solubility parameters (HSPs)

HSPs have been initially proposed for predicting the “solubility” of two chemicals based upon the similarity of their interaction energy.^{1, 2} From a thermodynamic point of view, a cohesive interaction of between molecules can be expressed as the energy density. The quantity can be estimated using a macroscopic parameter such as the vaporization enthalpy per molar volume. The first solubility parameter proposed by Hildebrand^{3, 4} is represented by a single component with the square root of the energy density (δ), and later Hansen divided it into three components: dispersion (δ_D), polar interactions or the Coulomb part (δ_P), and hydrogen bond contributions (δ_H). After assigning these three parameters to each solvent, we can plot them in the 3-dimensional cartesian coordinates, resulting in the “Hansen space”. By based on the “like dissolves like” concept, the distance in the HSP space (R_a) becomes a measure of the solubility. R_a for chemical species 1 and 2, is obtained with an empirical factor “4” for δ_D .

$$R_a^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2 \quad (1)$$

The result to the species 1 and 2 is interpreted as the shorter R_a , the better affinity.

The location of a “good” gelator in HSP space, however, should neither be so closed to that of a solvent, nor be so far; an appropriate R_a is required. Previous works^{5, 6} say that a single gelator should not be *perfectly* dissolved into the solvent. In our present systems with binary gelators, however, each gelator is *dissolved* into the solvent under an appropriate solvent choice. We indeed need detailed handling of the HSPs and Hansen space with using another manner that is employed for single gelator systems.

§S2. Materials and thermal measurements

2-1. Materials

Each gelator of 0.10 mol dm^{-3} was dissolved in an organic solvent. Their equivolume solutions of each gelator were mixed carefully to have a gel immediately. The mixture was heated up to $80 \text{ }^{\circ}\text{C}$ to obtain a sol state using a dry bath, and the sol system was stirred. The sample was then cooled down to room temperature by air to reobtain a gel state. Such a heating up—cooling down process was repeated for at least three times, and we got an isotropic gel.

We purchased 23 nonpolar (see Tables SA1 and SA2) and 7 polar (Table SA2) organic solvents in this study from FUJIFILM Wako, TCI, or Kanto. The gelators, or *p*-chlorophenol and AOT, were brought from FUJIFILM Wako and TCI, respectively. The chemicals but for AOT were used as received. Otherwise, AOT was dried in an oven at $80 \text{ }^{\circ}\text{C}$ for 3 d before use to remove any trace water.

Table S1. T_{drop} values of organogels depending on solvent⁽¹⁾

No.	Solvent groups	Solvents	$T_{\text{drop}} / ^\circ\text{C}^{(2)}$	$\sigma / ^\circ\text{C}^{(3)}$	$T_{\text{b, solv}} / ^\circ\text{C}^{(4)}$
1	I aromatics	benzene	24.8	3.0	80.1
2		butylbenzene	34.0	4.2	134.22
3		toluene	25.2	2.5	110.6
4		4- <i>tert</i> -butyltoluene	39.4	4.7	193
5		<i>o</i> -xylene	28.2	2.3	144.4
6		<i>m</i> -xylene	30.8	3.6	139.3
7		<i>p</i> -xylene	26.7	4.2	138.35
8		mesitylene	29.2	4.1	164.7
9	II acyclic alkanes (hydrocarbons)	hexane	60.9	3.2	68.7
10		heptane	60.1	3.5	98
11		decane	65.9	2.1	174.1
12		undecane	67.6	2.6	195.9
13		2,2,4-trimethylpentane	57.1	3.6	99.238
14	III acyclic alkane (other)	carbon tetrachloride	26.3	0.5	76.8
15	IV cyclic alkanes	cyclopentane	43.2	3.0	49.2
16		cyclohexane	48.2	1.4	80.7
17		methylcyclohexane	43.6	1.4	100.9
18		ethylcyclohexane	50.0	1.7	131.9
19		cycloheptane	47.4	2.6	118.48
20	V acyclic alkene	2-ethyl-1-butene	36.4	1.7	64.7
21	VI cyclic alkanes	cyclopentene	28.0	2.2	44.2
22		cyclohexene	30.2	2.7	83
23		cyclooctene	32.2	1.7	85.5

⁽¹⁾ Solvents that gel the gelators (AOT and *p*-chlorophenol) are written down in the Table.

⁽²⁾ Obtained in this study.

⁽³⁾ Standard deviation of T_{drop} .

⁽⁴⁾ Boiling point of solvent. Taken from SciFinderⁿ: <https://scifinder-n.cas.org/>

Table S2. Hansen solubility parameters of solvents and gelator

No.	Solvent group	Solvent / Gelator	$\delta D /$ (MP) ^{1/2}	$\delta P /$ (MP) ^{1/2}	$\delta H /$ (MP) ^{1/2}
Gelled solvents					
1	I aromatics	benzene	18.4	0.0	2.0
2		butylbenzene	17.4	0.1	1.1
3		toluene	18.1	1.4	2.0
4		4- <i>tert</i> -butyltoluene	16.9	1.7	2.0
5		<i>o</i> -xylene	17.8	1.0	3.1
6		<i>m</i> -xylene	18.0	2.3	2.3
7		<i>p</i> -xylene	18.0	1.0	3.1
8		mesitylene	18.0	0.6	0.6
9	II acyclic alkanes	hexane	14.9	0.0	0.0
10		heptane	15.3	0.0	0.0
11		decane	15.7	0.0	0.0
12		undecane	16.0	0.0	0.0
13		2,2,4-trimethylpentane	14.1	0.0	0.0
14	III perhaloalkane	carbon tetrachloride	17.8	0.0	0.6
15	IV cyclic alkanes	cyclopentane	16.4	0.0	1.8
16		cyclohexane	16.8	0.0	0.2
17		methylcyclohexane	16.0	0.0	1.0
18		ethylcyclohexane	16.2	0.1	0.1
19		cycloheptane	17.1	1.4	1.9
20	V acyclic alkene	2-ethyl-1-butene	14.9	1.7	3.5
21	VI cyclic alkenes	cyclopentene	16.7	3.8	1.7
22		cyclohexene	17.2	1.0	2.0
23		cyclooctene	16.9	2.1	3.5
“Sol” solvents					
31	VII polar ⁽¹⁾	acetonitrile	5.3	18.0	6.1
32		cyclopentanone	17.9	11.9	5.2
33		cyclohexanol	17.4	4.1	13.5
34		cyclohexanone	17.8	8.4	5.1
35		chlorocyclohexane	17.3	5.5	2.0
36		diethyl ether	14.5	2.9	4.6
37		ethanol	15.8	8.8	19.4
Gelator ⁽²⁾					

41	VIII	AOT	16.8	7.5	10.4
42		sulfosuccinic acid	18.7	18.2	31.2
43		3-methylheptane	15.2	0.1	0.1

⁽¹⁾ Solvents in which organogels are not formed are tagged as “polar” solvents. Details of chemical groups are omitted.

⁽²⁾ Including the gelator (AOT; No. 41) and the moieties of AOT (Nos. 42 and 42).

2–2. Thermal measurements

T_{drop} measurements

We employed a Mettler-Toledo DP 70 Drop Point system for T_{drop} measurements. The gel sample was placed in a cylindrical cup with a volume of approximately 0.6 cm^3 , and in the bottom of the cup there is a hole with a diameter 2.8 mm. System temperature was raised with a rate $1.0 \text{ }^\circ\text{C min}^{-1}$, which gives rise to liquefy the gel sample. The liquified sample drops off from the hole, which is analyzed to obtain the drop point dataset. Measurements were performed at least 6 times for a gel, and an average was taken to determine T_{drop} with an accuracy of $\pm 1.5 \text{ }^\circ\text{C}$, typically.

DTA

We use a home-built calorimeter for the differential thermal analysis (DTA). We monitor the temperature difference between the sample and reference by using a chromel-constantan thermocouple. In our measurements, the thermo-electro motive force was monitored by means of a nanovoltmeter (Keithley 2182A), where temperature was administrated with a temperature controller (Chino KP1000). When heating the system, we raised temperature with a rate of 3 K min^{-1} using a controller. Otherwise, the cooling process was conducted by air.

In the measurements, 1 cm^3 of the sample gel was loaded into a glass tube having a diameter of 8 mm. We froze the sample tube at the liquid nitrogen temperature, and enclosed the system by glasswork under an atmosphere of an inert gas: helium.

Figs. S1a–b demonstrate equipment and diagrams of T_{drop} and DTA measurements.

(a)

a1



a2



a3



Fig. S1a. Pictures of Mettler-Toledo DP 70 Drop Point system for T_{drop} measurements. (a1) System overview. (a2) A sample cup, where a hole is made in the bottom. Left: side view, right: top view. (a3) An adapter to hold the sample cup. The red arrow indicates the position where the cup is placed.

(b)

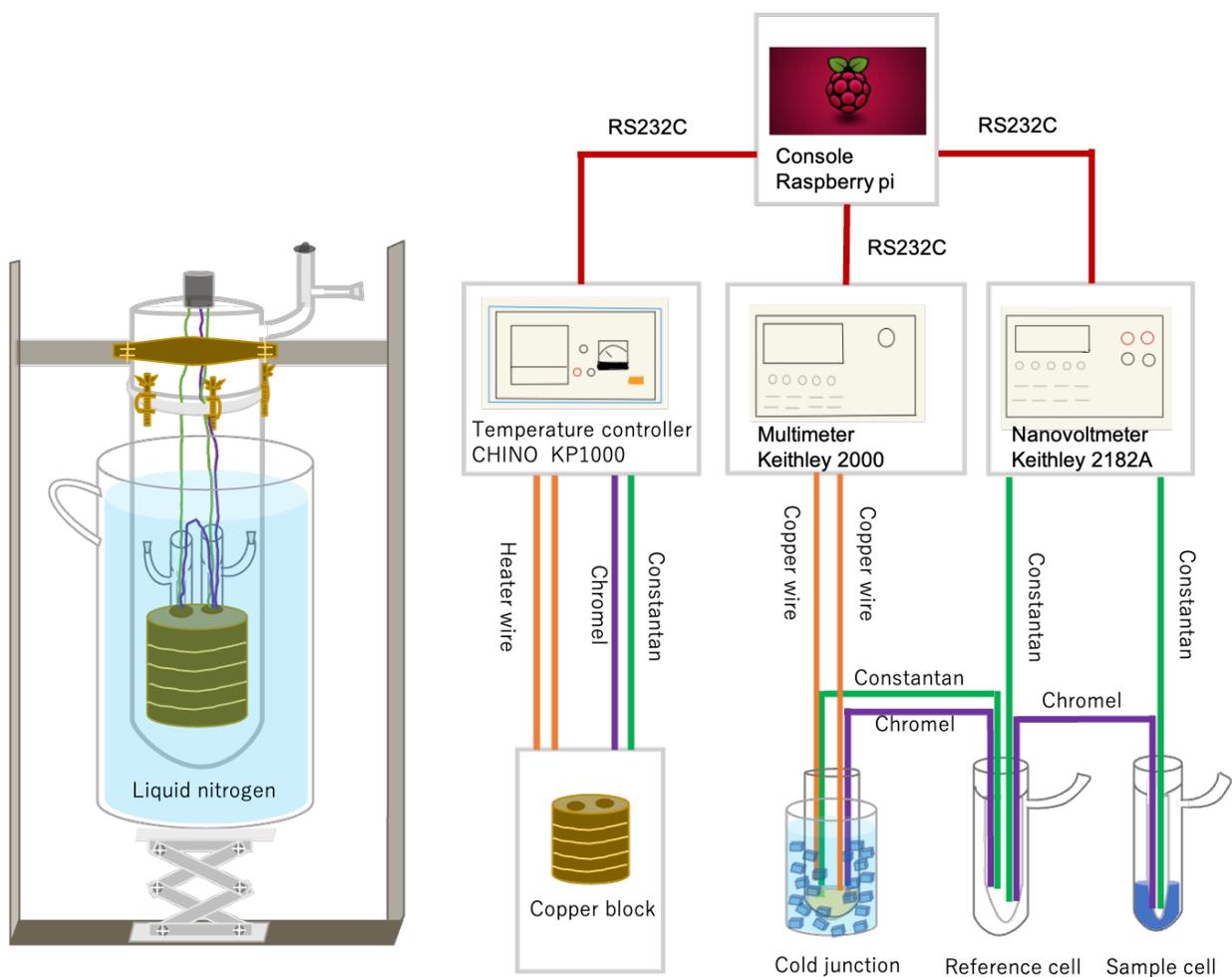


Fig. S1b. Schematic diagram for home-built DTA equipment we used in this study. Left: A schematic image of the external view of the DTA apparatus. Right: a schematic diagram of the inter-instrument connections.

§S3. Data analyses with HSPs

A package of Hansen solubility parameters were purchased from their website⁷ and we use the version 5.0.03 package. Some of Hansen solubility parameters for gelators and solvents are already preset in the package. If we cannot find the parameter for a substance, we input a molecular structure using SMILES (simplified molecular input line entry system) into the package to obtain the adequate parameters. We acquire a dataset ($2\delta D$, δH , δP) for a substance from the software, being processed for further analyses.

We note that all the parameters ($2\delta D$, δH , δP) particularly for gelators were obtained from the SMILES input. In the present study, we employ the parameters as given from the software package.

§S4. *k*-Fold cross validation for plots in Analyses I–V

4–1. Procedure

In this subsection we further analyze the plots in Analyses I–V (Fig. 1), using *k*-fold cross validation.⁸ This detailed analysis ensures applicability of the linear fitting drawn in Fig. 1.

We use the algorithm of cross validation as follows. From the R_a – T_{drop} data-sets, we randomly remove a solvent from each solvent group: aromatics, acyclic alkanes, cyclic alkanes, cyclic alkenes. Eventually, data-sets with 4 solvents are removed. As we used 23 solvents totally, 19 solvents are left for further analysis. The correlation of the R_a – T_{drop} data-sets in 19 solvents are fit linearly, and the slope and intercept of the line are determined.

We iterated this procedure for 5 times (5-fold), and obtained an averaged value of the slope and intercept. The averaged value is then compared with the "original" fitting result using the all 23 solvents.

4–2. Results

Table S3. Solvent choices for 5-Fold cross validation for linear fitting drawn in Fig. 1

No.	Solvent groups	Solvents	Run ⁽¹⁾				
			1	2	3	4	5
1	I aromatics	benzene	1	1	0	1	0
2		butylbenzene	1	1	1	1	1
3		toluene	1	0	1	1	1
4		4- <i>tert</i> -butyltoluene	1	1	1	1	1
5		<i>o</i> -xylene	0	1	1	1	1
6		<i>m</i> -xylene	1	1	1	0	1
7		<i>p</i> -xylene	1	1	1	1	1
8		mesitylene	1	1	1	1	1
9	II acyclic alkanes (hydrocarbons)	hexane	1	1	0	1	1
10		heptane	1	1	1	1	1
11		decane	1	0	1	1	1
12		undecane	0	1	1	1	0
13		2,2,4-trimethylpentane	1	1	1	0	1
14	III perhaloalkane	carbon tetrachloride ⁽²⁾	1	1	1	1	1
15	IV cyclic alkanes	cyclopentane	1	1	1	1	1
16		cyclohexane	1	0	1	1	1
17		methylcyclohexane	1	1	1	0	0
18		ethylcyclohexane	1	1	0	1	1
19		cycloheptane	0	1	1	1	1
20	V acyclic alkene	2-ethyl-1-butene ⁽²⁾	1	1	1	1	1
21	VI cyclic alkanes	cyclopentene	1	0	1	1	1
22		cyclohexene	1	1	1	0	0
23		cyclooctene	0	1	0	1	1

⁽¹⁾ In each run, a solvent is removed from solvent groups I, II, IV, and VI. Tags “0” and “1” are the solvent “removed” and “used” for analysis, respectively. The “0” solvents were chosen with a random number generator.

⁽²⁾ Solvents which are always used for analysis, because a single solvent is in the groups III and V.

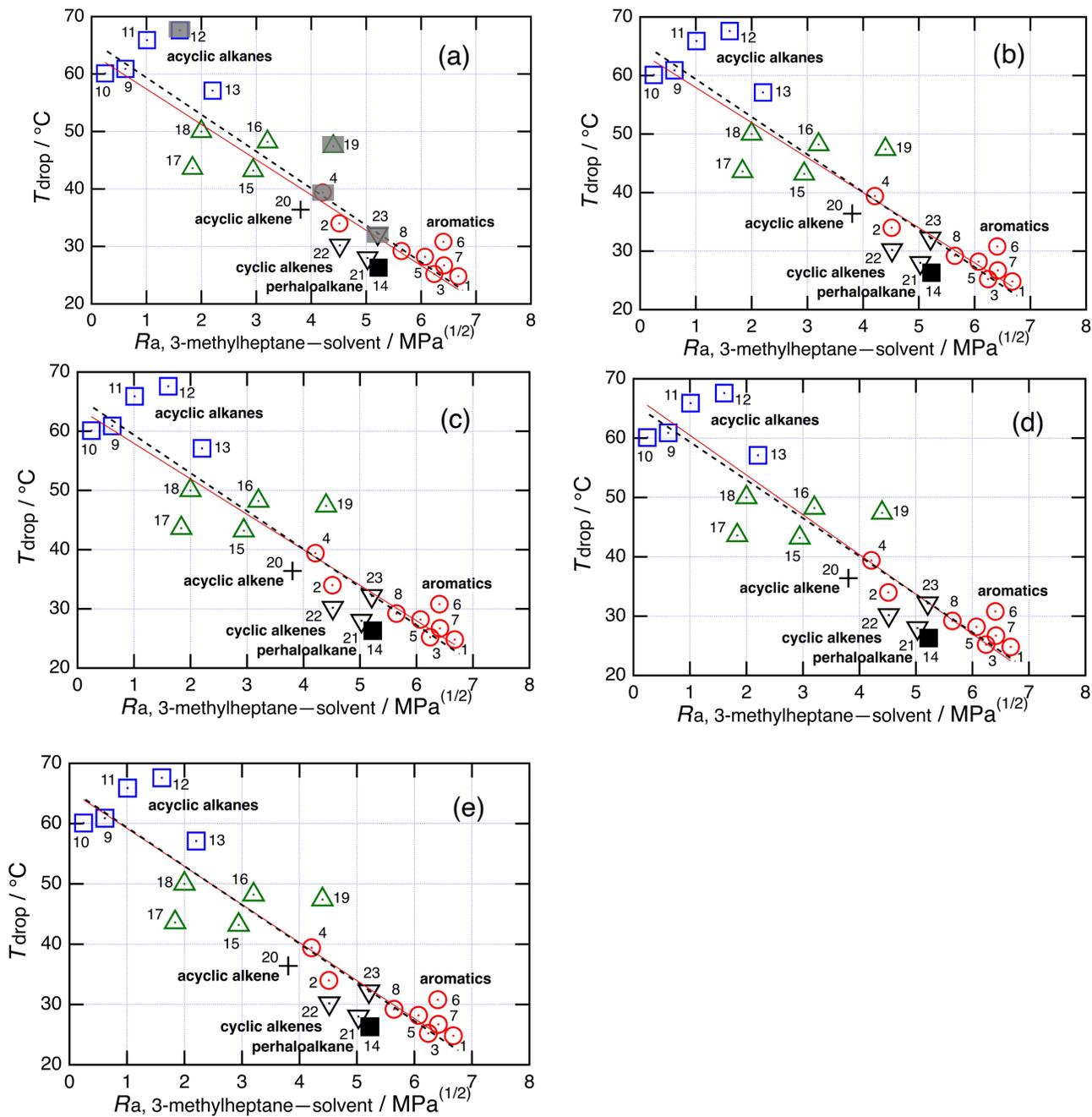


Fig. S2. Results for 5-fold cross validation for the $T_{\text{drop}}-R_a$ relation. The black dotted line stands for the fitting line where all the data-sets is employed. Panels a–e mean runs 1–5, respectively, in this analysis. In Panel a, as guide to eye, 4 data sets which were *not* employed for fitting (“0” solvents in Table S3) are shaded by gray color. The new fitting line after the solvent removal is shown in red. The detailed solvent data-sets in Panels b–e are shown in Table S3.

§S5. Schematic diagram of organogel breakdown with increasing temperature

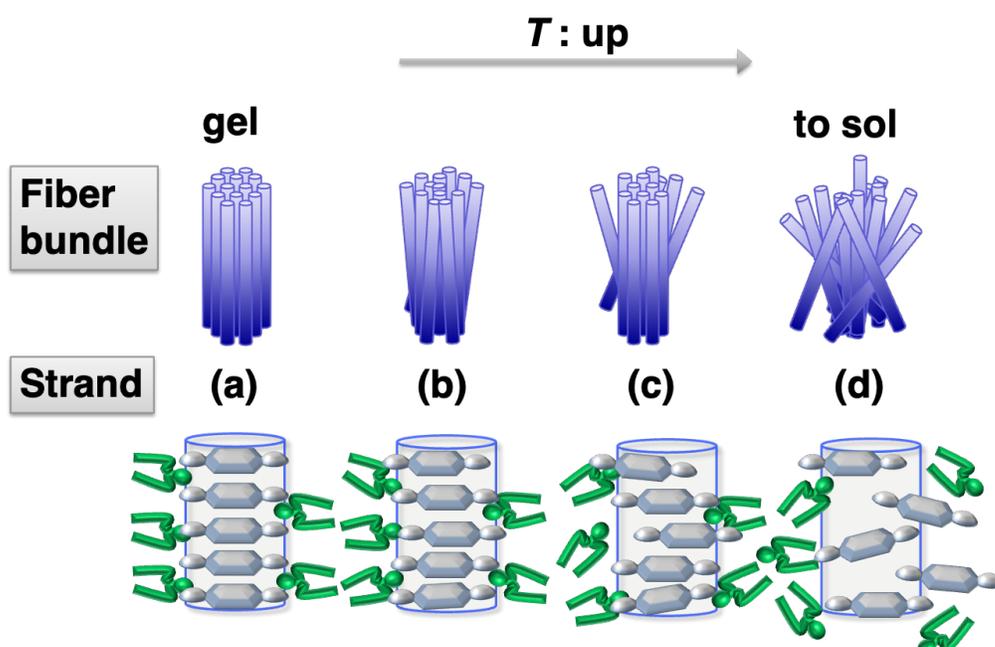


Fig. S3. A schematic diagram of gel–sol transition with heat, suggested by T_{drop} and DTA measurements. See Table S3 for details of States a–d. A part of the mechanisms above are found in the previous study.⁹

Table S4. Details of Phases a–d proposed in Fig. S2

State	$T / ^\circ\text{C}^{(1)}$	Measurements where applicable	Details
a	Room temperature	—	Gel state. The strand and fiber bundle are well organized
b	54.3	DTA	Some exterior of the fiber bundles peels off. But T_{drop} cannot be sensed as they have a sufficient organized strand structure
c	57.1	T_{drop}	T_{drop} is sensed with a more destroyed fiber bundle, but still some memories are in the strand
d	64.0	DTA	Toward sol state. Both of the fiber bundle and strand completely collapse above this temperature

⁽¹⁾For organogel in 2,2,4-trimethylpentane, as a typical.

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