Organogel formation rationalized by Hansen solubility parameters: dos and don'ts

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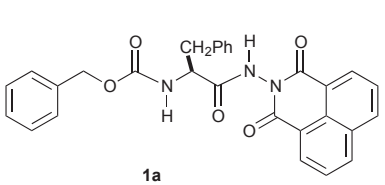
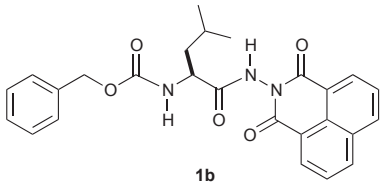
ELECTRONIC SUPPLEMENTARY INFORMATION

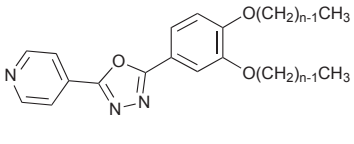
Formula of the LMWGs mentioned in this report:



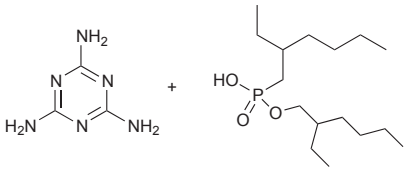
1a



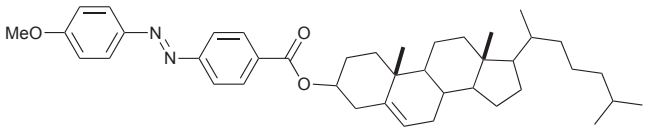
1b



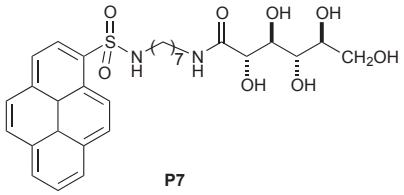
4-POXD-B8 (n= 8)
4-POXD-B12 (n = 12)



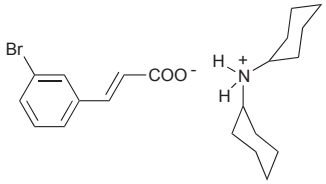
two-component LMWG



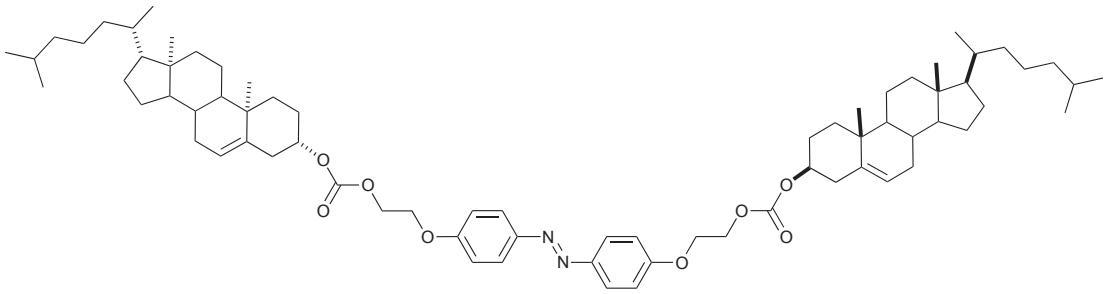
2Me



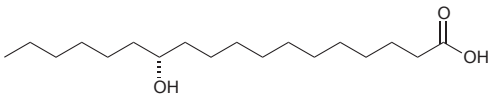
P7



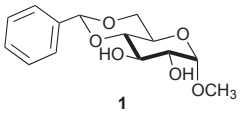
3-BrCIN



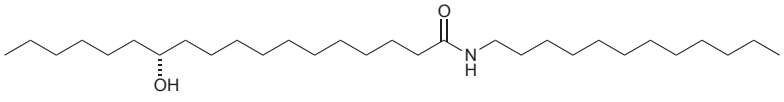
DCAZO2



12-hydroxystearic acid (12-HSA)



1



C12

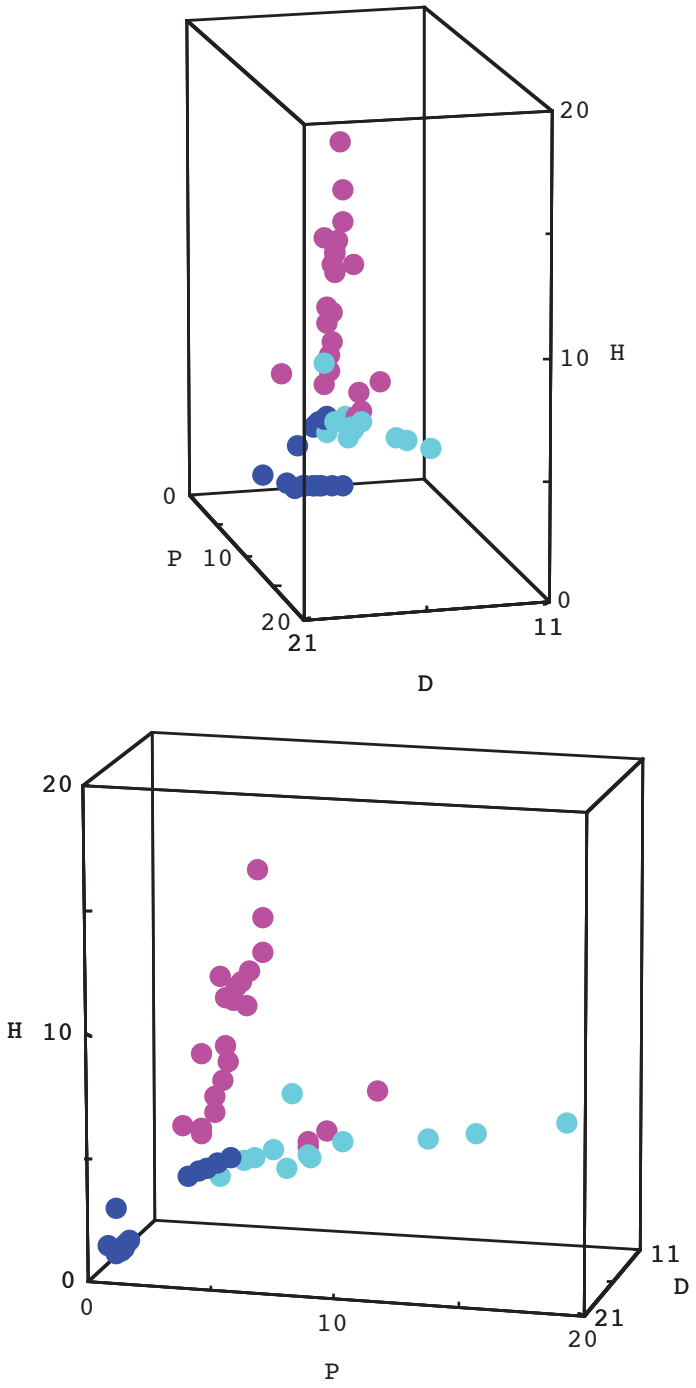


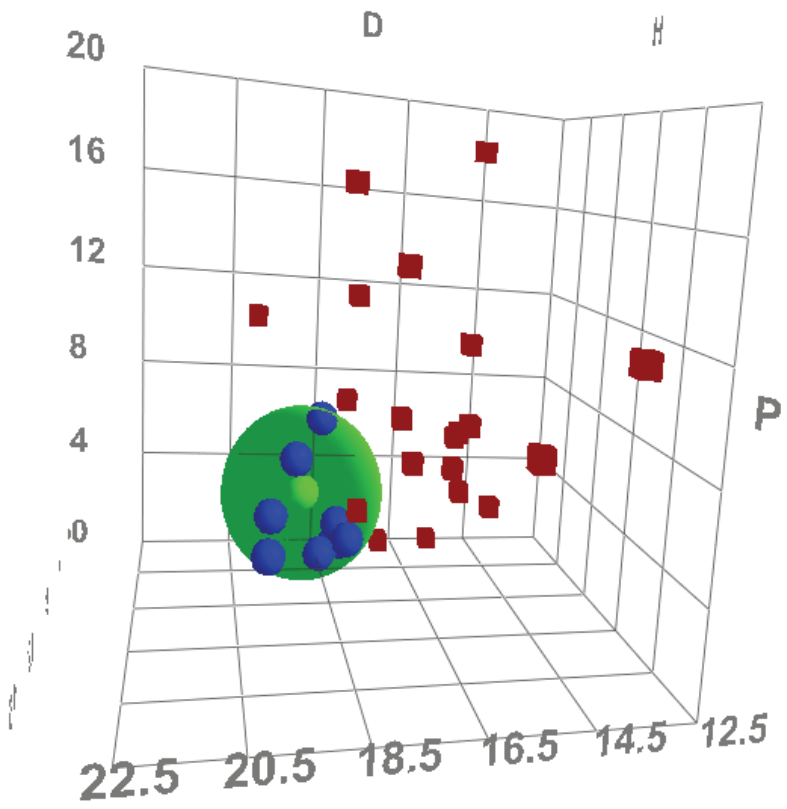
Fig. S1 Solubility data from Rogers *et al*.[1-3] for 12-hydroxystearic acid LMWG (12-HSA), represented in Hansen space. The same data as in Fig. 5 is plotted according to the following colour code. The good solvents (S) are represented by magenta points. The gelated liquids (G) are represented either in blue: gels with a hexagonal packing of 12-HSA (gels in alkanes, alkanethiols and CCl_4); or in cyan: gels with a triclinic packing (gels in nitriles, aldehydes, ketones and dichloromethane). *Each polymorph apparently corresponds to a distinct gelation domain*.

The solubility data from Jamart-Grégoire et al.[4] for amino acid based LMWGs **1a** and **1b** have been plotted in Fig. S2 according to the values of Hansen solubility parameters collected in Table S1.

Table S1 Hansen solubility parameters.[5,6]

Liquid	δ_d^s ($MPa^{1/2}$)	δ_p^s ($MPa^{1/2}$)	δ_h^s ($MPa^{1/2}$)
Acetone	15.5	10.4	7
Acetonitrile	15.3	18	6.1
Benzene	18.4	0	2
Carbon Tetrachloride	17.8	0	0.6
Chlorobenzene	19	4.3	2
Chloroform	17.8	3.1	5.7
Cyclohexane	16.8	0	0.2
Cyclopentanone	17.9	11.9	5.2
p-Diethyl Benzene	18	0	0.6
Diethyl Ether	14.5	2.9	4.6
Dimethyl Formamide (DMF)	17.4	13.7	11.3
Dimethyl Sulfoxide (DMSO)	18.4	16.4	10.2
Ethanol	15.8	8.8	19.4
Ethyl Acetate	15.8	5.3	7.2
Ethyl Benzene	17.8	0.6	1.4
Ethyl Propionate	15.5	6.1	4.9
Methanol	14.7	12.3	22.3
Methyl Acetate	15.5	7.2	7.6
Methyl Isobutyl Ketone (MIBK)	15.3	6.1	4.1
1-Methyl Naphthalene	19.7	0.8	4.7
Nitrobenzene	20	10.6	3.1
Octane	15.5	0	0
Tetrachloroethylene	18.3	5.7	0
Tetrahydrofuran (THF)	16.8	5.7	8
Toluene	18	1.4	2
p-Xylene	17.8	1	3.1
1,2-Diethyl Benzene	17.7	0.1	1
Tetrahydronaphthalene	19.6	2	2.9
Isopropyl Ether	15.1	3.2	3.2
Methylene Dichloride (Dichloromethane)	17	7.3	7.1
Ethylene Dichloride	18	7.4	4.1
Water	15.5	16	42.3

a)

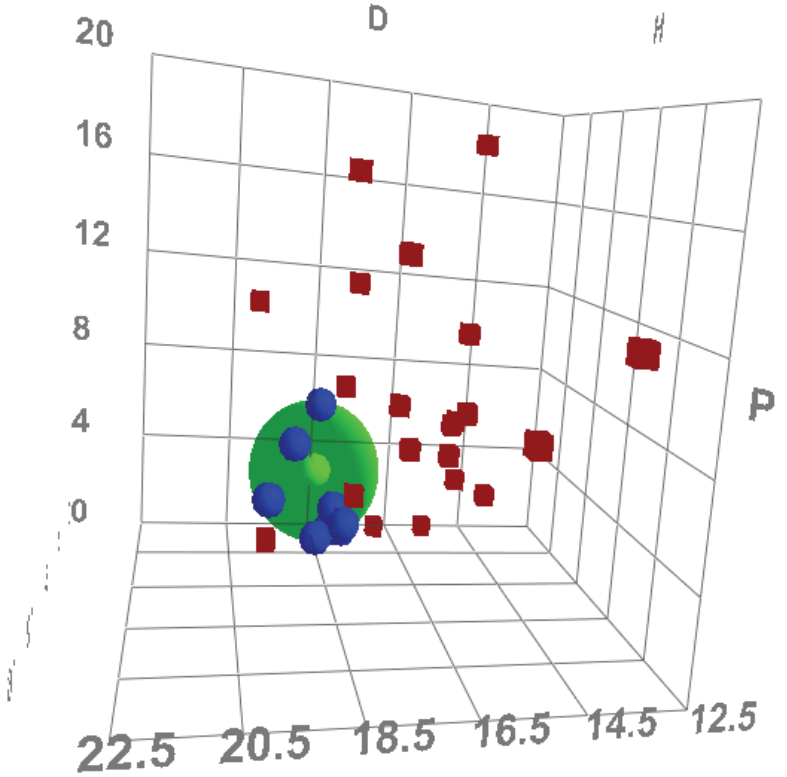


Gelation sphere :

centre
δ_d = 18.8 MPa$^{1/2}$
δ_p = 2.8 MPa$^{1/2}$
δ_h = 2.1 MPa$^{1/2}$

radius
R = 3.8 MPa$^{1/2}$

b)



Gelation sphere :

centre
δ_d = 18.4 MPa$^{1/2}$
δ_p = 2.8 MPa$^{1/2}$
δ_h = 0.9 MPa$^{1/2}$

radius
R = 3.2 MPa$^{1/2}$

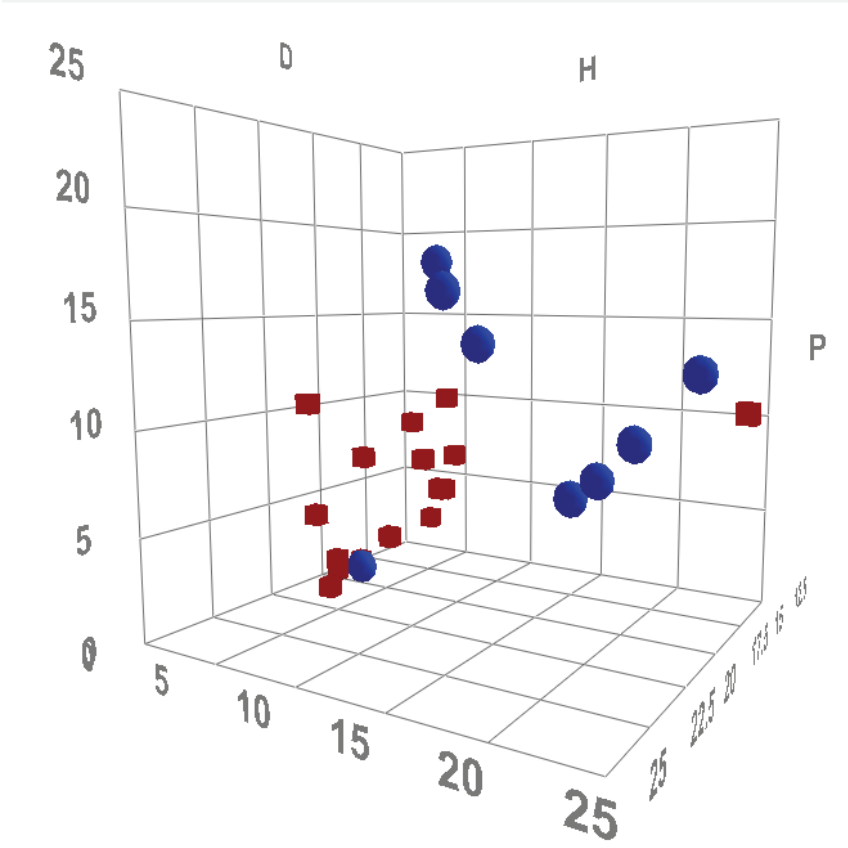
Fig. S2 Solubility data from Jamart-Grégoire et al.[4] for amino acid based LMWGs **1a** (a) and **1b** (b) (5g/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. The gelation sphere is green and its centre is light green. The plots are generated with the HSPiP software.[5,6]

The solubility data from Li et al.[7] for oxadiazole based LMWGs **4-POXD-B8** and **4-POXD-B12** have been plotted in Fig. S3 according to the values of Hansen solubility parameters collected in Table S2. Methylcyclohexane is an outlier both in this representation and in the original representation proposed by Li et al.[7]

Table S2 Hansen solubility parameters.[5,6]

Liquid	δ_d^s $(\mathrm{MPa}^{1/2})$	δ_p^s $(\mathrm{MPa}^{1/2})$	δ_h^s $(\mathrm{MPa}^{1/2})$
Acetone	15.5	10.4	7
Acetonitrile	15.3	18	6.1
Benzene	18.4	0	2
1-Butanol	16	5.7	15.8
Chlorobenzene	19	4.3	2
Chloroform	17.8	3.1	5.7
Cyclohexane	16.8	0	0.2
Diethyl Ether	14.5	2.9	4.6
Dimethyl Formamide (DMF)	17.4	13.7	11.3
Dimethyl Sulfoxide (DMSO)	18.4	16.4	10.2
Ethanol	15.8	8.8	19.4
Ethyl Acetate	15.8	5.3	7.2
Ethylene Dichloride	18	7.4	4.1
Ethylene Glycol	17	11	26
Heptane	15.3	0	0
Methanol	14.7	12.3	22.3
Methyl Acetate	15.5	7.2	7.6
Methyl Cyclohexane	16	0	1
Methylene Dichloride (Dichloromethane)	17	7.3	7.1
Methyl Ethyl Ketone (MEK)	16	9	5.1
Nitrobenzene	20	10.6	3.1
1-Propanol	16	6.8	17.4
Tetrahydrofuran (THF)	16.8	5.7	8
Toluene	18	1.4	2

a)



b)

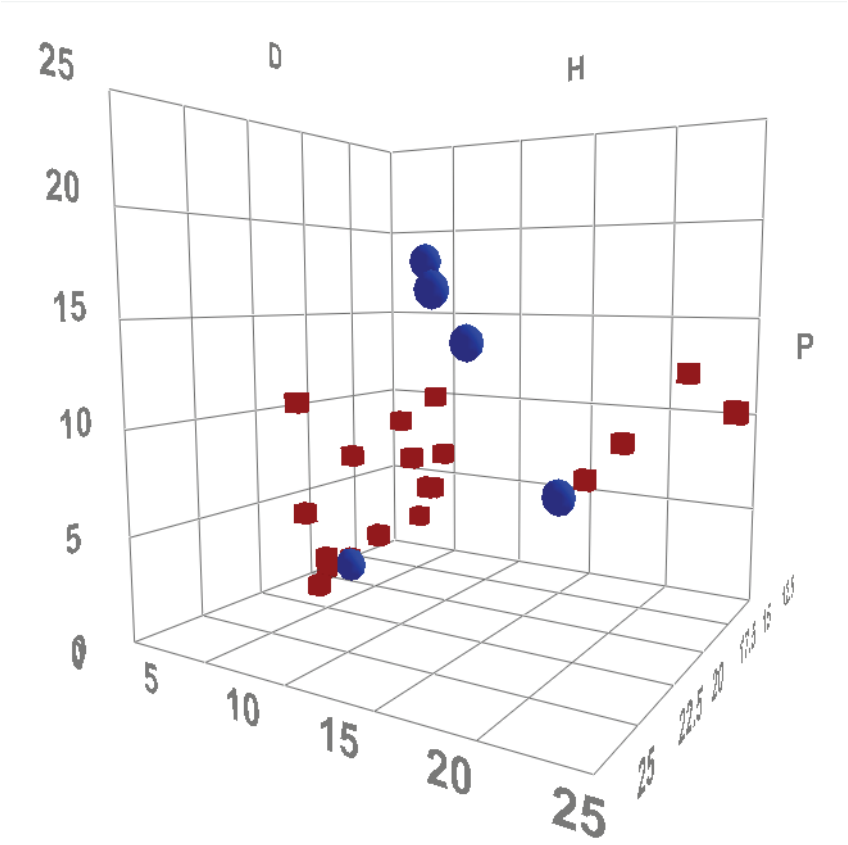
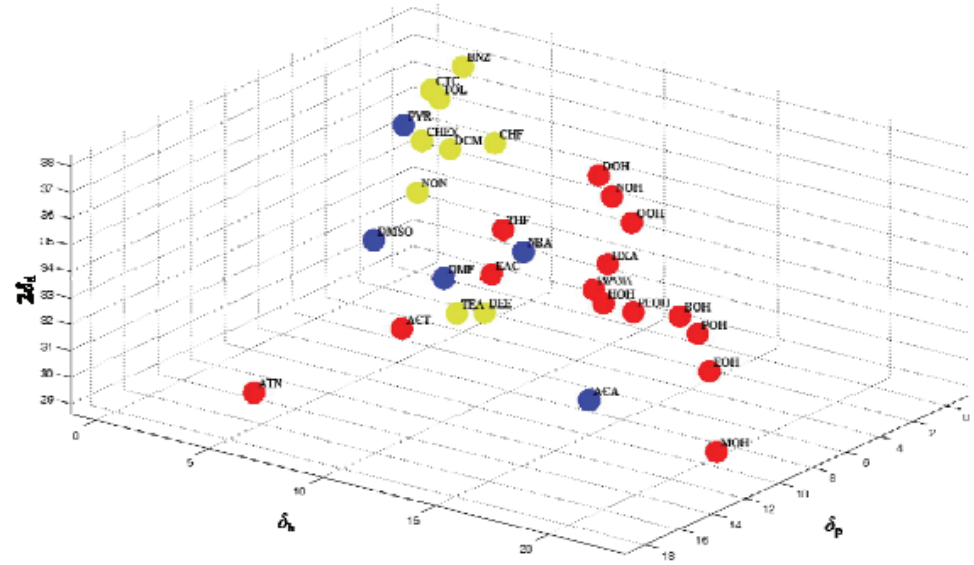


Fig. S3 Solubility data from Li et al.[7] for oxadiazole based LMWGs **4-POXD-B8** (a) and **4-POXD-B12** (b) (0.055mol/L), represented in Hansen space. The gelated liquids (G) are represented by blue points; both good solvents (S) and non-solvents (I) are represented by red points. The plots are generated with the HSPiP software.[5,6]

a)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CTC
TOL
PYR
CHEX
DCM
CHF
NON
DOH
BUH
OOH
THF
DMSO
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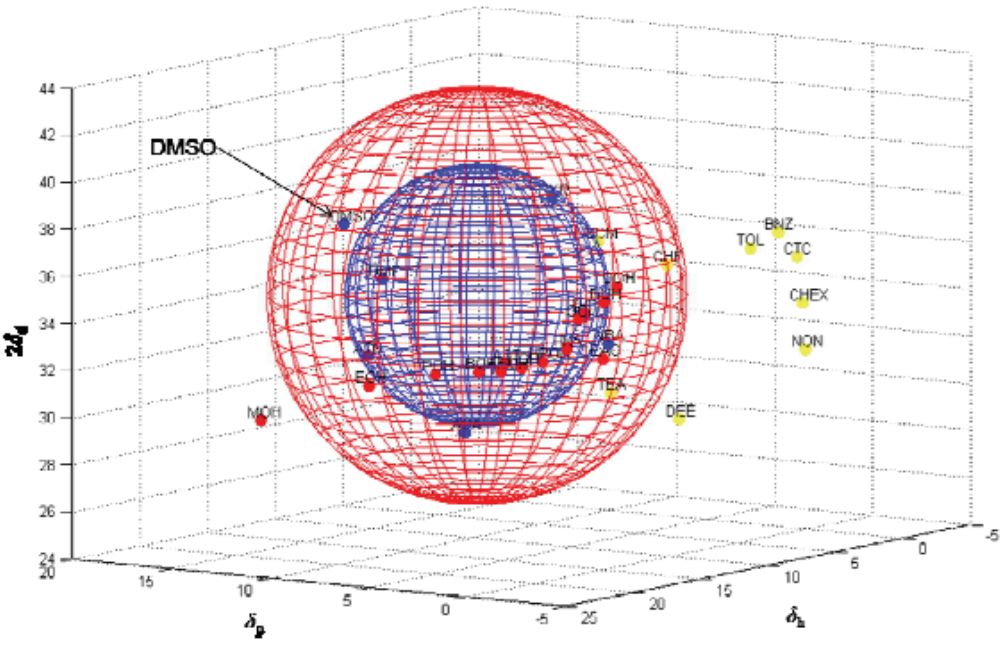
TEA
DEE
ACT
ATN
MCA
MOH
δ_d
δ_h
δ_p

b)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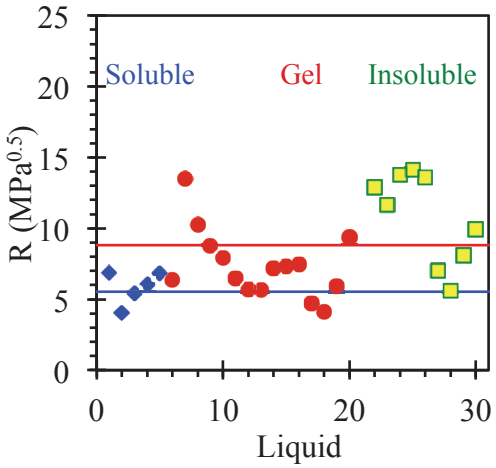
CTC
CHF
CHEX
NON
DEE
MOH
δ_d
δ_p
δ_h

c)



d)

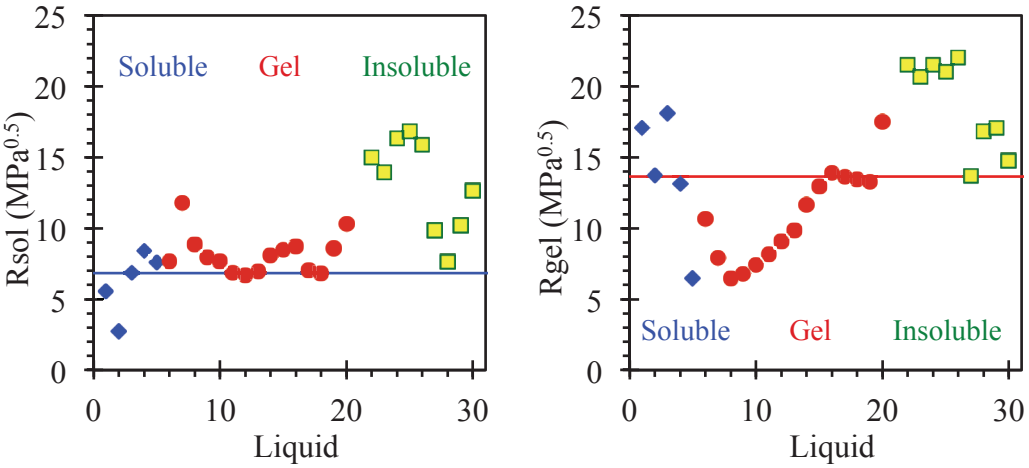


Fig. S4 Solubility data from Weiss et al.[8] for glucono-pyrenyl based LMWG **P7**, represented in Hansen space. The gelated liquids (G) are represented by red points; good solvents (S) by blue points and non-solvents (I) by yellow points. (a) Raw data. (b) Same data superimposed with concentric solubility and gelation spheres, as proposed in Figure S23 of the original publication.[8] (c) Distances calculated from the centre of the concentric spheres (δ_d = 17.1 MPa$^{1/2}$, δ_p = 10.08 MPa$^{1/2}$, δ_h = 9.58 MPa$^{1/2}$, R_{sol} = 5.53 MPa$^{1/2}$, R_{gel} = 8.79 MPa$^{1/2}$): *the correlation is poor (11 points out of 30 are outliers)*. (d) Distances calculated from the centres of two independent spheres: left: solubility sphere (centre δ_d = 17.8 MPa$^{1/2}$, δ_p = 11.2 MPa$^{1/2}$, δ_h = 11.9 MPa$^{1/2}$, radius R = 6.8 MPa$^{1/2}$) and right: gelation sphere (centre δ_d = 12.7 MPa$^{1/2}$, δ_p = 7.1 MPa$^{1/2}$, δ_h = 18.8 MPa$^{1/2}$, radius R = 13.6 MPa$^{1/2}$): *the correlation is slightly better (8 outliers). More data points are required to discriminate the two models*.

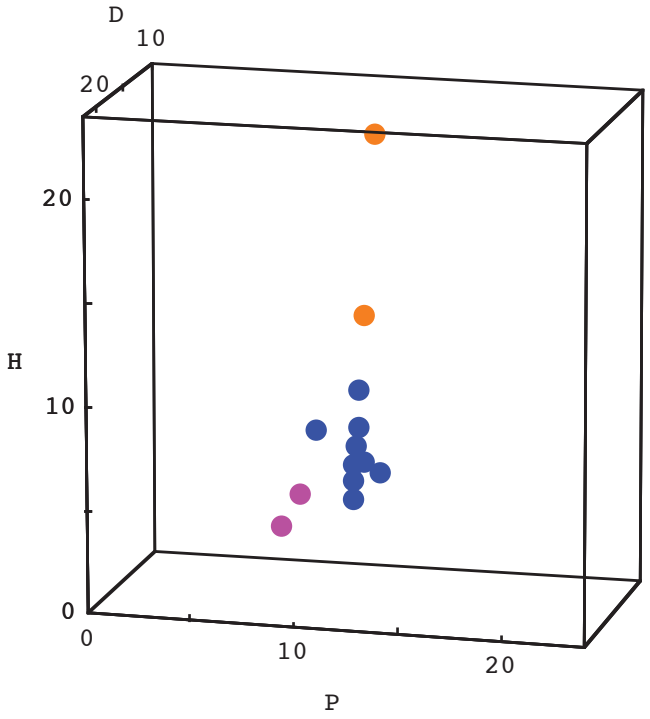


Fig. S5 Solubility data from Zhang et al.[9] for dicholesterol-linked azobenzene based LMWG **DCAZO2**, represented in Hansen space. The gelated liquids (G) are represented by blue points; good solvents (S) by magenta points and non-solvents (I) by orange points. The authors assume in their publication that the solubility and gelation domains share the same centre. *Additional data points would be required to validate this assumption*.

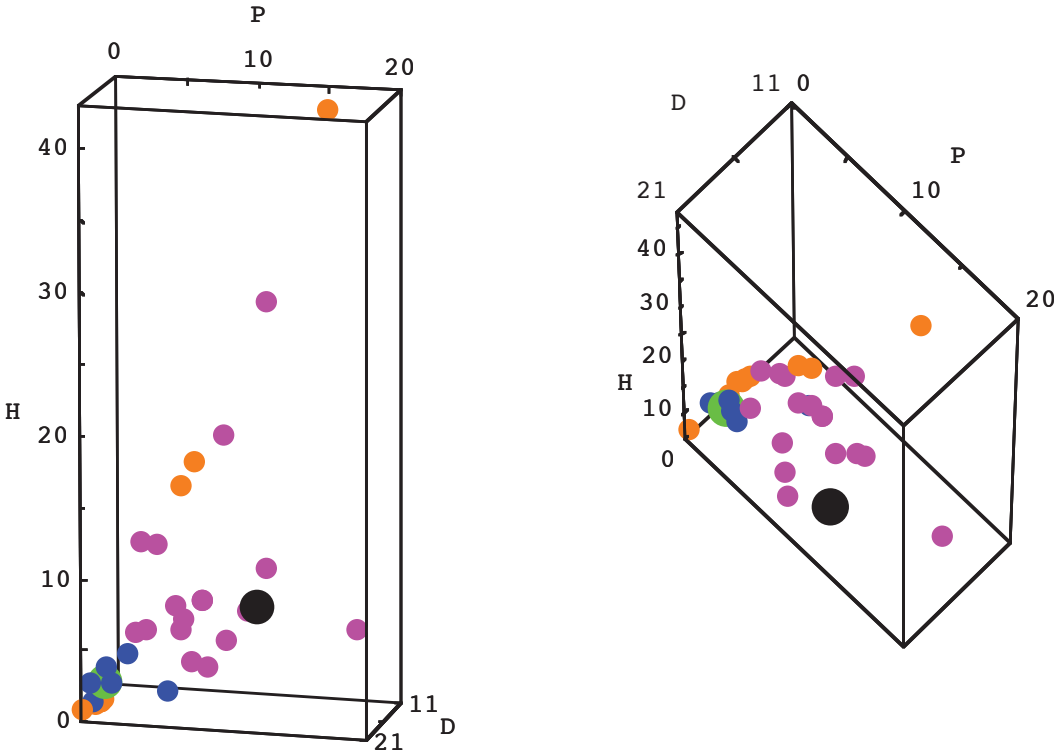


Fig. S6 Solubility data from Shinkai et al.[10] for glucose based LMWG **1** represented in Hansen space. Blue: gel; magenta: soluble; orange: insoluble. The black point represents the coordinates calculated with a group contribution method[11] for the gelator (LMWG **1**: δ_d = 19.6, δ_p = 12.0, δ_h = 8.4 MPa$^{1/2}$): *this point is far from the gelation domain (it is actually in the solubility domain)*. The green point is the centre of the gelation sphere determined by the present method (LMWG **1**: δ_d = 18.0, δ_p = 1.0, δ_h = 2.0 MPa$^{1/2}$).[12]

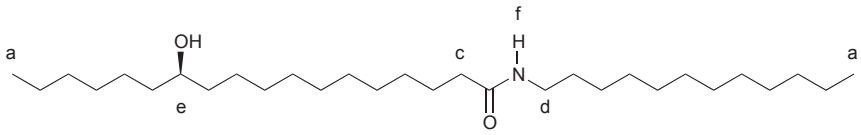


Fig. S7 Structure of hydroxystearic amide LMWG **C12**.

The synthesis of **C12** was adapted from reference 13:
12-hydroxystearic acid (**12-HSA**) was recrystallized according to reference 10 (mp 78.6 °C). To a cooled (at -5 °C) and stirred solution of ethyl chloroformate (2 mL, 21 mmol) in dry THF (50 mL) was added slowly a solution of **12-HSA** (6.43 g, 21 mmol) and triethylamine (3 mL, 21 mmol) in dry THF (50 mL) while maintaining the temperature at -5 °C. The mixture was stirred for an additional 40 min. Dodecylamine (4.36 g, 24 mmol) in 50 mL dry THF was added to the vigorously stirred solution at -5 °C, and the reaction mixture was kept at room temperature for 24 h. The solvent was removed under vacuum and the residue was washed successively with ethyl acetate (200 mL), 3N HCl (150 mL), aqueous 1M Na_2CO_3 (200 mL), water (250 mL) and diethylether (200 mL). The residue was dried under vacuum. A white powder (7.64 g, 76%) was obtained.

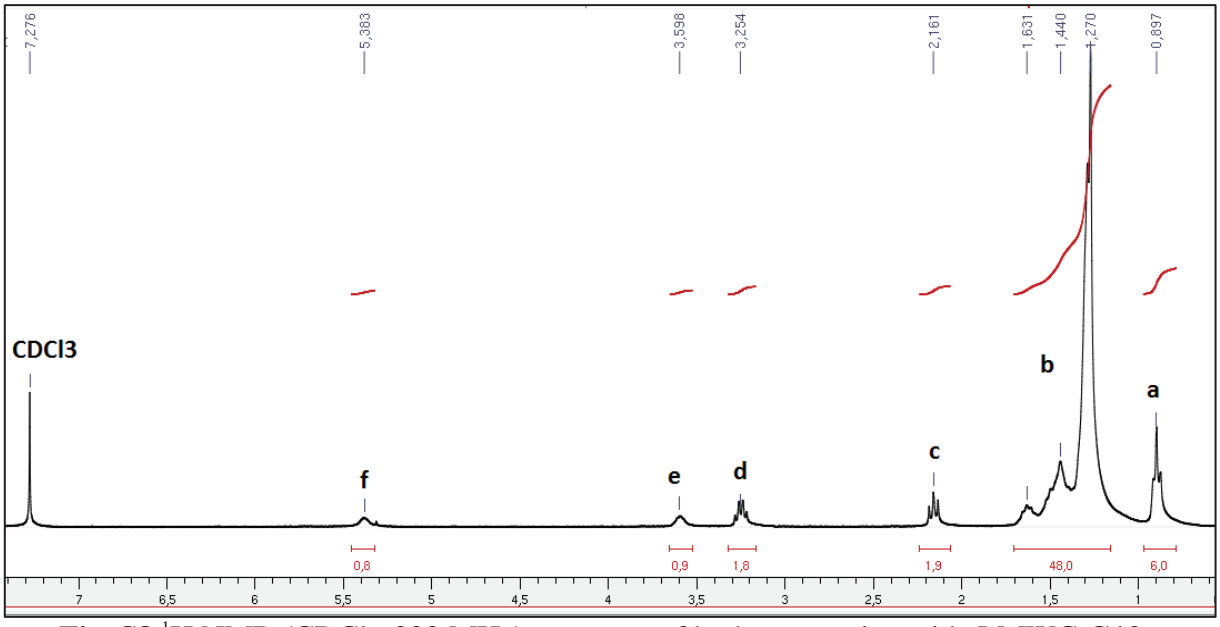


Fig. S8 ^{1}H NMR ($CDCl_3$, 200 MHz) spectrum of hydroxystearic amide LMWG **C12**.

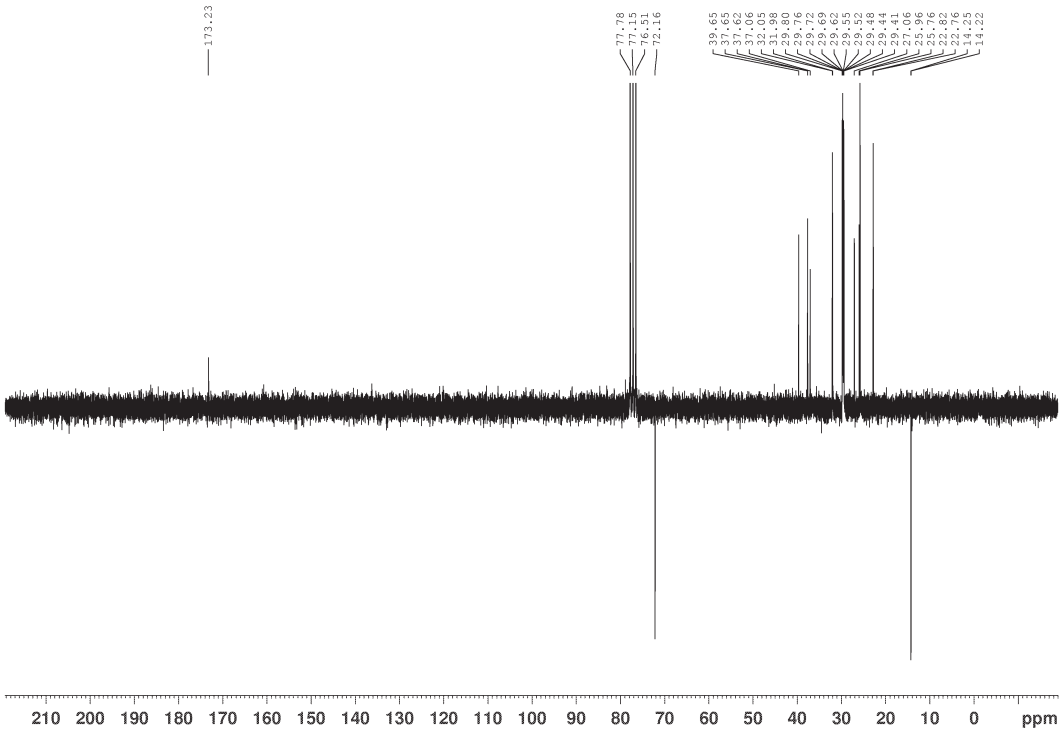


Fig. S9 ^{13}C NMR ($CDCl_3$, 200 MHz) spectrum of hydroxystearic amide LMWG **C12**.

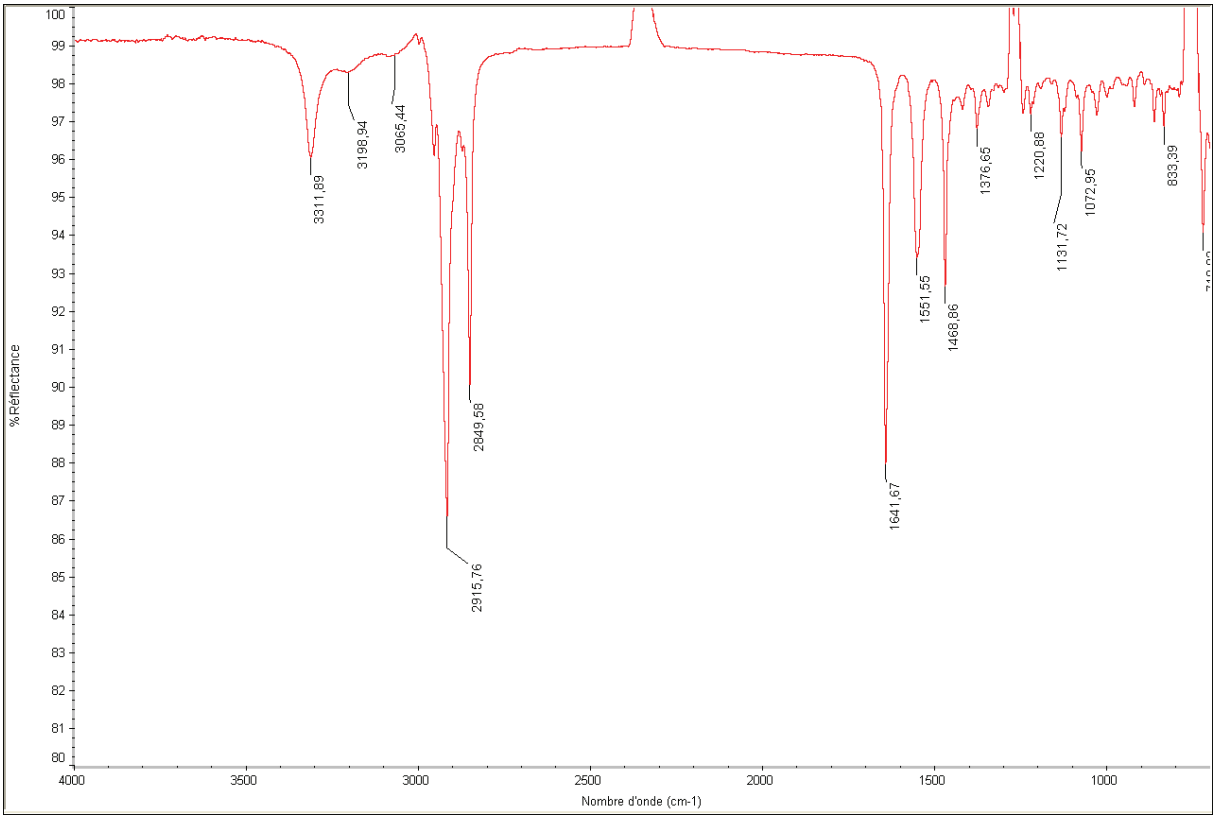


Fig. S10 FTIR spectrum of hydroxystearic amide LMWG **C12**.

Table S3 Gelation tests for hydroxystearic amide LMWG **C12**. First step: pure liquids.[a]

Liquid	Appearance[b]	δ_d^s ($MPa^{1/2}$)	δ_p^s ($MPa^{1/2}$)	δ_h^s ($MPa^{1/2}$)
Acetonitrile	I	15.3	18	6.1
Benzyl Alcohol	S	18.4	6.3	13.7
1-Butanol	S	16	5.7	15.8
t-Butyl Acetate	G	15	3.7	6
1-Chloropentane	G	16	6.9	1.9
Chlorobenzene	G	19	4.3	2
Cyclohexane	G	16.8	0	0.2
Cyclohexanone	G	17.8	8.4	5.1
Diacetone Alcohol	S	15.8	8.2	10.8
Dimethyl Formamide (DMF)	S	17.4	13.7	11.3
Dimethyl Sulfoxide (DMSO)	S	18.4	16.4	10.2
1,4-Dioxane	G	17.5	1.8	9
Ethanolamine	S	17	15.5	21
Hexadecane	G	16.3	0	0
Methanol	I	14.7	12.3	22.3
Methyl Ethyl Ketone (MEK)	G	16	9	5.1
N,N-Diethyl Acetamide	S	16.4	11.3	7.5
Propylene Carbonate	I	20	18	4.1
Propylene Glycol	S	16.8	10.4	21.3
Toluene	G	18	1.4	2
Water	I	15.5	16	42.3

[a] Gelation is tested by introducing 20 mg of gelator and 1 mL of liquid in a screw-cap vial, heating until dissolution and leaving the vial to cool on the bench.

[b] G: gel; S: soluble; I: insoluble or formation of a precipitate after cooling.

Table S4 Gelation tests for hydroxystearic amide LMWG **C12**. Second step: mixtures.[a]

Liquid 1	Liquid 2	Composition	Appearance[b]	δ_d^s (MPa$^{1/2}$)	δ_p^s (MPa$^{1/2}$)	δ_h^s (MPa$^{1/2}$)
1-Chloropentane	DMSO	0/100	S	18.4	16.4	10.2
		20/80	S	17.92	14.5	8.54
		40/60	I	17.44	12.6	6.88
		60/40	I	16.96	10.7	5.22
		80/20	G	16.48	8.8	3.56
		100/0	G	16	6.9	1.9
Cyclohexanone	Benzyl Alcohol	0/100	S	18.4	6.3	13.7
		20/80	S	18.28	6.72	11.98
		40/60	S	18.16	7.14	10.26
		60/40	S	18.04	7.56	8.54
		80/20	I	17.92	7.98	6.82
		100/0	G	17.8	8.4	5.1
Cyclohexanone	Butanol	0/100	S	16	5.7	15.8
		20/80	S	16.36	6.24	13.66
		40/60	S	16.72	6.78	11.52
		60/40	S	17.08	7.32	9.38
		80/20	I	17.44	7.86	7.24
		100/0	G	17.8	8.4	5.1
Cyclohexanone	Ethanolamine	0/100	S	17	15.5	21
		20/80	S	17.16	14.08	17.82
		40/60	S	17.32	12.66	14.64
		60/40	I	17.48	11.24	11.46
		80/20	I	17.64	9.82	8.28
		100/0	G	17.8	8.4	5.1
MEK	DMSO	0/100	S	18.4	16.4	10.2
		20/80	I	17.92	14.92	9.18
		40/60	I	17.44	13.44	8.16
		60/40	I	16.96	11.96	7.14
		80/20	I	16.48	10.48	6.12
		100/0	G	16	9	5.1
MEK	Propylene Carbonate	0/100	I	20	18	4.1
		20/80	I	19.2	16.2	4.3
		40/60	I	18.4	14.4	4.5
		60/40	I	17.6	12.6	4.7
		80/20	G	16.8	10.8	4.9
		100/0	G	16	9	5.1
Propylene Carbonate	t-Butyl Acetate	0/100	G	15	3.7	6
		20/80	G	16	6.56	5.62
		40/60	G	17	9.42	5.24
		60/40	I	18	12.28	4.86
		80/20	I	19	15.14	4.48
		100/0	I	20	18	4.1
Propylene Carbonate	Toluene	0/100	G	18	1.4	2
		20/80	G	18.4	4.72	2.42
		40/60	G	18.8	8.04	2.84
		60/40	G	19.2	11.36	3.26
		80/20	I	19.6	14.68	3.68
		100/0	I	20	18	4.1

Toluene	Benzyl Alcohol	0/100	S	18.4	6.3	13.7
		20/80	S	18.32	5.32	11.36
		40/60	S	18.24	4.34	9.02
		60/40	S	18.16	3.36	6.68
		80/20	S	18.08	2.38	4.34
		100/0	G	18	1.4	2
Toluene	Butanol	0/100	S	16	5.7	15.8
		20/80	S	16.4	4.84	13.04
		40/60	S	16.8	3.98	10.28
		60/40	S	17.2	3.12	7.52
		80/20	S	17.6	2.26	4.76
		100/0	G	18	1.4	2
Toluene	Diacetone Alcohol	0/100	S	15.8	8.2	10.8
		20/80	I	16.24	6.84	9.04
		40/60	G	16.68	5.48	7.28
		60/40	G	17.12	4.12	5.52
		80/20	G	17.56	2.76	3.76
		100/0	G	18	1.4	2

[a] Gelation is tested by introducing 20 mg of gelator and 1 mL of liquid in a screw-cap vial, heating until dissolution and leaving the vial to cool on the bench.
[b] G: gel; S: soluble; I: insoluble or formation of a precipitate after cooling.

REFERENCES

1. J. Gao, S. Wu and M. A. Rogers, *J. Mater. Chem.*, 2012, **22**, 12651.
2. S. Wu, J. Gao, T. J. Emge and M. A. Rogers, *Soft Matter*, 2013, **9**, 5942.
3. S. Wu, J. Gao, T. J. Emge and M. A. Rogers, *Cryst. Growth Des.*, 2013, **13**, 1360.
4. P. Curcio, F. Allix, G. Pickaert and B. Jamart-Grégoire, *Chem. Eur. J.*, 2011, **17**, 13603.
5. C. M. Hansen, Hansen Solubility Parameters: A User's Handbook 2nd Ed.; CRC Press LLC: Boca Raton, FL, 2007
6. S. J. Abbott, C. M. Hansen, H. Yamamoto, Hansen Solubility Parameters in Practice software, eBook, datasets, www.hansen-solubility.com
7. C. Zhao, H. Wang, B. Bai, S. Qu, J. Song, X. Ran, Y. Zhang and M. Li, *New J. Chem.*, 2013, **37**, 1454.
8. N. Yan, Z. Xu, K. K. Diehn, S. R. Raghavan, Y. Fang and R. G. Weiss, *Langmuir*, 2013, **29**, 793.
9. Y. Wu, S. Wu, G. Zou and Q. Zhang, *Soft Matter*, 2011, **7**, 9177.
10. O. Gronwald and S. Shinkai, *Chem. Eur. J.*, 2001, **7**, 4329.
11. E. Stefanis, C.Panayiotou, *Int. J. Thermophys.*, 2008, **29**, 568.
12. M. Raynal and L. Bouteiller, *Chem. Commun.*, 2011, **47**, 8271.
13. V. A. Mallia, M. George, D. L. Blair and R. G. Weiss, *Langmuir*, 2009, **25**, 8615.