



HAL
open science

Tunable two-component saccharide-based gels The effect of the co-operation of two glucofuranose-based compounds having different gelating abilities

Roman Luboradzki, Zbigniew Pakulski

► To cite this version:

Roman Luboradzki, Zbigniew Pakulski. Tunable two-component saccharide-based gels The effect of the co-operation of two glucofuranose-based compounds having different gelating abilities. *Supramolecular Chemistry*, 2009, 21 (05), pp.379-383. <10.1080/10610270802061176>. <hal-00513530>

HAL Id: hal-00513530

<https://hal.science/hal-00513530v1>

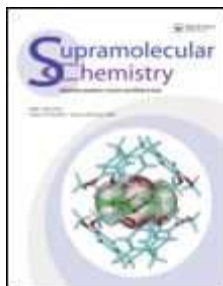
Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

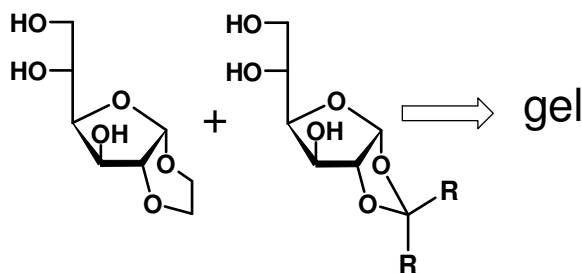


Tunable two-component saccharide-based gels The effect of the co-operation of two glucofuranose-based compounds having different gelating abilities

Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2007-0142.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	04-Mar-2008
Complete List of Authors:	Luboradzki, Roman; Institute of Physical Chemistry, Polish Academy of Sciences Pakulski, Zbigniew; Institute of Organic Chemistry Polish Academy of Sciences
Keywords:	gel, self-assembly, saccharide, X-ray structure



1
2
3
4 Addition of poor gelator
5 increases the thermal
6 stability of the the gel
7 formed by good gelator
8
9



Roman Luboradzki and
Zbigniew Pakulski

Tunable two-component
saccharide-based gels

1
2
3
4
5
6
7
8
9
10
11 **Tunable two-component saccharide-based gels. The effect of the co-operation of**
12 **two glucofuranose-based compounds having different gelating abilities.**
13
14

15
16 Roman Luboradzki*^a and Zbigniew Pakulski^b
17

18
19 ^aInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52 01-224
20

21
22 Warsaw, Poland, phone 48 22 3433225, fax 48 22 3433333, email romek@ichf.edu.pl
23

24
25 ^b*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52 01-224*
26

27
28 *Warsaw, Poland, phone 48 22 3432005, fax 48 22 6326681, email pakul@icho.edu.pl*
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 **Abstract**—The addition of 1,2-O-(ethane-1,2-diyl)- α -D-glucofuranose, which is
5 originally a poor organogelator, can support the gelating abilities of good
6 glucofuranose-based organogelators. The properties of such two-component gels can be
7 tuned by changing the proportion of the saccharides. A saccharide ability to form two-
8 component gels can be explained on the basis of its crystal structure, particularly the
9 way in which sugar molecules stack (or not) into hydrogen bond-based chains and the
10 architecture of these chains. The thermal stability of the obtained two-component gels
11 was characterized by measuring its T_{gel} temperature. SEM and XRD techniques were
12 used to characterized the xerogels.
13
14
15
16
17
18
19
20
21
22
23
24

25
26 *Keywords: Gel, Self-assembly, Saccharide, X-ray structure*
27
28
29

30 INTRODUCTION

31
32
33 In recent years, the development of new gelators of organic solvents as well as the
34 investigation of the gelating process and gel structure has received much attention.[1–
35 10] Gels derived from low-molecular-mass compounds have attracted special interest on
36 account of their unique features, potential applications and relative simplicity of the
37 gelator molecules. Low-molecular-mass gelators form gels, which fall within the
38 physical gels (in contradistinction to chemical gels) since only non-covalent interactions
39 between the gelator molecules are involved. The formation of the gel based on
40 spontaneous self-assembly of gelator molecules under non-equilibrium conditions such
41 as the cooling of oversaturated solutions is used as the typical preparation method.
42 According to the type of driving forces of molecular aggregation, low-molecular-mass
43 gelators can be classified into two categories: non-hydrogen-bond-based and hydrogen-
44 bond-based gelators. The title saccharides having free OH groups fall within the latter
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 group. The presence of intermolecular hydrogen bonds is responsible for self-
5 assembling of the gelator molecules, which leads to the formation of a fibrous
6 superstructure, as can be observed in TEM and SEM pictures of xerogels. The structure
7 of a particular fibril as well as the process of gel formation can be investigated by small
8 angle X-ray scattering (SAXS)[11]. Analysis of the crystal structure of the pure gelator
9 can shed light on its gelating ability. Despite significant progress in this field during the
10 last decade, the accurate design of a new gelator is still a hard task. The basic feature of
11 the gelator molecules is their ability to stack into one-dimensional chains. Thus, the
12 prediction of a new gelator can often be made per analogy according to the rule that if
13 the molecule looks similar to already known good gelators it will stack in a similar way
14 and thus also possess gelating abilities. The bis-urea compounds are an excellent
15 example of this concept [2]. The correlation between the hydrogen-bond network in the
16 bulk crystal and gelating ability was also shown for the class of pyranoside
17 derivatives[12-13]. On the other hand, saccharides having three free OH groups can
18 form different hydrogen-bond-based networks even if the configuration of the
19 saccharide ring remains unchanged: in other words they look similar but can pack in
20 quite a different manner, which seems to be responsible for increasing the margin of
21 unpredictability. Nevertheless, the “crystallographic approach” still seems to be a useful
22 tool, also for this class of gelators. Glucofuranose derivatives were chosen as they are
23 one of the simplest, smallest and most efficient gelators. Moreover, having an
24 unchanged furanose ring with three unprotected OH groups, they can be easily modified
25 by changing the hydrophobic fragment connected to the dioxolane C-2' carbon atom.

26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
A two-component gel can be defined as a system in which an individual component can
be present in an isotropic solution, and only the addition of the second component will

1
2
3
4 actually form a gel. In some cases however, systems containing a gelator and a second
5
6 component which modifies its behaviour and/or the properties of the gel can also be
7
8 assumed to be two-component gels.[14] Different systems have been used to generate
9
10 two-component gels, based on hydrogen-bonding interactions[15], π - π interactions[16],
11
12 metal ligand bonds[17] etc. The fact worth highlighting here is the necessity of co-
13
14 operation on a molecular scale between two components for a new structure to form.
15
16 From this point of view even two good gelators can form a two-component gel.
17
18
19

20
21
22 Two-component gels are significantly rarer than single-component systems. On the
23
24 other hand two-component systems have a vast degree of tenability. This allows
25
26 to design gels towards a novel form of functional gel-phase materials.
27
28
29
30
31

32 RESULTS AND DISCUSSION

33
34 Additionally to the previously reported class of saccharide-based gelators[18-19] we
35
36 synthesized 1,2-O-(ethane-1,2-diyl)- α -D-glucofuranose (**1**).[20] The reason behind this
37
38 was its molecular arrangement in a single crystal in which molecules of **1** assembled in
39
40 one-dimensional chains, as can be expected for a good gelator. Nonetheless, probably
41
42 because of the relatively small hydrophobic part connected to O2 and O3, this
43
44 compound was found to be a poor gelator, additionally with very low solubility in most
45
46 organic solvents, as Table 1 shows.
47
48
49

50
51 On the other hand, the hydrogen bond-based chains in the bulk crystal of **1** are very
52
53 similar to such chains observed in the crystal structure of a good gelator, namely 1,2-O-
54
55 isopropylidene- α -D-glucofuranose (**2**). (Figure 2)
56
57
58
59
60

1
2
3
4 This inspired us to use compound **1** as a material which can ‘support’ gelation. Because
5
6 of the perfect fit, the molecules of the gelator can be replaced by molecules of **1**. Thus,
7
8 the addition of **1** into the gelator-solvent mixture should lead (during the gelation
9
10 process) to a larger number of gelator fibrils, which should be reflected in the changed
11
12 mechanical and thermodynamical properties of the gel. Moreover the molar ratio of **1**
13
14 can be changed smoothly, allowing these properties to be tuned quite well. The
15
16 proposed mechanism is shown in Figure 3. In order to prove this concept, samples of
17
18 gels formed by **3** and **4** were prepared with the addition of different amounts of **1**, and
19
20 the thermal stability of those gels was tested. The gelator concentration was fixed as 1%
21
22 or 2% (wt/vol [g mL⁻¹]) and the concentration of **1** was 0, 0.01, 0.03, 0.06 and 0.12%
23
24 respectively. In **some** cases (mostly when CCl₄ was used) compound **1** tends to
25
26 crystallize as a separated phase, which simply leads to a mixture of crystals and gel
27
28 phase. However in several cases (**3**/toluene, **3**/benzene, **4**/toluene, **4**/benzene) good,
29
30 transparent gels were obtained. The T_{gel} of such systems depends strongly on the
31
32 concentration of **1** and, as Figure 4 shows, can increase significantly once a certain
33
34 concentration is exceeded. Additionally, the temperature range from the start to the end
35
36 of the process becomes wider, which may suggest that melting of such two-component
37
38 gels is a more complicated process than in simple one-gelator systems. To obtain a
39
40 visual insight into the aggregation mode, xerogels of **3**/benzene, **1/3**/benzene and dry
41
42 **1**/benzene microcrystals were prepared by the freezing-and-pumping method⁵. As
43
44 expected, gelator **3** forms a three-dimensional network containing a large number of
45
46 fibril-fibril junction points. A similar structure can be observed in **1/3**/benzene systems.
47
48 Pure **1** also forms a fibrillar network, but the number of junction points is significantly
49
50 lower and the fibrils are straight and longer. This picture may suggest self-supporting
51
52
53
54
55
56
57
58
59
60

1
2
3
4 precipitation (which is compatible with data from Table 1), as the ability to form a fibre
5 structure is not enough to act as a good gelator[13]. Powder X-ray analysis was
6 performed on dry samples of **3**/benzene, **1/3**/benzene and **1**/benzene. The **1**/benzene
7 XRD pattern shows peaks which can also be observed for crystalline **1** or calculated
8 from its crystal structure[21]. The XRD patterns for **3**/benzene and **1/3**/benzene show a
9 completely amorphous material. This confirms that **1/3**/benzene gel is not only a sum of
10 two separate networks of **3** and **1** but is a genuine two-component gel, where poor
11 gelator **1** modifies the thermal stability of the network formed by good gelator **3** and
12 vice versa, **3** modifies the behaviour of **1**.
13
14
15
16
17
18
19
20
21
22
23
24

25 26 27 CONCLUSION

28
29
30 In this paper we demonstrated how the “crystallographic approach” can help to design
31 not only a particular gelator, but also a two-component gel. Based on the similarity in
32 the crystal structure of different monosaccharides we proposed two-component systems
33 which can gelatinize different organic solvents. This tool seems to be particularly useful
34 for two-component (+ solvent) systems – much more complicated than one-component
35 typical gels.
36
37
38
39
40
41
42

43
44
45 Additionally we introduced the new two-component gels, whose properties can be
46 continuously changed just by gently changing the concentration of one compound.
47
48
49

50 51 EXPERIMENTAL

52 53 54 55 56 57 Materials

58
59
60

1
2
3
4 The saccharides were prepared according to literature procedure[19-20]. Solvents were
5
6 purified and dried according to literature methods.
7
8
9

10 11 **Gelation test procedure**

12
13 The gelation test was carried out as follows: the gelator was mixed in a closed-capped
14 tube with the appropriate amount of solvent to result in a concentration of 3% [g mL⁻¹]
15
16 (about 15 mg of gelator and 0.5 mL of solvent was used). The mixture was heated until
17
18 the solid was dissolved and then about one further minute. The solvent bp was usually
19
20 reached by this procedure. The test tube was cooled in air to 20 °C, left for 24 h at this
21
22 temperature and then turned upside down. When the gel was formed the whole
23
24 procedure was repeated with the concentration below 1%. Once we had found by
25
26 chance the gel formation in concentration over 3% (while at 3% it was marked as 'S'),
27
28 all the 'S' marked systems (solution in 3%) were checked in higher concentration until
29
30 we got either G (S→G) or P (S→P). In some cases, however, the solubility was so high
31
32 and the amount of the gelator so limited that a final answer could not be given. In the
33
34 case of 'I' at 3% starting concentration, lower concentrations were used in order to fully
35
36 dissolve the saccharide, as the presence of crystals can influence gelation (to ultimately
37
38 obtain either I→G or I→P). In addition to usual 'invert vial test', all the gels were
39
40 examined using an optical microscope to exclude self-supporting precipitation.
41
42
43
44
45
46
47
48
49

50 51 **Gel-Sol transition temperature**

52
53 The test tube containing the gel was put in a thermostated water bath. The temperature
54
55 was raised at a rate of 2°C/min. Here the T_{gel} was defined as the temperature at which
56
57 the gel turned into sol phase. If, at the beginning, the gel started to leak solvent, this was
58
59
60

1
2
3
4 defined as the start of the process which ran until the whole volume of the gel turned
5
6 into sol.
7
8
9

10 11 **SEM observations**

12
13 SEM observations were performed using a scanning electron microscope type DSM 942
14 (Zeiss, Germany) and Philips 515 in the secondary electron (SE) mode. The gel was
15 prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was
16 evaporated by a vacuum pump for about 8 h. Samples were fixed with conductive glue
17 to the SEM holder. Then the samples were coated with a thin layer of Au to protect
18 them from heat destruction and to maintain the real parameters of the observed details.
19
20
21
22
23
24
25
26
27
28
29

30 31 **XRD on xerogels**

32
33 Xerogels were prepared by using the same procedure as for SEM samples. The Bruker
34 D8 Advance diffractometer was used, with Cu(K α) radiation. Samples were measured in
35 the 2 θ range from 5 to 50°. Five scans were performed for each sample (each scan 12
36 hours) showing no time-dependent changes in the XRD pattern.
37
38
39
40
41
42
43
44
45

46 47 **Acknowledgments**

48
49 The authors acknowledge financial support from the Polish Ministry of Science and
50 Higher Education (grant No. N204 058 32/1514).
51
52
53

54 55 **References**

56
57
58 [1] Terech, P.; Weiss, R.G. *Chem. Rev.* **1997**, *97*, 3133–3159 and references therein.
59
60

- 1
2
3
4
5 [2] van Esch, J.; Schoonbeek, F.; de Loss, M.; Veen, E.M.; Kellogg, R.M.; Feringa,
6 B.L. In *Supramolecular Science: Where It Is and Where It Is Going*; Ungaro, R.,
7 Dalcanale, E., Eds.; Kluwer: Dordrecht, **1999**; 233–259.
- 8 [3] Hanabusa, K.; Okui, K.; Karaki, K.; Shirai, H. *J. Chem. Soc., Chem. Commun.*
9 **1992**, 1371–1373
- 10 [4] Hanabusa, K.; Yamada, Y.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed.* **1996**,
11 35, 1949–1950.
- 12 [5] Hanabusa, K.; Shimura, K.; Hirose, K.; Kimura, M.; Shirai, H. *Chem. Lett.* **1996**,
13 885–886.
- 14 [6] Hanabusa, K.; Kawakami, A.; Kimura, M.; Shirai, H. *Chem. Lett.* **1997**, 191–
15 192.
- 16 [7] De Vries, E.J.; Kellogg, R.M. *J. Chem. Soc., Chem. Commun.* **1993**, 238–240.
- 17 [8] Terech, P.; Furman, I.; Weiss, R.G. *J. Phys. Chem.* **1995**, 99, 9558–9566
- 18 [9] Gronwald, O.; Snip, E.; Shinkai, S. *Curr. Opin. Coll. Int. Sci.* **2002**, 7, 148–156.
- 19 [10] van Esch, J.; De Feyter, S.; Kellogg, R.M.; De Schryver, F.; Feringa, B.L. *Chem.*
20 *Eur. J.* **1997**, 3, 1238–1243.
- 21 [11] Grigoriew, H.; Luboradzki, R.; Cunis, S. *Langmuir* **2004**, 20, 7374–7377.
- 22 [12] Luboradzki, R.; Gronwald, O.; Ikeda, M.; Shinkai, S.; Reinhoudt, D.N.
23 *Tetrahedron* **2000**, 56, 9595–9599.
- 24 [13] Gronwald, O.; Sakurai, K.; Luboradzki, R.; Kimura, T.; Shinkai, S. *Carbohydr.*
25 *Res.* **2001**, 331, 307–318.
- 26 [14] Hirst, A.R.; Smith, D.K. *Chem. Eur. J.* **2005**, 11, 5496–5508
- 27 [15] Hanabusa, K.; Miki, T.; Taguchi, Y.; Koyama, T.; Shirai, H. *J. Chem.*
28 *Soc. Chem. Commun.* **1993**, 1382 – 1384.
- 29 [16] Maitra, U.V.; Kumar, P.; Chandra, N.; D'Souza, L.J.; Prasanna, M.D.;
30 Raju, A.R. *Chem. Commun.* **1999**, 595 – 596.
- 31 [17] Beck, J.B.; Rowan, S.J. *J. Am. Chem. Soc.* **2003**, 125, 13922 –
32 13923;
- 33 [18] Luboradzki, R.; Pakulski, Z. *Tetrahedron* **2004**, 60, 4613–4616
- 34 [19] Luboradzki, R.; Pakulski, Z. *Tetrahedron* **2005**, 61, 10122–10128
- 35 [20] Nagai, K.; Honda, T.; Kiho, T.; Ukai, S.; Tsuchiya, T. *Carbohydr. Res.*, **1989**
36 190, 165–180
- 37 [21] Lebuis, A-M.; Lee, D-S.; Perlin A.S. *Aust. J. Chem.* **1996**, 49, 299–303
- 38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 1

Solvent	Test results			
	1	2	3	4
Toluene	I→P	G	G*	G*
Benzene	I→P	G	G*	G*
p-Xylene	I→P	G	G*	G*
Carbon tetrachloride	I→P	G*	G*	P, PG
Nitrobenzene	P, SSP	G	G*	G*
Chloroform	I→P	G*	G	P, PG
Dibenzyl ether	I→P	G*	G*	G*
Cyclohexane	I→P	G*	P	P
n-Hexane	I→P	P	P	G*
n-Heptane	I→P	P	P	G*
Methanol	P	S	S	S
Ethanol	P	S	S→P	S→P
Acetonitrile	P	P	S→P	S
Ethyl acetate	I→P	P	P	S→G
1,4-Dioksane	P	S	S→P	S→P
THF	I→P	S	S	S→P
Water	P	S	S	S
Acetone	I→P	P	S	S→SSP

Abbreviations used: G, gel at 3.0 wt/vol%; G*, gel even under 1.0 wt/vol%; PG, partial gel; S, solution; P, precipitation; SSP, self-supporting precipitation; S→G, solution at 3.0 wt/vol% then gel at higher concentrations; S→P, solution at 3.0 wt/vol% then precipitation at higher concentrations; I→P, insoluble (not fully soluble at 3.0 wt/vol%) precipitation after dissolving at lower concentration.

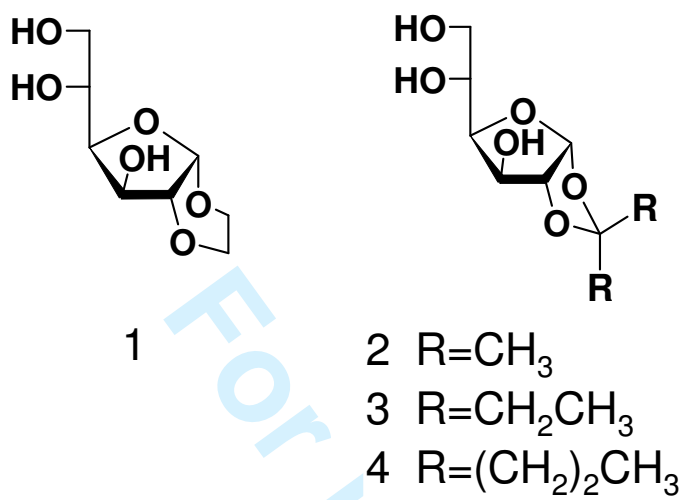


Figure 1

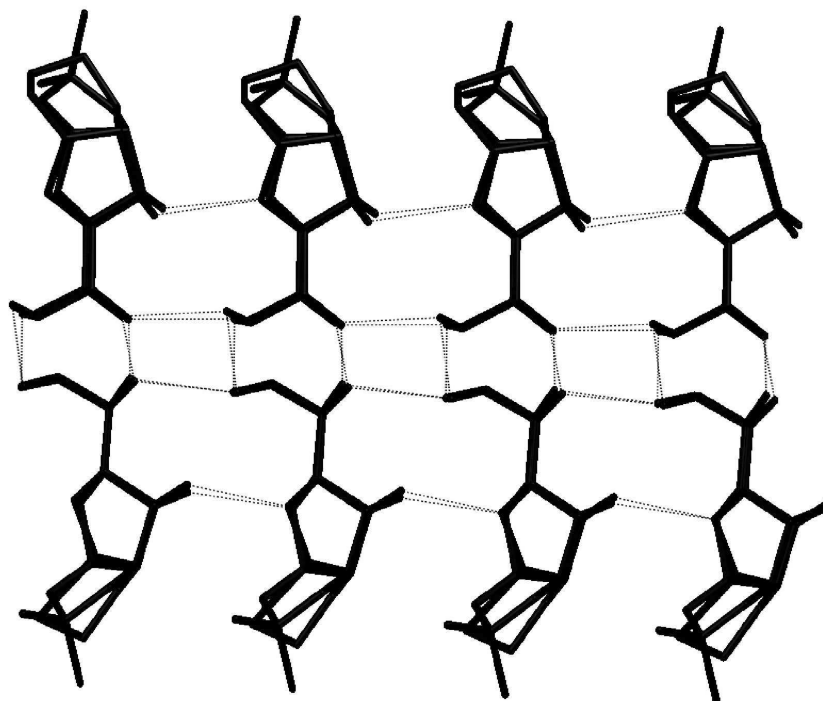


Figure 2

New Only

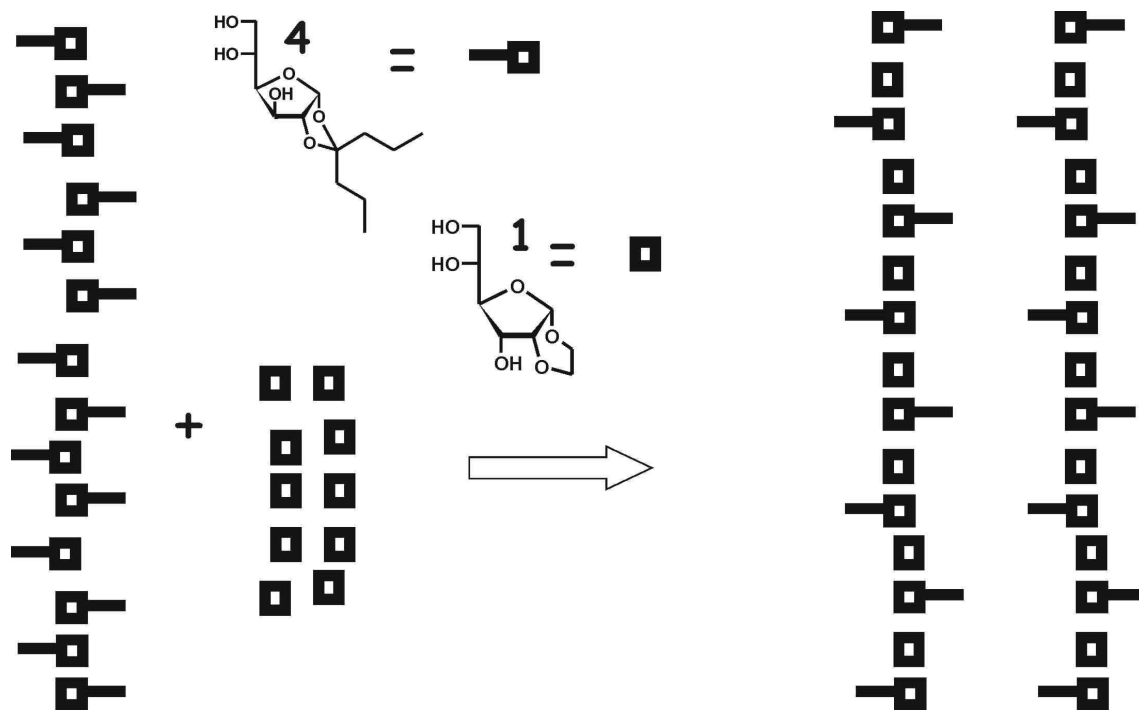


Figure 3

er Review Only

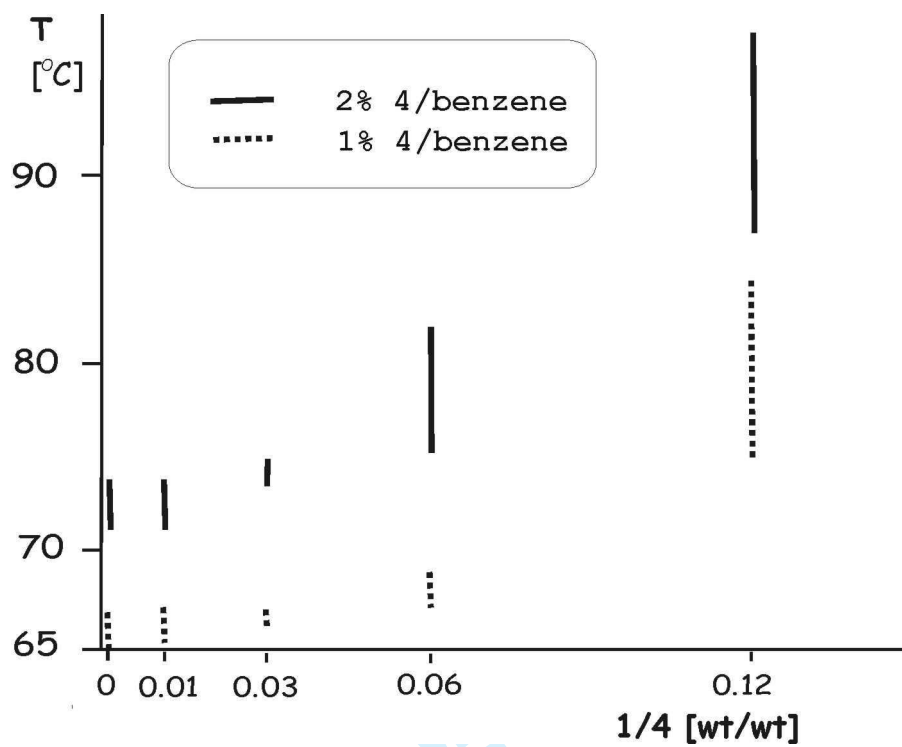


Figure 4

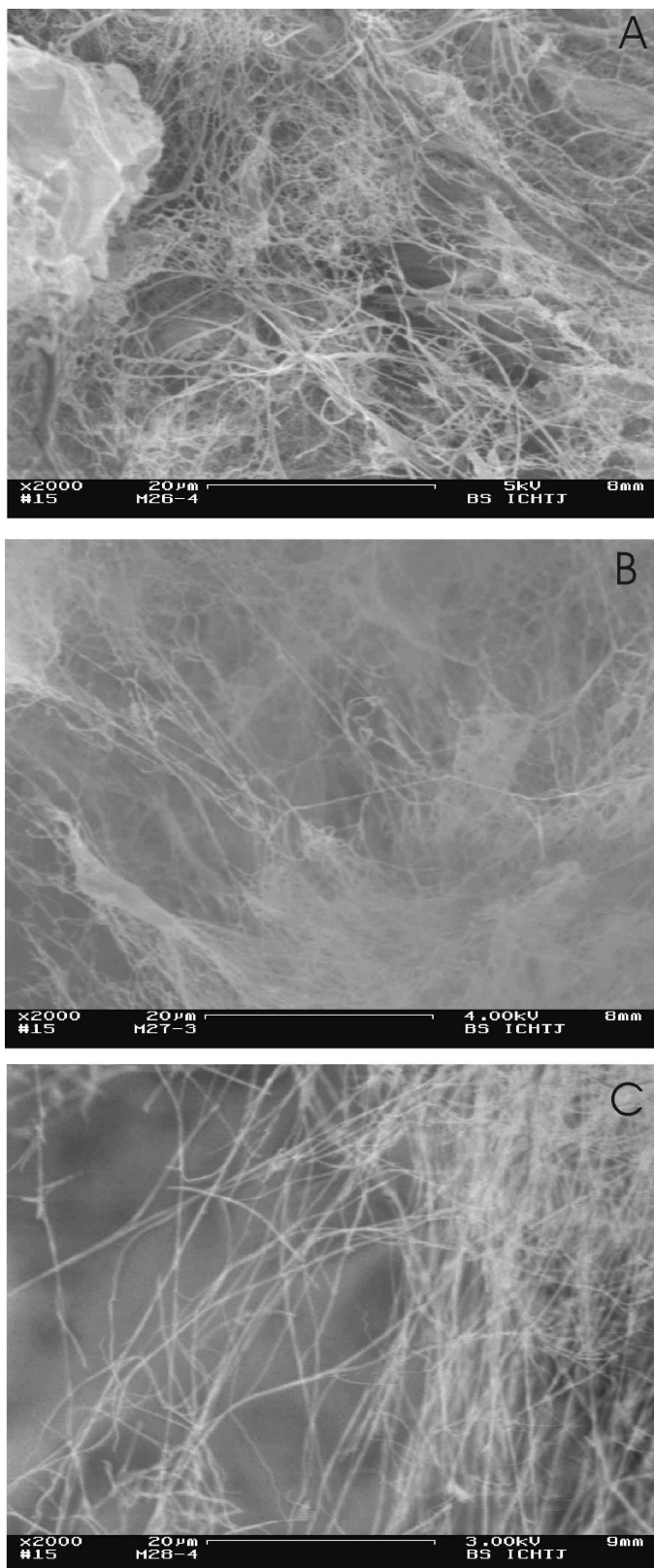


Figure 5

1
2
3
4
5
6
7 **Figure captions:**
8
9

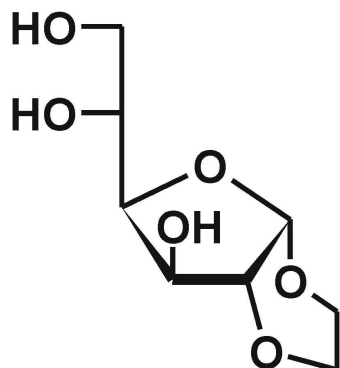
10
11 **Figure 1.** Structure of monosaccharides 1–4.
12
13

14
15
16 **Figure 2.** Least squares fit of two fragments of hydrogen bond-based chains observed in
17 the crystal structures of **1** and **2**. Fit based on all C4 atoms, hydrogen atoms have been
18 omitted for clarity. H-bond lengths (donor...acceptor) range from 2.728 Å to 2.816 Å for
19 **1** and from 2.758 Å to 2.878 Å for **2**, and may be assumed as typical
20
21
22
23
24
25
26
27

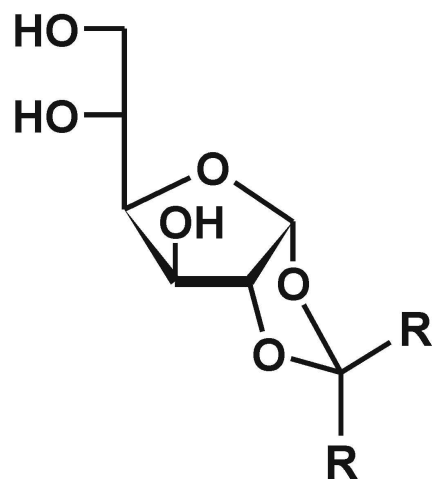
28 **Figure 3.** Possible mechanism of the way in which molecules of **1** can support the
29 gelation of **4**
30
31
32
33
34

35 **Figure 4.** T_{gel} against **1/4** [wt/wt] (poor/good gelator) ratio in **4**/benzene gels. Higher
36 concentrations of **1** usually could not be reached because of its low solubility, or the
37 solution of **1** became so over-concentrated during cooling that **1** started to crystallize
38 before compound **4** started to gelatinize the solvent.
39
40
41
42
43
44
45
46
47

48 **Figure 5.** SEM pictures of dried samples of A) **3**/benzene (0.5% wt./vol), B)
49 **1/3**/benzene (0.035% and 0.5% respectively), C) **1**/benzene (0.02%)
50
51
52
53
54
55
56
57
58
59
60

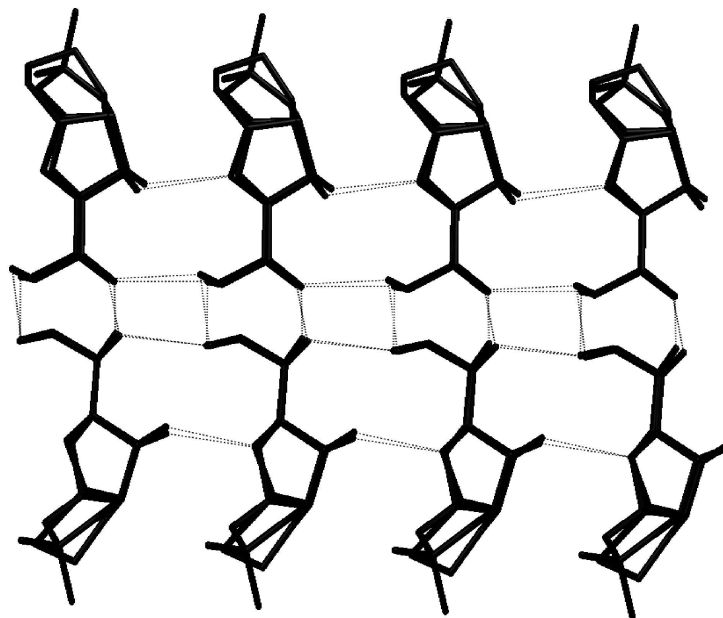


1

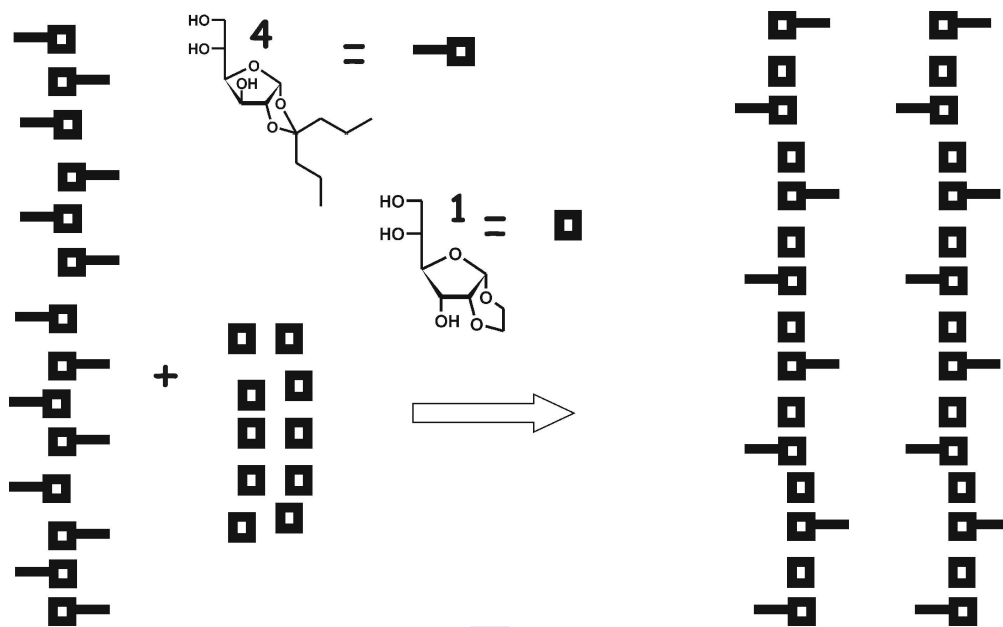
2 $R=CH_3$ 3 $R=CH_2CH_3$ 4 $R=(CH_2)_2CH_3$

Review Only

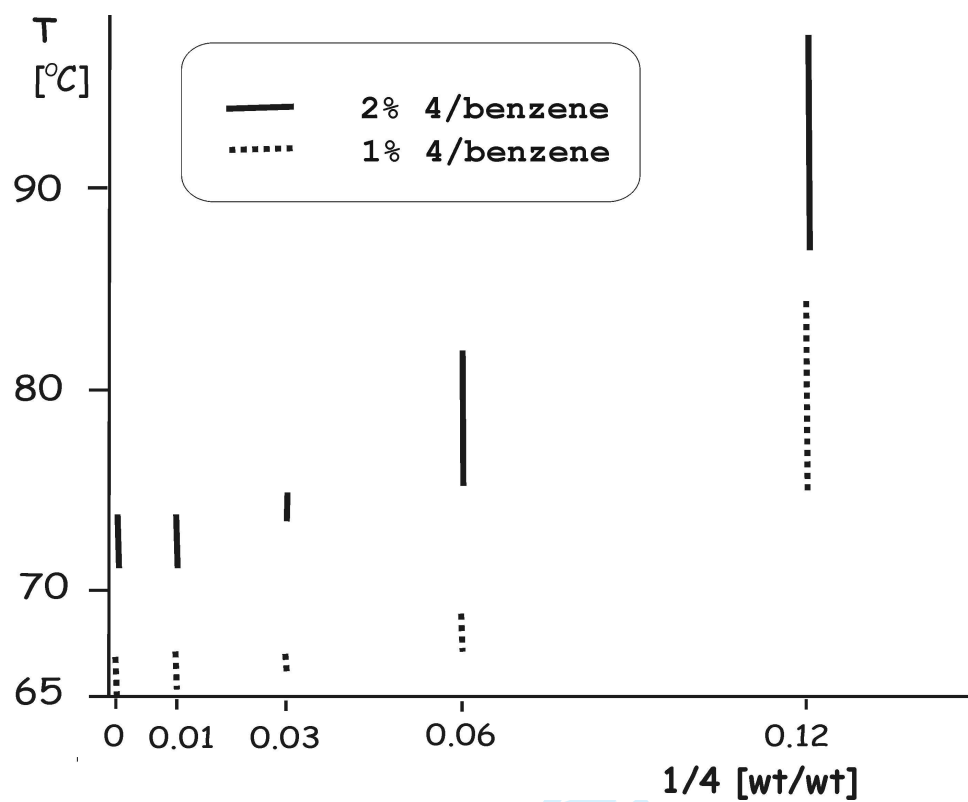
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



www Only



Review Only



View Only

