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PREPARATION AND CHARACTERISATION OF POLYACRYLONITRILE AND POLY(METHYL METHACRYLATE) GRAFTED CHITOSAN

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PREPARATION AND CHARACTERISATION OF POLYACRYLONITRILE AND POLY(METHYL METHACRYLATE) GRAFTED CHITOSAN

By

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بسم الله الرحمن الرحيم

ٱلرَّحۡمَٰنُ ﴿١﴾ عَلَّمَ ٱلۡقُرۡءَانَ ﴿٢﴾ خَلَقَ ٱلۡإِنسَٰنَ ﴿٣﴾ عَلَّمَهُ ٱلۡبَيَانَ ﴿٤﴾

إلى الشمعة التي تضيء طريقي في ظلمة الغربة..

إلى من صلواتها أنيسي في غربتي . . . إلى أمي . . .

إلى مثلي وقدوتي العليا...

إلى من يُفني جسده لإسعادي . . . إلى أبي . . .

إلى من ألتجئ إليهم في ضيقتي . . . إلى إخواني وأخواتي . . .

إلى من أجد عندهم الراحة والسعادة . . . إلى أصدقائي . . .

إلى كل من يعشق العلم والمعرفة . . . يتعلم ليعلم غيره...

إليكم جميعاً هذا العمل المتواضع...

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of thesis presented to the Senate of Universiti Putra
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for the degree Master of Science.

PREPARATION AND CHARACTERISATION OF POLY(ACRYLONITRILE) AND POLY(METHYL METHACRYLATE) GRAFTED CHITOSAN

By

FARAJ AHMAD FARAJ ABU-ILAIWI

July 1998

Chairman: Mansor Bin Ahmad, Ph.D.

Faculty : Science and Environmental Studies

Poly(acrylonitrile) (PAN) and poly(methyl methacrylate) were grafted onto chitosan in acidic medium by using cerium ammonium nitrate as initiator under nitrogen gas atmosphere. The grafting percentage showed dependence on initiator concentration, monomer concentration, acetic acid concentration, as well as time of the reaction and temperature of the reaction.

Extent of grafting, percentage of homopolymer formation, grafting efficiency and total conversion were estimated. The highest percentage of grafting of acrylonitrile achieved was as high as

2340% when the optimum conditions were used (cerium ammonium nitrate (CAN) = 0.015 mol. L^{-1}, acrylonitrile (AN) = 2.1 mol. L^{-1}, and acetic acid = 2%, the reaction time = 60 minutes and reaction temperature =50°C). The maximum percentage of grafting of methyl methacrylate was 450% when the optimum conditions were used (cerium ammonium nitrate (CAN) = 7.4 mmol. L^{-1}, methyl methacrylate (MMA) = 0.7 mol. L^{-1}, and acetic acid = 2%, the reaction time = 180 minutes and reaction temperature = 60°C). The resulting graft copolymers showed much hygroscopic compared to chitosan itself. Differential scanning calorimeter (DSC) and thermogravimetry analysis (TGA) studies showed that the graft copolymer of chitosan and chitosan are different in their thermal behaviour. Also thermogravimetry analysis (TGA) showed the temperature of the degradation for the copolymer. On the other hand, poly(hydroxamic acid) was prepared from chitosan-g-PAN with percentage of grafting 500%. Hydrogen capacity for the resin was calculated and water content was estimated. Absorption capacity for metal ions such as Cr^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+} was estimated. The absorption capacity for these metal ions follow the order: $Cr^{3+} > Co^{2+} > Pb^{2+} > Cu^{2+} > Fe^{3+} > Ni^{2+}$.

Abstrak tesis yang dikemukakan kepada Senat Universiti
Putra Malaysia bagi memenuhi keperluan
untuk ijazah Master Sains.

PENYEDIAAN DAN PENCIRIAN KITOSAN CANGKUK POLI(AKRILONITRIL) DAN POLI(METIL METAKRILAT)

Oleh

FARAJ AHMAD FARAJ ABU-ILAIWI

Jun 1998

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Fakulti : Sains dan Pengajian Alam Sekitar

Poliakrilonitril (PAN) dan poli(metil metakrilat) dicangkukkan pada kitosan di dalam medium berasid dengan menggunakan serium ammoniam nitrat sebagai mangkin di bawah gas nitrogen atmosfera. Peratus cangkukan bergantung kepada kepekatan mangkin, monomer, asid asetik, masa dan suhu tindakbalas.

Peratus cangkukan, peratus pembentukan homopolimer, kecekapan cargkukan dan pertukaran total telah dianggarkan. Peratus cangkukan akrilonitril adalah tinggi, iaitu 2340% di bawah keadaan optimum iaitu serium ammonium nitrat (CAN) = 0.015

$mol.L^{-1}$, akrilonitril (AN) = 2.1 $mol.L^{-1}$, asid asetik = 2%, masa tindakbalas = 60 minit dan suku tindakbalas = 50°C. Peratus cangkukan metil metakrilat adalah 450%. Keadaan optimum, tindakbalas mencangkukkan adalah seperti berikut, serium ammoniam nitrat (CAN) = 7.4 $mmol.L^{-1}$, metil metakrilat (MMA) = 0.7 $mol.L^{-1}$, asid asetik = 2%, masa tindakbalas = 180 minit dan suhu tindakbalas = 60°C. Keputusan menunjukkan bahawa kopolimer cangkuk adalah lebih higroskopik berbanding dengan kitosan. Kalorimeter pembiasan pembezaan (DSC) dan termogravimetri (TGA) menunjukkan suhu perguraian kopolimer yang berbeza. Selain itu, poli(asid hidroksamik) disediakan dari kitosan-g-PAN hasil peratusan cangkukkan sebanyak 500%. Kapasiti hidrogen untuk resin dan kandungan air dikira. Kapasiti penyerapan bagi ion-ion logam berat seperti Cr^{3+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, dan Pb^{2+} dikira. Kapasiti penyerapan bagi ion-ion logam ini adalah mengikut susunan: $Cr^{3+} > Co^{2+} > Pb^{2+} > Cu^{2+} > Fe^{3+} > Ni^{2+}$.

CHAPTER I

INTRODUCTION

Polysaccharides

Polysaccharides are widely used in variety of industrial and food applications. They are representing a broad family of materials with very similar molecular structure. Polysaccharides have played an essential role in the development of life on this planet, and constitute important members of the family of industrial water-soluble polymers[1].

Until recently, polysaccharides mainly originated from plant sources (e.g. starch, guar gum, and pectin) or were from marine origin (e.g. alginate, agar, and chitin). Microbial polysaccharides such as dextran and xanthan gum have found commercial applications[2].

Chitin and Chitosan

Chitin and chitosan are manufactured commercially in large scale from the outer shell of crustaceans (shrimp and crab). With the commercial availability of purified chitosan coupled with its ability to be used in a variety of forms (powder, solution, gel, film, fibre, bead, and membrane), chitosan is being used in many commercial applications[3].

New medical and biotechnology applications require high purity forms of chitin and chitosan to be made commercially. Chitosan is being evaluated in a number of medical applications. These include wound dressings, homeostatic agent, drug delivery system, and as a hypocholesterolemic agent[3].

Chitin and chitosan are the environmentally friendly, versatile, and modern materials. The importance of chitin and chitosan has grown partly because they represent a renewable and biodegradable source materials, and also of recent increased understanding of their functionality in biology, technological, biotechnological and medical applications[4]. As the second most abundant natural polymer, chitin, and its derivative chitosan, represent a great challenge both to the scientific community and to industry.

New derivatives of chitin and chitosan continue to appear, providing new solubility and useful properties. With the increasing availability of commercial products, coupled with chitin/chitosan's variety of forms (powder, solution, gel, films, fibre, bead, and derivatized), the need for continued research on the basic and applied aspects of chitin/chitosan would inevitably increase[3].

Graft Copolymerisation

A polymer is a high molecular-weight molecule composed of simpler low molecular-weight molecules, which are known as monomers. If a polymer consists of two or more different monomers then the resulting polymer is called copolymer. The copolymer is classified into four types depending on the sequences of monomers in the polymer backbone.

1. Random copolymers: There is no definite sequence of the monomers. The distribution of monomer is rather random. The random copolymer is represented as follows:

   $-A-A-B-A-B-B-A-A-B-B-B-A-B-$

2. Regular copolymers: Such molecules are characterized by some regular sequence of monomers in the polymer chain.

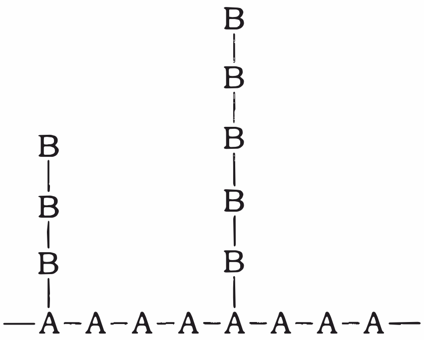
   $-A-B-A-B-A-B-A-B-A-B-A-$

3. Block copolymers: It is characterised by an arrangement where the block of one monomer is linearly connected to a block of another as follows:

   $-A-A-A-A-B-B-B-B-B-B-B-$

4. Graft copolymers: Graft copolymers are prepared by linking two different polymers but unlike block copolymers, structural sequence is such that one type of polymer is

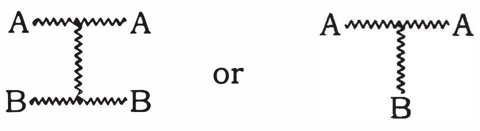
linked to the other through a branched structure. The structure is assumed as follows:



(**Note:** *A and B are two different monomeric units*)

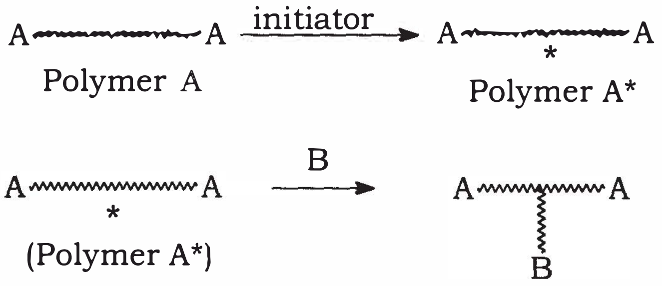
In general, there may be two ways by which graft copolymers can be synthesised.

- Cross-linking reactions of two polymer chains of different types.



where *A* is the polymeric
backbone and *B* is the
cross_ linker polymer

- Initiation of active sites on the polymeric backbone (A) when the monomers (B) can be grafted.



where A^* is a polymer having an active site.

Of the two methods, the second process has attracted the widest attention, and initiation has been carried out both by simple chemical means and by using suitable irradiation techniques. The active site may arise from the formation of radicals or ions of which the former again constitutes the main intermediate step by means of which the bulk of graft copolymerization work has been done.

In general, grafting means addition of side chains to the backbone polymer. Such side chains may be located at the surface or may be deeply penetrating. If the option is such that the grafting does not encompass the far interior of the backbone polymer, it may be envisaged that this will cause little perturbation in the molecular property of the backbone polymer. In addition it is known that the monomer does not usually penetrate into the ordered crystalline regions of polysaccharides but enters into the disordered amorphous regions. On the other hand, if the penetration of the side chains is deeper, major changes in the properties of graft copolymer may develop.

Scope of the Research

Polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) will be grafted onto chitosan in acidic medium by using cerium(IV) ammonium nitrate (CAN) as initiator under nitrogen gas atmosphere to produce biodegradable polymer. The effect of initiator concentration, monomer concentration, acetic acid concentration, as well as time and temperature of the reaction on grafting percentage will be examined to achieve the optimum conditions of the grafting.