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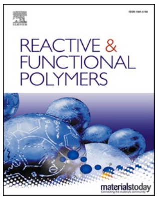

Perspective Article

D-galactose-based organogelator for phase-selective solvent removal and sequestration of cationic dyes

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ABSTRACT

Naturally occurring sugar-based monomers are attractive substrates in the design of functional glycopolymers. In this study, we report on the development of D-galactose based organogels of varying crosslink density capable of selective adsorption of dyes and solvents. Free radical polymerization of 6-*O*-methacryloyl-1,2;3,4-di-*O*-isopropylidene-D-galactose in the presence of nonamethylene glycoldimethacrylate generated novel crosslinked polymers OG10, OG15 and OG20 with 10, 15 and 20 wt% crosslinker, respectively. Depending on the nature of the solvent, OG10 undergoes swelling upto 935%. The negative zeta potential, as determined from DLS measurements, and the gelation ability suggested the potential utility of the polymer for dye removal from water. OG10 displayed significant adsorption of rhodamine B (RhB) (>95%), crystal violet (>93%), and methylene blue (>70%) dyes as well as the selective adsorption of >90% RhB from a solution containing both RhB and methyl orange. These porous organogels are also found to be suitable for phase-selective removal of organic solvents.

1. Introduction

Glycopolymers, a term used for both natural and synthetic carbohydrate-bearing polymers, have gained extensive attention over the past few decades to generate diverse architectures including crosslinked gels, amphiphilic block copolymers, dendrimers and other branched polymers [1,2]. Functionalization of carbohydrates along different carbon atoms for the synthesis of sugar-containing monomers has re-emerged as an essential area of research in the field of polymer technology [1,3]. Various polymerization methods such as free radical [1–7], Reversible addition-fragmentation chain-transfer (RAFT) [8–11], Atom-transfer radical polymerization (ATRP) [12–15], Ring-opening metathesis polymerization (ROMP) [5], Ring-opening polymerization (ROP) [14], click chemistry [16,17] etc. have been reported in the synthesis of linear glycopolymers as well as graft, block or random copolymers [8,9,13–15,18,19] and crosslinked glycopolymers [4,5,18,20]. Chemical crosslinking leads to the synthesis of gels, which renders the resulting biocompatible materials flexible and highly porous. These crosslinked three-dimensional interconnected network structure of polymers are capable of fluid absorption [21–23], based on which they can be classified as hydrogels (water immobilized) or organogels (organic liquid immobilized) [23].

The low-molecular weight gelators (LMWGs) and the polymeric gelators [23] have recently gained tremendous interest as new soft materials [24] in the field of chemistry, materials, biology, environment, biomedicine, oil-spill recovery, dye adsorption, biotechnology, cosmetics, food industry, and pharmaceuticals [16,21–23,25]. The conventional polymers that gelate organic solvent reported in literature consist of polyethylene, polyesters, poly(alkoxysiloxane), polyacrylates, and polycarbonates [23,26–34].

United Nations have adopted certain Sustainable Development Goals (SDGs) to address major global challenges in achieving a more sustainable future, where access to clean water for everyone is highlighted as one of the major concerns [35]. Water contamination from highly toxic dyes released from various industrial sources has become a threat to the environment as well as human health [36]. In order to protect the quality of water, commonly used methods for dye removal include membrane filtration, photochemical degradation, reverse-osmosis, ozonation, ion-exchange, biodegradation, precipitation/oxidation, electrocoagulation, and adsorption. Among these techniques, dye removal by adsorption is preferable as no harmful substance is formed [36–44]. Many LMWGs are widely used for selective gelation and dye removal from water [36,45–48]. LMWGs based on dipeptides were used for the removal of toxic dyes crystal violet (CV) and rhodamine 6G from water using xerogels prepared from toluene [46]. Similarly, 48 gelators based on the carboxybenzyl group were prepared by a two-step process

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that can instantly gel with crude oil to eliminate environmental pollution [48].

As compared to LMWGs, the polymeric materials gelate even at low concentrations, and their gelation ability can be tailored by modifying the backbone or the pendant groups [23]. Recently, polymeric materials [37,38,40–42,49] as gels have gained special attention as economic and efficient adsorbents for removal of dyes through hydrogen bonding, hydrophobic interactions, electrostatic interactions, and π-π interactions [41,44,46,47,50]. Ultra-light and superabsorbent cellulose nanofibril aerogels were assembled which were used to investigate the adsorption and desorption of cationic dye malachite green [51]. Poly(vinyl alcohol) (PVA)-based ultra-fast self-healing dimethyl sulfoxide based organogels were synthesized, which can adsorb methylene blue (MB) dye selectively with efficiency as high as 95.89% [41]. The β-D-glucose-based hydrogels prepared by RAFT polymerization with di(ethylene glycol) dimethacrylate as a divinyl crosslinker were used for the adsorption of cationic dyes RhB and MB, along-with load and release of silver nitrate [40].

Although there are several reports in the literature on the development of sugar-based hydrogels, the use of carbohydrate-containing organogels for selective dye removal and phase selective gelation has been less explored. The present study aims at establishing a simple, scalable approach towards the synthesis of novel chemically crosslinked polyacrylate-based organogels, bearing isopropylidene protected galactose as a pendant group for diverse applications. We also report on the application of these organogels in the selective removal of the organic phase from an aqueous-organic mixture as well as in the selective removal of cationic dyes.

2. Experimental

2.1. Materials

D-Galactose (extrapure, SRL), acetone (fisher scientific), 4-dimethylaminopyridine (DMAP, Alfa Aesar, 98%), methanol (rankem), and methacryloyl chloride stabilized with BHT (MACl, chemlabs, 97%) were used as received. Zinc chloride (dry) ($ZnCl_2$, CDH, 97%) was used after keeping under vacuum to remove traces of water. Benzoyl peroxide (BPO, Loba Chemie Pvt. Ltd.) was purified by recrystallization from chloroform-methanol prior to use. Nonamethylene glycoldimethacrylate (NMGDMA, TCI chem. Pvt. Ltd.) was purified by passing through activated basic alumina twice. Triethylamine (TEA, Fisher Scientific) was purified by distillation before use. Anhydrous tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were purchased from Sigma Aldrich and used without further distillation. Silica gel (mesh size 60–120 mm, Merck) was used for column chromatography.

2.2. Instrumentation

^{1}H and ^{13}C NMR measurements were performed on a Bruker DPX-400 instrument operating at 400 and 100 MHz, respectively using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal reference. Fourier-transform infrared (FTIR) spectra were recorded on KBr pellets using a Thermo Scientific Nicolet 6700 spectrometer to analyze different functional groups in the range 4000–400 cm^{-1} at 4 cm^{-1} resolution. Molecular weights were determined using gel permeation chromatography (GPC) on a Waters series 1515, equipped with Waters 1515 column. THF was used as the eluent at a flow rate of 1 mL/min at 30 °C. Calibration was done using polystyrene standards, and the samples were prepared in THF at 1 mg/mL concentration. Wide-angle X-ray diffraction (WAXD) patterns of finely powdered samples were obtained using Rigaku ultima IV X-ray diffractometer, using CuK$_\alpha$ radiation (0.154 nm) in the 2θ range of 5° to 50° at a scan rate 6°/min. Differential scanning calorimetry (DSC) thermograms were recorded using a DSC Q200 instrument in the temperature range 25–200 °C at heating/cooling/heating rate of 10 °C/min under dry nitrogen. Thermogravimetric analyses (TGA) were performed under nitrogen gas (flow rate as 20 mL/min) at 10 °C/min from 25 to 750 °C, using a Perkin-Elmer Pyris 6 TGA instrument. Swelling kinetics was recorded by immersing the solid dried gel in an excess amount of solvent and then weighing the swollen gel after 24, 48, and 72 h. The swelling was calculated using a standard equation (Eq. 1). The swelling ratio (%) was obtained by measuring the maximum amount of solvent taken by a fixed amount of the gelator.

$$\text{Swelling } (\%) = \frac{W_s}{W_d} \times 100 \tag{1}$$

where, W_s is the weight of blotted swollen gel and W_d is the weight of dried gel taken before swelling. The swelling studies were performed in different solvents. The gelator and the solvent were added in a sample vial and heated at 80 °C until the 'sol' state of the compound was visible. It was then cooled to room temperature slowly. The vials were inverted and kept undisturbed to observe the gel state of the mixture and the images were recorded. Field-emission Scanning Electron Microscopy (FESEM) was performed using JSM-7800F Prime instrument. FESEM micrographs were obtained for swollen and dried, cryofractured organogels. The absorption spectra were recorded on a PG instruments' T90+ UV–Visible spectrophotometer.

2.3. Synthesis of 1,2;3,4-di-O-isopropylidene-D-galactose (IpGal) (2)

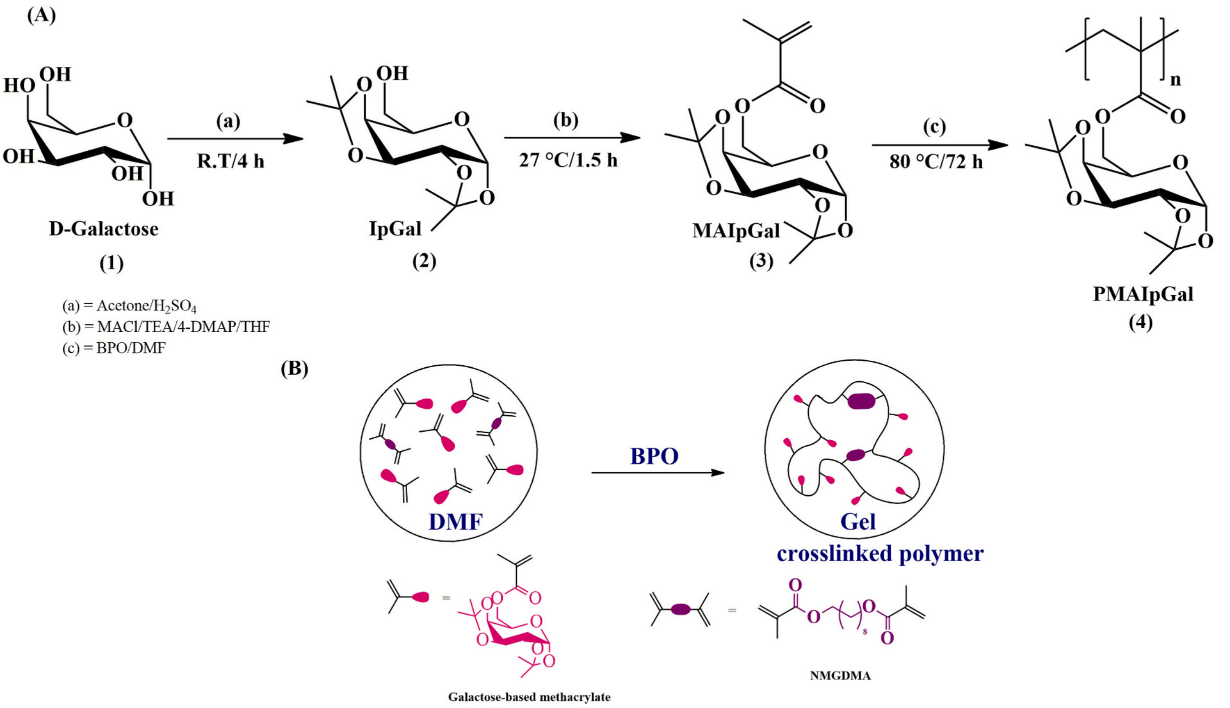
D-galactose (7 g, 38.8 mmol) and anhydrous $ZnCl_2$ (7.14 g, 52.4 mmol) were added to acetone (150 mL) followed by H_2SO_4 (0.84 mL) dropwise to the solution. It was allowed to react at room temperature for 4 h under nitrogen atmosphere until the starting material completely disappeared. The solution was neutralized with saturated Na_2CO_3 solution after the reaction. After filtration, the solvent was removed under reduced pressure on a rotary evaporator. It was further extracted with diethyl etherand dried over anhydrous Na_2SO_4. The organic solvent was evaporated, and the product **2** was obtained as a pale-yellow viscous oil in 75.6% yield which was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (1H, d, J = 5.2 Hz, anomeric proton C**H**), 4.62 (1H, dd, J = 8.0 Hz, 2.4 Hz, C**H**), 4.34 (1H, dd, J = 5.2 Hz, 2.4 Hz, C**H**), 4.28 (1H, dd, J = 8.0 Hz, 1.7 Hz, C**H**), 3.87–3.75 (3H, m, C**H** + C**H$_2$**), 2.14 (1H, m, O**H**), 1.45 (3H, s, C**H$_3$**), 1.33 (3H, s, C**H$_3$**), 1.25 (6H, s, 2C**H$_3$**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.9, 96.5, 71.8, 71.0, 70.8, 68.4, 62.5, 26.2, 26.1, 25.1, 24.5; FTIR ($\bar{\nu}$ (cm^{-1}) 3489 (br, O—H stretch), 2985, 2933 (C—H stretch), 1069 (C—O stretch).

2.4. Synthesis of 6-O-methacryloyl-1,2;3,4-di-O-isopropylidene-D-galactose (MAIpGal) (3)

2 (5 g, 19.2 mmol), TEA (8 mL, 57.6 mmol) and DMAP (2.35 g, 19.2 mmol) were added to anhydrous THF (60 mL) in a 250 mL round bottom schlenk flask. The mixture was cooled down to 0 °C and MACl (2.06 mL, 21.1 mmol) was added dropwise over a period of 30 min. The reaction mixture was kept at 27 °C to react under nitrogen atmosphere for 1.5 h. The reaction was monitored by thin-layer chromatography (TLC) with 15% ethyl acetate/hexane as the mobile phase. On completion of the reaction, THF was removed on a rotary evaporator, and it was redissolved in ethyl acetate. This was washed successively with 1 N HCl (2 × 30 mL), water (2 × 20 mL), saturated $NaHCO_3$ (2 × 30 mL), brine (2 × 20 mL), ammonia solution (2 × 20 mL) and brine (2 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the crude product obtained on removal of solvent was purified by column chromatography (5% ethyl acetate in hexane as the eluent) to obtain **3** in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (1H, s, **H**CH=C), 5.56 (1H, s, HC**H**=C), 5.54 (1H, d, J = 4.8 Hz, anomeric proton C**H**), 4.63 (1H, dd, J = 8.0 Hz, 2.4Hz, C**H**), 4.32–4.26 (4 H, m, 2 C**H** + C**H$_2$**), 4.08–4.06 (1H, m, C**H**), 1.94 (3H, s, C=C(C**H$_3$**)), 1.50 (3H, s, C**H$_3$**), 1.45 (3H, s, C**H$_3$**), 1.32 (6H, s, 2 C**H$_3$**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.20, 135.05,



Scheme 1. Schematic representation for: (A) Synthesis of galactose-based monomer (3) and linear chain polymer (4) using BPO initiator, and (B) crosslinking reaction using galactose based monomer with nonamethylene glycol dimethacrylate crosslinker.

124.78, 108.62, 107.74, 95.27, 70.10, 69.69, 69.51, 65.09, 62.62, 28.67, 24.94, 24.93, 23.96, 23.44, 17.26; FTIR ($\bar{\nu}$ (cm^{-1}) 2978, 2926 (C—H stretch), 1716 (C=O stretch), 1637 (C=C stretch), 1167 (C—O stretch).

2.5. *Synthesis of poly(6-O-methacryloyl-1,2;3,4-di-O-isopropylidene-D-galactose) (PMAIpGal) (4)*

3 (4.2 g, 12.7 mmol) and freshly recrystallized BPO (10.7 mg, 0.04 mmol) were dissolved in anhydrous DMF (21.4 mL) under argon and heated at 80 °C for 72 h. The resultant polymer was obtained by precipitation in cold methanol, filtered and dried (yield = 85%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.51 (1H, s, sugar anomeric proton **CH**), 4.63 (1H, s, **CH**), 4.29–3.97 (5H, m, **CH** + **CH$_2$**), 1.9–1.8 (2H, m, **CH$_2$**), 1.50–1.25 (12H, m, 4 **CH$_3$**), 0.88 (3H, m, C-C(**CH$_3$**)); FTIR ($\bar{\nu}$ (cm^{-1}) 2989, 2930 (C—H stretch), 1720 (C=O stretch), 1167 (C—O stretch).

2.6. *Synthesis of organogels*

3 (2 g), 0.25 wt% benzoyl peroxide (5 mg) and NMGDMA (10, 15 and 20 wt%) were added to DMF solvent (10.8 mL) under an argon purge and heated at 80 °C to synthesize the crosslinked polymers (labelled OG10, OG15, and OG20, respectively). The reaction was kept overnight for gelation under argon. The gel was washed with cold methanol and dichloromethane to remove any unreacted reagents and kept for drying under vacuum at 50 °C to obtain dried gels.

2.7. *Preparation of organogel*

1 mL of solvent was taken in a 5 mL sample vial, and finely crushed powder of gelator was added slowly with stirring at room temperature. The gelator was added till complete gelation has taken place and used for further characterization.

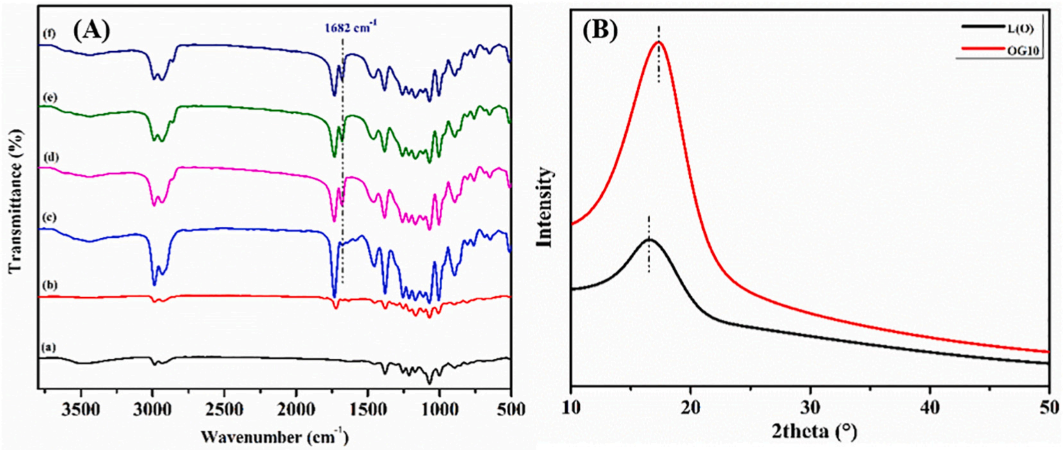


Fig. 1. (A) FTIR spectra of (a) IpGal, (b) MAIpGal, (c) linear polymer, (d) OG10, (e) OG15, (f) OG20; (B) XRD patterns for (a) linear polymer, and (b) OG10.

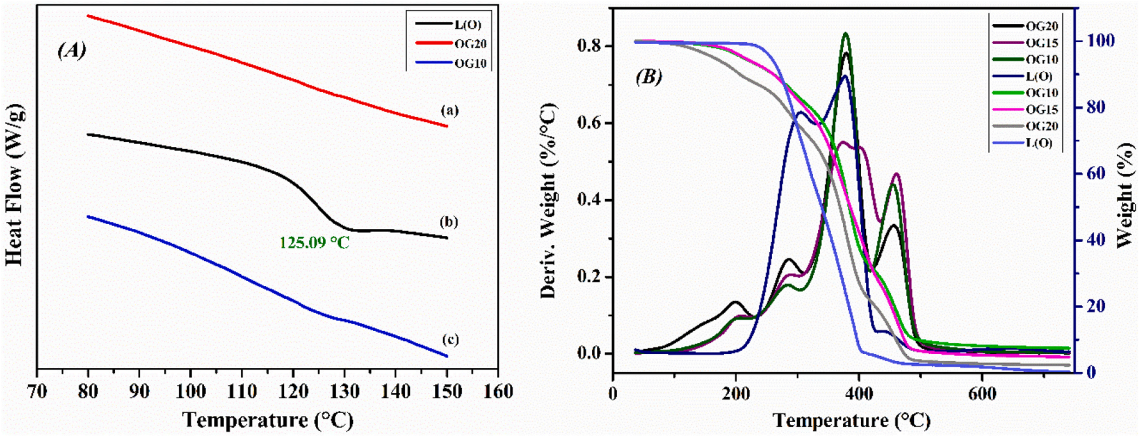


Fig. 2. (A) DSC thermograms of (a) OG20, (b) linear polymer, (c) OG10; (B) TGA and dTG thermograms of linear polymer, OG10, OG15 and OG20 representing thermal degradation of polymers.

3. Results and discussion

The presence of equally reactive secondary hydroxyl groups in carbohydrates restricts many reactions to be done selectively at the primary hydroxyl group. In galactose, hydroxyl groups are arranged in such a manner that they can be protected together with two isopropylidene units making the resultant product soluble in organic solvents. The synthesis of compounds **2** and **3** in Scheme 1(A) were done according to literature [5,7,10] with slight modifications and were confirmed by ^{1}H NMR. Further, compound **4** was synthesized by free-radical polymerization of **3** as shown in Scheme 1(A), and the crosslinked polymers according to Scheme 1(B). The formation of polymer was confirmed by ^{1}H and ^{13}C NMR, and FTIR spectroscopic techniques. Chemical structure of linear and crosslinked polymers were investigated by NMR, FTIR, XRD, DSC and TGA techniques.

3.1. Spectroscopy

^{1}H NMR signals in Fig. S1(a) show three distinct singlets at 1.3 (6H), 1.4 (3H) and 1.6 (3H) ppm attributable to isopropylidene protecting groups in IpGal. The protection is also confirmed by FTIR spectrum of IpGal as shown in Fig. 1. After protection of D-galactose, a broad O—H stretch was observed at 3489 cm^{-1} along with C—H stretches at 2985 and 2933 cm^{-1} and C—O stretch at 1069 cm^{-1} [7]. Subsequent reaction with methacryloyl chloride results in the monomer as a white solid (MAIpGal) after purification. This was confirmed by ^{1}H NMR in Fig. S1 (b) with olefinic protons appearing at 6.1 and 5.6 ppm and the signal for allylic methyl protons appearing at 1.9 ppm.

Also, from the FTIR spectrum in Fig. 1(A), it can be seen that the -OH stretch completely disappears in the protected galactose unit. The monomer shows a characteristic band at 1716 cm^{-1} attributable to the C=O functional group of the ester linkage. The absorption bands at 2978 and 2926 cm^{-1} corresponding to C—H stretch and at 1167 cm^{-1} corresponding to C—O stretch are observed in the spectrum as reported by Besenius et al. [5]. The free-radical polymerization of the synthesized monomer yields ~85% polymer (PMAIpGal) after precipitation in cold methanol. The formation of the polymer is accompanied by the disappearance of olefinic proton signals at 6.1 and 5.6 ppm as observed in Fig. S1(c).

A GPC instrument was used to determine the molecular weight of the polymer. The results depicted the GPC trace in low molecular weight (LMW) region, which found to be ~10,000 g/mol for polymer prepared with 0.63 M solution concentration. All the crosslinked polymers were prepared with the parameters optimized for linear chain polymer. The NMR spectrum of crosslinked gels was not observed due to their insoluble nature in all the solvents. The formation of crosslinked gels was also confirmed by their ability to swell in a variety of solvents. The crosslinking of MAIpGal with NMDMA (10, 15 and 20 wt%) shows no significant change in the FTIR spectra, indicating no evidence of any new functional group upon the formation of a crosslinked product. The small stretch at 1682 cm^{-1} which appears after crosslinking is attributable to the ester linkage of crosslinker present in the chains. The molecular packing and orientation were investigated by XRD patterns recorded for the linear and crosslinked polymers, represented in Fig. 1(B). The prominent peak shift from 2θ ~16.5^0 to 17.4^0 indicates the change in microstructure after crosslinking. The microstructural studies exhibit the broad peak clearly indicating the completely amorphous nature of both the polymers. This is attributed to the irregular random arrangement of gelator molecules in the dried state.

3.2. Thermal analysis

The absence of melting and crystallization peaks in DSC thermogram of the linear polymer indicates its amorphous nature, which is in accordance with XRD data. The glass transition temperature (T_g) for the linear polymer was observed at 125 °C [7] in the second heating curve, as shown in Fig. 2(A). No prominent T_g was observed in the second heating curve of the crosslinked polymer due to irregularity of crosslinking, which is attributed to the restricted segmental mobility of chains of an amorphous polymer. As shown in Fig. 2(B), the TGA thermograms reflect the high thermal stability of the polymer backbone. The dTG curves in the same image show four main stages of degradation of crosslinked polymers, and the curve recorded for linear polymer chain shows degradation in three significant stages. The first and second stages in linear polymer partially overlap. The first stage indicates 46% degradation of the polymer at 304 °C, which corresponds to the combined degradation of isopropylidene groups, pendant methyl unit, and the carboxylate group. The second step shows 49% degradation, which corresponds to the degradation of the pendant sugar moiety at 377 °C. The third step at 440 °C exhibited 5% degradation in the polymer.

This is similar to other thermally stable polymeric acrylate backbone as reported for other commercially available acrylate polymers [52–54]. The first peak around 200 °C in OG10, OG15 and OG20 is not observed in the linear analogue suggesting the degradation of the crosslinked network. Further, the degradation of the pendant sugar moiety was followed by the polymer backbone degradation at 440 °C. Moreover, the thermograms indicate a decrease in network stability with increasing crosslinker percentage owing to the enhanced rigidity due to tighter packing.

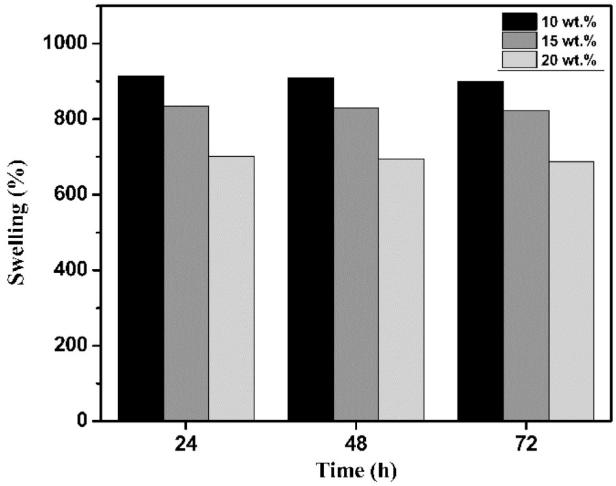


Fig. 3. Swelling ratio study of OG20, OG15, and OG10.

3.3. Swelling studies

The swelling or gelation capability of a polymeric gel depends on various factors, including, the structure of the polymer chains, as well as the crosslink density [40]. The swelling behavior is also based on the type of interaction of gelator with the solvent or gelator-gelator interaction, such as H-bonding, Van der Waal forces or dispersion forces, which include dipole-dipole, dipole-induced, and instantaneous dipole-induced forces [55]. The swelling studies were performed for OG10, OG15 and OG20 crosslinked polymers in DMF, and the weight of swollen gel was recorded until no increase in weight was observed after blotting the surface of the gel. The experiments were performed for 72 h, though the weight of the swollen polymer did not increase after 24 h. In Fig. 3, the results represent the swelling ratio values as 915%, 834%, and 702% respectively in $CHCl_3$. The swelling of gels was enhanced with a decrease in crosslinking ratio due to increased porosity of the crosslinked network structure, which is also evidenced from morphological studies. The diffusion of the solvent into the gel is slower and prevented when the matrix is highly crosslinked that leads to a reduction in swelling capacity [49].

As the crosslinking in OG10 with 10 wt% of crosslinker amount shows the maximum swelling ratio among the three, it was used to study swelling behavior in other organic solvents. The gelation test for OG10 was carried out in 16 different organic solvents of various dielectric constants (ε) using the vial inversion method as represented in Fig. 4, to determine the solvent uptake amount by the polymer. The stable gel formation is evident with 1,4-dioxane, DMF, THF, chloroform, dichloromethane, toluene, and ethyl acetate, whereas in DMSO, acetonitrile, and diethyl ether, no such swelling was observed. Also, the material was not swellable in highly polar (water and methanol), and non-polar (n-hexane) solvents. The swelling ratio data in Table S1 shows the swelling to be highest in chloroform (935%); the solvent with neither highest nor lowest ε. Thus, the observed swelling did not show any direct correlation to dielectric constant [40].

3.4. Morphological studies

The morphologies of the chloroform-based gels prepared from OG10, OG15, and OG20 were investigated using FESEM, and the images are shown in Fig. 5. The images of cryo-fractured lyophilized xerogels indicate a three-dimensional co-continuous, entangled fibrous bulk morphology. The surface of the dried gels was found to be macroporous with a random distribution of pores. The formation of such macropores occur as the solvent enters the network of the gelator upon swelling. The absorption of solvent by the gelator expands the polymer matrix where the solvent pockets are formed after lyophilization, which appear as pores in the microscopic images. A high crosslink density leads to a compact network in the gel as the solvent absorption is difficult leading to a smaller mesh size in the matrix as observed for OG20 with ~0.1 μm pore size as seen in Fig. 5(a). The pore size measured for OG15 was found to be ~0.5 μm and ~ 0.9 μm for OG10 as estimated from the FESEM images in Fig. 5. The size of pores decreased from 0.9 to 0.1 μm with the increase in crosslinker content from 10 wt% to 20 wt%. As the crosslinker amount increases, the number of crosslinks increase, thereby leading to the formation of a more compact polymer matrix.

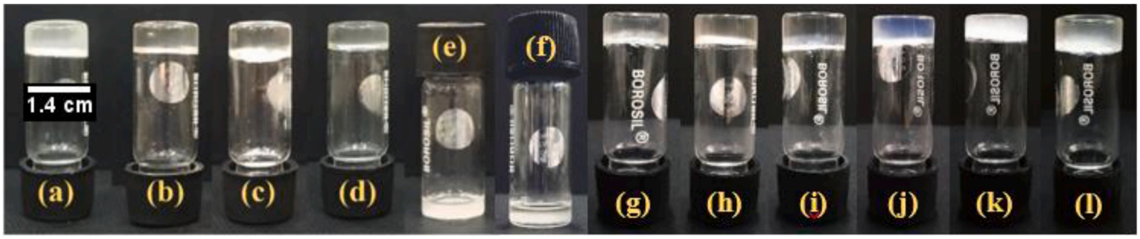


Fig. 4. Swelling studies of OG10 in (a) toluene, (b) THF, (c) chloroform, (d) 1,4-dioxane, (e) diethyl ether, (f) DMSO, (g) DMF, (h) DMAc, (i) 1,2-dichloroethane, (j) o-dichlorobenzene, (k) o-xylene, (l) ethyl acetate.

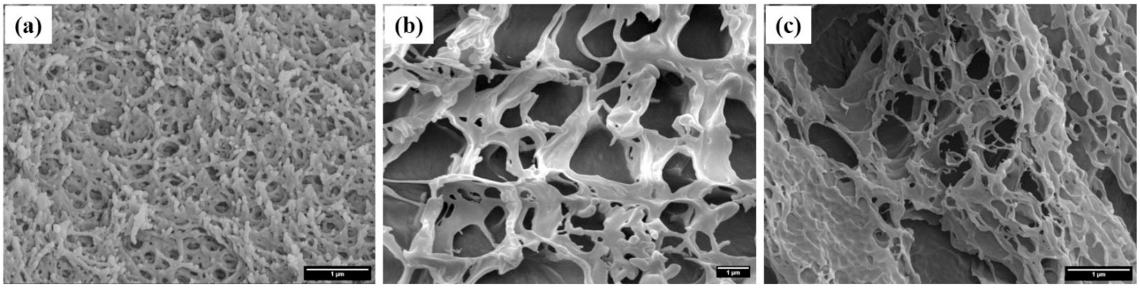


Fig. 5. FESEM images of cryofractured lyophilized organogels (a) OG20 (b) OG15 (c) OG10.

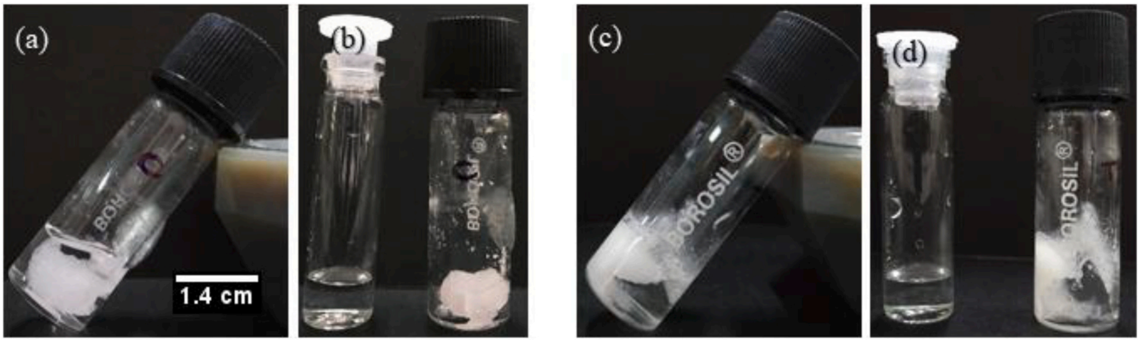


Fig. 6. (a) chloroform absorbed by the gelator, (b) water separated from the chloroform-water mixture; (c) toluene absorbed by the gelator, (b) water separated from the toluene-water mixture.

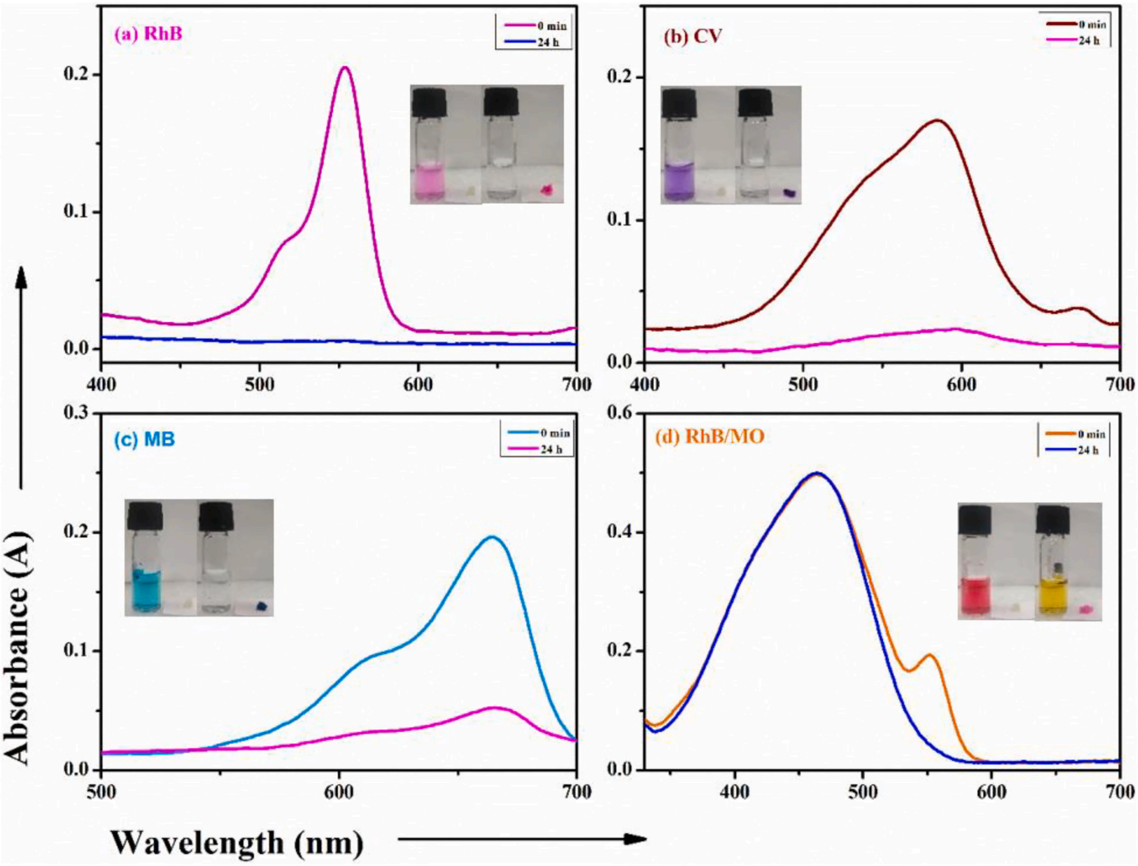


Fig. 7. UV spectra demonstrating dye adsorption by OG10 gel in 24 h (a) RhB (b) CV (c) MB, and (d) RhB/MO.

3.5. *Phase-selective organogelation studies*

Phase-selective organogelation has always been challenging in mixtures of solvents when water is one of the components. The first phase-selective gelator was introduced in 2001 by Bhattacharya et al. to address recovery after oil spills. Further, on this basis, Debnath et al. also developed few LMWGs as phase-selective organogelators in 2008 [46]. Interestingly, it was found that the organogels in the present study selectively gelate organic solvent from oil/water mixtures. The studies were carried out by taking 1:1 toluene/ water mixture with 100 mg of OG10. The mixture was shaken vigorously and kept undisturbed at room temperature. The gelation was observed in the toluene layer selectively, as shown in Fig. 6, which could be easily separated from water, and gelator can be reused as well. Also, after organic solvent separation, the gel weight was observed as 771 ± 20 mg with chloroform, and 506 ± 10 mg with toluene which accounts for nearly 100% organic solvent separation from water. Hence, the hydrophobic nature of the organogelator can be used for selective removal of chloroform or toluene from their aqueous mixtures.

3.6. *Dye-adsorption studies*

The surface charge of the crosslinked polymer was measured in terms of zeta potential using DLS instrument. The negative magnitude of the surface charge suggested the potential use of the polymer towards the adsorption of positively charged dyes. The preliminary studies were conducted using cationic dyes as well as a mixture of cationic and anionic dyes. The tests were performed with 10 mg of OG10 gel in 1.5 mL dye solution (0.0125 mg/mL) of RhB, CV, MB and RhB/MO each. The solutions were kept at room temperature for 24 h for dye

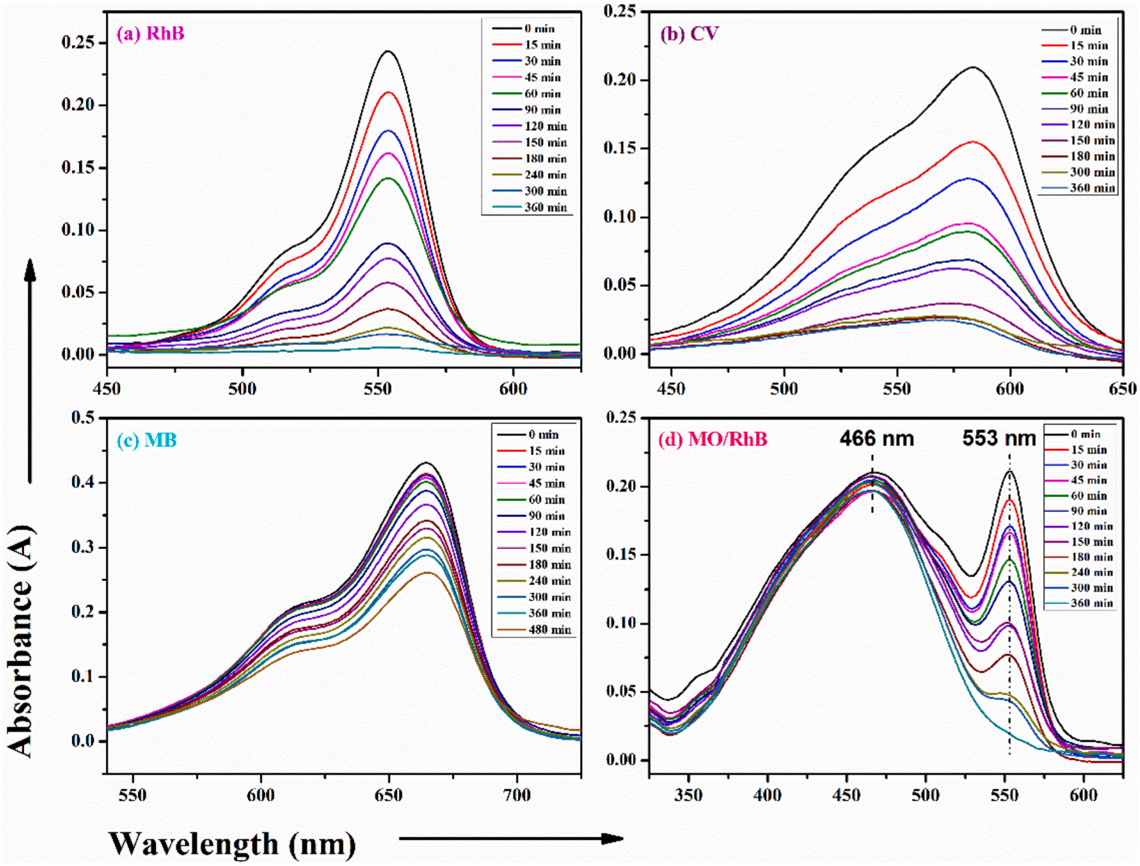


Fig. 8. UV spectra showing a time-dependent dye adsorption studies using OG10 gel for: (a) RhB (b) CV (c) MB, and (d) RhB/MO.

adsorption. The initial and residual dyes in the solution were detected using UV–Visible spectroscopy, as shown in Fig. 7. The UV curves clearly indicate the adsorption of all the cationic dyes by the organogel. The color of all the dye solutions nearly disappeared within 24 h. Also, the data shows >90% of RhB and CV, and > 70% of MB were adsorbed by the gel.

Based on these preliminary results, further kinetic studies on the adsorption of RhB, CV and RhB/MO were carried out with 10 mL dye solution (0.00625 mg/mL), and that of MB with 10 mL dye solution (0.003125 mg/mL) using 40 mg of swollen gel. The time-dependent dye adsorption was monitored using UV–Visible spectroscopy. As can be seen in Fig. 8, the concentration of RhB and CV decreased with time with almost complete adsorption in 360 min., whereas with MB, only 36% ± 2% of dye was adsorbed in the same time. The gel took longer to adsorb MB than RhB and CV, as observed in Fig. 7(c) with >70% of MB dye adsorbed in 24 h. Also, adsorption studies with a mixture of anionic (MO) and cationic (RhB) dyes showed selective removal of RhB. This was accompanied by a significant color change from orange to yellow, the color of MO in water. UV–vis studies showed the disappearance of the peak at 553 nm corresponding to the absorption maximum of RhB dye (Fig. 8(d)). The gel selectively adsorbs cationic dyes due to the negative charge associated with the surface of the crosslinked polymer, which is measured in terms of zeta potential as −5.53 mV.

4. Conclusions

Protected D-galactose containing acrylate-based linear and crosslinked polymers were synthesized by free-radical polymerization. For OG10, the swelling was found to be 412% in DMF, 480% in THF, 552% in toluene, 619% in 1,4-dioxane, and 935% in $CHCl_3$ solvent. No direct correlation was found between the dielectric constant and swelling ratio. The FESEM micrographs confirmed the porous morphology for all the compositions, and the pore size decreased with increase in crosslinker amount due to tighter packing of the network. The zeta potential of the crosslinked polymer was measured as −5.53 mV, suggesting the ability of the material to adsorb cationic dyes selectively. The adsorption studies with OG10 on cationic dyes showed 90% ± 3% dye adsorption for RhB, 36% ± 2% for MB, and 88% ± 2% for CV in 360 min. Additionally, the selective adsorption of 85% ± 2% of cationic RhB dye from a mixture of RhB/MO was demonstrated. Since the gel adsorbed dyes from water, this organogel can potentially be used for the removal of various toxic cationic dyes from water. Also, it is found to undergo phase selective organo-gelation from organic-aqueous solvent mixtures. The adsorption is nearly 100% suggesting its potential for use in solvent recovery.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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