Synthesis and Characterization of Allyl Pentaerythritol Cross-linker

Anamica* and Pande Poorn Prakash
Department of Chemistry and Environmental Science, M.M.M. University of Technology Gorakhpur-273010, U.P., INDIA
*anamicamishra72@gmail.com

Abstract
Conventionally, cross-linkers are used for the preparation of polymer-based gels. In this study, we report the synthesis and characterization of allyl pentaerythritol: a novel cross-linker based on pentaerythritol. The synthesized cross-linker allyl pentaerythritol has been characterized by elemental analysis (C, H, N and O) and by Fourier-transform infrared (FT-IR) and 1H Nuclear magnetic resonance (1HNMR) spectra. The cross-linked polymers were prepared by utilizing the synthesized cross-linker in different concentration.

The swelling capacity of the synthesized polymers has been studied and it was found that some of the polymer samples behave like super-absorbent polymers. These polymeric gels can be utilized in various applications viz. as a catalyst, for heavy metal removal, for dye removal, for anion removal from water etc.

Keywords: Pentaerythritol, allyl chloride, allyl pentaerythritol, polyol-based cross-linker.

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 fluid[1]. The gels show great significance 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 having various bio-applications[5]. In this study, we report the synthesis of a pentaerythritol based cross linker and also the preparation of polymer-gels with the help of cross-linker. The prepared gel can be utilized as a catalyst, heavy metal removal, dye removal, sanitary pads, anion removal from water etc. The work on these applications is under process and preliminary results are highly promising.

In the preparation of cross-linkers, the hydroxy containing group (natural polymers and biopolymers) has been utilized commonly. Due to their low cost and biocompatibility, these bio-materials are of much interest for the researchers[6,7]. The gels can be degraded easily which make them an excellent material in various applications. Different hydroxy containing group such as starch, cellulose and chitosan have been used in the synthesis of cross-linkers[8-10]. Stevenson et al[11] used ribose crosslinking agent in gelatin films, Karvandian et al[12] reported glucose cross-linker in bone scaffolds and Hudson et al[13] studied collagen cross-linking agent in bone pathobiology. Park et al[15] prepared alginate-based gel. Liu et al[14] studied chitin-based acrylate superabsorbent.

This study comprises synthesis and characterization of polyol based cross-linker. We have synthesized the cross linker using a polyol pentaerythritol. Pentaerythritol is a polyol, which is prepared by poly-addition reaction between formaldehyde and acetaldehyde and used in paints, plastics, cosmetics and explosives.

Material and Methods

Reagents: Pentaerythritol, sodium hydroxide, allyl chloride, ethyl acetate, sodium chloride and anhydrous sodium sulphate were purchased from SRL chemicals. The chemicals were used after purification.

Synthesis of Allyl Pentaerythritol: Pentaerythritol (5 gm) and aqueous sodium hydroxide (7 gm NaOH, in 7 ml water) were added to 250 ml round bottom flask equipped with a magnetic stirring bar. The flask was sealed and heated at 80°C with constant stirring for 90 minutes. After that, the contents were cooled and vessel was opened. Then, 15 ml allyl chloride was added into it under inert atmosphere and the mixture was stirred for 24 hours. The temperature was increased to 100°C for two hours. Then the contents were stirred over night at 40°C temperature. Reaction mixture was cooled to room temperature, placed in an ice bath, opened and diluted with ice water to dissolve sodium chloride salt.

The reaction mixture 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. Allyl pentaerythritol (AP) was obtained in liquid form. The synthesized compound AP is ($C_{17}H_{24}O_4$) M.W. 292, Yield: 67%. Elemental anal.: (Calc) Found %: C (69.86) 69.84, H (8.21) 8.20 and O (21.91) 21.90.

Characterization: Elemental analyses of C, H, N and O percentage were obtained by using an elemental analysers Euro-E 3000 instrument. FT-IR Spectrometer Perkin Elmer Spectrum GX Range: 10,000 cm^{-1} to 370 cm^{-1} was used to analyse polyol based crosslinker sample. Nuclear Magnetic Resonance (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.

Results and Discussion

All the hydroxide groups of pentaerythritol react with sodium hydroxide to form sodium salt which further reacts with allyl chloride resulting in the formation of tetra allyl pentaerythritol (polyol based cross-linker) (figure 1). The cross-linker is further utilized for the formation of gels.

IR: The IR spectra of AP is shown in figure 2 and different absorption peaks are shown in table 1. IR spectral data shows hydroxy absorption peak at 3430 cm^{-1}. Absorption peak at 3081 cm^{-1} indicates the presence of =C-H group and stretching peak at 1646 cm^{-1} confirms the presence of C=C group in compound. The peaks at 1422 cm^{-1}, 1452 cm^{-1} show -CH- group near to double bonded carbon and peak at 1088 cm^{-1} shows -C-O- stretching, =C-H bending peaks are at 925 cm^{-1}.

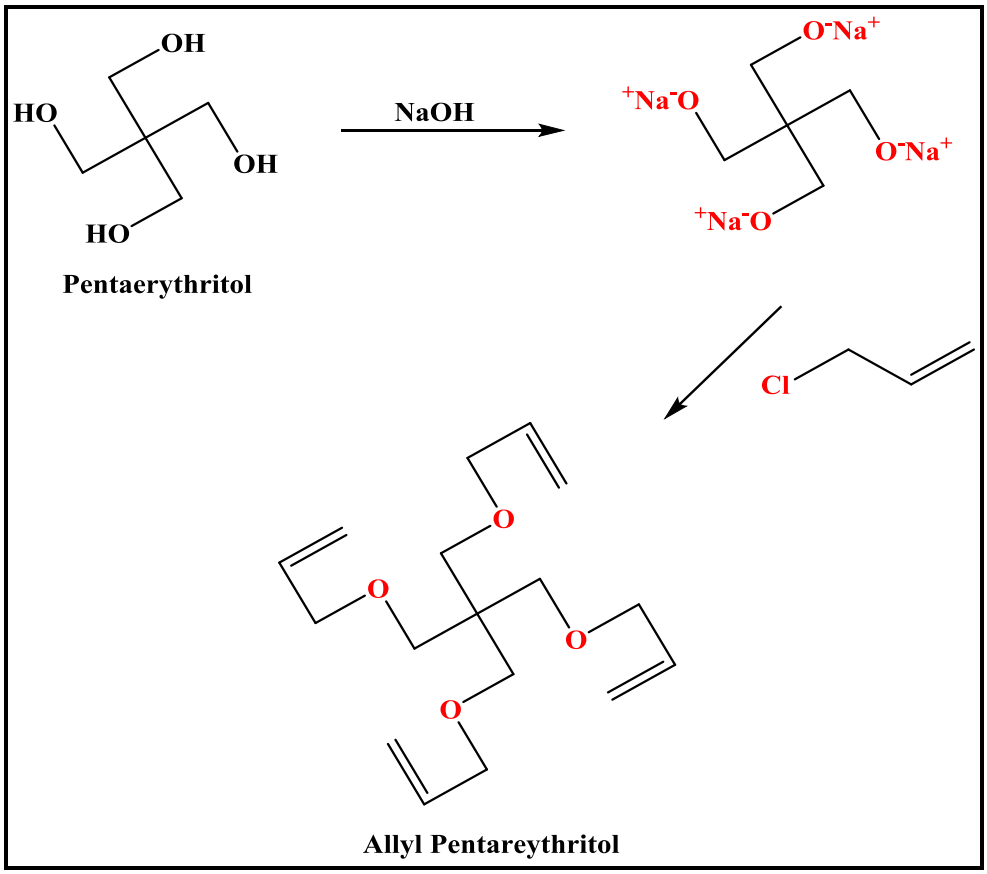


Fig. 1: Formation of AP cross-linker from pentaerythritol

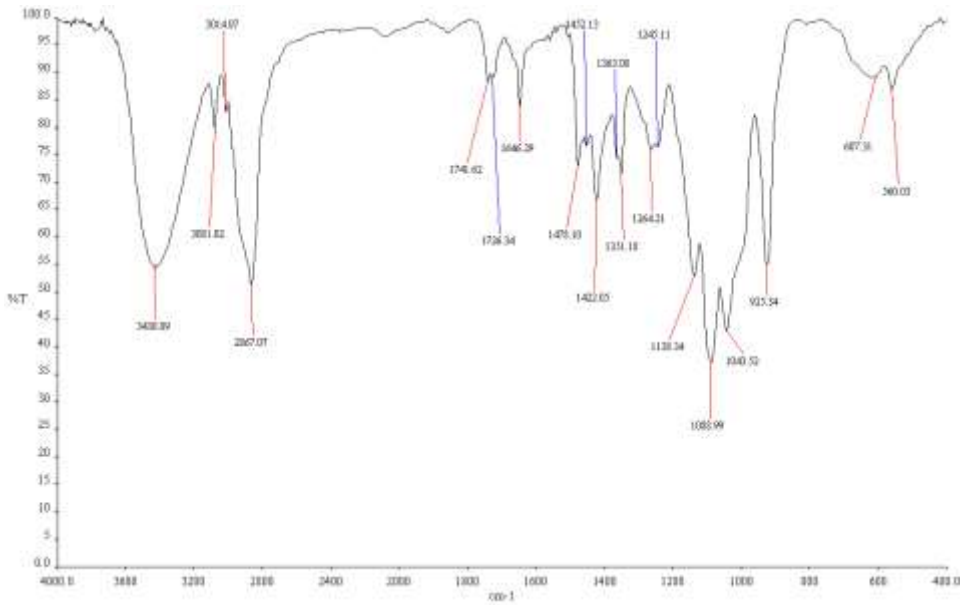


Fig. 2: IR spectra of AP

Table 1
IR spectra of Allyl pentaerythritol

IR (in cm^{-1})	**Allyl Pentaerythritol**
-O-H stretching	3430 cm^{-1}
-C=C-	1646 cm^{-1}
-C-O stretching	1088 cm^{-1}
=C-H Stretching	3081 cm^{-1}
=C-H bending	925 cm^{-1}

^{1}HNMR: The ^{1}HNMR spectra of AP shows the peak of different proton of allyl group as H^a, H^b, H^c between δ 5-6. While in the case of pentaerythritol, there are no peaks between δ 5-6. The ^{1}HNMR peaks of synthesized polyol based cross-linker are shown in figure 3. ^{1}H-NMR (in deuterated DMSO): δ 5.89 (t, 4H, $=CH_a$-), 5.24 (d, 4H, $=CH_b$), 5.23 (m, 4H, $=CH_c$), 4.04 (d, 8H, -O-CH_2), 3.4 (s, 8H, -C-CH_2). The ^{1}HNMR data of different proton as H^a, H^b, H^c, -O-CH_2 in linker is shown in figure 4.

The pentaerythritol based cross-linker is used in the formation of gels. Gels have been prepared by the polymerization of sodium salt of acrylic acid in the presence of cross linker. Acrylic acid monomer is used to prepare gel in the presence of potassium persulphate initiator and AP cross-linker (figure 5).

In our studies, the best samples of these superabsorbent gels can absorb about 217 times water (about 21700 % of their original weight) in 46 hours. These gels can be used in various applications such as in personal care materials, biomaterials, drug-delivery systems, bio-sorbent, pharmaceutical, construction, forestation, agriculture, environmental and industrial applications. In water management, the gel is used for required and unwanted water management depending on their particular usages.

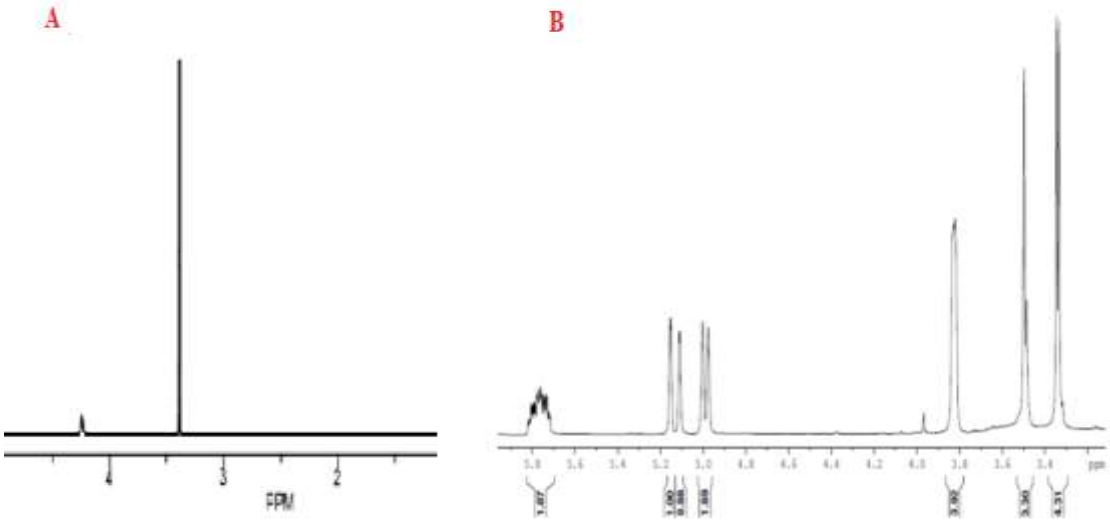
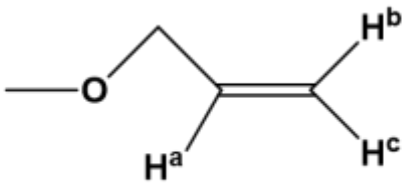


Fig. 3: ^{1}HNMR Spectra of (A) Pentaerythritol (B) AP



^{1}HNMR (in δ)	**Allyl Pentaerythritol**
H^a	5.89 (t, 4H)
H^b	5.24 (d, 4H)
H^c	5.23 (m, 4H)
-O-CH_2-	4.04 (m, 8H)

Fig. 4: ^{1}HNMR spectra data of proton in different environment

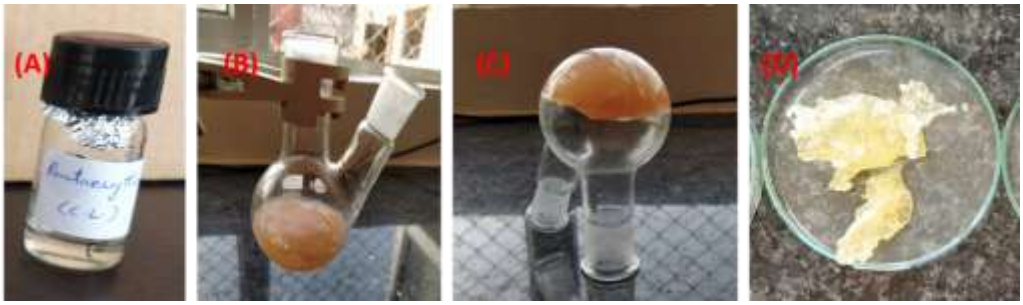


Fig. 5: Formation of (B-D) gel with the help of (A) cross-linker

Conclusion

From the spectral data (IR, ^{1}HNMR), it can be concluded that allyl groups are linked to pentaerythritol group at four places (-OH group positions). The method used to prepare cross-linker is very simple and convenient. There is no difficulty during preparation and isolation of cross-linker. Gels have been prepared by the use of the cross linker easily and found to act as super absorbents.

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