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ARTICLE TYPE

Enantiomeric organogelators from D-/L- arabinose for phase selective gelation of crude oil and their gel as a photochemical micro reactor

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Enantiomeric D- or L- arabinose based low molecular-weight organogelators (LMOGs), accessible in a single synthetic step from D-/L- arabinose have been found to be efficient gelators for aromatic solvents and refined and crude oil. The organogel has also been successfully used as a micro reactor for a photochemical reaction.

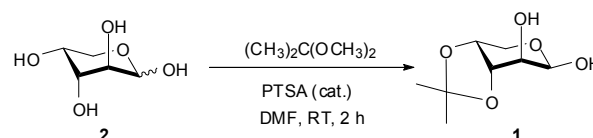
Low Molecular Weight Organogelators (LMOGs) are a relatively new class of soft materials that are attracting a lot of attention due to their potential applications in diverse fields.¹⁻² Most of the LMOGs are based on a wide variety of small molecules such as steroids,^{2a,3} amino acids,⁴ monosaccharides,⁵ polyaromatic compounds⁶ and ureas.⁷ Recently, the use of various organogels for catalysis and as micro-reactors has been reported and reviewed wherein the role of the rheology, morphology and chirality of the organogelator are proposed to have important roles in guiding the reactivity and selectivity of the reactions.⁸ In this context, organogel systems have been reported that guide the enantio-differentiating dimerization of substituted anthracenes.⁹ An elegant work on the effects of supramolecular assembly via gelation, on the stereoselectivity of the conjugate addition to cyclohexanone has also been reported.¹⁰ Quite a few chiral organogelators have been reported in literature, mainly bearing steroid, amino acid and carbohydrate moieties.^{2a,3,4,5} However, most of these suffer from the limitation that only one of the enantiomers of the gelator molecule has been explored, mainly due to the lack of easy and feasible access to the other enantiomer. A few chiral organogelators and organogels in both the enantiomeric forms have also been reported.¹¹ However, more of such simple chiral gelators for which both the enantiomers are easily accessible is desirable. Our group is involved in the development of novel uses of carbohydrate based materials for different purposes including asymmetric catalysis and as chiral micro-reactors via organogel formation. As a simple and easy source of enantiomeric gelators, arabinose is a good alternative since both the enantiomers are available commercially and cheaply. Herein, we report our findings of the gelation properties of the easily synthesized compounds D- and L- 3,4-O-isopropylidene-arabinose (**1**) and the application of the organogel for phase selective organogelation (PSOG) of crude oil and as a micro-reactor for photochemical reactions.

The desired compounds D-/L- **1** were synthesized following the method reported by Kiso and Hasegawa¹² exclusively as the β-anomers (Scheme 1). The products were characterized by

standard procedures and the data corresponded well with the reported and calculated values.¹³

Preliminary gelation studies were carried out with enantiopure D-**1** and L-**1** separately with benzene. The gelation studies showed both enantiopure D-**1** and L-**1** to be very good gelators at very low concentration levels. The Minimum Gelator Concentration (MGC) was 0.5% (w/v) (Fig. 1a and b) which are amongst the lowest for this category of organogelators and thus D-**1** and L-**1** qualifies as supergelators. Similar gels were also formed at higher concentrations. All the gels were thermo-reversible in nature. The gel to sol transition temperature (T_g) of the 0.5% benzene organogel was found to be 46-48 °C.

The benzene organogel from D-**1** and L-**1** were characterized by optical microscopy (Fig. S29, ESI[†]) and Scanning Electron Microscopy (SEM). The SEM micrograph of the benzene xerogel of D-**1** (Fig. S30a, ESI[†]) confirmed the 3-D fibre network in which the solvent is trapped. The xerogel from L-**1** was also characterized by SEM and showed a similar fibre structure (Fig. S30b, ESI[†]). To establish the true gel-like properties, the rheological studies were also carried out.¹⁴ The rheological experiments with the benzene gel at 1% (w/v) concentration was carried out by a frequency sweep experiment at a constant stress (Fig. 2). In the linear viscoelastic region of the gel, the ratio of the values of G' to G'' varied from about 3-8 showing that it is a weak gel. The gels from D- or L- isomers being physically and structurally very similar, the rheological properties of the gel from L-**1** were also expected to be the similar as that with D-**1**. The gelation property of racemic-**1** was also studied and it was



Scheme 1 Synthesis of organogelator D-**1**. The same reaction was also applied for the synthesis of L-**1**

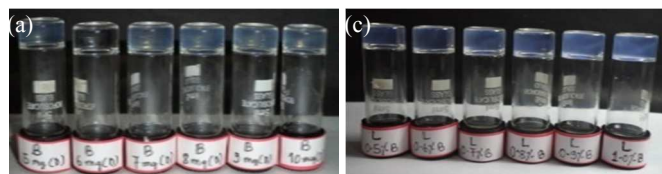


Fig. 1 Organogels of benzene at 0.5%, 0.8%, 0.9% and 1% (w/v) concentrations of (a) D-**1** and (b) L-**1**

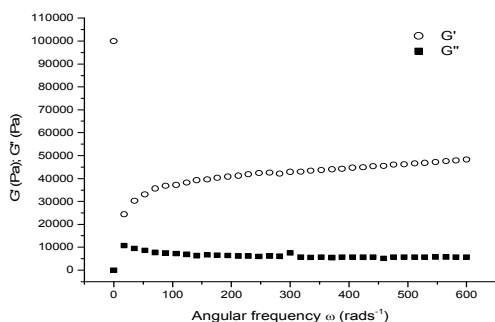


Fig. 2 Rheology (frequency sweep) of the 1.0% (w/v) organogel from D-1 and benzene. G' = storage modulus, G'' = Loss modulus

found that in the racemic form, **1** was not able to gel benzene even up to concentrations of 2% (w/v).

The gelation experiments with other solvents revealed enantiopure D-1 or L-1 to be a selective gelators for aromatic solvents such as toluene, *ortho*-xylene, *meta*-xylene, *para*-xylene and chlorobenzene (Table 1, detailed study with other solvents is presented in the ESI†). However the more polar nitrobenzene did not yield any gel even up to concentrations of 5%. In addition, both the enantiopure gelators also formed gels with hexane. All the gels were thermally reversible. The MGCs were 0.5% (w/v) for all the above solvents. The values of T_g at the MGC for the D-1 gels are presented in Table 1. The variation of T_g with concentration was also studied for all the gels (Graphs 1 and 2, ESI†). The gels for enantiopure D-/L-1 with any particular solvents were very similar in nature with respect to the T_g and gel structure (See ESI†). Expectedly once again, racemic-1 did not form any gel with any of the above solvents.

The gelation ability of D-/L-1 is consistent with the hypothesis of such types of organogelators where H-bonding plays the most important role in the self assembly of the gelator molecules. In a case such as this where the gelator forms a gel through H-bonding, strongly polar or even moderately polar solvents disrupt the intermolecular H-bonding preventing self assembly and thus result in the lack of gel formation. The lack of gelation ability of the racemic-1 is interesting and once again demonstrates the difficulty in predicting the exact requirements for gelation ability.

The gelation of petroleum products has been the topic of several studies in recent times, especially with the intention of remediation of oil spills and its recovery.^{2e,14} With the potential for such applications we decided to explore the possibility of D-/L-1 being able to form gels with petrol and diesel. The studies revealed both D-/L-1 to be a very good gelator for petrol and diesel. The lowest concentration of D-/L-1 which was able to gel petrol or diesel was 0.3% (Fig. 3g and 3h). The T_g for the petrol and diesel gels at MGC were 63-64 °C and 59-60 °C respectively.

Although many studies have studied the gelation of various refined forms of petroleum products, none has studied the gelation of crude petroleum, to the best of our knowledge. This neglected aspect is especially relevant in view of the numerous instances of environmental pollution due to accidents of ocean liners transporting crude oil or of mid ocean oil rigs. To address this issue we have carried out and report for the first time, the gelation experiments of crude oil using D-/L-1. The gelation experiments demonstrated that a concentration of 0.5% (w/v) or

Table 1 Gelation studies of D-1 in various solvents at various concentrations

Solvent/Conc. ^a	0.3%	0.5%	1.0%	2.0%	5%	MGC (T_g °C) ^b
Benzene	S	G	G	G	G	0.5% (46-47)
Toluene	S	G	G	G	G	0.5% (54-55)
<i>o</i> -Xylene	S	G	G	G	G	0.5% (48-49)
<i>m</i> -Xylene	S	G	G	G	G	0.5% (48-49)
<i>p</i> -Xylene	S	G	G	G	G	0.5% (44-45)
Chlorobenzene	S	G	G	G	G	0.5% (45-46)
Nitrobenzene	S	S	S	S	S	-
Hexane	S	G	G	G	G	0.5% (42-43)

^a w/v; ^b T_g at MGC, S = Soluble, G = Gel.

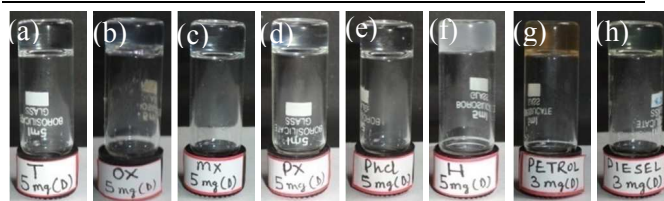


Fig. 3 Gel formation photos of D-1 in (a) toluene 0.5% (w/v) (b) *o*-xylene 0.5% (w/v) (c) *m*-xylene 0.5% (w/v) (d) *p*-xylene 0.5% (w/v) (e) chlorobenzene 0.5% (w/v) (f) hexanes 0.5% (w/v) (g) petrol 0.3% (w/v) (h) diesel 0.3% (w/v)

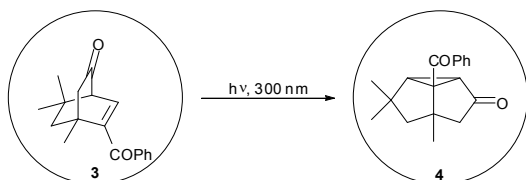
higher of D-1 was able to efficiently gel a sample of crude oil (Fig. 4a, T_g = 46-47 °C).

Towards the objective of remediation of oil spills, an important area of research today is phase selective organogelation (PSOG).^{2f,15} Although there are a few reports of the PSOG of petrol and diesel, the same for crude oil which is equally important is conspicuously absent. For this purpose the gelation ability of D-/L-1 in a biphasic system consisting of crude oil and saline water was studied, whereby it was found that addition of a concentrated petrol solution of L-1 to the crude oil layer resulted in the selective gelation (Fig. 4d) of the latter.

Finally, the suitability of the organogel for applications as a micro-reactor was tested by carrying out the photochemical reaction of **3** (Scheme 2).¹⁶ Organogels from D-/L-1 are ideal for photochemical reactions due to the lack of any light absorbing chromophore in the gelator itself. A mixture of **3** and D-/L-1 in benzene was warmed and subsequently allowed to cool to room temperature, when a gel was formed. The gelled mixture upon irradiation at 300 nm for 1 h yielded the product **4** (88%) similar to the previously reported¹⁶ solution state photochemical reaction of **3**. The gelator was also recovered from the mixture after column chromatography. This serves as a proof of concept of the suitability of our gels as a micro-reactor.



Fig. 4 (a) A sample of crude oil before gelation (b) A gelled sample of crude oil and D-1 at 0.5% (w/v) concentration (c) A biphasic system of saline water and crude oil before addition of the gelator (d) The biphasic system of water and crude oil after gelation of the crude oil with D-1.



Scheme 2 Photochemical reaction of **3** incorporated in a gel of benzene and D-/L-1

Conclusions

In conclusion we have been able to develop a very simple chiral LMOG that is easily accessible in both the enantiomeric forms in single steps from commercially available precursors. The enantiopure gelator is selective for oil like solvents. Interestingly, the racemic **1** is not able to form gels at all. The critical gelation concentration is very low and either of the pure enantiomers can be used effectively for the gelation of petrol, diesel and crude oil. The phase selective gelation of crude oil from a mixture of crude oil and water makes the gelator suitable for real world application in the remediation of crude oil spills. As demonstrated the organogel is also suitable for use as a micro-reactor for photochemical reactions.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, methods, Tables, Spectra and Figures for characterization and comparison of the D-gel with the L-gel. See DOI: 10.1039/b000000x/ See DOI: 10.1039/b000000x/

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