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Partially acetylated or benzoylated arabinose derivatives as structurally simple organogelators: Effect of the ester protecting group on gel properties

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Abstract: Sugar based low molecular weight gelators (LMWGs) have been used for various applications since long time. In this work, we report structurally simple, ester protected arabinosides as low molecular weight organogelators (LMOGs) that are able to gel aromatic solvents as well as petrol and diesel. Studies on the mechanical strength of the gels through detailed rheological experiments indicate that the gels from the 1,2-dibenzoylated arabinose gelator possesses better mechanical properties than the 1,2-diacetylated gelator. These results are interpreted in terms of the tendency of the former to form fibres with comparatively lower diameter than the latter; based on detailed FESEM and AFM studies. Investigation of the interactions responsible for the self-assembly of gelators through IR and WXRD spectroscopy reveal that the primary interactions responsible for it is H-bonding between the hydroxyl groups and the ester C=O which is absent in the solid state of the gelators. In addition, pi interactions present in the 1,2-dibenzoylated derivative results in the more regular arrangement which in turn leads to better mechanical properties of its gels compared to that of the 1,2-diacetylated gelator.

Introduction

Low Molecular weight Gelator (LMWG) based gels are a class of soft materials that have attracted a lot of attention in recent years due to their wide applications.[1,2] The potential applications of these gels include stimuli responsive materials[3,4] (including stimuli such as changes in temperature, chemical environment, pH, light, temperature and others), drug delivery and tissue engineering,[5,6] waste water treatment and environmental remediation,[7] optical applications[8] and as self-healing materials.[3c,9] The LMWGs are based on a wide variety of compounds ranging from steroids,[10] amino acids and peptides,[11,12] molecules with conjugated π-systems and/or polyaromatic hydrocarbons,[13,14] ureas and thioureas,[15] nucleosides and nucleobases,[16,17] dendrons and dendrimers[18] and carbohydrates.[19] During gelation, these small molecules self-assemble into supramolecular structures through a variety of non-covalent forces such as H-bonding, Van-der-Waal's forces, hydrophobic interactions, π-π stacking, CH-π and dipole-dipole interactions and halogen bonding.[20-23]

Amongst carbohydrates, many monosaccharide derivatives are known to be LMWGs, from the widely popular dibenzylidine sorbitol (DBS) derivative known since a long time; to more recent ones.[19b]. The design of supramolecular gelators based on sugars revolve around one of the following basic strategies – (i) protection of the 4,6-OH groups in the parent hexose sugar as the benzylidine[24-26] (ii) synthesizing amphiphilic monosaccharide derivatives either as glycosides of moieties that are well known to induce gelation such as steroids, long chains, and polyaromatic hydrocarbons[27-29] or as protecting groups on

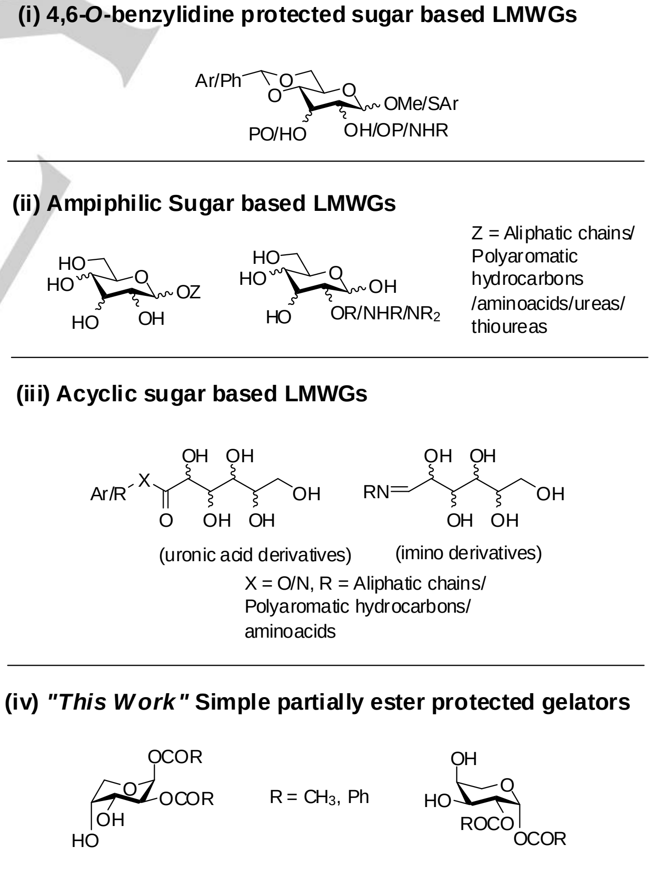

Figure 1. (i) – (iii) Typical structural classes of previously reported monosaccharide based LMWGs and (iv) "This work"

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one of the hydroxy (or amino) groups[30-31] and (iii) putting additional hydrophobic/H-bond inducing substituents, that are known to induce gelation properties, on the acyclic sugar as imines or aldonic acid esters/amides (Figure 1).[32]

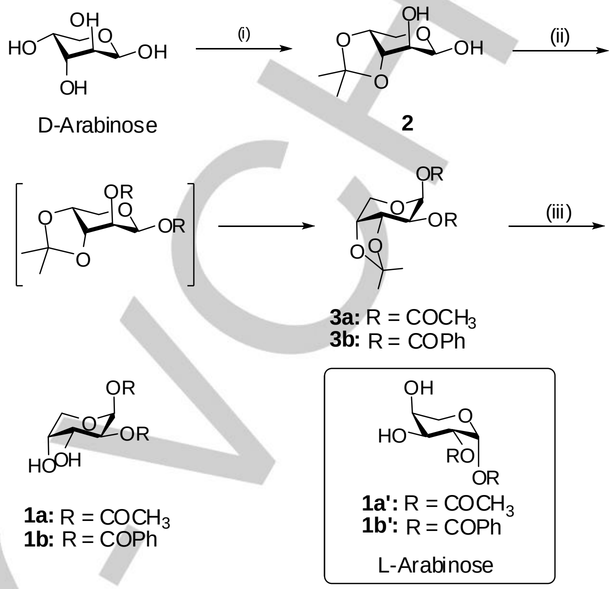
Each of these structural classes of monosaccharide based gelators present some disadvantages such as the instability of acetonide/benzylidine protected sugars under acidic conditions, the requirement of multiple synthetic steps involving protection and deprotection and the implementation of the stereoselective glycosylation. The difficulties associated with the selective protection/deprotection of monosaccharides can be lessened to some extent by designing gelators based on pentose sugars which have one less hydroxyl group that requires to be manipulated. This has been demonstrated previously by us when we reported an arabinose based supergelator that was accessible in one single synthetic step.[33] Similarly, we have also reported triazolyl arabinoside derivatives as phase selective gelators of petrol, diesel and crude oil.[34] Additionally, amongst sugars, arabinose based gelators provide the unique opportunity towards the synthesis of economically feasible enantiomeric gelators that may be required for chiral applications such as in asymmetric catalysis and as chiral micro-reactors.[35]

In the present work we report simple partially ester protected arabinose derivatives as LMOGs for aromatic solvents (Figure 1). The structurally simple gelators bear minimal and simple protecting groups and are easily synthesized in three simple steps. Two types of ester groups, *viz*. acetate and benzoate have been explored for the gelation ability. Significant differences in the mechanical properties have been found for the two gels through rheological studies. Again, the structural simplicity of the protecting groups have enabled detailed mechanistic studies to probe the interactions responsible for self-assembly mechanism leading to the variation of their mechanical properties.

Results and Discussion

Synthesis and structure of the gelators

We synthesized the gelators D- or L-**1a** and D- or L-**1b** from commercially available D- or L- arabinose in three simple steps (Scheme 1). First, the D- or L- arabinose was converted to the monoacetonide D- or L- **2** by reacting with 2,2-dimethoxy propane using catalytic *p*-TSA, following a previously reported procedure.[28,31] The exclusive β-nature of the monoacetonide in the 4C1 conformation, as reported by Kiso[36] and others,[37] was confirmed by its 1H-NMR spectra. Diacetylation of **2** using acetic anhydride and pyridine in the presence of catalytic Dimethylaminopyridine (DMAP) converted **2** to the 3,4-isopropylidine-1,2-diacetate derivative **3a**. The conversion of **3a** to the compound **1a** was carried out by treatment of the former with acetic acid and water. Similarly dibenzoylation of **2** using benzoic anhydride and pyridine followed by removal of the acetonide gave the corresponding 1,2-dibenzoyl arabinopyranoside **1b** as the β-anomer in the 1C4 conformation. Similarly, the enantiomeric compounds **1a'** and **1b'** were also synthesized from L-arabinose.



Scheme 1. Synthesis of gelators **1a** and **1b**. Reagents and conditions: (i) 2,2-Dimethoxypropane, *p*-TSA (catalytic), DMF, RT, 2 h; (ii) Ac_2O, pyridine, RT, 2 h or Bz_2O, pyridine, RT, 5 h; (iii).AcOH:H_2O (7:3), 85 °C, 2 h. L-arabinose derivatives **1a'** and **1b'** were synthesized similarly.

Gelation properties

Initial gelation experiments using **1a** and **1b** revealed that they were able to gel several aromatic solvents (Table 1) as well as petrol and diesel. The gelation tests were performed by the simple inversion test. For this the required amount of the gelator in 1 mL of any solvent was taken in a capped vial and then heated till the compound completely dissolved. Then the vial was set aside to cool. In all the cases of the successful gelation, it occurred almost instantly which was observed by inverting the vial, wherein, the material was able to hold its own weight. Other solvents were also tested but both **1a** and **1b** were unable to congeal them.

The Minimum Gelation Concentrations (MGC) for all the solvents was 0.3% (w/v) for both **1a** and **1b** as well as **1a'** and **1b'**. Experiments to explore the variation of the gel-sol transition temperature T_g with the concentration of the gelator revealed that the thermal stability of the gels could be increased by increasing the gelator concentration (Figure 2). The thermal reversibility of the gels was also evident from heating cooling cycles which showed that the gels were thermally reversible up to more than 10 heating-cooling cycles. Also, the gels were stable up to many months under conditions to prevent loss of solvents through evaporation.

A very interesting property of the gelators was also observed when the gelation was studied with racemic mixtures of the **1a** and **1b**. Unlike the pure enantiomers, the racemic mixtures

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Table 1. Gelation abilities of compounds **1a** and **1b**.

Solvent	**1a,**[a] **(MGC, T_g)**	**1b, (MGC, T_g)**[b]
Benzene	G, (0.3%, 53-54 °C)	G, (0.3%, 51-52 °C)
Toluene	G, (0.3%, 51-52 °C)	G, (0.3%, 52-53 °C)
o-xylene	G, (0.3%, 48-49 °C)	G, (0.3%, 57-58 °C)
m-xylene	G, (0.3%, 49-50 °C)	G, (0.3%, 56-57 °C)
p-xylene	G, (0.3%, 51-52 °C)	G, (0.3%, 55-56 °C)
Chlorobenzene	G, (0.3%, 47-48 °C)	G, (0.3%, 48-49 °C)
Hexane	PG	PG
Dichloromethane	S	S
Chloroform	S	S
Ethyl acetate	S	S
Acetonitrile	S	S
Methanol	S	S
n-butyl alcohol	S	S
Amyl alcohol	S	S
DMF	S	S
DMSO	S	S
Water	S	S
Petrol	G, (0.2%, 56-57 °C)	G, (0.2%, 55-56 °C)
Diesel	G, (0.2%, 55-56 °C)	G, (0.2%, 58-59 °C)

[a] G = Gel, PG = Partial Gel and S = Solution; [b] MGC (Minimum Gelation Concentration) are presented as % (w/v).

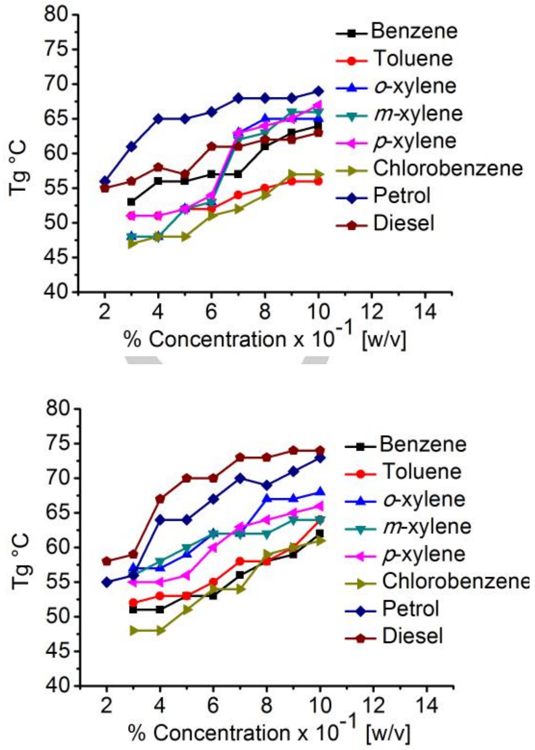

Figure 2. Variation of Gel-sol transition temperature (T_g) with concentration of gelator (a) **1a**; (b) **1b**.

obtained by mixing equal amounts of the D- and L- isomers were unable to gel any of the aromatic solvents. Such an unique property of arabinose based gelators has also been observed before.[33,34] Another interesting feature of the gels was their stability under exposure to ultrasound and UV-light. Many organogels from LMOGs have been reported to be responsive to ultrasound, UV-light. The stability of the gels from **1a** and **1b** to ultrasound therefore could be a useful property with potential for applications in the presence of ultrasound and UV-radiations such as micro-reactors for chemical reactions.

Mechanical properties of the gels.

To study their response to mechanical stress, oscillatory rheological studies of the organogels from both **1a** and **1b** were performed at uniform concentration of 1% (w/v). Two types of experiments were carried out for each of the gels *viz*. the Dynamic Strain Sweep (DSS) experiments and the Dynamic Frequency Sweep (DFS) experiments. The graphs obtained from the rheological experiments are presented in the accompanying Supporting Information (Figures S3-S17) and the summary of the results are presented in Table 2. From the DSS experiments, values of γ were obtained. The value γ represents the strain at which the storage modulus (G′) becomes equal to the loss modulus (G″) and represents the limiting strain beyond which the material behaves more like a fluid than a viscoelastic solid. For any particular solvent, comparison of the values of γ shows that in general **1b** was able to form gels that are more resistant to strain than the gels from **1a** as indicated by the higher values of γ for the former. From the DFS experiments, plots of the linear viscoelastic range of the gels and the values of the ratio of the loss modulus (G″) to the storage modulus (G′), in the linear viscoelastic region, represented by tan δ, were obtained. As can be seen in Table 2, the tan δ values any particular solvent was lower for the gels from **1b** than that of the gel from **1a**, indicating that **1b** formed stronger gels than **1a** for the solvent.

Morphological studies through FESEM and AFM.

To rationalize the mechanical properties of the gels obtained through rheological experiments, the detailed FESEM and AFM experiments were carried out in order to reveal the microstructure of the gels. From the micrographs obtained (Figures S18 to S33, Supporting Information), it could be generally concluded that the gelators self-assembled to form

Table 2. Summary of the rheological properties of the organogels from **1a** and **1b**.

Organo-gelator	Solvent	γ (%) x 10^{-2}	G' (Pa)[a] x 10^3	G″ (Pa)[b] x 10^3	tan δ [c]
1a	Benzene	5.99	38.62	14.93	0.38
	Toluene	2.96	36.62	12.90	0.35
	o-xylene	16.93	61.40	25.10	0.41
	m-xylene	6.54	26.40	7.09	0.27
	p-xylene	14.50	12.22	3.80	0.31
	PhCl	5.56	13.40	4.805	0.39
	Petrol	52.43	6.29	2.82	0.45
	Diesel	50.31	0.931	0.411	0.46
1b	Benzene	35.8	3.58	0.876	0.24
	Toluene	50.10	1.35	0.211	0.18
	o-xylene	25.30	1.73	0.315	0.18
	m-xylene	25.91	7.30	0.975	0.14
	p-xylene	20.82	13.80	1.468	0.10
	PhCl	11.73	22.50	4.283	0.20
	Petrol	70.83	0.866	1.96	0.24
	Diesel	62.34	0.377	0.60	0.16

[a] G' = Storage modulus; [b] G″ = Loss modulus; [c] tan δ = G″/G'.

dense, fibrillar, entangled networks resulting in gelation of the solvents. Also, from the micrographs of the gels from compound **1a** it was observed that that the fibres in benzene, toluene, *m*-xylene and chlorobenzene gels were much thicker than those of *o*-xylene and *p*-xylene. Again the fibers from the xerogels of petrol and diesel showed much more cross-linking which led resulted in the formation of stronger gels. The micrographs for the xerogels from compound **1b** showed the formation of collapsed ribbon like structures compared to those from **1a**. Once again, the stronger natures of the petrol and diesel gels from **1b** were justified by the observation of more extensively cross-linked fibres.

These observations were further confirmed by Atomic Force Microscopy (AFM) experiments of the *m*-xylene gels of **1a** and **1b** which offered better visual insight into the morphologies of the gels (Figure 3). High resolution 3D images to study the surface topography obtained by AFM showed a series of mountain like 3D images for both the gels from both **1a** and **1b** (Figures 3b and 3d). From the 2-D image of **1a** gel, the diameter of the individual fibres was measured to be 50 – 65 nm and aggregation through intertwining was also observed (Figure 3a). From the AFM image of **1b** gel, fibres of approximate diameter 25 – 32 nm were measured (Figure 3c). It is well known that the mechanical properties of fibre based materials are strongly dependant on the fibre diameter – the smaller the diameter, better are the mechanical properties.[38] It can be also concluded that the ribbon like structures observed in the FESEM images were formed through aggregation of the smaller fibres that were observed in AFM image.

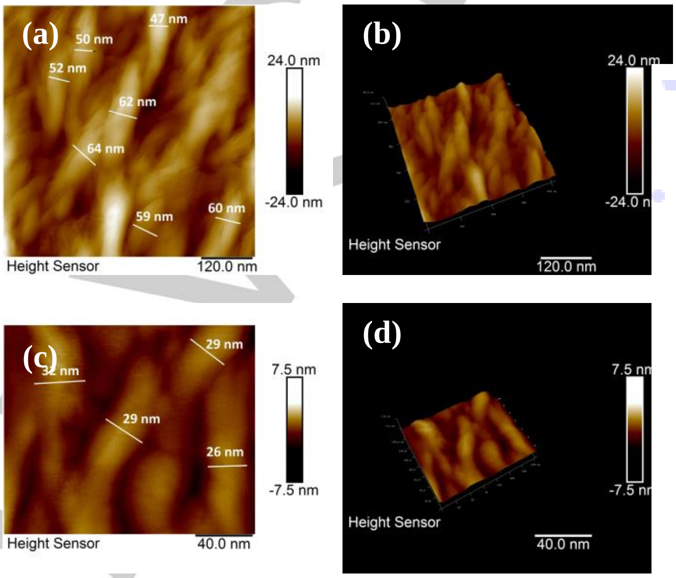

Figure 3. AFM images of the *m*-xylene organogels. (a) 2-D image of organogel from **1a**; (b) 3-D image of organogel from **1a**; **(c)** 2-D image of organogel from **1b**; (d) 3-D image of organogel from **1b**.

Mechanism of the self-assembly of the gelators

The self-assembly of the gelators occurred through the strong H-bonding between the free hydroxyl groups and the carbonyl of the acetates or the benzoates to yield 1-dimensional fibres which further underwent crosslinking to generate the 3-D network. The involvement of H-bonding in the self-assembly process was proven by FTIR studies (Figure 4). In the FTIR spectra the peak for the OH groups at 3345 cm^{-1} (suggesting strong H-bonding) in the crystalline powder state of **1a** shifted to 3354 cm^{-1} in the benzene gel (Figure 4a). The blue shift indicates the weaker H-bonding in the gel state compared to the crystalline state The involvement of the C=O in the H-bonding during self-assembly was also proven by the red shift in the carbonyl absorption from 1738 cm^{-1} (typical of a non-H-bonded ester C=O) in the solid state to 1729 cm^{-1} in the gel state (benzene). Taken together, the IR absorption data suggest that, while in the solid crystalline powder state, the H-bonding interactions are present purely between the OH groups, in the gel state, the gelator **1a** self-assembles through additional H-bonding interactions between the OH and the C=O groups. In

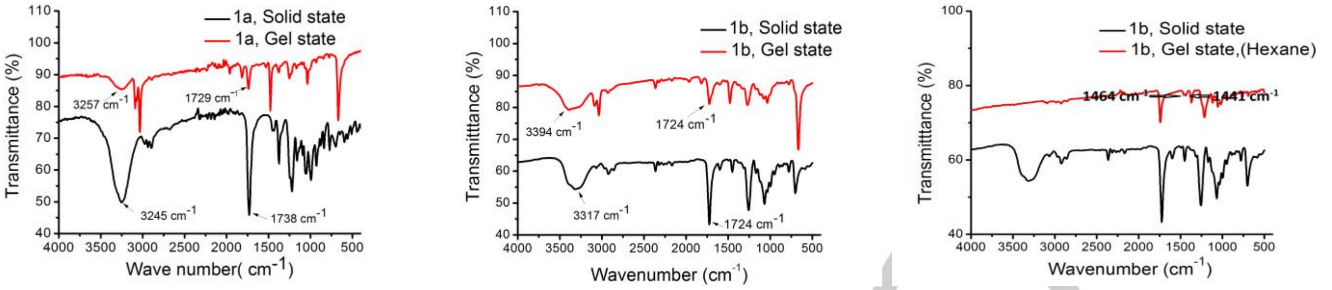

Figure 4. IR spectra. (a) Crystalline solid state and benzene gel of **1a**; (b) Crystalline solid state and benzene gel of **1b**; (c)) Crystalline solid state and hexane gel of **1b**.

case of **1b** the initial OH stretching frequency at 3317 cm^{-1} in the solid state was blue shifted to 3394 cm^{-1} in the benzene gel state proving H-bonding. Again, the C=O stretching frequency at 1724 cm^{-1} present in the crystalline state (typical of a non-H-bonded conjugated ester) was also present in the benzene gel. However, an additional broad peak appeared as a shoulder at 1695 cm^{-1} in the latter, clearly indicating the involvement of the C=O in the self-assembly process. This also suggests that it is probably only one of the two benzoyl groups that actually takes part in the H-bonding. Further confirmation of the π interactions of the phenyl group during self-assembly of **1b** could be obtained from its hexane gel. Whereas, in the pure solid, the aromatic C=C stretching appeared as a single peak at 1440 cm^{-1}, in the hexane gel two peaks corresponding to 1464 cm^{-1} and 1441 cm^{-1} appeared; indicating π interactions in the gel state (Figure 4c). This additional π-interaction during self-assembly of gelator **1b** is therefore, responsible for the stronger nature of its gels compared to the **1a** gels where only H-bonding interactions are present.

The more organized structure of the self-assembled **1b** was also evident from the WXRD spectra of the corresponding xerogels (Figures S34 and S35, Supporting Information). While both the diffractograms showed periodic peaks, the number of peaks for the **1b** xerogel were fewer than that in the spectra of the xerogel of **1a** indicating better organization and self-assembly.

Conclusions

In conclusion, this work reports two synthetically simple sugar based super-organogelators that involve partially ester protected arabinose moiety. The structural simplicity of the gelators implies that they have very few kinds of interaction that results in the self-assembly during gelation. Rheological characterizations of the gels indicate that the gels from the dibenzoylated arabinose gelator is mechanically more robust than the diacetylated arabinose gelator. Spectroscopic studies revealed that the increased mechanical strength of the latter is due to the presence of thicker and more extensively cross-linked fibres under the same conditions. This in turn is due to the involvement of H-bonding as well as π interactions in the former compared to the latter where the self-assembly is only due to H-bonding. These gels are stable under ultrasound and photochemical irradiation, which could be useful for carrying out reactions in these media, a work that is being pursued presently. Again, applications of the gelators towards oil-spill remediation through phase selective organogelation of crude-oil is also being pursued at present.

Experimental Section

1. Gelation tests

Gelation test were carried out by adding exact weights of compounds **1a** or **1b** individually to 1 ml of appropriate solvent in a vial. The vial was sealed and the suspension was heated to dissolve the compound providing a clear solution. It was then allowed to cool after which gelation was tested by inverting the sample vial. If the inverted vial was able to hold the system, it was considered as a gel.

2. Determination of the minimum gelation concentration (MGC)

1 ml of solvent was taken in 5 ml of sample vial, 1 mg of gelator **1a** or **1b** was added to the solvent which was then heated till a clear solution was obtained. Then the solution was cooled and the vial inverted to confirm gelation. If partial or no gelation was observed, the cycle was repeated adding 1 mg of 1a or 1b at the beginning of each heating cooling cycle till complete gelation of the solvent was observed by inversion of the vial.

3. Rheological experiments

Rheological properties of gel sample were determined by using a Bohlin Gemini-2 Malvern rheometer using parallel plates (25 mm, stainless steel). The gap between the parallel plates was 500 micron. The experiments were carried out for either of compounds **1a** or **1b** at 1% (w/v) concentration. The gel samples were placed on parallel plates by spatula in such a way that it covered the surface of the parallel plates. The different tests Dynamic strain sweep (DSS) and Dynamic Frequency sweep (DFS) were performed to determine the viscoelastic nature of the gels. DSS experiment were carried out at a constant frequency of 1 Hz at temperature 25 °C. The strain value was determined at a point where tan $\delta = 1$ ($G'' > G'$). Variation of storage modulus (G') and loss modulus (G'') was tested within frequency range of 1Hz to 100 Hz at strain of 0.001 % by DFS experiments.

4. Field emission scanning electron microscopy (FESEM)

The experiments were performed by using a Zeiss supra-55 FESEM. The xerogels of the samples were prepared by drop-casting a hot 1% (w/v) solution of gelator **1a** or **1b** in gelling solvent on a glass slide (2mm x 2mm) and drying them overnight in air inside a vacuum dessicator. The xerogel was then placed on a stub which was then coated with gold by a Quorum -Q150RES sputter coater under vacuum of 5 x 10-5 millibar and a current of 20 mA for 2 minutes.

5. Atomic force microscopy (AFM)

The experiments were performed by using a Bruker Dimension Icon instrument. The samples were prepared by drop-casting a dilute solution of gelator **1a** or **1b** in benzene solvent on a glass slide (2mm x 2mm) and drying them overnight under vacuum inside a desiccator. AFM images of the samples were obtained using Tapping Mode at 1 Hz scanning rate with a silicon cantilever tip (RFESP-MPP-21100-10) at a resonance frequency of 75 kHz and a spring constant of 3 Nm^{-1}.

6. Wide Angle X-ray scattering (WXRD)

The xerogels of the sample were prepared by dissolving **1a** (100 mg) or **1b** (100 mg) in 10 mL of benzene in a beaker and drying them overnight in a vacuum desiccator. The WXRD diffractogram of the samples were recorded on a Proro AXRD diffractometer. X-rays of wavelength 1.54 Å was used.

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Keywords Gels • Carbohydrates • Self-assembly • Supramolecular Chemistry • Pi interactions

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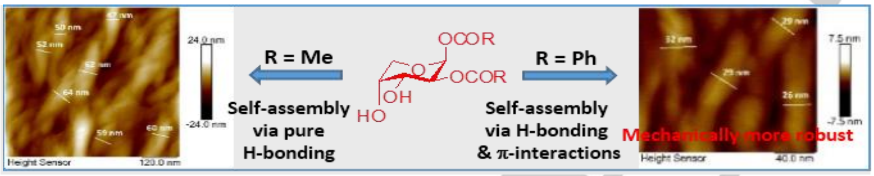

Structurally simple partially acetylated or benzoylated arabinose derivatives are reported as gelators. The reasons for the greater mechanical robustness of the former compared to the latter is investigated and reported.

*Rajkamal, Navendu P. Pathak, Tanmoy Halder, Shubhajit Dhara, Somnath Yadav**

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Partially acetylated or benzoylated arabinose derivatives as structurally simple organogelators: Effect of the ester protecting group on gel properties