RSC Advances

Characterization and phase transition study of a versatile molecular gel from a glucose-triazole-hydrogenated cardanol conjugate†

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The synthesis and gelation properties of a structurally simple, renewable-resource-based glucose-triazole-hydrogenated cardanol conjugate (GTHCC) are reported. The conjugation of hydrogenated cardanol and glucose was done using a triazole linker employing copper(ı) mediated acetylene azide cycloaddition 'click' chemistry in the key step. The GTHCC was found to form four different classes of gels; namely, (i) hydrogel from aqueous-protic solvents, (ii) organogel from non-polar solvents, (iii) gel from vegetable oil and (iv) gel from petroleum oil. In a water–methanol (1 : 1) mixture, the conjugate acted as a stable thermoreversible supergelator, even at a very low gelator concentration of 0.03% w/v. Unlike glycoside-based gels derived from hydrogenated cardanol and glucose, the GTHCC is stable under acidic as well as basic conditions, owing to the covalent linkages in the tether. The intrinsic fluorescence of the hydrogel was found to be sensitive towards a gel–sol transition.

Introduction

Gels are abundant and widely studied soft materials with various applications in pharmacology, material science, cosmetics, lubrication, pollution control, electronics, sensing, chromatography and surface engineering.[1–8] Different gels can be classified on the basis of the medium which they hold.[7] The formation of a molecular gel in different media mainly depends upon non-covalent forces like π–π stacking, hydrogen bonding, hydrophobic interactions and van der Waals forces.[1,7–10] Molecular hydrogels could be formed by the assembly of low molecular weight organic molecules into fibrous networks, which entrap solvent molecules. The development of new molecular gels has been a continuing and fascinating area of applied organic chemistry research.[1] A major challenge in this field is unravelling the preparation of structurally simple molecular gels, generated from inexpensive and renewable raw-materials and using convenient synthetic routes, for high volume applications.

Molecular gels from sugar-based compounds are highly attractive for development owing to their intrinsic chirality, biocompatibility and natural abundance.[11] Such gelators have applications as advanced materials, drug delivery systems, for separating biomolecules or for the formation of supramolecular architecture.[12] It occurred to us that the conjugates derived from

a sugar (polar head) and a hydrogenated cardanol (3-pentadecylphenol; a non-polar tail) could display gelation properties.[13] Cardanol is a low-cost raw material that is generated in industrial quantities from cashew nut shell liquid (CNSL), which is a by-product of the cashew industry.[14] Hydrogenated cardanol serves as a raw material for technologically relevant surface active products.[3,14] Previously, John and co-workers studied the applications of the cardanyl glucoside (1-*o*-3′-*n*-(pentadecyl) phenyl-α-ᴅ-glucopyranoside) and its siblings, and their gelation properties.[14,15] However, glucoside-based gels are susceptible to hydrolysis under acidic conditions which limits their applications. We have now designed a glucose–triazole-hydrogenated cardanol conjugate (GTHCC) **1** which is robust, stable under acidic or basic conditions and can be prepared readily by applying a copper(ı) mediated acetylene azide (CuAAC) click reaction. The GTHCC designed by us is a new class of compound, and it contains a polar glucose head connected through a triazole incorporated linker to the benzene ring with a 15C nonpolar tail (Fig. 1). The conjugate **1** is robust, as the hydrogenated cardanol and the glucose units are linked covalently through the tether, which incorporates the
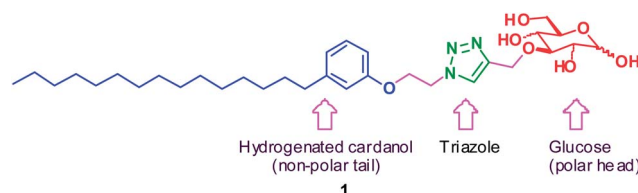
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Fig. 1 Structure of the glucose-triazole-hydrogenated cardanol conjugate (GTHCC) **1**.

1,4-disubstituted triazole unit. Gels which show thermoreversible sol–gel transitions are an important class of gels and have been studied widely.[7] Thermoreversible hydrogels exhibit a sol–gel transition at a certain temperature, which occurs as a consequence of a sudden change in the solvation state.[7,8] We report here the synthesis and thermosensitive gelation properties of a glucose–triazole-hydrogenated cardanol conjugate (GTHCC) **1** (Fig. 1) that satisfies the above criteria.

Experimental section

Materials and general methods

For the synthesis and characterisation of the glucose-triazole-hydrogenated cardanol conjugate, all the reagents and solvents were purchased from Sigma-Aldrich, E-Merck or SRL, India. Melting points were uncorrected and were determined using open-ended capillary tubes on a VEEGO VMP-DS instrument. Thin layer chromatography (TLC) was performed with silica gel-G (SRL, India) or silica gel GF-254 (E-Merck) using hexanes–ethyl acetate as the eluent, and the spots were visualized with a short exposure to iodine vapor or UV light. Column chromatography was carried out on silica gel (100–200 mesh, Acme Synthetic Chemicals, India). Hexanes used in column chromatography refer to the 60–80 °C boiling mixture. Infra Red (IR) spectra were recorded as KBr pellets on a Bomem MB104 spectrometer or a Nicolet-6700 spectrometer. Specific rotations were recorded in $CHCl_3$ on a Rudolph Research Analytical Automatic Polarimeter. The ^1H nuclear magnetic resonance (NMR) (400 MHz), ^{13}C NMR (100 MHz) and Distortionless Enhancement by Polarization Transfer (DEPT) spectra were recorded as dilute solutions in a mixture of $CDCl_3$ and CCl_4 (1 : 1) or DMSO-d_6 using a Bruker 400 MHz NMR spectrometer with tetramethyl silane (TMS) (0 ppm) as the internal standard; J values are given in Hz. ^1H NMR spectral data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constant and integration. High resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer using the electron spray ionization mode. 1-(2-bromoethoxy)-3-pentadecylbenzene **2** (ref. 16) and the propargyl glucose diacetonide ether **4** (ref. 17) were prepared according to literature procedures. Cardanol was purchased from Sabari Industries, Sedurapet, Pondicherry and hydrogenated in a Paar Hydrogenation Apparatus. All other starting materials or reagents were purchased from SRL India and used as received.

All the solvents used for the gel preparation and gel characterisation experiments were of spectroscopic grade. Triple-distilled water was used for the experiment, which was prepared using alkaline permanganate solution. Dynamic light scattering (DLS) analysis was carried out with a Malvern Zetasizer nano series, with a path length of 1 cm. The wavelength of the laser used was 632.8 nm and the scattering angle was kept at 90°. Viscosity measurements were performed using an SV-10 Vibro Viscometer. FT-IR spectra were recorded using a Perkin Elmer Spectrum FT-IR instrument. The scanning electron microscope images were taken using an F E I Quanta FEG 200 – High Resolution Scanning Electron Microscope. Differential Scanning Calorimetric measurements were performed using a TA-DSC Q-200 instrument. Fluorescence emission and fluorescence anisotropy measurements were performed using a Fluoromax-4 fluorescence spectrophotometer. Rheological measurements of the storage (G') and loss (G'') modules were taken for the GTHCC gel in (A) water–methanol (1 : 1), and (B) cyclohexane solvents at 20 °C, using a Physica MCR301 rheometer in the cone plate configuration (25 mM diameter, 1.002° angle and gap size 52 μM), which was equipped with a thermocouple unit. Measurements were conducted with the strain rate held at 1.00%. Temperature dependence was studied for the GTHCC in water–methanol (1 : 1) using temperature intervals of 1 °C min^{-1}, over the range 15–55 °C.

Gelation test

The gelation ability of the GTHCC in different fractions of water–alcohol mixtures was determined by weighing 5–50 g L^{-1} of the compound and adding them to different solvents and oils. Then the mixtures were heated until the solutions became transparent, and were allowed to cool at 23–20 °C. Gel formation was checked by the tube inversion method.[18]

Synthetic scheme for materials

The synthesis of the GTHCC is straightforward and goes through a CuAAC reaction between glucose diacetonide propargyl ether **4** and hydrogenated cardanol based azide **3** as the pivotal step (Scheme 1). The azide **3** was prepared from the corresponding bromide **2**. The acetonide protecting groups in the GTHCC diacetonide **5** could be stripped sequentially or selectively to provide mono-acetonide **6** or GTHCC **1**. A small fraction (<3%) of the β-anomer of **1** is preferentially crystallized from column fractions during the column chromatographic purification of a 1 : 1 mixture of α and β-anomers. The ^1H NMR spectrum of GTHCC **1** in $CDCl_3$ displayed broad peaks for the hydrogens on the glucose portion, indicating intermolecular hydrogen bonding and aggregation. GTHCC was peracetylated to **7** with acetic anhydride in pyridine. Both the mono-acetonide **6** and peracetylated product **7** did not show any inter-molecular associations in $CDCl_3$. Full descriptions of the synthetic procedures and the molecular characterisation data are given in the ESI.†

Results and discussion

Gelation properties

GTHCC **1** was tested for its gelation properties in different aqueous-protic solvent mixtures, vegetable oil, petroleum oil and non-polar organic solvents; the results are given in Table 1 (ESI Table 1†). It was found that when using GTHCC as a low molecular weight gelator, four different classes of gel could be found; that is, (i) hydrogel from aqueous-protic solvent mixtures, (ii) organogel from non-polar solvents, (iii) gel from vegetable oil and (iv) gel from petroleum oil. The GTHCC formed a hydrogel in a mixture of water and methanol, or water and ethanol, at the initial concentration of 5 g L^{-1}. The critical gelation concentration (CGC) of GTHCC was determined for the

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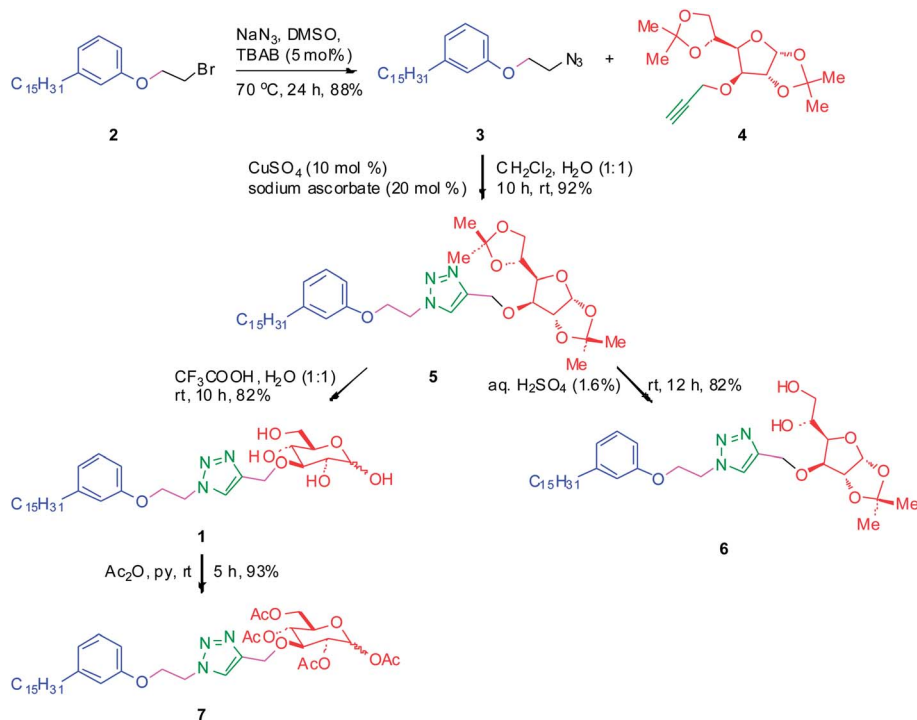
Scheme 1

different fractions of the water–methanol and water–ethanol solvent mixtures (ESI Table 1†). The best gelation ability was observed in the water–methanol (1 : 1) mixture, where CGC was reached at 0.25 mg mL^{-1}. The CGC of GTHCC hydrogel is less than 0.03% (w/v). Therefore, GTHCC in a water–methanol (1 : 1) mixture can be regarded as a supergelator. Thus 1 belongs to a group of low molecular weight compounds which have a CGC of less than 1% (w/v).[7,19,20]

The GTHCC hydrogel formed from the water–methanol mixture (1 : 1) was stable for several days at room temperature. When the hydrogel was heated above 53 °C it formed a clear transparent solution, which indicates the complete conversion

Table 1 Results for the gelation test of GTHCC (at 5–50 g L^{-1}) at room temperature[a]

Aqueous–protic solvent mixture	State	T_{gs}
Water–methanol (1 : 1)	Gel (CGC = 0.025%, 0.25 mg mL^{-1})	42 °C
Water–ethanol (1 : 1)	Gel (CGC = 0.08%, 0.8 mg mL^{-1})	33 °C
Water–n-propanol (1 : 1)	Solution	
Water–n-butanol (1 : 1)	Solution	
Water	Precipitate	
Methanol	Solution	
Ethanol	Solution	
n-Propanol	Solution	
Butanol	Solution	
Non-polar organic solvent		
Cyclohexane	Gel (CGC = 2%, 20 mg mL^{-1})	
Toluene	Gel	
Vegetable oil		
Coconut oil	Gel	
Mustard oil	Gel	
Soybean oil	Gel	
Petroleum oil		
Petrol	Gel (CGC = 3.5%, 35 mg mL^{-1})	
Diesel	Gel	

[a] T_{gs} = gel–sol transition temperature; CGC = Critical Gelation Concentration at 23–20 °C.

of the gel into a sol state (Fig. 2). Upon gradual cooling the hydrogel could be reproduced, which shows that the molecule is a thermoreversible supergelator. The GTHCC formed stable hydrogels even with 0.1 M aqueous HCl and methanol (1 : 1), and 0.1 M aqueous NaOH and methanol (1 : 1), solutions. This indicates that the hydrogel is stable in highly acidic as well as basic conditions.

Rheology and fluorescence studies of the gel

The formation of a true gel and the sol–gel transition temperature are reliably inferred from the measurement of the rheological parameters of the sample.[21–24] Fig. 3 shows the frequency dependence of the storage modulus (G') and loss modulus (G'') of GTHCC gels in (A) water–methanol (1 : 1) and (B) cyclohexane solvents. The results show linear regions of G' and G'' with a frequency sweep (1–100 rad s^{-1}). There is no change and crossover observed in the storage modulus and loss modulus of either gel over the frequency range. The storage modulus (G') is the dominant variable in both cases, which is the most important characteristic of a molecular gel.[21,22] Moreover, both the storage and loss moduli are almost independent of the frequency, indicating a gel-like behaviour. The frequency measurements indicate that the gels did not show any change in rheological properties over the frequency range.

Fig. 4 shows the changes in the storage modulus (G') and the loss modulus (G'') at an angular frequency of 10 rad s^{-1}, as a function of temperature for the GTHCC gel in the water–methanol (1 : 1) solvent mixture. The crossover point of the G' and G'' above 49 °C gives an indication of the transition from the solid gel state to the fluid sol state.[22,23] This result suggests that above 49 °C the GTHCC gel formed in the aqueous methanolic medium is converted to a sol state.

The gelation process of GTHCC in the water–methanol mixture (1 : 1) is also studied by dynamic light scattering (DLS) analysis. The DLS analysis has shown that the gelation process involves a change of hydrodynamic diameters, with a mean diameter from 22–23 nm to 5–7 μm (Fig. 5, 6, 7(B) and ESI Fig. 1†). In the sol state (57 °C), the DLS histogram plot (ESI Fig. 1(A)†) indicates the formation of a micellar structure which has a hydrodynamic diameter distribution from 20–50 nm. Generally the diameters for micellar structures are in the range of 1–300 nm.[25,26] In the gel state the distribution of the hydrodynamic diameters increases due to the assembly of larger

Fig. 2 Demonstration of the thermoreversible supergelator characteristics of a GTHCC hydrogel formed from a water–methanol mixture (1 : 1).

micellar aggregates, which show a diameter distribution in the range 3–5 μm (ESI Fig. 1(B)†). Fig. 7(B) shows the plot for the changes in mean diameter of the hydrogel with the variation of temperature. An abrupt increase in micellar size has been observed at 49 °C, which is due to the intermicellar interaction leading to the formation of larger micellar aggregates. After 42 °C the mean diameter increases sharply due to larger aggregates, which are assembled together to form large fiber networks or gels. DLS studies of the GTHCC hydrogel indicate that the gelation process involves different modes of aggregation. The differential scanning calorimetric (DSC) analysis of the hydrogel in the water–methanol (1 : 1) mixture provides further insight into the changes observed in the physical state of the sample. The endothermic peaks in the DSC plot represent the gel–sol transition temperature (T_{gs}) which provides information regarding the interaction of the gelator molecules. Multiple endothermic transition peaks have been observed in the DSC plot of the hydrogel (Fig. 7(A)), which is due to the gelation process of GTHCC in the water–methanol (1 : 1) mixture involving various modes of aggregation. There is a sharp endothermic transition at 42 °C (T_{gs}), which happens due to the melting of the gel to higher micellar aggregates, whereas the small endothermic transition at 49 °C is due to the dissolution of larger micellar aggregates to micellar structures, which is confirmed by DLS analysis. The viscosity studies of the GTHCC hydrogel in the water–methanol (1 : 1) mixture provide valuable information regarding the behaviour of the gel with the variation of temperature. The viscosity of the hydrogel decreases with an increase in temperature (Fig. 7(C)). A sharp decrease in viscosity was observed after 49 °C and after 54 °C it remains constant due to its complete conversion from a gel state to a sol state.

The intrinsic fluorescence emission and fluorescence anisotropy (Fig. 7(D) and ESI Fig. 4†) of GTHCC provides more useful information regarding the gelation process in the water–methanol (1 : 1) mixture. The GTHCC hydrogel in the water–methanol (1 : 1) mixture gives an emission at 300 nm. The hydrogel gives a higher emission intensity in the gel state at low temperatures, whereas with an increase in temperature the emission intensity decreases (Fig. 7(D) and ESI Fig. 4†). A sharp decrease in fluorescence intensity is observed at 50 °C and after 54 °C it remains constant due to a complete conversion to a sol state. The decrease in fluorescence intensity with increase in temperature is observed due to an increase in the non-radiative decay process with the conversion of the gel to a sol state. The fluorescence anisotropy measurement of the GTHCC hydrogel shows a similar trend in fluorescence emission. A higher fluorescence anisotropy is observed in the gel state, indicating a highly rigid and compact structure formed by the GTHCC hydrogel, which restricts its rotational motion. With an increase in temperature the fluorescence anisotropy decreases, due to the melting of the hydrogel to a sol state, which increases the molecular rotation of the molecules.

From the above study of four conceptually different investigations: DLS, DSC, viscosity and fluorescence parameters, it is concluded that the gelation process of the GTHCC supergelator in a water–methanol (1 : 1) medium involves the formation of three different states of GTHCC aggregation at different
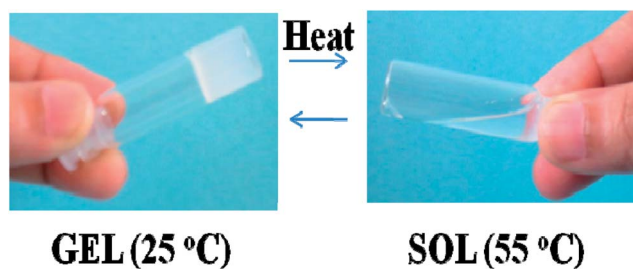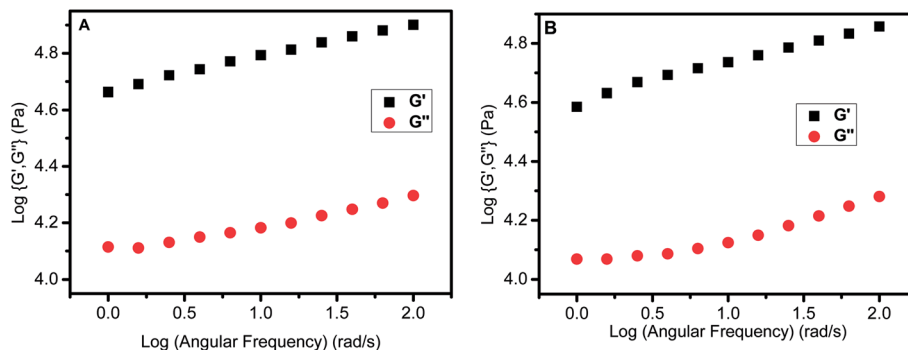
Fig. 3 Frequency dependence of the storage modulus (G') and the loss modulus (G'') of GTHCC gel at 20 °C in (A) water–methanol (1 : 1) and (B) cyclohexane (strain rate 1.00%).
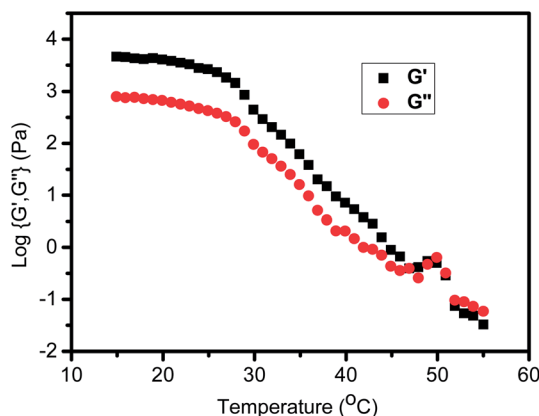

Fig. 4 Temperature dependence of the storage modulus (G') and the loss modulus (G'') of GTHCC gel in water–methanol (1 : 1) at a frequency of 10 rad s^{-1}. [GTHCC] = 2 mg mL^{-1}.
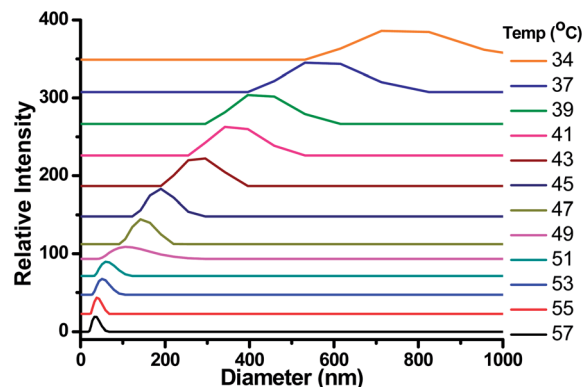

Fig. 6 DLS plot for distribution of the hydrodynamic diameter of GTHCC with the variation of temperature in water–methanol (1 : 1) solvent ([GTHCC] = 2 mg mL^{-1}).
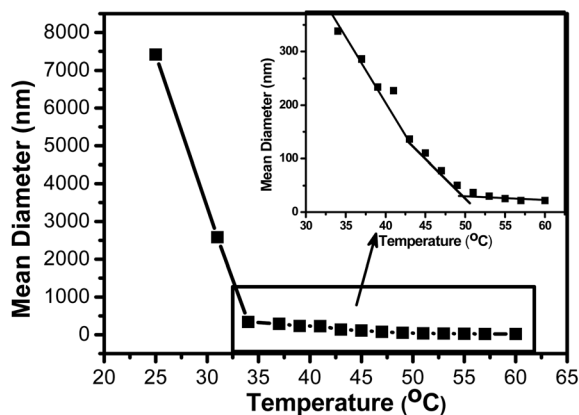

Fig. 5 Dynamic Light scattering (DLS) plot for the variation of mean diameter of hydrogel with the variation of temperature in water–methanol (1 : 1), ([GTHCC] = 2 mg mL^{-1}). (Error = ±5%).

temperature ranges: at higher temperatures, above 49 °C, the transparent sol state causes the compound to exist in a micellar organization; on decreasing the temperature, to between 38 °C to 44 °C, higher micellar aggregates form; and the gel phase forms below 27 °C.

Morphology of gel

HR-SEM images (Fig. 8(A) and ESI Fig. 3(A)†) of a dried gold-coated hydrogel of GTHCC in a water–methanol (1 : 1) mixture showed the formation of a spongy sheet -like structure which has cavities of μm scale inside it. From the HR-SEM images it can be concluded that the molecules of GTHCC assemble over one another to form a sheet-like structure, and the cavities formed by these assemblies entrap solvent molecules through capillary forces and surface tension.[14] This observation suggests that the van der Waals hydrophobic interactions between the nonpolar hydrogenated cardanol tails and the triazole linker could be the main driving force for the gelation properties of the compound. The FT-IR data (ESI Fig. 2†) of the hydrogel in the deuterated water–methanol (1 : 1) mixture show a broad peak at 3450 cm^{-1}, indicating intermolecular hydrogen bonding between the –OH groups of the GTHCC conjugate.[27] Neither mono-acetonide **6** nor peracetylated GTHCC **7** formed a gel at concentrations of up to 5 mg mL^{-1} in the mixture of water and methanol (1 : 1), indicating that intermolecular hydrogen bonding is also crucial for gelation. Thus, along with van der Waals hydrophobic interactions, intermolecular hydrogen bonding plays an important role in formation of a supergelator with an exceptionally high gelation capacity.
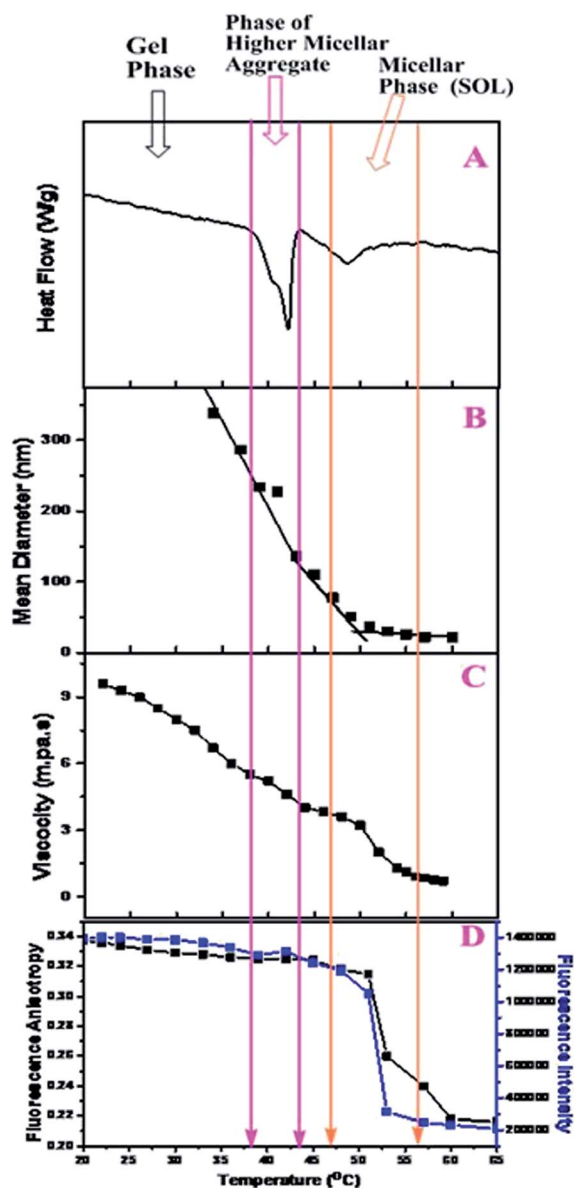
Fig. 7 (A) Endothermic plot of differential scanning calorimetric analysis; (B) Dynamic Light scattering (DLS) plot for the variation of mean diameter of hydrogel with the variation of temperature; (C) plot for the viscosity of the hydrogel with the variation of temperature; (D) plot for fluorescence intensity and fluorescence anisotropy of the GTHCC hydrogel (λ_{ex} = 274 nm and λ_{em} = 300 nm), in water–methanol (1 : 1) solvent, ([GTHCC] = 2 mg mL^{-1}). (Error = ±5%).

Significantly, the GTHCC **1** was found to induce gelation in non-polar aprotic solvents like cyclohexane and petrol. The HR-SEM image of the GTHCC gel in cyclohexane shown in Fig. 8(B) is comprised of twisted and interconnected sheets. At 500 nm magnification (ESI Fig. 3(B)†) the GTHCC gel displayed the fibrous nature of the interconnected sheets. The HR-SEM images suggest that the hydrophobic interactions between the nonpolar hydrogenated cardanol tails and the triazole linker are the main driving force for the gelation of the compound in cyclohexane. A similar observation was reported by the John research group for cardanyl glucoside gelation in cyclohexane.[14]
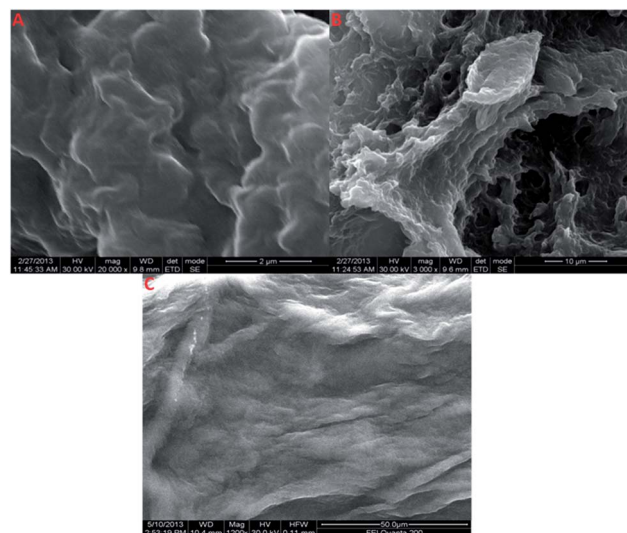

Fig. 8 HR-SEM images of the GTHCC gel in (A) water–methanol (1 : 1), (B) cyclohexane and (C) petrol.

The HR-SEM image of the GTHCC gel in petrol shows that the compound aggregates to form entangled fibre networks (Fig. 8(C)). The CGC of GTHCC in petrol is 3.5%. In a physical mixture of water and petrol, the addition of GTHCC forms a phase-selective gel with the petrol, which separates from the water and forms a layer that floats. This observation could have implications in oil-slick management. The studied morphology of GTHCC gel in different solvents displays significant variations in the morphology of self-assembled systems.

Conclusion

In conclusion, we present a glucose-triazole-hydrogenated cardanol conjugate (GTHCC) as a new type of molecular gel, which is synthesized using hydrogenated cardanol and glucose which are sufficiently cheap and are from renewable natural resources. GTHCC forms four different classes of gels in aqueous-protic solvent mixtures, non-polar organic solvents, vegetable oils and petroleum oils, which are well supported by rheological measurements. In a water–methanol (1 : 1) mixture it shows highly stable thermoreversible supergelation ability. The DLS, DSC, viscosity measurements, intrinsic fluorescence emission, fluorescence anisotropy measurements and SEM analysis shows the formation of micellar structures (20–50 nm diameters) in the sol state. Intermicellar aggregation leads to the formation of larger micellar structures and the interaction of larger aggregates to form sheet-like spongy gel networks which entrap the solvent molecule by surface tension effects in the water–methanol (1 : 1). Owing to the long non-polar tail and polar glucose head, GTHCC induces gelation even in non-polar aprotic solvents like cyclohexane and petrol.

Acknowledgements

References

1 N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821.

2 S. Kiyonaka, K. Sugiyasu, S. Shinkai and I. Hamachi, *J. Am. Chem. Soc.*, 2002, **124**, 10954.

3 G. John and P. K. Vemula, *Soft Matter*, 2006, **2**, 909.

4 S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan and G. John, *Angew. Chem., Int. Ed.*, 2010, **49**, 7695.

5 A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed.*, 2008, **47**, 8002.

6 S. P. Bhuniya and B. H. Kim, *Chem. Commun.*, 2006, **17**, 1842.

7 *Gels Handbook*, ed. Y. Osada and K. Kajiwara, Academic Press, London, 2000, vol. 1, The Fundamentals.

8 F. E. Fages, *Topics in Current Chemistry, Low Molecular Mass Gelators*, Springer, Berlin, 2005, p. 256.

9 H. Y. Lee, S. R. Nam and J.-I. Hong, *J. Am. Chem. Soc.*, 2007, **129**, 1040.

10 P. Terech, in *Molecular Gels*, ed. R. G. Wiess, Kluwer Academic Publishers, The Netherlands, 2004.

11 P. K. Vemula, J. Li and G. John, *J. Am. Chem. Soc.*, 2006, **128**, 8932.

12 Z. Yang, G. Liang, M. Ma, A. S. Abbah, W. W. Lu and B. D. Xu, *Chem. Commun.*, 2007, **8**, 843.

13 H. S. P. Rao, A. K. Mishra, M. Kamalraj and J. Swain, Preparation and properties of sugar–triazole cardanol conjugates, Provisional Indian Patent application no.: 4611/CHE/2013, 2013.

14 V. S. Balachandran, S. R. Jadhav, P. K. Vemula and G. John, *Chem. Soc. Rev.*, 2013, **42**, 427.

15 G. John, J. H. Jung, M. Masuda and T. Shimizu, *Langmuir*, 2004, **20**, 2060.

16 O. A. Attanasi, G. Mele, P. Filippone, S. E. Mazzetto and G. Vasapollo, *ARKIVOC*, 2009, (viii), 69–84.

17 (*a*) V. Baliah, A. Ekambaram and T. S. Govindarajan, *Curr. Sci.*, 1954, **23**, 264; (*b*) A. Roy, S. K. Sahabuddin, B. Achari and S. B. Mandal, *Tetrahedron*, 2005, **61**, 365–371.

18 A. R. Hirst, I. A. Coates, T. R. Boucheteau, J. F. Miravet, B. Escuder, V. Castelletto, I. W. Hamley and D. K. Smith, *J. Am. Chem. Soc.*, 2008, **130**, 9113.

19 D. K. Smith, *Molecular Gels: Nanostructured Soft Materials in Organic Nanostructures*, ed. J. L. Atwood and J. W. Steed, Wiley-VCH, Weinheim, Germany, 2008, p. 111.

20 K. Tiefenbacher, H. Dube, D. Ajami and J. Rebek, Jr, *Chem. Commun.*, 2011, **47**, 7341.

21 P. Rajamalli, P. S. Sheet and E. Prasad, *Chem. Commun.*, 2013, **49**, 6758.

22 D. R. Nisbet, K. E. Crompton, S. D. Hamilton, S. Shirakawa, R. J. Prankerd, D. I. Finkelstein, M. K. Horne and J. S. Forsythe, *Biophys. Chem.*, 2006, **121**, 14.

23 A. K. A. S. Brun-Graeppi, C. Richard, M. Bessodes, D. Scherman, T. Narita, G. Ducouret and O. W. Merten, *Carbohydr. Polym.*, 2010, **80**, 555.

24 Y. Ikeuchi, H. Tanji, K. Kim and A. Suzuki, *J. Agric. Food Chem.*, 1992, **40**, 1751.

25 T. Dwars, E. Paetzold and G. Oehme, *Angew. Chem., Int. Ed.*, 2005, **44**, 7174.

26 P. Rajamalli, S. Atta, S. Maity and E. Prasad, *Chem. Commun.*, 2013, **49**, 1744.

27 A. Awasthi and J. P. Shukla, *Ultrasonics*, 2003, **41**, 477.