

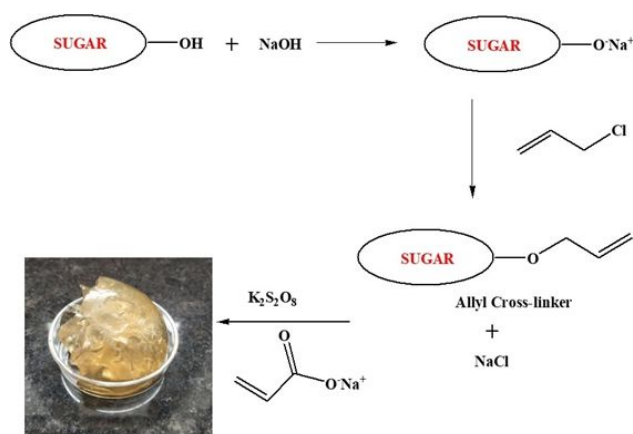
SYNTHESIS AND CHARACTERIZATION OF A NOVEL SUGAR BASED CROSS-LINKER

ANAMICA* and Poorn Prakash PANDE

Department of Chemistry and Environmental Science, M.M.M. University of Technology Gorakhpur-273010, U.P., India

Received February 13, 2020

There are very few literature reports on the synthesis of monosaccharide based cross-linkers. A novel monosaccharide sugar-based cross-linker was synthesized by using D-mannitol, and allyl chloride in basic medium at low temperature (40°C) under inert atmospheric conditions. We have used a new synthetic scheme which does not involve the use of autoclave at high temperature and pressure for carrying out allylation with allyl chloride. The synthesized product has been characterized by, Fourier-transform infrared (FT-IR) spectra and ¹H Nuclear magnetic resonance (¹H NMR) spectra. The formation of allyl mannitol was also confirmed with the help of elemental analysis of C, H and O. Cross linked polymer gel samples were prepared by polymerizing acrylic acid monomer alongwith the synthesized cross-linker at different concentrations. Aqueous gels have been prepared from the cross-linked polymers and their swelling capacity has been studied. It has been found that these gels act as superabsorbent materials. The optimum ratio of cross-linker and acrylic acid monomer for the preparation of gel having highest swelling capacity (~ 28000% of water) was found to be 0.03 g crosslinker with 12.0 g. monomer.



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INTRODUCTION

Gels are three-dimensional cross-linked network of polymeric chains, which transport ionic groups. These are the materials, which can absorb large amount of liquids much greater than their weight under load or without load such as biological fluids.¹ The gels show great potential in solving problems related to ecological, industrial and biological fields.²⁻⁴ After swelling in water gel resembles with living tissues, and can be used as biomaterial in various bio-applications.⁵ The potential of gels is enhanced by the linking through a variety of crosslinkers. The synthesized gels are used as a catalyst, in heavy metal removal, in dye

removal, in sanitary pads, in anion removal from water etc.

In the preparation of cross-linker, the natural compounds and biopolymers are commonly used. Due to their low cost and biocompatibility, these bio-materials are of much interest for the synthesis of cross-linkers for the researchers^{6,7} The gels can be degraded easily, which make them an excellent material in various applications. Different polysaccharides such as starch, cellulose, and chitosan have been used in the synthesis of cross-linkers.⁸⁻¹⁰ There are many literature studies about the preparation of polysaccharides-based linkers but only a few reports are available on the preparation of monosaccharides and oligosaccharides based

* Corresponding author: anamicamishra72@gmail.com

crosslinking agents.^{11,12} Mallory Stevenson *et al.* have used ribose crosslinking agent in gelatin films,¹³ Farnaz Mazaheri Karvandian *et al.* reported glucose cross-linker in bone scaffolds,¹⁴ and David M. Hudson *et al.* studied collagen cross-linking agent in bone pathobiology.¹⁵

This paper comprises the synthesis, characterization of a sugar based cross-linker allyl mannitol (AM) and preparation of polymer-gels based on this cross-linker. D-Mannitol is a type of sugar alcohol used in diabetic foods as sweetener and in medication. It is also used to reduce pressure in eyes. Naturally mannitol is isolated from sea-weed (20%) and tree (80%).

EXPERIMENTAL

1. General

D-mannitol, sodium hydroxide, allyl chloride, ethyl acetate, sodium chloride, and anhydrous sodium sulphate were purchased from SRL chem. Pvt Ltd. India. The chemicals were used after purification. The solvents were used of analytical grade. The structure of the synthesised products was confirmed by elemental analysis, C, H, N and O. Elemental analysis was performed on an elemental analyser's Euro-E 3000 instrument. FT-IR Spectrometer Perkin Elmer Spectrum GX Range: 10,000 cm^{-1} to 370 cm^{-1} (in KBr discs) were used to analyse crosslinker. ^1H Nuclear magnetic resonance (^1H NMR) spectra were obtained with a Bruker Advance III 400 MHz spectrometer on samples dissolved in dimethyl sulfoxide (DMSO). The chemical shifts are given in δ (delta) from tetramethyl silane.

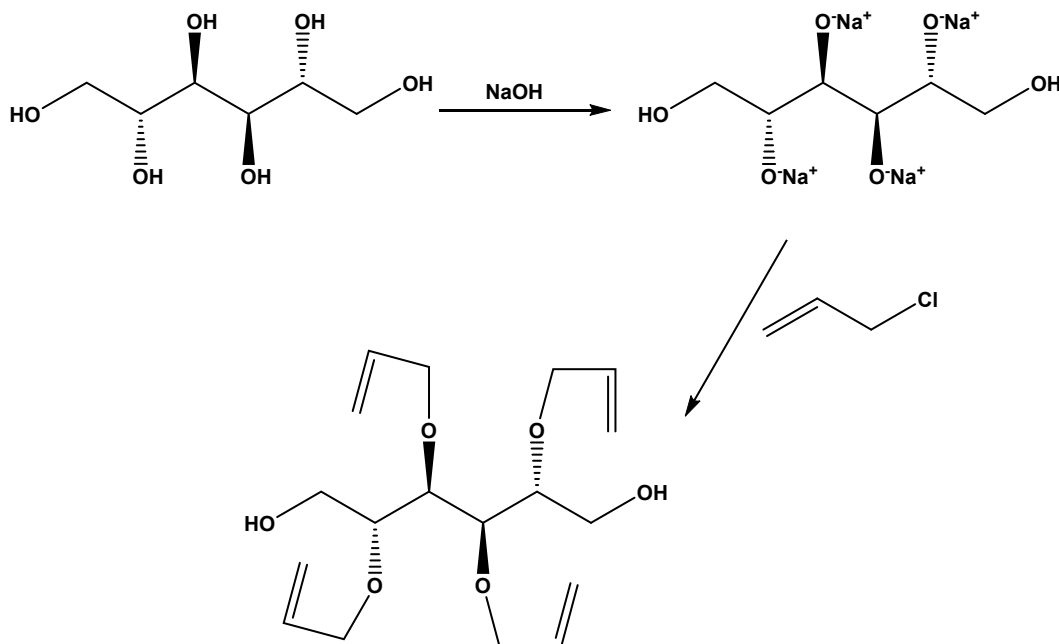
2. Synthesis of Allyl Mannitol

A 250 mL R.B. flask equipped with a magnetic stirring bar was taken. D-mannitol (5.469 g, 30 mmol) aqueous NaOH

(4.8 g, 120 mmol) NaOH dissolved in 7 mL water) was added to the flask. The flask was sealed and heated at 80°C with constant stirring for 90 minutes. After that, the flask was cooled, opened and allyl chloride (9.39 g, 120 mmol) was added and the mixture was stirred for 24 hours at 40°C under nitrogen atmosphere. The temperature of reaction was increased to 100°C for two hours. Then the contents were further stirred for 60-72 hours. Reaction mixture was cooled at room temperature, placed in an ice bath, the flask was opened and ice water was added to dissolve sodium chloride formed during the reaction. The product was extracted with ethyl acetate. The combined organic layers were washed with water and brine respectively, dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure at 40-50°C. A pale-yellow coloured liquid was obtained. The synthesized compound allyl mannitol is ($\text{C}_{18}\text{H}_{30}\text{O}_6$) M.W. 342, Yield: 68%. Elemental anal.: (Calc) Found %: C (63.16) 63.12, H (8.77) 8.75, and O (28.07) 28.04.

3. Synthesis of Polymer gel

Acrylic acid (12 g) was dissolved in distilled water (20 mL) and neutralized with 8.3M sodium hydroxide (20 mL). After that the contents were transferred into a 2-neck round bottom flask, equipped with magnetic stirring bar and fitted with condenser. The reaction is carried out in an inert (N_2) atmosphere. The desired quantity allyl cross-linking agent was added to the flask, followed by the addition of 1 ml potassium persulfate solution (10%, KPS). The reaction mixture was placed in a water bath at 40°C and continuously stirred. When an exothermic reaction started, the reaction mixture was removed from water bath. The reaction was allowed to take place about two hours, for completing the reaction. The obtained gelled mass of polyacrylic acid was dried at 80°C for 24 hours. The dried crystal-like solid was grinded for further investigations. Similarly, different polymer gel samples were prepared using different amount of crosslinking agent.



Scheme 1 – Formation of cross-linker from D-mannitol sugar.

RESULTS AND DISCUSSION

1. Preface

D-mannitol based cross-likier was synthesized from D-mannitol and allyl chloride in basic medium. The formation of product allyl mannitol (AM) was confirmed with the help of elemental analyses, FT-IR and ¹HNMR spectroscopy.

2. Study of FT-IR

The IR spectrum of allyl mannitol is shown in Figure 1, and different absorption peaks are shown in Table 1. IR spectral data shows hydroxyl absorption band at 3419 cm⁻¹. Absorption band at 2920 cm⁻¹ indicates the presence of C=C-H group and stretching band at 1646 cm⁻¹ confirm the presence of C=C group in compound. The peaks at 1425 cm⁻¹, 1455 cm⁻¹ show -CH- group near to double bonded carbon, and peak at 1089 cm⁻¹ shows -C-O- stretching. =C-H stretching and bending peaks are at 3080 cm⁻¹, 926-994 cm⁻¹.¹⁶⁻¹⁸

3. Study of ¹HNMR

The ¹HNMR spectra of allyl mannitol show the peak of different proton of allyl group as H^a, H^b, H^c between δ5-6. While in the case of D-Mannitol, there are no peaks between δ5-6. The ¹HNMR

peaks of synthesized sugar based cross-linker is shown in Figure 2. ¹H-NMR (in deuterated DMSO): δ 6.0 (t, 4H, =CH_a-), 5.34 (d, 4H, =CH_b), 5.1 (m, 4H, =CH_c), 4.0 (d, 8H, -O-CH₂), 3.94 (s, 2H, -OH), 3.57-3.51 (m, 4H, -CH₂-OH), 3.40 (m, 4H, -CH₂-), 3.50 (m, 4H, -CH₂-). The ¹HNMR data of different proton as H^a, H^b, H^c, -O-CH₂ in linker is shown in Figure 3.

4. Application-Gel formation

The spectral data (IR, ¹HNMR) it can be concluded that allyl groups are linked to D-mannitol group at four places (secondary OH group positions). Likes some other allyl cross-likier, this crosslinker contain four ally groups which can be used in formation of gels. Gels have been prepared (Figure 4) by the polymerization of sodium salt of acrylic acid in the presence of potassium persulfate initiator and allyl mannitol cross-linker. In our studies these superabsorbent gels can absorb about 281 times water and 28115 % of their original weight. These gels can be used in various applications such as in personal care materials, biomaterials, drug-delivery systems, bio-sorbent, pharmaceutical, construction, reforestation, agriculture, environmental and industrial applications. In water management, the gel is used for required and unwanted water management depending on their particular usages.

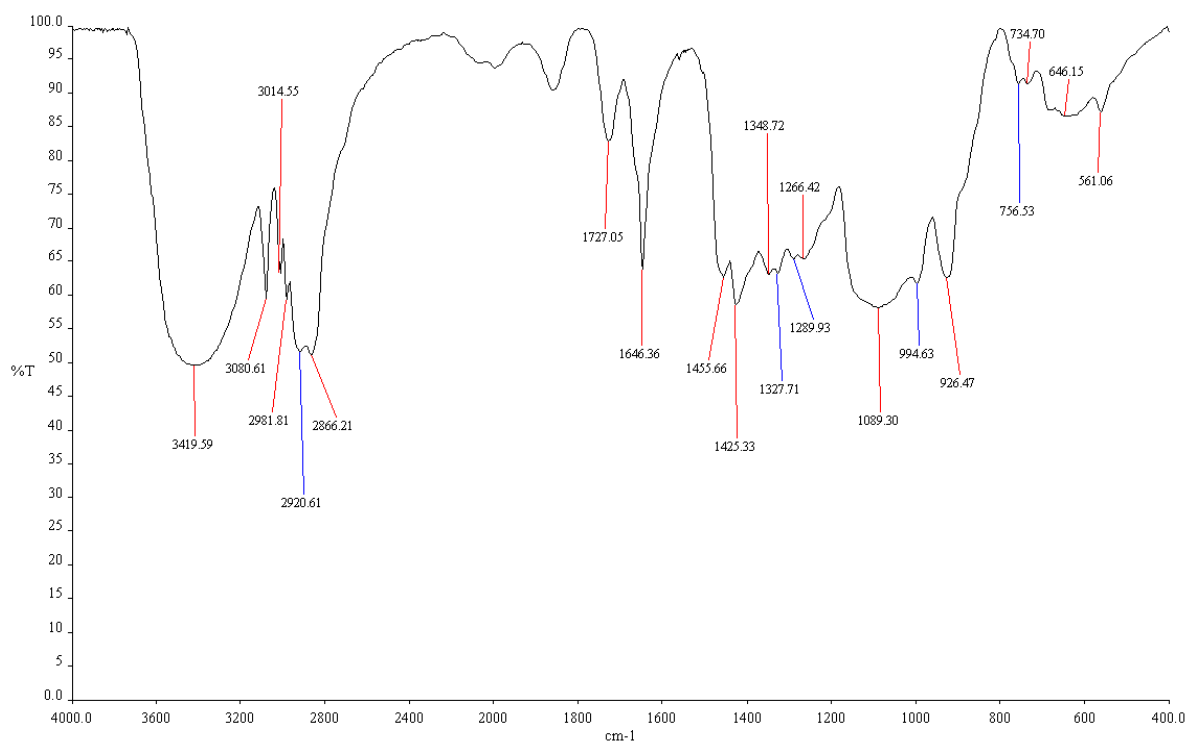


Fig. 1 – IR spectra of Allyl D-Mannitol.

Table 1
IR Frequency of Allyl D-mannitol cross linker

IR (in cm^{-1})	Allyl Mannitol
-O-H stretching	3419 cm^{-1} , ¹⁶
-C=C-	1646 cm^{-1} , ¹⁷
-C-O stretching	1089 cm^{-1} , ¹⁸
=C-H Stretching	3080 cm^{-1} , ¹⁷
=C-H bending	$926\text{-}994 \text{ cm}^{-1}$, ¹⁷
-C=C-H	2920 cm^{-1} , ¹⁷
-C=C-CH ₂	1425 cm^{-1} , 1455 cm^{-1} , ¹⁷

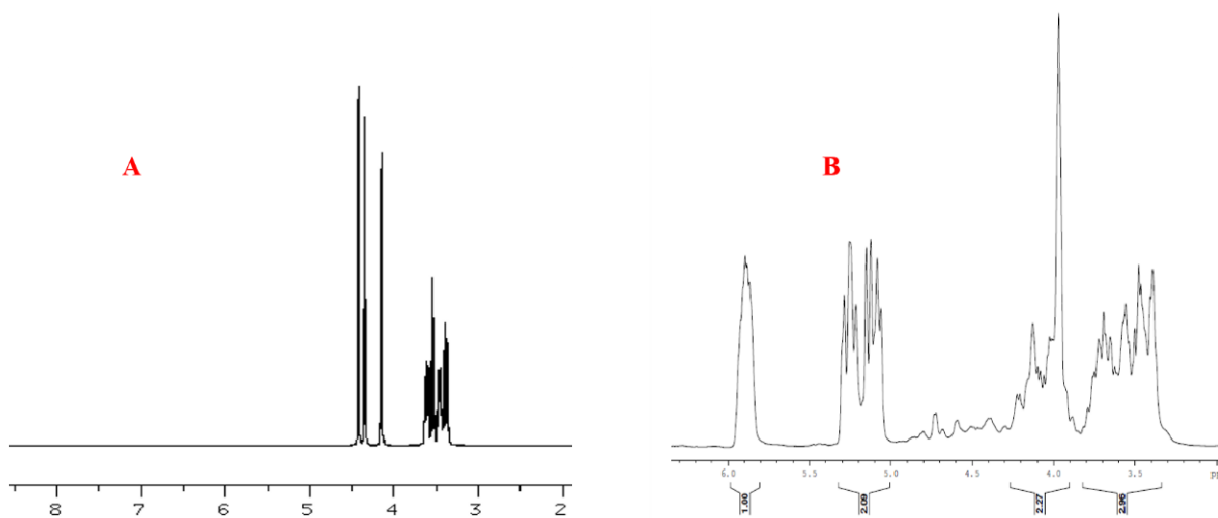


Fig. 2 – ¹H NMR Spectra of (A) D-mannitol (B) Allyl-mannitol.

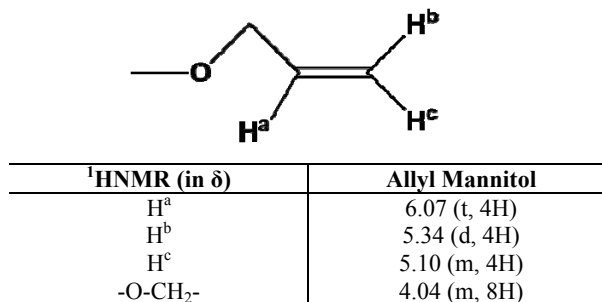


Fig. 3 – ¹H NMR spectra data of proton in different environment.

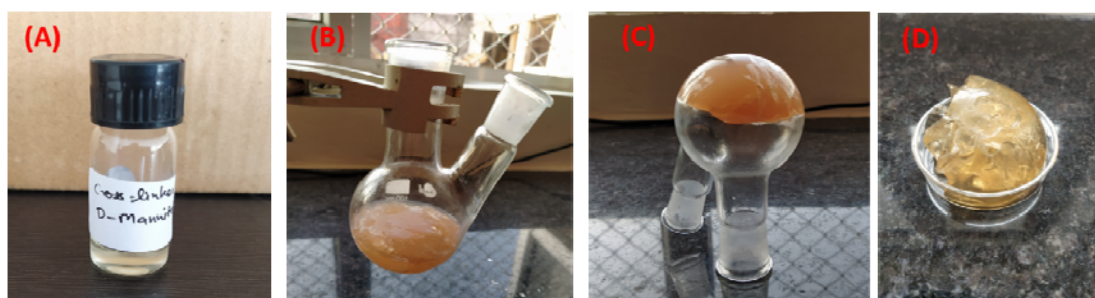


Fig. 4 – Formation of gel (B-D) with the help of cross-linker (A).

Table 2

Swelling Capacity study at 180 minutes

Cross Linker AM (g)	Time (min.)	Weight of SAP sample (g)	Weight of swelled SAP (g)	Swelling capacity g liquid/g SAP	Swelling capacity %
0.03	180	0.5	117.0837	233.1674	23316.74
0.06	180	0.5	13.6335	26.2670	2626.70
0.09	180	0.5	23.2623	45.5246	4552.46
0.12	180	0.5	15.2282	29.4572	2945.72
0.18	180	0.5	25.1561	49.3122	4931.22

Table 3

Swelling Capacity study at 46 hours

Cross Linker AM (g)	Time (hour)	Weight of SAP sample (g)	Weight of swelled SAP (g)	Swelling capacity g liquid/g SAP	Swelling capacity %
0.03	46	0.5	141.0772	281.1544	28115.44
0.06	46	0.5	73.4627	145.9254	14592.54
0.09	46	0.5	61.2729	121.5458	12154.58
0.12	46	0.5	63.6819	125.3638	12536.38
0.18	46	0.5	60.2112	119.4224	11942.24

5. Swelling Capacity of polymer gel

The swelling capacity of the synthesized polymeric gels were studied by tea-bag method.

Tea-Bag Method (in distilled water): The synthesized polymer gel sample (0.5 g) [W_0] was placed into a pre-weighed tea bag and it was sealed. The sealed tea bag was placed in a 250 mL beaker filled with distilled water, and it was left for desired time (180 minutes or 46 hours) for swelling. After that the tea bag was removed from beaker, and excess amount of water was removed from swollen gel by hanging bag until, no liquid was dripping off. The swelled tea bag was weighed [W_1] and the swelling capacity of polymer gel was calculated by following equation 1.

$$FreeSwell = \frac{w_1 - w_0}{w_0} \quad (1)$$

The swelling capacity (SC) of synthesized polymer gel at 180 minutes and 46 hours were determined. Five different cross-linked polymer gel samples have been synthesized using different concentrations of allyl mannitol crosslinker. The swelling capacity of these polymer gel samples were calculated which are shown in Tables 2 and 3. From the table (2 and 3), it can be seen clearly that the swelling capacity of polymer gels is high when the amount of cross linking agent (CLA) used is the lowest (*i.e.* 0.03 g crosslinker in 12.0 g. acrylic acid monomer used during the synthesis of gel). As the amount of cross-linker (CLA) used in the synthesis of polymer gel increases, the swelling

capacity (SC) of the super absorbent polymer gel (SAP) decreases.

$$CLA \propto \frac{1}{SC}$$

CONCLUSIONS

A novel cross-linker, allyl mannitol has been synthesized by allylation of mannitol, using a new and easy synthetic scheme where allylation has been carried out with allyl chloride at low temperature (40 °C) without using an autoclave. The process of the synthesis of the cross linker is very simple and convenient, and the cross-linker is eco-friendly as it is sourced from a naturally occurring sugar. In synthesis of cross linker with allyl chloride, four secondary alcoholic hydrogens of mannitol are easily replaced by allyl groups. From the spectral data (IR, ¹HNMR), it has been confirmed that allyl groups are linked to D-mannitol group at four places. Cross-linked polymer gel samples have been synthesized using acrylic acid monomer and allyl mannitol cross-linker in the presence of potassium persulfate initiator. The synthesized gels show high water adsorption capacity and behave as super absorbents. The methods used in synthesis of crosslinker and polymer gel-preparation are convenient and cost effective. These hydrogels have shown promising results for their application as superabsorbent polymers.

Acknowledgements. One of the authors (Anamica) gratefully acknowledges a research cum teaching fellowship from MMM University of Technology, Gorakhpur under Technical Education Quality Improvement Program (TEQIP), of Ministry of Human Resource Development, Government of India.

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