

# STUDY OF MODIFICATION OF POLYSACCHARIDES VIA ATOM TRANSFER RADIAL POLYMERIZATION FOR APPLICATION AS A CORROSION INHIBITOR: A REVIEW

Nishad Rajendra Vaidya<sup>1\*</sup>

<sup>1</sup>*Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India*

\* Corresponding author: Nishad Rajendra Vaidya, E-mail address: nishad2vaidya@gmail.com

## Abstract -

Polysaccharides are being viewed as an alternative to their non-renewable counterparts owing to their eco-friendliness and sustainability. Availability of hydroxyl groups and feasibility of their modification can be potentially utilised for functionalization or grafting purpose. Grafting of bio based polysaccharides using Atom Transfer Radical Polymerization (ATRP) is a versatile technique. This review emphasizes on grafting of some of the polysaccharides by ATRP to increase the durability and number of heteroatoms on the backbone of polysaccharides, which could be used as an effective tool for making corrosion inhibitor.

**Keywords-** Polysaccharides, grafting, ATRP, anti-corrosion

## 1. INTRODUCTION

Polysaccharides are the bio-polymers with monosaccharide repeating units linked by glycosidic bonds. They are commercially used in food, cosmetics, clinical as well as pharmaceutical industries [1-3]. Some promising features such as biodegradability, nontoxicity, biocompatibility, make them versatile and thus suitable for applications in various fields. Presence of polar functional groups, high molecular weight and relatively rigid backbone are some of the main factors which affect the physico-chemical behavior of polysaccharides. They can withstand upto 200°C temperature and have high glass transition temperature ( $T_g$ ) as well as softening temperature, which together contribute to the high cohesive forces between their chains [4]. Chemical modifications such as esterification [5], etherification [6], quarterisation [7], urethane formation [8], free radical reaction [9] and amination [10] can furthermore enhance the

properties of polysaccharides. One of the convenient and common routes to modify the natural polysaccharide is graft polymerization. There are three different approaches of grafting classified as grafting from, grafting to and grafting through [11]. Generally, free radical polymerization is employed in such reactions which lead to the formation of homopolymer along with copolymer [12]. Atom Transfer Radical Polymerization (ATRP) has many advantages over the grafting methods for polysaccharide modifications. This technique was first reported by K. Matyjaszewski and M. Sawamoto in 1995 [13, 14]. Atom Transfer Radical Polymerization consists of the formation of carbon – carbon bond between alkyl halides, commonly known as an initiator and alkenes which lead to polymer chain formation with controlled molecular weight, low poly-dispersities and diverse functionality [15, 16].

As of now, most of the bio-based polymers have been studied as corrosion inhibitors efficiently in both acidic and basic media which have proved a decrease in corrosion rate [17]. An approach of grafting monomeric substituents on the polysaccharide has been proved better in binding to the substrate [18]. Even though most of the studies have investigated, if grafting could be made especially by ATRP, the properties of polysaccharides as a corrosion inhibitor would be enhanced by increasing the durability and tensile strength of the coating. This review discusses the modification of selective polysaccharides via ATRP so as to put a step forward to introduce the heteroatoms in the chemical structure which would felicitate the anti-corrosion properties efficiently.

### 1.1 AGAROSE

Agarose is a linear polysaccharide which consists of 3-O-linked  $\beta$ -D- and 4-O linked 3,6-anhydro- $\alpha$ -L-galactopyranose obtained from seaweeds [19]. Agar grafted quaternized poly [2-(dimethylamino) ethyl methacrylate] (Ag-g-QPDMAEMA) copolymers were prepared via grafting from ATRP as anti-bacterial agents [20]. The process is summarized in scheme 1 (Figure 1). The agarose was dissolved in dimethyl acetamide while 2-bromopropionyl bromide (BiBB) was added dropwise at 0°C to the above mixture in the presence of triethylamine as catalyst. By varying the macroinitiator to monomer ratio, 2-(dimethylamino) ethyl methacrylate (DMAEMA) was polymerised onto the macroinitiator via ATRP using copper(I) bromide (CuBr)/ 2,2'-bipyridyl (bipy) catalyst system at 60°C in dimethylformamide to graft different lengths of PDMAEMA on the backbone of agarose. Finally, 1-bromobutane was used to quaternize tertiary amine moieties of PDMAEMA thus to introduce cationic features. Minimum inhibitory concentration (MIC) values were shown by quaternary graft copolymers against gram negative that is *Staphylococcus aureus* and gram positive *Escherichia coli* bacteria and hemotoxicity in rabbit red blood cells. Ag-g-QPDMAEMA grafted copolymer can be used as hydrogels at a high concentration which could act as antibacterial agent to hinder biofilm formation in bacterial suspensions. This research typified the agarose based antibacterial agents with versatile biomedical applications which can be stretched to modification of agarose with other quaternary ammonium salts. However, this study also developed the antibacterial function of polymeric quaternary ammonium salts from solutions to substrate surfaces without the use of any complicated reaction chemistry.

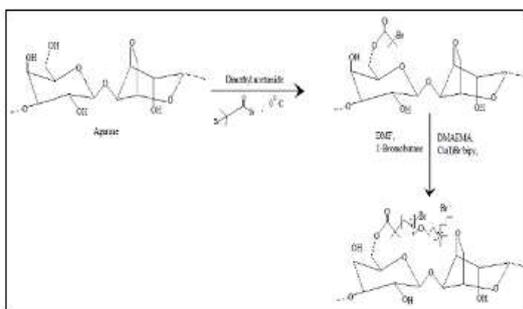


Fig.1: Synthesis of Ag-g-QPDMAEMA [20]

Hydrophobically modified agarose grafted poly (N,N-dimethylamino-2-ethyl methacrylate) (PDMAEMA) was synthesised by using graft from ATRP technique as shown in scheme 2 (Figure 2) [21]. Agarose initially reacted with palmitoyl chloride in N-methyl pyrrolidone at 80°C in presence of pyridine at various amounts as a catalyst. Light brown precipitate of acylated agarose was then reacted with 2-bromopropionyl bromide (BiBB) to prepare agarose macroinitiator (AgBr) in dichloromethane in presence of pyridine at 0°C. Finally, ATRP of varied amount of 2-(dimethylamino) ethyl methacrylate (DMAEMA) was carried out using agarose macroinitiator (AgBr) in presence of dioxane as a solvent at 85°C. The molar ratio used for the grafting was [AgBr]: [copper(I)chloride (CuCl)]: [N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA)]: [dioxane]= 1:5:10:2500. The polymerization followed first order kinetics with high conversion (64-87%). pH study of the product stated the solubility in aqueous solution (pH range from 5-6).

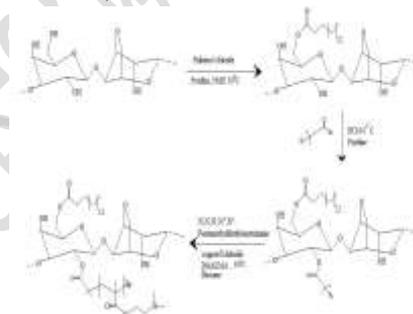


Fig. 2: Synthesis of Ag-g-PDMAEMA [21]

### 1.2 GUAR GUM

Guar gum is an uncharged ground endosperm of guar beans [22]. It consists of linear carbohydrate polymer structure- straight chain of D-mannose unit connected by  $\beta(1\rightarrow4)$  glycoside linkage and D-galactose unit linked with  $\alpha(1\rightarrow6)$  bonds. The average ratio of galactose to mannose is 1:2. Guar gum is water soluble polysaccharide, which gently forms a viscous colloidal solution in water.

Graft copolymer of 4-aminoantipyrine (AAP) and guar gum macroinitiator (GGBr) via ATRP using grafting from technique was synthesised at 50°C by scheme 3 (Figure 3) [23]. In first step hydroxyl groups of guar gum was reacted with 2-bromoisobutyryl imidazole at 65°C using lithium chloride (LiCl) /dimethyl sulfoxide (DMSO) for 24 h and the product was precipitated in methanol. The creamy green coloured solid product was obtained

using soxhlet extraction for 48 h and vacuum drying at 50<sup>o</sup> C for further 48 h.

In second step, ATRP of 4-aminoantipyrine (AAP) was carried out using GGBr in presence of 2,2'-bipyridyl (bipy) as a catalyst and copper(I)bromide (Cu(I)Br) as a ligand in presence of water under nitrogen atmosphere. Optimum reaction conditions such as effect of 4-aminoantipyrine concentration, effect of guar gum macroinitiator concentration, effect of Cu(I)Br/bipy concentration ratio and the effect of temperature on the rate of copolymer formation were studied. The optimum ratio of [AAP]: [GGBr]: [Cu(I)Br]: [bipy] was found to be 100:1:1:2. Thus the product obtained with polydispersity 1.28 has higher thermal stability but lower glass transition temperature as compared with guar gum [23].

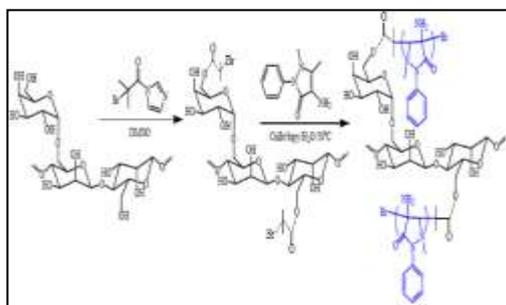


Fig. 3: Synthesis of AAP-g-GGBr [23]

### 1.3 LOCUST BEAN GUM

Locust bean gum is a non-ionic versatile polysaccharide also known as carob gum or carbon bean gum [24]. It is hydrophilic in nature and has vivid applications in food industry, drug delivery, tissue engineering etc. [25]. It has 4 linked D-mannopyranosyl units and every 4<sup>th</sup> or 5<sup>th</sup> chain unit is substituted on 6<sup>th</sup> carbon with D-galactopyranosyl unit. Solubility of locust bean gum is affected by change in pH. Locust Bean gum has good solubility in lithium chloride / dimethyl sulfoxide system.

Well defined locust bean gum grafted copolymers were synthesized by two step grafting process at ambient temperature using water as shown in scheme 4 (Figure 4) [26]. In the first step, initiator sites were introduced on locust bean gum backbone by the reaction of hydroxyl groups with 2-bromoisobutyric acid in presence of lithium chloride (LiCl)/ dimethyl sulfoxide (DMSO) at 65<sup>o</sup>C for 24 hours. For the same purpose, 1, 1'- carbonyl diimidazole in anhydrous dimethyl sulfoxide was reacted with 2-bromoisobutyric acid to form acid imidazolide at ambient temperature. In a separate beaker locust bean gum was added to the LiCl/DMSO solution at 150<sup>o</sup>C until highly viscous

and clear solution was formed. The resulting acid imidazolide solution was then added to the locust bean gum / lithium chloride-dimethyl sulfoxide solution slowly. The molecular weight and polydispersities of polysaccharide before and after macroinitiator synthesis were affected by the concentration of acid imidazolide.

Further, by using a significant molar ratio of [Initiator]: [Cu(I)Br]: [bipy]=1:1:2 a range of monomers such as methacrylate, acrylamide and styrenic monomers were grafted on to locust bean gum. After a few minutes, solution became viscous indicating rapid polymerization. Catalytic copper was removed using basic alumina or silica. High molecular weight grafted product was obtained indicating complex nature of the copolymer as compared to the starting macroinitiator [26].

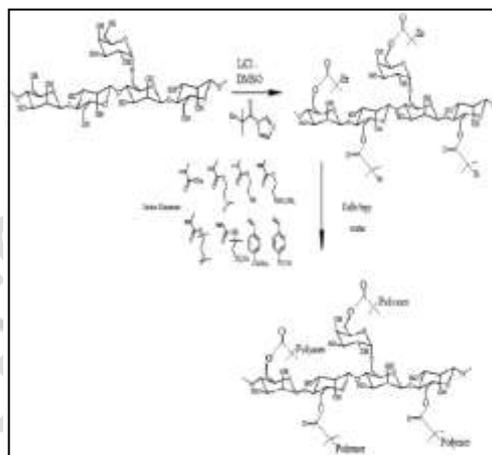


Fig. 4: Grafting of copolymers based on locust bean gum by ATRP [26]

### 1.4 TAMARIND KERNEL GUM

Tamarind kernel gum [27] is a water soluble polysaccharide with the ratio of galactose: xylose: glucose equal to 1: 2.25: 2.8. It consists of branched (1→5)- $\alpha$ -L-arabinofuranan and unbranched (1→4)- $\beta$ -D-galactopyranan linkages.

Recently, a copolymer of tamarind kernel gum and polymethacrylic acid was successfully synthesized using surface initiated ATRP technique for dye removal application [28]. Well defined tamarind kernel gum based macroinitiator (TKPBr) was synthesised in first step by dispersing tamarind kernel gum in a mixture of pyridine and dimethyl formamide at 75<sup>o</sup>C. 2-bromo-2-methylpropionyl bromide was added dropwise in the above solution in presence of ice and the solution was made to stand still for 8 h. The tamarind kernel gum macroinitiator (TKPBr) was then precipitated in excess amount of double distilled water and vacuum dried at 55<sup>o</sup>C for 12 h.

In second step, ATRP of methacrylic acid was carried out using TKPBr in presence of CuBr/bipy in dimethyl formamide as solvent at 65°C for 3 h. Finally, the product was filtered, washed with water and dried in vacuum at 50°C for 24 h. The various grades of product were synthesised with variation in temperature, time and concentration of CuBr/bipy. Optimum conditions like effect of temperature, effect of CuBr/bipy ratio were studied for rate of conversion. The optimum ratio of CuBr: bipy was found to be 2:3. Adsorption studies were carried out further for methyl blue and erichrome black T dyes which showed better adsorption capacity in both acid as well as basic media along with efficient desorption process which could regenerate the copolymer.

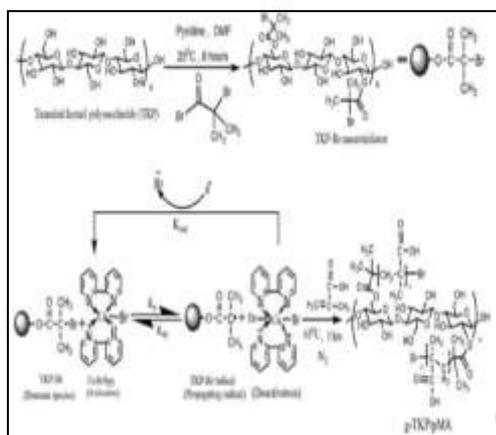


Fig. 5: Synthesis of tamarind kernel gum-g-poly(methacrylic acid) [28]

## 2. CONCLUSION:-

Combination of different synthetic techniques for preparing a precise structure is becoming a necessity with an increase in demand for various modified hybrid materials. Non-toxicity, biodegradability and biocompatibility of bio-based materials offer great potential applications in various fields. ATRP is a versatile method to insert various functionalities into the polysaccharide structure. We observed in this review that ATRP acts as a powerful technique for the preparation of architectures of polysaccharides based hybrid materials. This could be extended for the application of those modified materials as a corrosion inhibitor which could enhance the molecular size, durability and applicability. Along with this, the review paper also highlights the use of grafting from technique and the properties of final product which depends upon the reaction conditions.

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