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ARTICLE TYPE

Exploration, synthesis and studies of gel forming simple sugar-chalcone derivatives

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Simple sugar chalcone derivatives have been obtained by the aldol condensation of various *β*-C-glycosidic ketones with aromatic aldehydes under basic condition. Aglycon dimer chalcone, an unexpected cleavage product of sugar chalcone was obtained under the same condition as a by-product. Zn-mediated reduction of sugar-chalcone resulted in the formation of the corresponding reduced product. Products were characterized using NMR (^{1}H, ^{13}C), mass spectroscopy and elemental analysis. Few of the sugar-chalcone derivatives exhibited the gelation property and their morphology was studied using FESEM and HRTEM.

Introduction

Low-molecular-weight organogelator (LMOG) is an important class of soft matters which has received an increasing attention in recent years due to their easy fabrication into soft materials. It also has a wide applications in the field of sensing, catalysis, oil recovery, template synthesis of nanoporous materials etc.[1] It is very important to design suitable gelator molecules involving H-bond forming site and π–π stacking unit including van der Waals forces, electrostatic attraction and hydrophobic interaction which are necessary for the gelation.[2]

Chalcone and their derivatives are found to be well-known intermediates for the synthesis of various heterocyclic compounds. They exhibit a broad spectrum of biological activities[3] such as antiinflammatory, antituberculosis, antifungal, antimalarial, antileish-manicidal, anticancer etc.. The simple unsubstituted chalcone itself shown to inhibit the proliferation of human breast cancer cells.[4] In addition, hydroxy chalcones are also reported to induce apoptosis in melanoma cells.[5] Few of the chalcones are under investigation for antiblood platelet coagulation and antihaemostasis.[6] Isoliquiritigenin, a liquorice chalcone has been used as a phosphodiesterase III inhibitor for the treatment of cardiovascular diseases.[7] Moreover, there are only few reports on the organogelator based simple chalcone derivatives. However, chalcones with nitro group[8] and polycatenar type derivatives[9] have shown to exhibit gelation property. In continuation of our on-going research in the area of saccharide and gelation chemistry,[10] we have reported simple sugar-chalcone derivatives, which prone to form gel with different solvents and also about the dimer which has been formed from the cleavage of the sugar chalcone derivatives.

Results and discussion

Synthesis and characterization of sugar chalcone derivatives

4,6-*O*-butylidene-ᴅ-glucopyranose was synthesized by adopting the literature procedure.[11] (4,6-*O*-Butylidene-*β*-ᴅ-glucopyranosyl) propan-2-one (**2**), 2,3,4,6 tetra-*O*- acetylated-*β*-ᴅ-glucopyranosyl-propan-2-one (**3**), 2,3,4-xylose tetra-*O*-acetylated-*β*-ᴅ-pyranosyl-propan-2-one (**4**) were synthesized following the literature procedure.[12] The reaction of various sugar protected propane-2-one, **2-4** with aromatic aldehydes using pyrrolidine as catalyst resulted in 80-90% of the corresponding *α*,*β*-unsaturated compounds, **5-22** and **1-8** in **ESI** which upon reduction[13] using Zn/NH_4Cl in EtOH/H_2O gave the corresponding reduced chalcone derivatives, **23-29** in 59-84% yield (**Scheme 1**, Also see **ESI**). Reduction was carried out under neutral condition. Since most of the chalcone derivatives were partially soluble in ethanol, the reaction temperature was maintained from 40-50 °C. However, the compound, **29** was obtained in good yield by the reduction of its precursor[13] using Ethanol:DMSO solvent mixture in the ratio 9:1. But, the reduction of partially protected sugar-based ferrocenyl-chalcone[14] did not give any expected product under the given condition. Remarkable chemoselective carbon-carbon double bond reductions were observed in all the cases and the labile functionality like ketone was unaffected under these conditions. Structure of the synthesized sugar chalcone derivatives, **5-22** and **1-8** in **ESI** were determined by (^{1}H, ^{13}C) NMR spectroscopy, mass spectroscopy and elemental analysis. The appearance of two doublets at δ 7.89 and δ 6.94 with J value of 16.5 Hz each, corresponds to the *trans*-alkene protons whereas the two aromatic protons appeared as two singlets and the unreacted aldehyde proton appeared as a singlet at δ 9.95 in ^{1}H NMR spectrum for the compound, **15**. It also notably exhibited a

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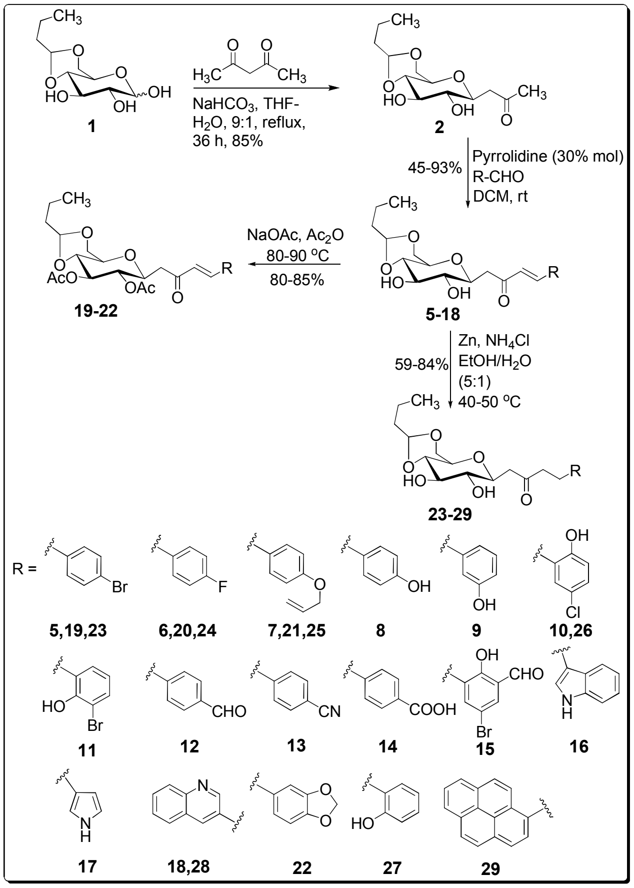
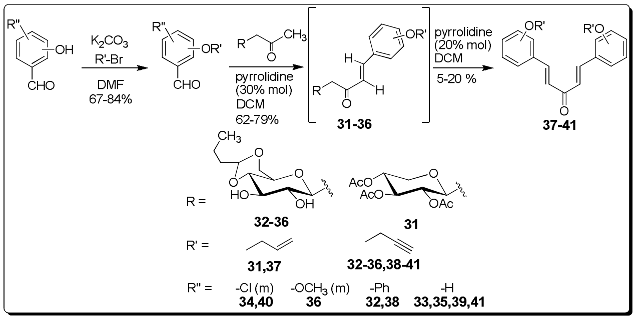
large coupling constant for the H-1 signal ($^3J_{H1,H2}$ ~ 9.5 Hz), indicating a *trans*-diaxial orientation of H-1 and H-2 as expected for a *β*-D-configured glucopyranose moiety.[13] The aldehyde carbon appeared at 198 ppm whereas the *α*-,*β*-unsaturated carbonyl carbon resonated at 195 ppm in ^{13}C NMR, gave further confirmation for the formation of sugar-chalcone product, **15**. The pyrene based sugar-chalcone derivative,[15] was synthesized and reduced using Zn to furnish the pyrene based sugar ketone derivative, **29**. In ^{1}H NMR spectrum of compound, **29** the characteristic methylene peaks were appeared as two multiplets in the region 3.1-3.0 and 2.8-2.6 ppm whereas two peaks at 45 ppm and 27 ppm corresponds to the methylene carbons in ^{13}C NMR confirmed the formation of the reduced product. From the DEPT-135 experiment (**See ESI**) the appearance of six peaks on one side of the base line corresponds to the six methylene carbons further confirmed the formation of the sugar ketone derivative, **29**.



Scheme 1 Synthesis of sugar-chalcones, **5-22** and its reduced derivatives, **23-29**.

Dimer formation

The unexpected allyl and propargyl dimers, **37-41** was obtained as a by-product in the aldol condensation between 2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosylpropane-2-one with 4-allyloxybenzaldehyde and also from the aldol condensation of 4,6-*O*-butylidene*β*-D-glucopyranosyl-propane-2-one with propargyloxy-napthaldehyde/o-propargyloxybenzaldehyde/m-chloropropargyloxybenzaldehyde/p-propargyloxybenzaldehyde respectively [**Scheme 2**]. Reaction condition was optimized to increase the yield of the dimer. However, *O*-alkylation was carried out as first step followed by aldol condensation to reduce the polarity of the dimer which inturn reduces the resolution factor (R_f) of the product thus minimizes the difficulty in isolation of the product using column chromatography. The yield of the dimer was obtained in the range of 5-20%.



Scheme 2 Synthesis of chalcone-dimer, **37-41**.

The structure of the synthesized dimers are shown in **Figure 1**. The formation of the dimer was confirmed from [^{1}H, ^{13}C] NMR and also from DEPT-135 experiments [**See ESI for more details**]. It is very clear from the ^{1}H NMR spectrum of compound **38**, that the dimer would have been formed only from the aldol condensed product because of the retainity of the *trans*-alkene double bonds which has a *J* value of 16.2 Hz. The dimer formation is also confirmed from ^{13}C NMR where the alkene carbons were observed at 136 ppm and 114 ppm. In addition, the characteristic carbonyl carbon was observed at 191 ppm. The cleavage of the sugar part was further confirmed from DEPT-135 experiment where one single peak for -OCH$_2$ group only was observed. The formation of the dimer product is also characterized from 2D experiments [**See ESI for more details**].

Mechanism for the formation of dimer product may be through the imine formation of the sugar-chalcone with the base (pyrrolidine) and the mechanistic pathway is not so clear. Pyrrolidine is a weak base and it could not produce the intermediate (enolate). Thus, the addition of pyrrolidine to the sugar-chalcone is expected to undergo enamine reaction followed by sugar cleavage which may result in the formation of the dimer. However, the exact mechanism is still ambiguous.

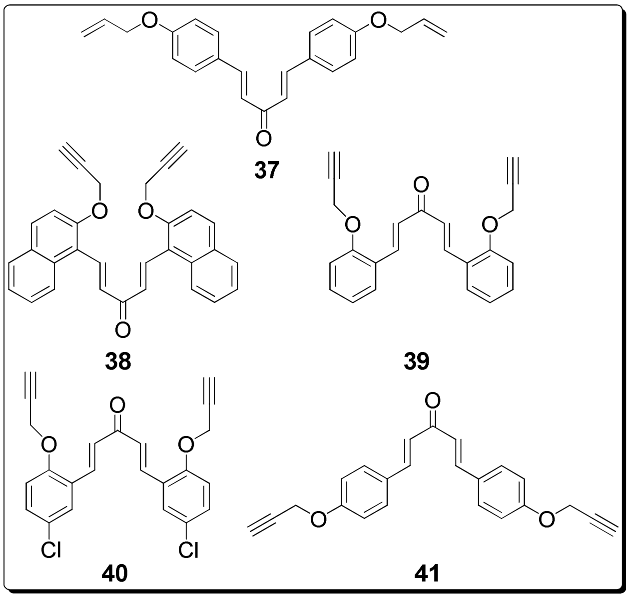


Figure 1 Proposed structure of the unexpected dimers, **37-41**.

Gelation experiment

Gels which are visco-elastic material was obtained by inversion tube method where the compound was reluctant to flow after heating followed by cooling [**Figure 2**]. Critical gelation concentration (CGC) means the minimum amount of compound which is trapped by the solvent. It actually judges the quality of the gel. In general, low CGC refers to a good gelator.

Forty six different sugar derivatives such as sugar-chalcone derivatives, sugar ketones, aldol product and the dimer were synthesized and tested for gelation in both solvents as well as solvent mixtures [**See ESI for more details**]. An appropriate amount of gelator was weighed and dissolved in a suitable solvent. It is then heated until dissolution or boiling point of the solvent and the homogeneous solution is allowed to cool at room temperature to obtain the gel. The sugar-chalcone derivatives, **8, 9, 21, 33** & **35** formed gel in different solvent at low CGC of 1.5, 1.5, 1.9, 1.6 and 1.8 wt/v% respectively. However, compounds **7** & **32** (CGC: 1.0 & 1.2%) form gel at a relatively lower concentration compared to the other derivatives. This may presumably be due to the high degree of hydrogen bonding and also because of the molecular architecture core and surface moiety. From the gelation studies, it is found that the sugar ketones, aldol product and the dimers did not form gel. It may be due to the absence of conjugation in the case of sugar ketone and aldol product and absence of the hexose sugar in the case of dimers. This further confirmed the necessity of the presence of hexose sugar and conjugation for gelation.

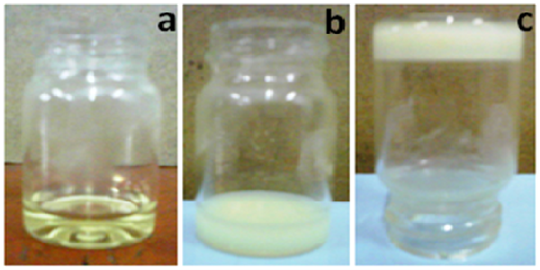


Figure 2 Representation of the formation of gel, **9** in $CHCl_3$, (a), after heating; (b), on cooling and (c), gel in inverted position.

Morphological studies

Morphology of the compounds that form gel were studied using FESEM and HRTEM analysis. SEM images of the compounds **7-9**, **21**, **3** (**see ESI**), **30**, **32** & **35** were obtained and its representative images are shown in **Figure 3**. Sugar chalcone derivatives, **7**, **21** & **3** (**see ESI**) which possessed allyloxy as side chain showed fibrous network, smooth non-fibrous surface and also embedded flake-like morphology respectively. The difference in the morphology is due to the difference in the protecting group present in the saccharide moieties. Thus, it is obvious from the results that nature of the protecting group in the saccharide also affects the morphology of the gel. Compound, **9** which has the hydroxy group in the meta position self assembles to form globules which was linked to each other through thin nanometer sized tape-like structure. Compound, **8** showed non-fibrous cluster-like morphology. Similar morphology has been observed with propargylated sugar-chalcone derivative, **35**. Compound, **30** did not form gel and the morphology was observed as particle-like structure. SEM image of the compound **32**, showed baggasse-like morphology, which on magnification was observed as a lamellar structure. Moreover, compounds which possess the fibrous network could trap more solvent compared to that of the lamellar structure has been well documented from FESEM analysis. Thus, the compound **32**, could not trap the solvent much as in the case of compound, **7** because of its lamellar morphology.

The internal morphology of the compound, **7** before and after gelation was studied using HRTEM analysis. The compound, **7** before gelation had rod like morphology whereas interestingly the same compound after gelation showed intertwined fibrous-like morphological structure. Moreover the gelator compound, **7** has a fibrillar network where the fibres which are in the nanometer scale join together to form a rope-like morphology. Also the joined fibres found to be intertwined in the right-hand side fashion. Hence, the appearance of intertwined structure clearly confirms the self assembly of the molecule. The HRTEM image of the compound, **7** before and after gelation is shown in **Figure 4**.

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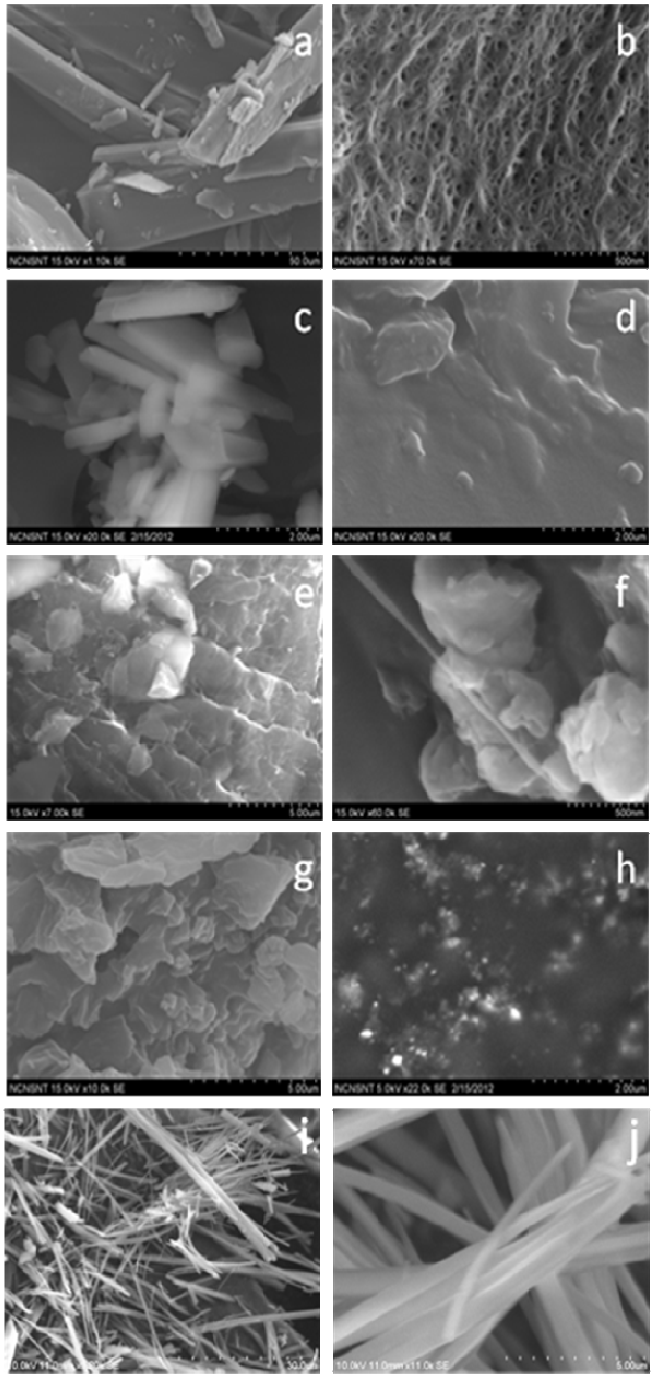

Figure 3 FESEM images (with different magnification) of compounds, (a), **7** before gelation [50 μm]; (b), **7** in DMSO+H_2O, after gelation [500 nm]; (c), **3** (**see ESI**) in DMSO+H_2O [2 μm]; (d), **21** in DMSO+H_2O [2 μm]; (e), **8** in $CHCl_3$+MeOH [5 μm]; (f), **9** in $CHCl_3$ [500 nm]; (g), **35** in EtOAc [5 μm]; (h),**30** in EtOAc [2 μm]; (i), **32** in $CHCl_3$ [30 μm] and (j), **32** in $CHCl_3$ [5 μm].

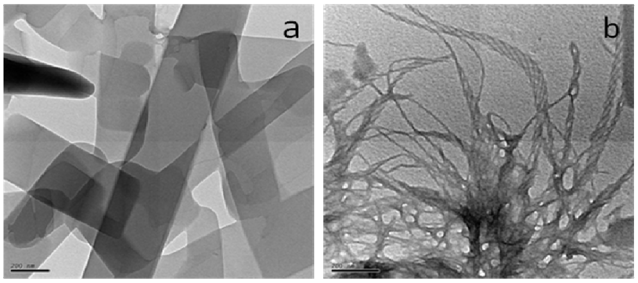

Figure 4 HRTEM image fo compound, **7** (200 nm): (a) solid and (b) gel in DMSO;H_2O mixture (10;1)

Correlation of present and previously reported results:

Gel formation was not observed for the compound, **31** which has the pentose sugar, allyloxy functionality and also α,β-unsaturated group. This clearly picturises that only the presence of $\pi-\pi$ interaction is not sufficient for gel formation. However, the formation of gel is also favoured by the presence of hexose sugar moiety. The previous work reported[16] in our laboratory which was related to the transformation of chalcone into various heterocyclic derivatives like pyrazole, spirooxindolopyrrolidines and pyrrolizidines failed to form gel. Recently, it was reported[17] that the sugar chalcone containing the halogen group crystallized but does not favour the gel formation and the crystallization is due to the presence of hydrogen bonding whereas similar derivative containing the hydroxy or allyl group substituent does not form crystal but rather formed gel. Additional experiment was conducted to rule out the existence of hydrogen bonding. In this process, compound, **8** which possess the hydroxyl group was propargylated but it was observed that the propargylated product, **35** did not lose its gelation property. Futhermore, it was reported[14] in the literature that the sugar-chalcone having the hydroxy group in the ortho position formed a crystal whereas the same derivative which possess the hydroxyl group in the meta or para position forms gel. Morphology of both the compound, **8** & **9** were analyzed using SEM and its representative images were shown in **Figure 3**.

Gel properties depend on various factors, such as time[18], temperature,[19] solvent,[20] composition, structure of the gelators[21] and even the use of different isomers. Solvent plays a vital role in the gelation process. The polarity of the solvent and the gelator has significant importance in the gelation. Hence the choice of solvent should be made with utmost care. Gelator, 7 has a good self-assembled structure (**Figure 3b**) with less polar solvents and it failed to gelate with more polar solvent like methanol or ethanol. Moreover from the SEM image, it is very clear that a minimal change in the structure of the chalcone and also with the change of the solvent, there has been a dramatic change in the morphological structure (**Figure 3**). This clearly portrays the high significance on the effect of solvent on gelation. When DMSO and water mixture was used in the ratio 10:1, the compound, 7 formed a clear gel whereas on increasing the volume of water resulted in precipitation. Hence, it is not only the solvent but also the solvent ratio has a severe impact on gelation. Moreover, it is also reported in the literature[22] that the solution or precipitate

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would be formed if the gelator-solvent interaction is too strong or too weak.

^{1}H NMR experiment of gelator

The gel formation of compound **8** is also evident from ^{1}H NMR experiment which was carried out before and after heating [**Figure 5**]. It was observed from the experiment that the peaks were broad before heating. It may be because of the self assembly of the compound whereas the same derivative after heating gave a well resolved spectra. Generally, broadening of NMR signal can be infuenced by either self-assembly or ligand exchange. In this case, the association of molecules was obtained from the ^{1}H NMR studies of the compound, **8**. The aggregation of molecule was observed in $CDCl_3$-DMSO solvent mixture in the ratio 1:4 at room temperature. On increasing the temperature by maintaining the solvent mixture ratio, the disaggregation was observed as evidenced from the splitting of broad peaks. In addition, the broadening may be either due to the exchange of the molecules between the solution and the gel states or limited tumbling of the molecules resulting in increased anisotrophy.

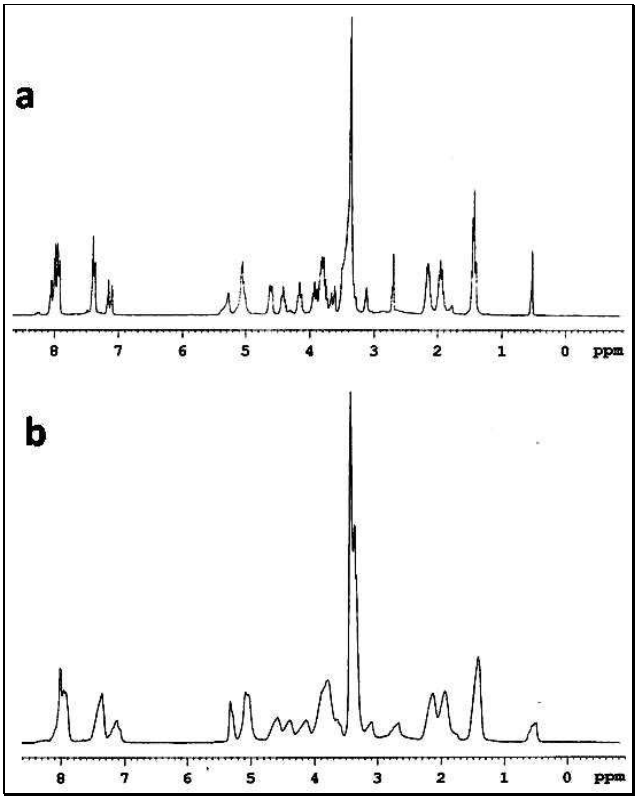

Figure 5: ^{1}HNMR spectra of compound **8** recorded in $CDCl_3$ + DMSO solvent mixture in 1:4 ratio (a) after heating, (b) before heating.

Thermal studies

The thermal properties of the sugar-chalcone was understood from DSC studies. DSC was taken for the compound as such in the solid state. The compound was then formed gel in DMSO-H_2O solvent mixture. DSC was then taken for the gel sample prepared. The peaks observed in both the cases were overlapped. The overlapped DSC graph is shown in **Figure 6**

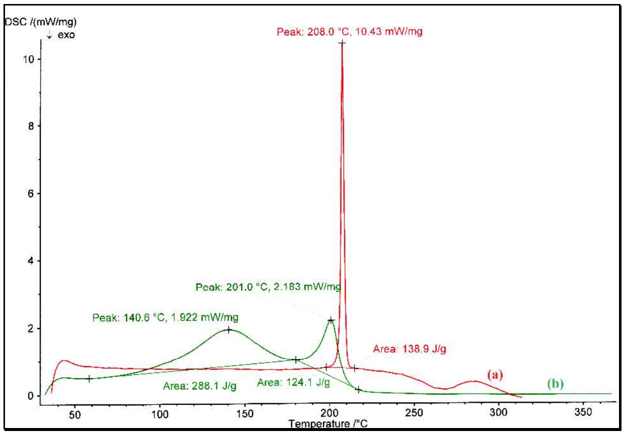

Figure 6 Differential Scanning Calorimetry (DSC) of the organogelator, **7**, (a) solid and (b) gel (DMSO + H_2O)

The melting peak of **7** was observed at 208 °C with ΔH value of 138.9 J/g in the solid phase whereas the same compound in the gel state melted at 201 °C with ΔH value of 124.1 J/g. The peak observed at 140 °C represents the liberation of both the water as well as the DMSO. Generally, the ΔH value of the gel dependent on the nature of the solvent used for gelation was well reported in literature.[23] The difference between the melting point of the solid **7** and the same compound in its gel form gives the stability of the gel formed. In general, if the difference is too wide it is said to be a good gelator. Here, in this case the difference in the melting temperature (T_m) between the solid and gel was found to be exactly 7 °C. Hence, the gel formed from the compound **7** was found to be a good gelator.

XRD studies

One of the side product which is the aldol product that was obtained from the aldol condensation of 4,6-*O*-butylidine-*β*-D-glucopyranosylpropan-2-one with 2-nitro benzaldehyde crystallized in ethylacetate and its ORTEP view is shown in the **Figure 7**. The crystallographic parameters of the crystal **30** are represented in **Table 1**.

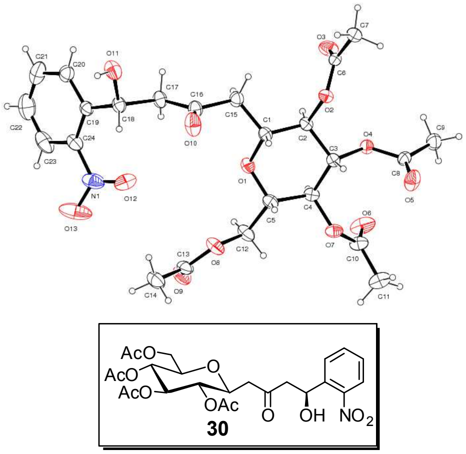

Figure 7 ORTEP view of compound **30** (top), Structure of the compound **38** (below).

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Table 1 Crystallographicic data for compounds, **30**

Parameters	**30**
Formula	$C_{24}H_{29}NO_{13}$
Formula weight	539.48
Crystal system	Monoclinic
Space group	P21
a (A)	9.523(5)
b (A)	5.419(5)
c (A)	26.034(5)
α (deg)	90.000(5)
β (deg)	95.631(5)
γ (deg)	90.000(5)
V (A3)	1337.0(14)
Z	2
Calculated density (mg/m^3)	1.340
μ (mm^{-1})	0.110
T (K)	293 (2)
No. of unique reflections	4783
No. of observed reflections	4630
R1, Rw	0.0396, 0.0963
GOF	568
Crystal habit	Needle, Colorless

The hydrogen bonding in the compound, **30** is represented in **Figure 8**. Eventhough it possessed hydroxy group it did not favour gelation, it may be because of the presence of electron withdrawing substituent (-NO_2 group attached to the phenyl moiety). Though it does not form gel, the SEM image of the compound **30** was obtained for comparison with the gel forming sugar-chalcones. From the SEM image, the morphology of the compound **30** was found to be particle-like structure.

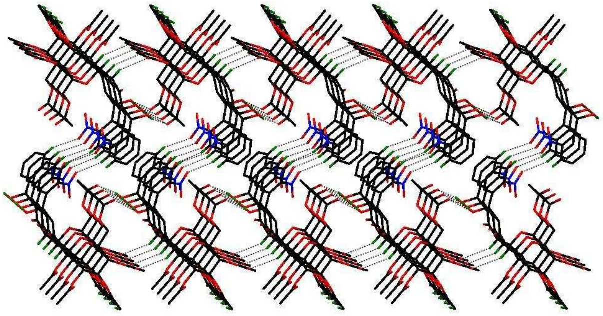

Figure 8 Hydrogen bonding interaction of compound, **38**

Conclusion

Thus, we have designed and synthesized several sugar-chalcone derivatives, which prone to form organogel. From the gelation studies it was obvious that even the position of hydrogen bonding substituent affect the gelation. Thus, it is concluded that for gelation of the propargylated or allylic sugar-based compound, π−π stacking of the double or triple bond plays a vital role. In addition, the self assembly of the sugar-chalcone compounds also depends on the position of the hydrogen bonding substituent. Moreover, it was found that the compounds which have electron donating groups formed gel whereas the compounds which possess the electron withdrawing group did not favour gelation. It was summarised that the compound for gel formation in sugar chalcone system should possess a hexose sugar, chalcone system, hydrogen bond forming site and also the π−π stacking.

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Notes and references

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