



**IGNITED MINDS**  
Journals

*Journal of Advances in  
Science and Technology*

*Vol. VIII, Issue No. XV,  
November-2014, ISSN  
2230-9659*

**SYNTHESIS AND UTILIZATION OF RESINS  
THROUGH FUNCTIONALIZATION OF  
POLYSACCHARIDE**

AN  
INTERNATIONALLY  
INDEXED PEER  
REVIEWED &  
REFEREED JOURNAL

# Synthesis and Utilization of Resins through Functionalization of Polysaccharide

Nitika Kohli<sup>1\*</sup> Dr. Arun Kumar Suthar<sup>2</sup>

<sup>1</sup>Research Scholar, Jodhpur National University, Rajasthan

<sup>2</sup>Assistant Professor

**Abstract – In vision of quickly increasing interest in the amino polysaccharide chitin as a functional biopolymer, a recent development of basic and application studies in chitin chemistry is reviewed as well as some basic aspects of this specialty biomass resource. A special emphasis is placed on the controlled modification reactions to prepare chitin derivatives with well-defined structures and thereby to construct sophisticated molecular architecture having various superior functions. Of soluble precursors reported, A-phthaloyl-chitosan has proved particularly useful and made possible series of regioselective and quantitative substitutions thus far difficult. One of the important achievements based on this organ soluble precursor is the synthesis of non-natural branched polysaccharides that have sugar branches at a specific site of the linear chitin or chitosan backbone.**

## INTRODUCTION

Increasing environmental concern and the need for decreasing the dependence on fossil based raw materials have fueled research towards the possibilities of making use of renewable sources. Polysaccharides can be found in vast amounts in nature, cellulose being the most common organic polymer. High levels of sophistication have been formed during the evolution of biological systems, for instance, wood consists of cellulosic nanostructures having high strength 1, 2. These biocompatible and biodegradable structural materials have drawn increasing attention in various research fields ranging from materials science to medical applications 3, 4.

Cellulose consists of beta-D-glucopyranose units linked together by acetal functions at C4 and C1 positions (Figure 1). The degree of polymerization (DP) varies according to the source and the pretreatment of the biopolymer, wood pulp having a typical DP of 300-1700 5. The cellulose molecules are assembled to elementary fibrils and fibrillar bundles called microfibrils, which are located in the plant cell wall constituting the framework of the cell along with other wall polymers such as hemicelluloses and pectins 2.

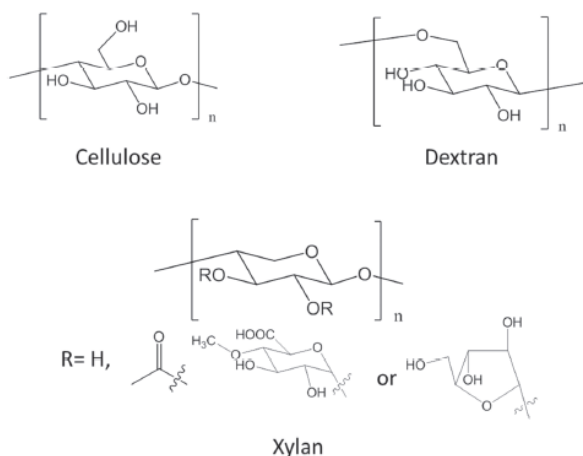
This nanostructure, often termed nanofibrillated cellulose 6, can be extracted by mechanical disintegration of pulp fibers 7-10 and is usually obtained as a water suspension with a solid content below 2 weight-%. The fibrils have an entangled network structure 11 - 13. Characteristics of the

obtained fibrils are a small diameter and high aspect ratio and because of its high strength 1, it is an interesting material as a reinforcing element in polymer composites for various applications.

Hemicellulose is the most abundant polysaccharide family next to cellulose, present as a component in most plant cell walls. In hardwood species, the main hemicellulose type is xylan, which predominantly consists of D-xylopyranoside units (Figure 1) connected by  $\beta$ -(1 $\rightarrow$ 4) -linkages along with acetyl-, glucuronic acid and species dependent side groups 14. Among other methods, xylan can be conveniently extracted from biomass by alkali extraction 15, 16, where the acetyl groups are also hydrolyzed rendering the backbone hydroxyl groups available for derivatization reactions. Xylans and xylan derivatives have found applications in the paper and food industry as well as pharmaceutical applications 16, 17.

Dextran is a water soluble microbial polysaccharide predominantly consisting of linear alpha-1,6-linked glucopyranose units (Figure 1), and a small amount of branching at 1 $\rightarrow$ 2, 1 $\rightarrow$ 3 or 1 $\rightarrow$ 4 depending on the source 18.

Dextran is biodegradable and resists protein adsorption as well as cell adhesion, making it suitable for biomedical applications, such as plasma volume expansion and artificial tears 18, 19.



**Figure 1. Structural units of cellulose, dextran and xylan. Typical xylan substituents are Oacetyl-, methylglucuronic acid and arabinose-residues.**

Chemical derivatives of polysaccharides have a long history; cellulose nitrate, sulfate, acetate and carboxymethyl cellulose being the oldest cellulose derivatives having industrial significance. The reactions used for derivatisation involve the numerous hydroxyl groups on the polysaccharide macromolecule, the hydroxyl group acting as a nucleophile towards an electron deficient carbon, forming the covalent bond 5, 20.

The tendency of polysaccharides to absorb water can become a problem when these natural polymers have to be chemically tailored, since water restricts the chemical reactions available for these modifications. Drying of the polysaccharides or using problematic solvents to do the chemical alteration is neither economical nor environmentally benign 20, 41. For example, the use of NFC for making polymer composites usually requires removing the water through solvent-exchange procedures and by chemical modification of the surface of NFC fibrils to obtain better compatibility with polymers 13 and this may lead to destruction of the original nanostructure of the fibrils 42.

Polysaccharides possess unique structures combined with reactive groups that allow the design of structures and hence of properties. Chemical modification is the most important path to adapt the properties to targeted application and even to develop novel functional polymers and advanced materials based on biomass. The hydroxyl groups show the typical reactions of low-molecular alcohols, i.e., they can form ethers and esters.

Chemical modification of cellulose has been already carried out commercially for many decades and in particular ethers and esters of cellulose find applications in various fields including cosmetics, food, constructing materials, paper, oil well drilling as well as in pharmaceutical applications and as filters,

membranes and films. It is interesting to note that commercial chemical modifications have not been limited to some ethers including methyl-, ethyl-, hydroxyalkyl-, and carboxymethyl moieties and some esters including acetate, propionate, butyrate, phthalic acid half ester and to products with two or even three of the functional groups mentioned.

## SYNTHESIS OF FUNCTIONALIZED POLYSTYRENE RESINS

The use of solid-supported reagents and scavengers have become increasingly popular in organic chemistry as their use bypasses the purification difficulties associated with traditional solution-phase reactions whilst retaining the beneficial aspects, such as ease of reaction monitoring (TLC, LC-S, NMR, etc.). Solid-supported reagents also enable the use of excess reagents to drive the reaction to completion, without complicating the work up procedure.

Simple filtration, washing and solvent removal is all that is required to work up the reactions, which is particularly beneficial to high throughput synthesis. 1 Attaching toxic or hazardous compounds to a solid support reduces the risks associated with the reagent. Simple filtration of solid supported catalysts also means that the catalyst can be recovered, regenerated and reused, reducing the cost associated with these reagents. The simple work up techniques associated with polymer-supported reagents and scavengers also make the use of automation a real possibility. Robots can carry out all the manipulations required and large libraries can be generated quickly and efficiently.

Perhaps the most important insoluble support for organic synthesis is cross-linked polystyrene. Derivatize polystyrene can be made either by copolymerisation of styrene, divinylbenzene<sup>2</sup> and functionalized styrene, or in a more divergent fashion by functionalizing a polystyrene starting material. The functionalization of polystyrene has been achieved by two methods with relatively small diameter (175 mm) polystyrene beads: (1) by direct lithiation of the polystyrene<sup>3</sup> and (2) by halogen-metal exchange.<sup>4</sup> These procedures are not applicable nor optimized for relatively large diameter (O150 mm) cross-linked polystyrene functionalization.

Beads with diameters greater than 150 mm possess optimal handling properties. Larger diameter resins (O150 mm) are free flowing, greatly reducing the problem of static often associated with smaller diameter resins, which makes these smaller resins more difficult to manipulate. The rate of filtration of the larger diameter beads is faster, with none of the polymer support passing through the filter. This is often a problem with the smaller diameter beads requiring the reaction mixture to be re-filtered. Although smaller diameter beads often have

increased chemical reaction rates, this needs to be balanced by the improved handling and increased functionality per bead associated with larger beads.

In this study we report on the development of a cost effective method of derivatizing 4-bromopolystyrene, in one step, to generate a range of functionalized resins. Moreover, this methodology can be used on small and large diameter (up to at least 600  $\mu$ m) beads of polystyrene. These reagents can be used as polymer-supported reagents, scavengers or supports for target oriented and diversity oriented synthesis.

Triphenylphosphine polystyrene (1) is one of the most successful polymer-supported reagents developed, as it avoids the need for troublesome purification to remove triphenylphosphine oxide. Triphenylphosphine is used in a wide range of reactions, including Mitsunobu,<sup>5</sup> halogenation<sup>6</sup> and Wittig<sup>7,8</sup> reactions. Furthermore, it is commonly used as a ligand for metal catalyzed reactions, such as the Suzuki reaction.<sup>9</sup> Polymer-supported triphenylphosphine, on cross-linked polystyrene, is usually synthesized by bromination followed by lithiation of the polystyrene. The lack of complete selectivity in this process results in less chemically defined resin (1b). Higher quality polymer supported triphenylphosphine has been synthesized by many different methods such as ring opening metathesis polymerization of norbornadiene structures,<sup>10–12</sup> and radical co-polymerisation<sup>2</sup> of diphenyl-(4-vinylphenyl)phosphane, styrene and cross-linkers; however, these resins are either expensive or not commercially available.

## FUNCTIONALIZATION OF THE POLYSACCHARIDE CHITIN

Polysaccharides are widely distributed in nature. Their molecular structures and hence their properties vary over a broad range. They have been regarded primarily as structural materials and as suppliers of water and energy. These structures are considered less significant than other natural polymers such as proteins and nucleic acids in view of their biological functions. They are, however, attracting increased attention as their inherent biological activities and physicochemical properties are being better understood. Polysaccharides will therefore become increasingly important in various fields since they possess unique structures and characteristics that are quite different from those of typical synthetic polymers.

Of the many kinds of polysaccharides, cellulose and chitin are the most important biomass resources; cellulose is synthesized mainly in plants, whereas chitin is synthesized mainly in lower animals. In fact, they are the most abundant organic compounds on earth and estimated to be produced at levels approaching  $10^{11}$  tons annually. Although cellulose has been studied extensively, only limited attention

has been paid to chitin, principally from its biological properties. Despite its huge annual production and easy accessibility, chitin still remains an unutilized biomass resource primarily because of its intractable bulk structure.

Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide groups at the C-2 positions in place of hydroxyl groups (Scheme 1). In addition to its unique polysaccharide architecture, the presence of amino groups in chitin is highly advantageous for providing distinctive biological functions and for conducting modification reactions. Chitin is thus expected to have a much higher potential than cellulose in many fields. It is a specialty biopolymer having specific properties including biodegradability, biocompatibility, and bioactivity, and it is therefore interesting not only as an abundant resource but also as a novel type of functional material. Special emphasis has been put on the chemical modifications of chitin to explore its full potential. Modifications of chitin are, however, generally difficult owing to a lack of solubility, and the reactions under heterogeneous conditions are usually accompanied by various problems including poor extent of reaction, difficulty in regioselective substitution, structural non-uniformity of the products, and partial degradation of the desired products under severe reaction conditions. Therefore, many efforts have focused on the exploration of facile modification reactions that may open a way to use chitin more effectively. As a consequence, the recent progress in chitin chemistry is noteworthy, and some results and experimental procedures have been compiled into a handbook. Studies on its applications are also quite encouraging, and several commercial products have appeared in the market recently.

### Sources of chitin and chitosan-

Chitin occurs in a wide variety of species, from fungi to the lower animals. Arthropod shells (exo-skeletons) are the most easily accessible sources of chitin. These shells contain 20-50% chitin on a dry weight basis. From a practical viewpoint, shells of crustaceans such as crabs and shrimps are conveniently available as wastes from seafood processing industries and are used for the commercial production of chitin. Other potential sources for chitin production include krill, crayfish, insects, clams, oysters, jellyfish, algae, and fungi. Krill is likely to be the most promising source in the future.

Squid pens also contain chitin that is classified as  $\beta$ -chitin. This material is distinguished from the ordinary  $\alpha$ -chitin in crustacean shells according to the difference in crystalline structure.  $\beta$ -Chitin has weaker intermolecular forces and is quite attractive as another form of chitin having some characteristics considerably different from those of  $\alpha$ -chitin. The

chemistry of (3-chitin is rapidly advancing, although this starting material is less abundant and is not yet produced commercially. The cell walls of some fungi (Zygomycetes) contain chitosan as well as chitin and these may be used as sources of chitosan. Practically, however, chitosan is more easily prepared by the deacetylation of chitin.

#### Preparation of chitin-

A-Chitin is produced commercially from crab and shrimp shells, which contain calcium carbonate and proteins as the two other major components. Pigments are also contained in small quantities. Further-more, the chitin molecules are assumed to have polypeptide side chains attached covalently to some of the C-2 amino groups through amide linkages. Chitin is the most stable substance against acid and alkali among these components and not is soluble in ordinary solvents. Accordingly, it can be isolated as a residue which remains after decomposing the other substances present in the shell with acid and alkali.

The shells are first cleaned and treated with diluted hydrochloric acid at room temperature to remove calcium carbonate. The decalcified shells are then cut into small flakes or are pulverized and heated in 1-2 mol/l sodium hydroxide near 100°C to decompose the proteins and pigments. Chitin is obtained as an almost colorless to off-white powdery material, There are some free amino groups besides acetamide groups, and the degree of deacetylation for the isolated chitin is around 0.1. Proteases may be used to remove some of the proteins under mild conditions.

(3-Chitin can be isolated from squid pens in a similar but simpler manner, since squid pens are composed almost exclusively of chitin and proteins with only trace amounts of metal salts. Moreover, the molecular packing of (3-chitin is less tight. Squid pens can be treated with hydrochloric acid and sodium hydroxide under mild conditions to give (3-chitin. When the isolated chitin is pulverized within an ultra-centrifugal mill, a white fluffy cotton-like material is obtained. During the isolation procedure, some of the acetyl groups are removed, and the resulting chitin has a degree of deacetylation near 0.1.

#### Preparation of water-soluble chitin -

Chitin can be dissolved into aqueous sodium hydroxide as the alkoxide form, the so-called alkali chitin. When chitin is steeped in concentrated aqueous sodium hydroxide and treated with crushed ice, an alkali chitin solution results. Under these conditions, N-deacetylation proceeds rapidly in solution. An alkali chitin solution in 10% sodium hydroxide left at room temperature for 70 h gives a product with about 50% deacetylation that is soluble even in neutral water. Higher or lower deacetylations often fail to lead to complete solubilization, leading to swollen gels. The degree of deacetylation should be 0.45-0.55 for good

water-solubility. Alternatively, random N-acetylation of chitosan to a degree of acetylation of about 0.5 gives rise to a water-soluble product (Scheme 2).

## FUNCTIONALIZATION OF DI- AND POLISACCHARIDES

The family of polysaccharides that remains in our circle of interest are cyclodextrin. Cyclodextrin (CyDs) are macro cyclic oligosugars most commonly composed of 6, 7 or 8 glucosidic units bearing 1,4- $\alpha$ -glycoside bond, so-called  $\alpha$ -,  $\beta$ - or  $\gamma$ -CyD. Each of the chiral glucose units is in a rigid 4C1 chair conformation, thus giving the macro cycle shape of a hollow truncated cone with all of the secondary hydroxyl groups located on the wider rim, while all of the primary hydroxyl groups are on the narrower rim. The primary and secondary hydroxyl groups on the outside of the CyD make it water-soluble. CyDs have been studied extensively as hosts in supramolecular chemistry.<sup>5,6</sup> The choice of structure of CyDs is of particular importance for supramolecular host-guest complexes, which are the basis of most cyclodextrin applications in medicine, catalysis, separation and sensor technology as well as the food chemistry.

In the initial period, my research interests were concentrated on the functionalisation of sucrose in interesting and useful products in perfumery and food industry.

Methods for the selective functionalisation of carbohydrates are useful both for the direct transformation of unprotected sugars to low added value derivatives, and for the subtle protection-deprotection strategies in multistep syntheses of complex molecules. In the case of sucrose, which can be considered as a promising raw material for the chemical industry because of its exceptional availability, the presence of eight hydroxyl groups provides an interesting field of experimentation aiming at the control of the regioselectivity and/or the degree of substitution.<sup>7,8</sup> Among the numerous chemical reactions involving the alcohol function, the acetalation reaction is extensively used in the case of carbohydrates, mostly for protection purposes. The fragility of the glycosidic bond of sucrose under acidic conditions, (because of its fructofuranosidic nature) is a strict limitation to acid-catalysed acetalations. Only very reactive carbonyl compounds are reactive enough under appropriate acidic conditions which preserve the disaccharidic integrity of the molecule. Notably, the transacetalation reaction of  $\alpha,\beta$ -unsaturated dialkylacetals has been shown to occur under mild conditions by Gelas and co-workers.

Sensitivity to the acidic glycoside bond in sucrose has encouraged researchers to seek methods for the preparation of derivatives without bond cleavage. Such requirements are fulfilled by one pot procedure, in which I have obtained cyclic acetals of sucrose in

the presence of lanthanides deposited on the ion exchange resin. As a result, cyclic acetals can be obtained with very good yields without damaging the glycosidic bond. My research was inspired by the work of Yu et al., who used lanthanides embedded in resin for the synthesis of simple acetals of aldehydes and ketones. In addition, I have showed that the catalyst can be recovered and reused without loss of capacity.

Natural or synthetic macrocyclic molecules are interesting compounds for various applications in supramolecular chemistry. The characterizing feature of supramolecular chemistry is that carefully designed synthetic structures (hosts) recognize target molecules (guests) and form a supramolecular complex through noncovalent interactions. A supramolecular complex is formed when there is attractive interaction between host and guest that includes H-bonding, aromatic-aromatic  $\pi$ -stacking, electrostatic and hydrophobic forces. The development of artificial receptors able to form complexes with specific guest has been important to the progress of supramolecular host-guest chemistry. In designing a suitable hosts you have to consider parameters like host size, charge, character of the donor atom, according to the properties of target molecules. The optimal preorganization of host and guest are obtained in the complementarity of the binding sites of host and guest. Suitable neutral host types known for binding cationic molecules are crown ethers, podands, cryptands, cyclophanes and calixarenes. Very often crown ethers constitute the main part of construction of macrocycles. Crown compounds are capable of selective binding to metal, ions, organic compounds, and neutral molecules.<sup>16</sup> When the metal cation radius exactly fits the size of the crown units, it usually forms a 1/1 host/guest complex. In cases when the cation is larger than the crown cavity, a particularly interesting phenomenon is observed, consisting in formation of complexes with 2/1 stoichiometry (sandwich-type complex). Crown ethers and azacrown ethers are important molecular receptors that are currently being used in biological model systems. It has been also shown that sugars are well known to be versatile chiral entities that are particularly suitable for the design of chiral receptors. Crown ethers containing various carbohydrate moieties have received much attention in recent years.<sup>17</sup> Usually, the sugar moieties are mono-, di-, or trisaccharides which are directly incorporated into the crown macrocycle itself or grafted on as pendant arms.<sup>18</sup> Host-guest chemistry, and among others the sugar macrocycle, is emerging as one of the key elements of science and nanotechnology, that aims to improve systems that exhibit higher association constants and greater selectivity.

The use of cesium and sodium cations as a "template" is a successful strategy for the preparation of sugar cryptands. Suitable sucrose and cellobiose derivatives were received in good yields and I have shown that

the size of the metal cation determines the structure of the obtained macrocycles.

## CONCLUSION

Despite the fact that chitin is one of the most substantial structural materials for many living organisms and has a huge annual production, its utilization has been scarcely developed. Application is limited mostly to water treatment in the form of chitosan only in a negligible amount. It may therefore be referred to as the 'last biomass resource'. The delay in basic and application studies on chitin is ascribable to this material's inherent intractable nature.

Chitin is thus one of the most important natural polymers and it has a high potential for providing novel types of polymeric materials with various advanced functions. Owing to advancements in basic chitin chemistry, the fundamental understanding of the complicated characteristics of this amino polysaccharide is progressing. Under these circumstances, a great variety of potential applications have been suggested; including toiletry ingredients, water absorption and moisture retention agents, medicines, virucidal, bactericidal, and fungicidal agents, biocompatible and biomedical materials, bioactive materials, supports for enzyme and cell immobilization, polymeric reagents, specialty fabricated materials such as films, fibers, papers, and membranes, metal cation adsorbents, and agrochemical agents for seed coating, improved growth, and soil amendment. Some applications seem quite promising.

## REFERENCES

- Brower, J.B., Ryan, R.L., Pazirandeh, M. (1997). Comparison of ion exchange resins and biosorbents for the removal of heavy metals from plating factory, *Environmental Science and Technology*, Vol. 31, pp. 2910-2914.
- Creswell, M. W.; Bolton, G. L.; Hodges, J. C.; Meppen, M. (2008). *Tetrahedron*, 54, 3983.
- For a comprehensive list of ROMP-based polymers see (2003): *Polymeric Materials in Organic Synthesis and Catalysis*; Buchmeiser, M. R., Ed.; Wiley-VCH.
- Kitagawa, K.; Inoue, A.; Shinokubo, H.; Oshima, K. *Angew (2000). Chem., Int. Ed.*, 39, 2481.
- Kurita K. (2007). In: Arshady R, editor. *Desk reference of functional polymers: synthesis*

and applications. Washington, DC: American Chemical Society. p. 239.

Kurita K. (2007). In: Goosen MFA, editor. Applications of chitin and chitosan. Lancaster, PA: Technomic Publishing, p. 79.

Kurita K. In: Muzzarelli R, Jeuniaux C, Gooday GW, (2006). editors. Chitin in nature and technology. New York: Plenum, p. 287.

Pelletier, J. C.; Kincaid, S. (2000). Tetrahedron Lett., 41, pp. 797–800.

Tokura S, Nishi N. In: Zakaria MB (2004). Muda WMW, Abdullah P, editors. Chitin and chitosan. Malaysia: University Kebangsaan, p. 67.

---

### Corresponding Author

**Nitika Kohli\***

Research Scholar, Jodhpur National University,  
Rajasthan

E-Mail – [nitikohli68@yahoo.com](mailto:nitikohli68@yahoo.com)