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Bertajuk

CHEMICAL MODIFICATION OF POLYMERS:

Current and Future Routes for Synthesizing New Polymeric Compounds

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CHEMICAL MODIFICATION OF POLYMERS: CURRENT AND FUTURE ROUTES FOR SYNTHESIZING NEW POLYMERIC COMPOUNDS

ABSTRACT

Chemical modification of polymers is one of the methods used to synthesize new polymeric compounds. It is the most active fields of research in polymer sciences for the past 30 years and enables us to introduce functional or reactive groups into polymers, to alter polymer surfaces, to provide side chain substituents, etc. Important products of polymer modification include polymeric reagents, functionalised resins, catalyst and media for trapping reaction interdiates, organometallic polymers acid carrier for active molecules. This lecture gives an overview of our work on preparation and application of poly(hydroxamic acid) resins, lipase modification and immobilization for hydrolysis of palm oil and fatty ester syntheses, and graft copolymerization of sago starch.

Poly(hydroxamic acid) resins are successfully prepared from several synthetic polymers and poly(methyl acrylate) grafted sago starch. Conversion of the starting polymers into the desired resins is carried out by a simple one-step reaction. *N*-phenyl and *N*-methyl derivatives of poly(hydroxamic) are also synthesized and characterized. Based on the ability of the resins to form complexes with many metal ions, several new application are proposed. These include separations of metal ions , use as active membrane for zinc ion selective electrode, preparation of ligand ion exchangers for removal fluoride and arsenate ions and use as a water sorbent.

Several synthetic polymer are identified as suitable carriers for lipase immobilization. Although this enzyme can be immobilized by both chemical and physical techniques, the latter seems to be the best method for this purpose. Lipase is also modified by chemical attachment of hydrophobic groups. These modifications reduce the hydrolytic activity, enhance the lipolytic nature of the enzymes and produce more thermostable enzymes that are better catalysts in organic media. Immobilization of the modified enzymes are also studied and the results indicate that they are useful for ester syntheses. The possibility of producing lipase using immobilised cells are also investigated. These polymers are used for the carriers and the best system is obtained when poly(urethane) is used as the matrix and the cells are immobilized by an adsorbtion technique.

In graft copolymerization of vinyl monomer onto sago starch study, various monomers are successfully grafted onto the backbone polymer. Grafting levels are dependent upon the type of initiator, amount of the monomer and sago starch as well as the reaction temperature and period. Based on grafting reactions of methyl acrylate and acrylonitrile onto sago starch, a new rate of equation of polymerization and a new kinetics model for graft fraction are proposed. Characterizations of the grafted products are carried out use TGA, FTIR spectrophotometry, SEM microscopy and differential scanning calorimetry. Further investigations indicate that the copolymers produced are suitable for use as hydrogels and matrices for hydroxamic acid and amidoxime chelating resins.

INTRODUCTION

Polymers are large molecules containing long sequences of one or more species of atoms or groups of atoms jointed together by primary bonds. Copolymers are polymers whose molecules contain two or more different types of repeat units (Table 1). Polymers are formed by linking together monomers through a polymerization process.

Table 1. Examples of monomers, polymers and copolymers

Monomer	Polymer/copolymer
Ethylene	Poly(ethylene)
Propylene	Poly(propylene)
Tetrafluoroethylene	Poly(tetrafluoroethylene)
Styrene	Poly(styrene)
Methyl methacrylate	Poly(methyl methacrylate)
Vinyl chloride	Poly(vinyl chloride)
Acrylonitrile	Poly(acrylonitrile)
Ethylene glycol	Poly(ethylene glycol)
Ethylene glycol & terephthalic acid	Poly(ethylene terephthalate)
Hexamethylene diamine & sebacic acid	Poly(hexamethylene sebacate)(nylon 6.10)
Styrene & Acrylonitrile	Poly(styrene-co-acrylonitrile)
Styrene & butadiene	Poly(styrene-co-butadiene)

The amount of polymeric materials used by industry is enormous as they are used almost everywhere. The most important applications of polymers are in packaging, construction, electronics, furniture, toys and recreation, appliances, medical supplies, transport, agriculture, apparel, footwear and industrial equipment.

The global polymer industry's output was estimated at around US$75 billion in the year 1998 with growth at around 6% per year. In most European countries, the polymer consumption is about 100kg/person/year [Mulder, 1998]. In 1999, the Malaysia polymer industry achieved a turnover of about RM7.2 billion and contributed to about 2.5 percent of the country's gross domestic product. It was estimated that there were around 1200 plastic product manufacturers which provided job opportunities to about 87000 people. In the year 2000, the total production of polymer products was estimated to be RM8.5 billion, an increase of 15% from the turnover of 1999. Polymer manufacturers exported 44% of their products (estimated about RM3.7 billion) which represents a 23% increase over 1999. The polymer industry in Malaysia is expected to continue to grow in the next 20 years as the demand for polymers still strong, especially in electrical and electronic sector, telecommunications, packaging, automotive, advanced composites and construction.

Packaging is the most economically important of application of polymers. Polymer packaging may consist of bags, bottles, boxes, crates, foil and loose fills. Higher grade forms of packaging include blood bags and CD boxes. Important advantages of using polymers as packaging material are low weight, have good processability and are corrosion free. These characteristics lead to cost reduction, for example the transportation of packaged

goods. In Malaysia, the plastics packaging business employs of around 25000 out of 87000 workers in the plastics industry, contributes to about 30% of the total production of plastic products and accounts for 35% of the total plastics exported yearly. Malaysia is one of the major producers of plastic bags and film in Asia.

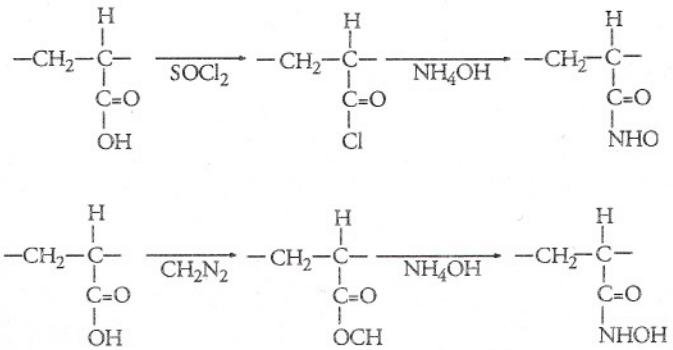
Chemical modification of polymers is one of the methods used to produce new polymeric materials to extend application of the existing polymers. Modification may be carried out as an existing polymer does not have the required properties, and there is difficulty in synthesizing a new monomer and / or the monomer is not stable under the polymerization conditions. The applications of the products include non-material uses such as polymeric reagents which consist of a reactive function bound to an insoluble support, functionalized resins which are used as ion exchangers, chelating agents, reagent for organics syntheses, catalysts and media for trapping unstable reaction intermediates, organometallic polymers which may be useful as semiconductors, and vehicles for carrying active molecules such as hormones and drugs[Akelah and Moet, 1990].

Since chemical modification of polymers is very diverse and has grown to cover a wide range of topics, this lecture is limited to an overview of our work on preparation, characterization and application of poly(hydroxamic acid)s; lipase modification and immobilization for hydrolysis of palm oil and fatty ester syntheses; and graft copolymerization of sago starch to produce hydrogels and chelating ion exchange resins.

PREPARATION , CHARACTERIZATION AND APPLICATION OF POLY (HYDROXAMIC ACID) RESINS

Hydroxamic acids, a group of compounds with the general formula R-CO-NHOH, are very important chelating agents as they form stable complexes with a large number of metal ions and widely used in analytical chemistry [Agrawal ,1980]. They are also as constituents in growth factors, food additives, antibiotics, tumour inhibitors, antifungal agents, cell division factors and enzyme inhibitors [Kurzak *et al.*, 1992; Holmes,1996].

Early preparative methods of hydroxamic acid resins were based on poly(carboxylic acid)s (Scheme 1) [*Petrie et al.*,1965].

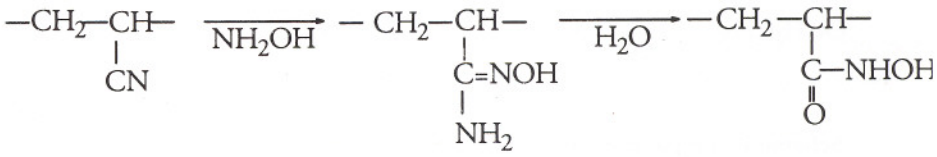


Scheme 1. Preparation of poly(hydroxamic acid) resin from poly(carboxylic acid).

Since then a large number of poly(hydroxamic acid)s derived from various starting polymers including poly(styrene)[Phillip and Fritz, 1980] and poly(acrylonitrile) [Vernon and Kyffin, 1977] have been prepared. Although hydroxamic functional groups have been successfully attached onto the polymers the kinetics of extraction and hydroxamic acid capacity should be improved for them to be useful as an ion exchanger. In addition, preparation techniques which involve several reaction steps are not only tedious but may also contaminate the resins with other functional groups.

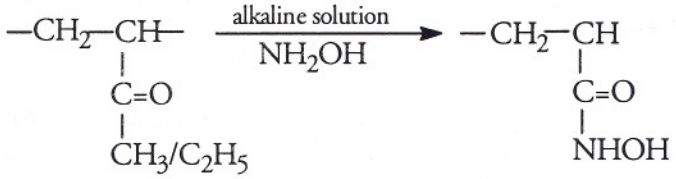
Our research on poly(hydroxamic acid) resins started in 1978 with the aim of producing poly(hydroxamic acid) resins with desirable properties of an ion exchanger such as fast rate of extraction and high capacity for targeted metal ions. In addition to this, we also explored the possibility of using this ion exchanger for new applications. Our first attempt to prepare the resin was using poly(divinyl benzene-acrylonitrile) copolymer as a starting material. This copolymer was synthesized from its monomers i.e. divinyl benzene and acrylonitrile by suspension polymerization. A number of crosslinked poly(hydroxamic acid) ion exchange resin were successfully prepared. By incorporating poly(ethyl acrylate) into the copolymer, the resin in bead form was successfully produced. The copper capacity of the optimized resin at pH2 was 2.13 mmol/g, with time taken to occupy 50% the resin sites with this metal ion only 5 minutes [Wan Yunus, 1980]. The uptake of Au(III), Al(III), Ag (I), Fe(III), Mn(II), Ni(II) and Co(II) ions as a function pH was studied and several new applications including recovery and separation of gold (III) and silver (I) [Vernon and Wan Yunus, 1981] were demonstrated.

Synthesis of the hydroxamic acids from poly(acrylonitrile) is simple because it involves only treatment with hydroxylamine, however, since, the production of the hydroxamic acid is through the formation of amidoxime groups (Scheme 2), the product is contaminated by this group, which is also a chelating group capable of forming stable complexes with few metal ions and is also used as a functional group for chelating resins.



Scheme 2. Conversion of acrylonitrile group into the hydroxamic acid.

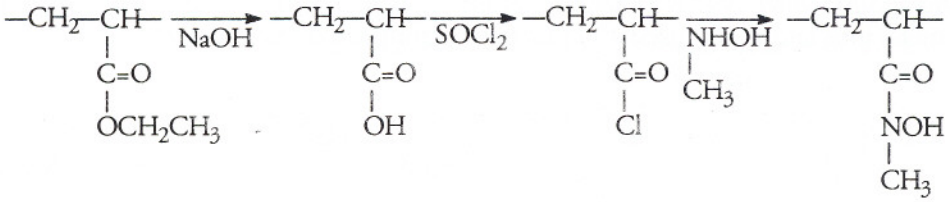
Treatment of esters with hydroxylamine is a common procedure used to prepare hydroxamic acids. Based on this reaction, we have synthesized and converted crosslinked poly(ethyl acrylate)[Wan Yunus and Ahmad, 1988] and poly(methyl acrylate) [Haron *et al.*, 1992] into hydroxamic acid resins (Scheme 3). The advantages of using poly(ester)s as starting materials for the resin preparation in addition to the simple synthetic route, the high resin capacity, its favourable kinetics of extraction, the resin produced is also free from amidoxime group contamination.



Scheme 3. Conversion of ester (methyl or ethyl acryclate) group into the hydroxamic acid.

Synthetic polymers are obtained from petroleum products which are in limited supply. These polymers may also create disposal problems as they are not easily degraded in the environment. As an attempt to reduce the environmental problem created from disposal of spent poly(hydroxamic acid) resins we used poly(methyl acrylate) grafted sago starch as a starting material for the resin preparation [Lutfor,1999, Lutfor et. al., 2001b]. Incorporation of the starch in the matrix may enhance biodegradability of the hydroxamic acid resin as this natural polymer is highly biodegradable.

In an addition to the type a chelating group used to form a metal ion complex, the stability of the complex is also affected by substituent group attached to the functional group. In order to study the effect of substituted groups on the selectivity of poly(hydroxamic acid) resin towards metal ion complexation, resins containing N-methyl and N-phenyl hydroxamic were synthesized. Our early attempt to synthesize N-methyl hydroxamic was through hydrolysis of the ester group, formation of acid chloride and treatment of the acid chloride with N-methyl hydroxyl amine [Wan Yunus and Baharom, 1986] (Scheme 4).



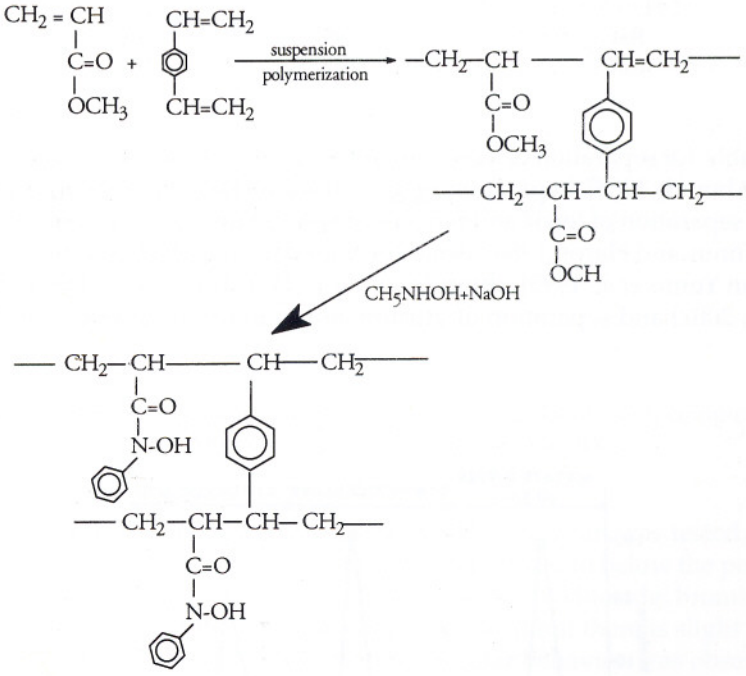
Scheme 4. Preparation of poly(N-methyl hydroxamic acid) resin from crosslinked poly(ethyl acrylate).

This preparation procedure involves four reaction steps (including preparation of the crosslinked poly(methyl acrylate) from ethyl acrylate and divinyl benzene). Only 21% conversion of carboxylic acid groups into hydroxamic acid was observed because the conversion of the carboxylic acid into the acid chloride is not efficient.

Later we investigated the possibility of preparing the resin by directly reacting crosslinked poly(methyl acrylate) with N-methyl hydroxylamine and successfully produced the resin with hydroxamic acid capacity of 2.9 mmol [Balchi, 1998]. This method of preparation

produces a higher hydroxamic acid content (of about 40%) and involves only polymerization of monomers and a one step modification of polymer to obtain the desired polymer.

Another derivative of hydroxamic acid that was studied was N-phenyl hydroxamic acid. When poly(styrene) was used as a starting polymer, the metal ion capacity of the resin produced was low. The introduction of the group onto the polymer required several steps of polymer modification [Phillip and Fritz, 1980]. Scheme 5 describes our method of synthesis of poly(N-phenyl hydroxamic acid) resin from crosslinked poly(methyl acrylate). Conversion of the ester in the starting polymer into the hydroxamic acid is a simple one step reaction but also produces a reasonably high hydroxamic acid capacity [Awang, 1995; Awang *et al.*,1996].



Scheme 5. Preparation of poly(N-penhyl hydroxamic) acid from methyl acrylate.

The ability of the hydroxamic acid group to form metal complexes of different stability has been extensively studied to find analytical applications of poly(hydroxamic acid) resins. Among applications reported by other groups of researchers interested in this area are extraction of iron from various alkaline salts; separation of iron from copper, nickel and cobalt; separation of copper from lead, separation of uranium from neodymium; separation of cobalt from copper and nickel; and separation of chromium, copper and iron from plating bath effluent .

We have studied the behaviour of our resin that was prepared from poly(acrylonitrile) towards some metal ions and found that the resin could completely sorb gold and silver ions; separate gold from silver, iron and copper; and extract and separate uranium [WanYunus,1980]. Using the resin prepared from poly(ester), we have demonstrated that the resin could be used for quantitative extraction of iron and copper ions from several concentrated alkaline and alkaline earth metal solutions (Table 2)[WanYunus and Ahmad, 1988].

Table 2. Recoveries of iron and copper ions from various concentrated salt solutions.

Solutions	% of metal ion recovery	
	Fe	Cu
NaCl	103	102
KCl	98	100
CH_3COONa	100	100
$BaCl_2$	99	98
$CaCl_2$	100	100

It is also suitable for separation of ions from iron-copper-nickel ions solution(Figure 1)[Wan Yunus and Ahmad, 1988], separation of gold from nickel, cobalt and zinc [Wan Yunus *et al.*, 1996c], separation of ferric and ferrous ions[Wan Yunus and Haron, 1996], extraction of tin [Wan Yunus and Haron,1988], isolation of gold from cyanide solution [Wan Yunus et al, 1990a; Wan Yunus *et al*, 1995], chloride solution [Wan Yunus *et al.*, 1996] and sediments [Haron *et al.*, 2002] and separation of yttrium and uranium from xenotime [Haron et al., 2001].

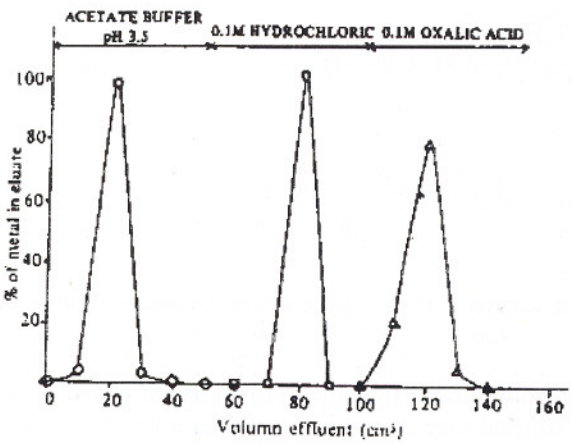
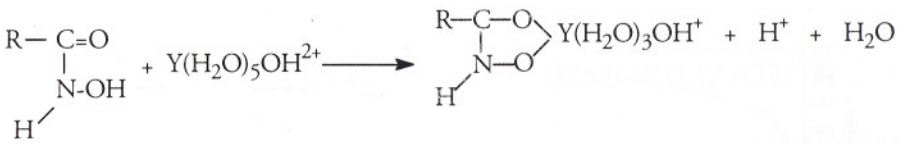


Figure 1. Iron-coper-nickel separation.
(o) nickel, (□) copper, (Δ) iron.

Another new application for hydroxamic acid resin which is apparently not reported by any other research group is the use of metal ion loaded poly(hydroxamic acid) resin as a matrix for ligand ion exchangers. For example, poly(hydroxamic acid) resin loaded with yttrium ion [Haron *et al.*, 1995] can be used for sorption of fluoride ions. The sorption of fluoride ion was accompanied by a pH increase as the exchange mechanism involves the release of hydroxide ions (Scheme 6).



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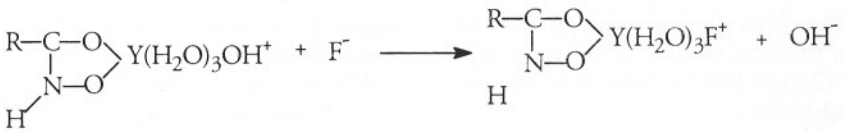


II

Scheme 6. Mechanisms of yttrium-poly(hydroxamic acid) complex formation (I) and its anion exchane (II).

The rate of fluoride ion exchange was fast and when the resin was tested for removal of fluoride ion from wastewater samples, the ion was reduced to below the permissible level by just a single treatment with the resin. The presence of chloride, bromide, iodide and nitrate ions does not affect the efficiency of the removal but there is slight interference in the presence of phosphate and sulphate ions. Similar behavior was observed when the resin was loaded with cerium ion [Haron and Wan Yunus, 2001]. This study has been extended to sorption of arsenate by iron (III)-poly(hydroxamic acid) complex [Haron *et.al*, 1999].

Another potential application of poly(hydroxamic acid) resins is as a water sorbent or hydrogel [Lutfor *et al.*, 2001d] . We have investigated the swelling behavior of the resin prepared from poly(methyl acrylate) grafted sago starch and observed the maximum absorbency in water was around 190g water / g for the hydroxamic acid sample synthesized from the starting material containing 31% sago starch (Figure 2). The water sorbency in sodium chloride (Figure 3) and other salt solutions decreases with the increase of the salt concentration due to deswelling behavior of the adsorbent occurred when the concentration of the external solution is increased, especially for multivalent salts.

We have also demonstrated that zinc complex of hydroxamic acid could be used for construction of a membrane for an inexpensive zinc selective electrode. The electrode produced gave linear response over a concentration range of 5 x 10^{-4}M to 2 x10^{-2}M of determinant. The slope of linearity is close to the theoretical Nerst slope, 2.303 RT/nF, which is 29.78 mV per decade for n=2 at 27°C. The membrane was useful in the pH range of 4.5 to 6.0 and has working life of at least 4 weeks. The presence of copper, chromium, lead, barium, sodium and potassium ion did not interfere with the zinc ion concentration determination [Kassim *et al.*,1992].

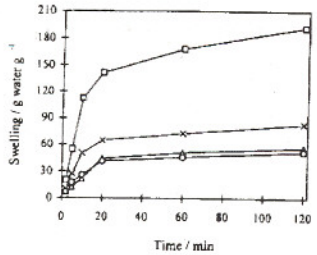


Figure 2. Plots of swelling absorbent in distilled water as a function of time at different sago starch % (-□-sago 31%; -x- sago 43%; -Δ- sago 56%; -o- sago 66%) .

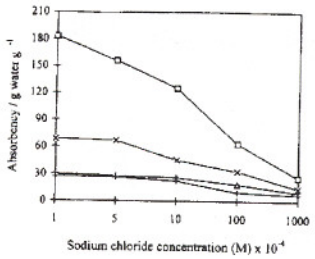


Figure 3. Absorbency obtained using various concentration of sodium chloride solution (M) at different sago starch % (-□-sago 31%; -x- sago 43%; -Δ- sago 56%; + sago 66%)

To conclude discussion of our work on preparation, characterization and application of poly hydroxamic acid resins, it can be said that

1. Poly(hydroxamic acid) resins were successfully prepared from poly(acrylonitrile) poly(ethyl acrylate), poly(methyl acrylate) and poly(methyl acrylate) grafted sago starch. The resins produced from the first three starting materials were in the bead form. The conversion of the starting polymers into hydroxamic resins was through a simple one step reaction but produced high hydroxamic acid capacity and good kinetics of extractions.

2. N-methyl and N-phenyl derivatives of poly(hydroxamic acid) resin were also successfully synthesized from poly(methyl acrylate). These resins were also prepared by a simple one-step conversion process of the starting material. The products were also in bead form and were found to exhibit high metal ion capacity and good kinetics of exchange.

3. Based on the ability of the hydroxamic acid group to form complexes with many metal ions, new applications of the resins have been proposed. These include separation of nickel and lead, extraction of gold from sediments, and from cyanide and chloride solutions, extraction of tin ion, separation of ferrous and ferric ions and use as an active membrane for zinc ion selective electrode.

4. The ability of the hydroxamic acid group to form stable complexes with metal ions has also been exploited for preparing ligand ion exchangers. Cerium and yttrium complexes were successfully used for fluoride ion removal while the ferric ion complex was used for sorption of arsenate ion.

5. The product obtained by attaching hydroxamic acid groups onto poly(methyl acrylate) grafted starch, can be used as hydrogels in addition to their use as a chelating ion exchanger. Introduction of the starch in the polymer matrix makes the product more environmental friendly as this natural polymer is biodegradable and produced from a renewable resource.

LIPASE MODIFICATION AND IMMOBILIZATION

Lipases are a class of enzymes (natural polymeric species) that normally hydrolyze a variety of long-chain acyl esters. Under controlled conditions, they can also catalyze esterification and several other synthetic reactions (Scheme 7).

(1) Hydrolysis of Ester

(2) Synthesis of Ester

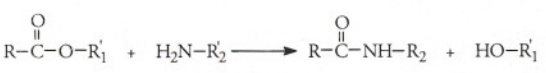
(3) Transesterification

(3.1) Acidolysis

(3.2) Alcoholysis

(3.3) Interesterification

(3.4) Aminolysis



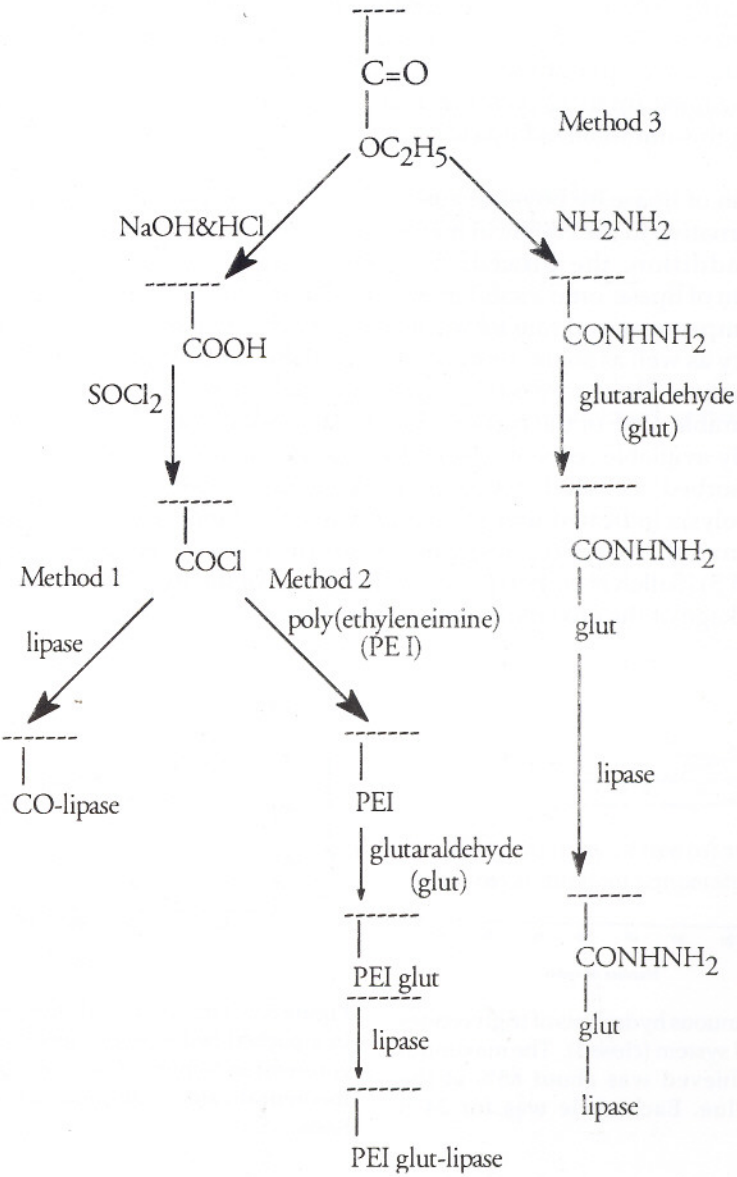
Scheme 7. Types of reactions catalyzed by lipase.

Although they are useful biocatalysts for many industrially important applications such as hydrolysis of fat, modification and synthesis glycerides and esters, their applications in industry are limited owing to difficulties in separation of the enzymes from the substrates and the products and/or the instability of the enzymes under operational conditions, as well as the biphasic nature of the reactions.

Lipases have been modified to improve or to obtain desired properties such as specific activity, solubility in organic solvents and enhancement of activity and stability to make them useful for industrial applications. One of the common methods used for lipase modification is immobilization i.e. the localization or confinement of the enzyme. The advantages of lipase immobilization include ease of isolation of the catalyst, increase of enzyme stability and possibility of continuous and repeated usage of the enzyme.

Lipase immobilization has been extensively studied. Methods used involve both chemical (where covalent bonds are formed with the lipase) and physical (where weaker interactions and mechanical containment of the enzyme is used) techniques on various carriers. The objectives of our involvement in this research is to find suitable catalysts for biotechnological modification palm oil and synthesis of fatty esters. Both chemical and physical techniques of lipase immobilization are used in our study but the results show that the physical methods are more encouraging.

To chemically immobilize lipase onto poly(ethyl acrylate-divinyl benzene) beads, three methods were used (Scheme 8).



Scheme 8. Chemical method of immobilization of lipase onto poly(ethyl acrylate-divinyl benzene)

Although a fairly large amount of lipase was successfully bonded onto the matrix using all three methods, lipase activity, was found to be very low, especially the lipase immobilized through the formation of poly (carboxylic acid)(Methods 1 and 2). This is probably due to the low affinity of the substrate (olive oil) for the lipase on the hydrophilic surface of the matrix. The lipase activity was improved when the enzyme was immobilized through partial conversion of the ester group into the hydrazide form (Method 3). Full activity was retained up to 12 cycles of a laboratory scale semi-continuous hydrolysis of olive oil using this immobilized lipase [Salleh *et al.*, 1988].

Immobilization of lipase by physical adsorption of on the polymer beads seems to be an attractive alternative to the chemical method as it produces high expressed activity of the enzyme. In addition, the procedure is simple and cheap. Typical procedure of immobilization of lipase onto a solid matrix is shaking the carrier in the enzyme solution at a chosen temperature and rate for a selected period. Polymer sorbents produced in our own laboratory as well as some commercially available sorbents were used as carriers for the immobilization. These sorbents are vinyl type polymers, so they thermally stable and chemically durable. One of the carriers that we successfully used was Amberlite XAD-7, a commercially available sorbent. Using this matrix, the lipase from *Candida rugosa*, was physically adsorbed. The study using this enzyme preparation in a packed bed reactor for olive oil hydrolysis indicated that the lipase was very stable. The half life for the closed system was around 80 days (cycles) whereas for the open system it was about 150 days (Figures 4 and 5) [Salleh *et al*, 1991]. Steady reduction of the hydrolysis efficiency may be due to the leakage of the enzyme from the matrix.

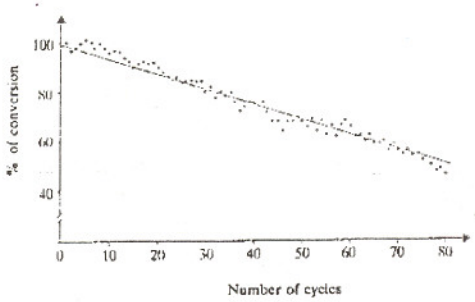


Figure 4. Continuous hydrolysis of triglycerides in a packed bed system (closed). The maximum conversion achieved was about 65% of the theoretical value. Each cycle was for 24 h duration.

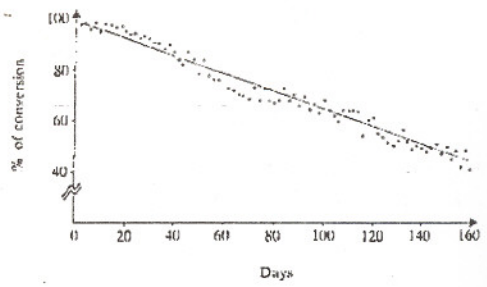


Figure 5. Continuous hydrolysis of triglycerides in a packed bed system (open). The maximum conversion achieved was about 90% of the theoretical value. Sampling was done on daily basis.

Carrier surface hydrophilicity or hydrophobicity is another important factor determining the expressed activity of an enzyme immobilized onto the matrix. We have compared the activity of the lipase immobilized onto unmodified poly (methyl methacrylate) beads and those with the carboxylic acid and hydroxide groups modified. The best result was obtained when the adsorption was carried out using the purified unbuffered enzyme solution immobilized onto the unmodified beads. The amount of protein adsorbed onto the polymer

increased with the increasing polymer-enzyme contact period but the expressed hydrolytic activity decreased after about 60 min. of exposure. The hydrolytic activity of the enzyme also varied with the bead size of the matrix (Table 3) and its optimal hydrolysis temperature shifted from 37 to 45(C (Figure 6). It was also observed that the immobilized enzyme was more stable than the free enzyme (Figure 7).

Table 3. Effect of bead size on specific hydrolytic activity of lipase immobilized onto poly(methyl methacrylate)

Bead size, μm	**Specific hydrolytic activity, unit/min/g**
75-300	67-44
300-850	18-93
850-1,700	14.01

Its operational half life when it was packed in a column in a closed system was 40 days (Figure 8).

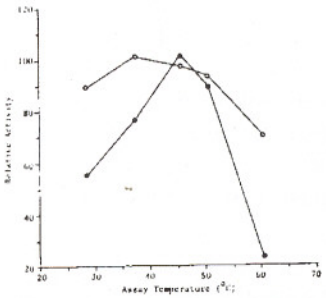


Figure 6. Temperature profile for free (o) and immobilized lipase (●).

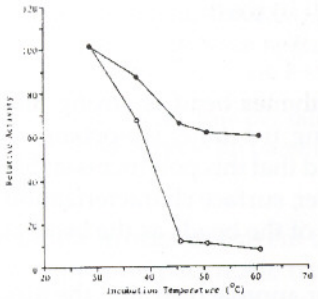


Figure 7. Activity of free (o) and immobilized lipase (●) at different temperatures.

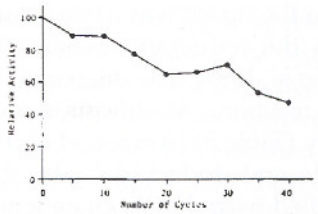


Figure 8. Operational stability of immobilized lipase. The substrate was replaced every 24h, but readings were recorded every 5 d.

One of the disadvantages of using non-crosslinked poly(methyl methacrylate) is that it may swell excessively in organic solvents. Organic solvents are sometimes required in order to improve the efficiency of lipase-catalysed reactions. As an attempt to produce a polymeric material which is strong and insoluble in aqueous solutions and organic solvents, we have prepared synthetic polymer beads by a suspension polymerization technique using methyl acrylate, methyl methacrylate and divinyl benzene [Wan Yunus *et al*, 1995a]. We found that the copolymer beads containing 62% methyl acrylate, 33% methyl methacrylate and 5% divinyl benzene was the best carrier for lipase immobilized by adsorption (Table 4). Optimum immobilization was observed when the lipase was purified, dissolved in water and shaken with the carrier at the rate of 50 rev/min for 30 min.

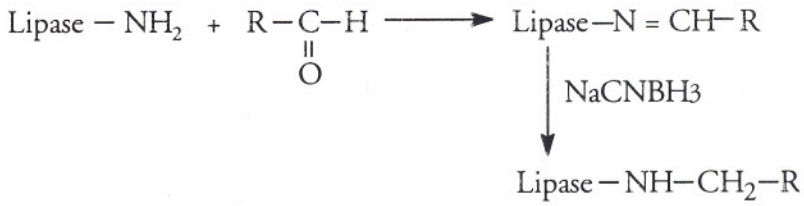
Table 4. Amount and specific activity of lipase adsorbed onto various copolymer beads

Methyl methacrylate/ Methyl acrylate ratio by weight	Lipase adsorbed (mg/g)	Specific hydrolytic activity (U/min/g)
20:80	3.10	17.22
35:65	4.05	38.33
50:50	3.24	36.39
65:35	3.26	23.33
100:0	1.85	17.22

This polymer bead is strong and insoluble in aqueous solution and organic solvents including n-octane, iso-octane, diisopropyl ester, n-hexane and cyclohexane. It is also expected that this polymer is stable towards heat and chemicals as it is a vinyl type polymer. However, surface characterization suggests that the lipase adsorption is only on the outer surface of the beads as the bead porousity is low.

Another approach to alter the original properties of lipases to make them suitable for use in industrial processes is through chemical reaction in which a modifier is chemically attached to the enzyme. This modification may change the microenvironment of the enzyme which consequently alters or improves its properties. We also tried this approach in our study; three type of modifiers i.e. poly(ethylene glycol), aldehydes and imidoesters, were used.

Attachment of aldehydes onto the lipase was carried out by reductive alkylation using sodium cynoborohydride as the reductant (Scheme 9)[Ampon *et al.*, 1991a,1991b, 1993a,19993b,1994,1997; Basri *et al.* 1997]. The degree of the modification depends on the type of aldehyde used in the reaction. Modification reduces the estrolytic activity but improves esterification activity (Table 5) [Ampon et al.,1991b; Salleh et al.,1990]. Lipase derivatised with octaldyhyde and dodecyldehyde gave products which are more thermostable than those modified with shorter chain length aldehydes.



Scheme 9. Reductive alkylation of lipase.

Table 5. Activity of reductively alkylated lipase

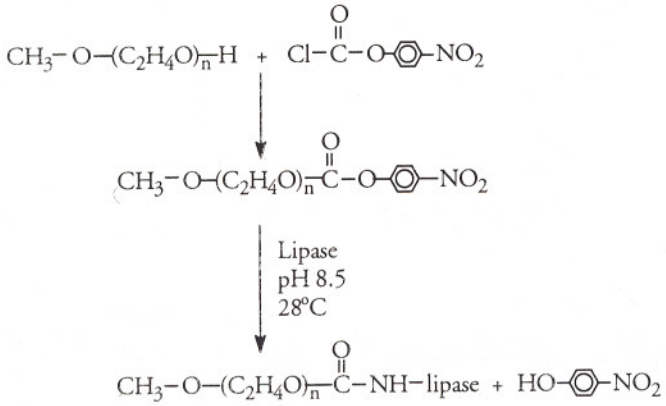
Carbonyl compounds	% modification	Estrolytic[a] activity	Synthetic[b] activity
None	0	65.8 (100)	0.354 (100)
Acetaldehyde	55	39.7 (60)	0.896 (253)
Propionaldehyde	58	26.0 (40)	0.646 (18.2)
Benzaldehyde	41	7.9 (12)	0.771 (218)
Octaldehyde	39	6.1 (9)	0.438 (124)
Dodecylaldehyde	46	4.0 (6)	0.417 (118)

[a]Activity measured in an emulsified aqueous system containing 50 volumes of olive oil and 50 volumes of water, with poly(vinyl alcohol) as an emulsifier. Percent activity compared to the unmodified lipase is (in parentheses).

[b]Expressed in terms of micromoles of FFA removed from the reaction mixture per minute per milligram protein and as percent activity compared to unmodified enzyme (in parentheses).

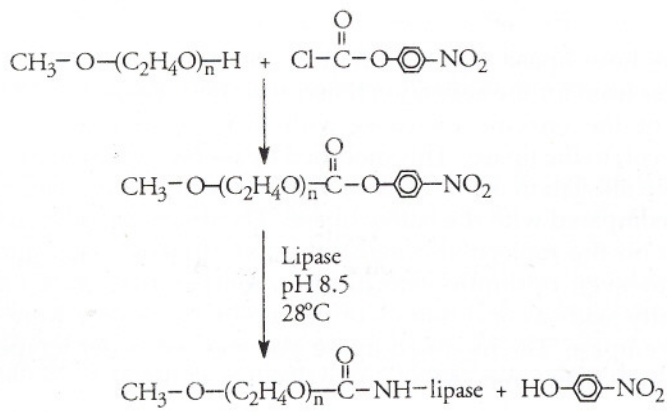
It is also observed that alkylated lipase is relatively more stable in organic solvent than the native enzyme. When this modification was extended to porcine pancreatic trypsin, it resulted in about 5 to 6 fold increase of sugar esterification activity of the enzyme in DMF [Ampon, 1991a].

Scheme 10 shows how lipase was modified by poly(ethylene glycol); p-nitrophenyl chloroformate was used for the activation [Basri *et al.*,1991, Basri *et al.*,1995]. The degree of modification of the enzyme increases with increase of molar ratio of activated poly(ethylene glycol) to the lipase. This modified lipase behaves similarly to the product from the reductive alkylation, i.e. it exhibits higher specific ester synthesis activities in organic solvents compared with the native lipase. The degree of enhancement of lipase activity depends on the molecular weight of poly(ethylene) used and the extent of modification. However, optimum esterification temperature (40°C) and degree of preference for fatty acids as acyl donors of the modified enzyme were very similar to those of the native lipase. The modified lipase also showed better temperature, solvent and storage stabilities than unmodified lipase [Basri *et al.*, 1995].



Scheme 10. Poly(ethylene glycol) modification of lipase

In another study, modified lipase was prepared through amidation with imidoester hydrochlorides of different hydrophobicity (Scheme 11). Here again we found out that the modified lipase exhibits higher esterification activity but lower fat hydrolysis than those of native enzyme. The enzyme that was modified with the high molecular weight imidoesters shows higher activity. The best organic solvent for this synthesis is benzene. The modification does not affect the optimum temperature of esterification (Figure 9) but produces an enzyme which is more stable towards heat (Figure 10) and exposure to organic solvents (Figure 11). The highest synthetic activity is recorded when myristic acid is used for the ester synthesis [Basri *et al.*, 1994].



Scheme 11. Amidation of lipase with hydrophobic imidoester

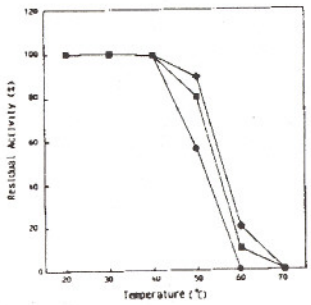


Figure 9. Optimum esterification temperature of native lipase (-●-) and lipase modified with imidoester I (-♦-) and imidoester VI (-■-).

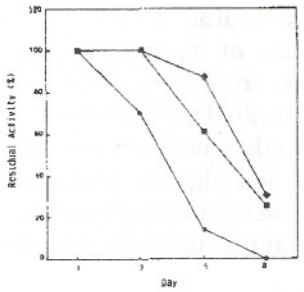


Figure 10. Stability of native lipase (-●-) and lipase modified with imidoester I (-(-) and imidoester VI (-♦-) in benzene at room temperature for various time intervals.

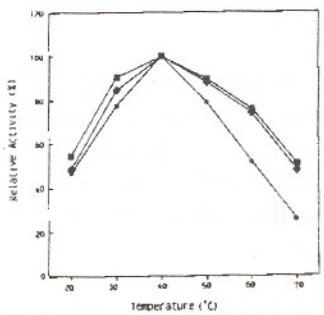


Figure 11. Thermostability of native lipase (-●-) and lipase modified with imidoester I (-■-) and imidoester VI (-♦-). Samples were incubated at various temperatures and the activity was determined after 1 h.

These modified enzymes were also immobilized onto solid supports such as synthetic polymers and inorganic adsorbents [Basri, *et al.*, 1996]. Immobilization of the modified lipase showed higher activity than that observed for immobilization of native enzyme. When the same poly(ethylene glycol) modified enzyme was immobilized onto polymer beads, we found that those adsorbed on Amberlite XAD-7 (poly(methyl methacrylate)) gave the highest esterification activity, followed by poly(carboxylic acid) and Amberlite XAD-2 (poly (styrene)). The lipase also favoured medium-chain fatty acids to long-chain fatty acids as acyl donors. However, alcohol selectivity of the enzyme was unchanged upon immobilization.

Immobilization of microbial cells is another attractive technique for enzyme immobilization. It offers several advantages including ability to catalyze multistep and continuous reactions, elimination of the tedious enzyme isolation and purification procedures. In addition, reactions can be carried out at higher cell concentration and ease of products harvesting. We also studied the possibility of producing lipase using immobilized cells. Using poly (2-hydroxy ethyl methacrylate) [Razak *et al.*, 1996], polyurethane [Salleh *et al.* 1997, Mohd et. al, 1991] and alginate [Zakaria *et al.*, 1992] we have successfully immobilized lipolytic cells. These cells were physically immobilized either by adsorption or entrapment. It was found that polyurethane was the best matrix for immobilization.

The following conclusions summarize our work on lipase modification and immobilization to date

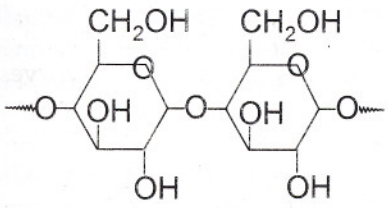
1. Although lipase can be immobilized onto synthetic polymers by both chemical and physical techniques, the latter seems to be the best method as the products offer advantages such as high expressed activity and good stability in addition to a simple procedure for immobilization. Several synthetics polymers have been identified as suitable carriers for the enzyme.

2. Modification of lipase by chemical attachment of hydrophobic groups alters several enzyme properties. Such modification reduces the hydrolytic activity but enhances the lipolytic nature of the enzyme. The chemical modification also produces more thermostable enzymes that are better catalysts in organic media. These enzymes are also suitable for immobilization onto polymer matrices and the products are useful for ester syntheses.

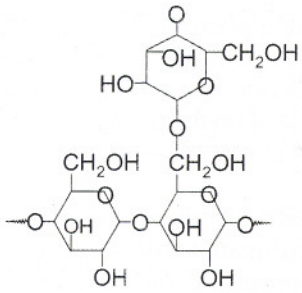
3. Lypolytic cells were also successfully immobilized onto poly(2-hydroxyethyl methacrylate), poly(urethane) and alginate by physical techniques. It is found that adsorption is a more favorable technique for cell immobilization. Polyurethane is the best matrix for this purpose.

GRAFT COPOLYMERIZATION OF VINYL MONOMER ONTO SAGO STARCH

Starch, is a natural polymer composed of repeating 1, 4-α-D-glucopyranosyl units (anhydroglucose units [AGU]). It is a mixture of linear and branch components, namely amylose and amylopectin (1 and 2). It has been used as a substrate for graft copolymerization of vinyl monomers as they can be easily grafted onto it. The products are potentially useful for many commercially important applications such as hydrogels, flocullants, ion exchangers, adhesives, sizes, thickeners, resins and plastics. Starch is cheap, readily available, renewable and biodegradable.

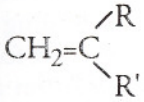


(1) Amylose (1, 4-α-D-glucose)



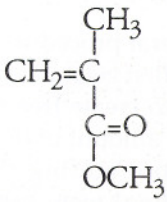
(2) Amylopectin (1, 4-α-D-glucose with 1, 6-D-glucose branch

The general formula of vinyl monomer (3) and several specific examples (4-8) are given below. These monomers polymerize through free radical polymerization.

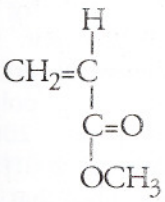


(3) General formula

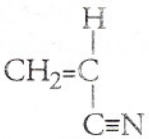
(4) Styrene



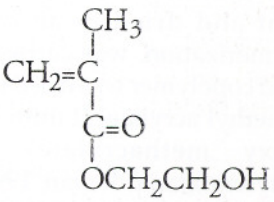
(5) Methyl methacrylate (MMA)



(6) Methyl acrylate (MAA)



(7) Acrylonitrile



(8) 2-hydroxyethyl methacrylate (HEMA)

Vinyl polymer grafted starches are copolymers in which a starch is used as a backbone (main chain) polymer and vinyl monomer becomes a branched polymer. In order to attach the branched polymer, a radical has to be created on the backbone polymer and this is achieved through chemical reaction, exposure to radiation or mastication. Grafting of hydrophillic vinyl monomers may produce products that can be utilized as thickness, absorbents, sizers, adhessives or flocculants, while graft copolymerization of hydrophobic monomers onto starch may produce resins and plastics.

Sago starch is extracted from sago palm tree. Like other starches, it does not dissolve in water but gelatinizes if it is heated in water at 75°C. It is produced commercially and ranked as fifth among important commodities in Malaysia (after palm oil, petroleum, rubber and cocoa) with the production capacity of 30,000 ton / year. Annual production in Southeast Asia of sago starch is 60 milllion ton.

Sago starch supply in Malaysia is mainly from Sarawak where about 20,000 hectare of its land is cultivated with sago trees. Although it is produced in modern factories, its quality varies depending on the quality of water supply, the method of extraction and the mode of transportation. Production of starch from sago palm tree is very attractive as one matured tree produces up to 550 kg

Graft copolymerization of sago starch is one of the possible ways to modify the properties of sago starch. We carried out this study with the objective of synthesizing new polymeric materials in hope that with new properties, it can be used for new applications. Currently the price of this commodity is very low (about 40 sen / kg) and its uses are mainly limited to food additives and animal feeds.

The general procedure for grafting vinyl monomers onto sago starch is as follows: The starch is first gelatinized by heating its suspension in water at 80°C for 30 min. The initiation process to create free radicals on the polymer backbone was carried out by adding the required amount of initiator to the gelatinized sago starch and allowing it to react for 15 min before adding the monomer. All the reactions (gelatinization, initiation and propagation) were carried out under nitrogen gas atmosphere. The reaction mixtures were continuously stirred and the reaction temperatures were controlled by placing the reaction flask in a thermostated waterbath. The product was precipitated using a suitable solvent and dried in an oven. Removal of homopolymer formed during the copolymerization, was carried out by Soxhlet extraction using a suitable solvent. The purified copolymer was dried in an oven. Using this procedure we have successfully grafted poly(methyl acrylate) [Lutfor *et al.*,2000a], poly(acrylonitrile)[Lutfor *et al.*,2001a], poly(2-hydroxy methacrylate) [Rusli, 2001], poly(acrylic acid) [Bin, 2001], poly(styrene)[Janarthanan, 1999], poly(methyl methacrylate)[Fakhru'l-razi *et al.*, 2001] and poly(MAMOA)[Najjar, 2002] onto sago starch. Further investigations show that this procedure could be used to prepare poly(2-acrylamido-2-methyl-propane-sulfonic acid) grafted chitosan using potassium persulfate as redox initiator [Najjar *et al.*, 2000]. The optimum conditions for graft copolymerization of some vinyl monomers onto sago starch are in Tables 6a to 6f.

Table 6a. Optimum conditions for preparation of PMA-g-sago starch

Temperature	:	50°C
Reaction period	:	60 min.
$[H_2SO_4]$	:	0.175 molL^{-1}
[AGU]	:	0.135 "
[CAN]	:	8.77×10^{-3} "
[MA]	:	0.803 "

Results:

[MA] / molL^{-1}	% Grafting	% Efficiency
0.178	17.4	85.9
0.389	54.3	84.4
0.592	77.0	84.3
0.803	130	82.4
1.1017	123	65.5

Table 6b. Optimum conditions for preparation of PAN-g-sago starch

Temperature	:	50°C
Reaction period	:	90 min.
$[H_2SO_4]$	:	0.190 molL^{-1}
[AGU]	:	0.146 "
[CAN]	:	9.52×10^{-3} "
[MA]	:	0.650 "

Results:

[MA] / molL^{-1}	% Grafting	% Efficiency
0.35	26.6	96.3
0.50	62.3	96.6
0.65	82.4	96.8
0.80	79.3	83.8

Table 6c. Optimum conditions for preparation of poly(HEMA)-g-sago starch

Reaction period	:	3h
Temperature	:	40°C
Amount of HEMA	:	0.17 mol
Amount of ceric ammonium nitrate (CAN)	:	1.0×10^{-3} mol
$[HNO_3]$	:	0.01m

II

Reaction period	:	2h
Temperature	:	40°C
Amount of potassium persulphate (PPS)	:	5×10^{-3} mol
Amount of HEMA	:	0.05 mol

PPS > CAN

Table 6d. Optimum conditions for PMMA grafted sago starch

I

Reaction temperature	:	70°C
Reaction period	:	2h
Amount of CAN	:	2.0 mmol
Amount of HNO_3	:	0.4 mmol
Amount of MA	:	1.41 mmol

Percentage of grafting: 246%

II

Reaction period	:	50°C
Temperature	:	1.5h
Amount of MA	:	47 mmol
Amount of PPS	:	1.82 mmol

Percentage of grafting: 90%

Table 6e. Optimum conditions for poly(styrene) grafted sago starch preparation

Reaction temperature	:	50°C
[HNO_3]	:	0.01M
Amount of styrene	:	350 mmol
Amount of CAN	:	1.68 mmol
Reaction period	:	2 h

Percentage of grafting: 53.92%

Table 6f. Optimum conditions for preparation of PMA and PAA grafted sago starch

PAA		
Temperature	:	40°C
Reaction period	:	1.5h
Amount of PPS	:	10 mmol
Amount of monomer	:	21.9 mmol
PMA		
Temperature	:	50°C
Reaction period	:	1.5h
Amount of monomer	:	87 mmol
Amount of PPS	:	8.33 mmol

To find the optimum conditions of graft copolymerization of each monomer, reaction period, temperature, and concentration of monomer and initiator were varied. When the copolymerization is carried out in the presence of a crosslinker, an interpenetrating polymer network is produced [Najjar, 2002].

The following compositional parameters are used to express the graft levels:

$$\text{Percentage of grafting (Pg)} = \frac{\text{weight of grafted polymer}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency(Ge)} = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer+ weight of homopolymer}} \times 100$$

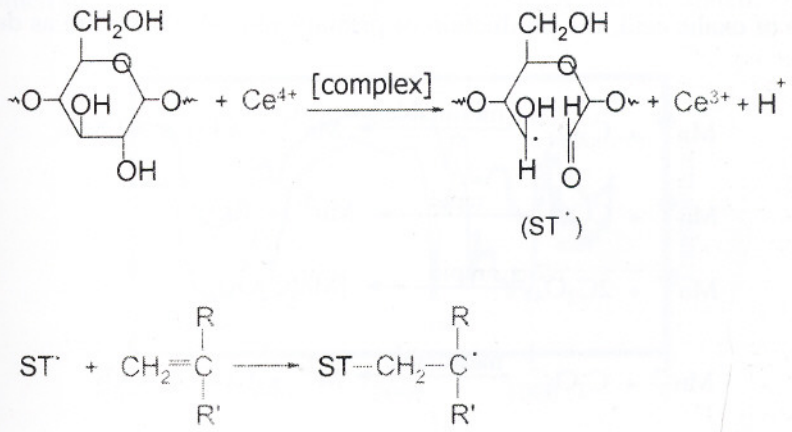
$$\text{Rate of graft polymerization (Rg)} = \frac{\text{weight of grafted polymer}}{\text{(m.w. of monomer) x (reaction time, s) x (volume, L)}} \times 1000 (\text{mol L}^{-1}\text{s}^{-1})$$

$$\text{Percentage of homopolymer} = \frac{\text{weight of grafted homopolymer}}{\text{total weight of polymer produced}}$$

Our study indicates that the extent of grafting depends on the type of vinyl monomer used in the copolymerization. Except for styrene, other monomers investigated are easily grafted on sago starch. The percentage of grafting of styrene onto the starch under optimum conditions is only 54% (Tables 6e).

Initiation of the polymerization was carried out using either ceric ion, potassium persulfate or potassium permanganate. A reaction mechanism for the initiation by ceric ion which involves a complex formation and produces cerous ion in addition to the production of transient free-radical species capable of initiating vinyl polymerization is given in Scheme 12.

Initiation:



Scheme 12. Reaction mechanism of iniation by ceric ion.

When potassium persulfate is used as the iniator, the formation of active centers is initiated by sulfate radical and other free radical species which are produced as an aqueous solution of persulfate is heated (Scheme 13).

$$S_2O_8^{--} \longrightarrow 2SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + H_2O \longrightarrow HSO_4^- + HO^{\cdot}$$

$$2HO^{\cdot} \longrightarrow HOOH$$

$$2HO^{\cdot} + HOOH \longrightarrow H_2O + HO_2^{\cdot}$$

$$S_2O_8^{--} + HO_2^{\cdot} \longrightarrow HSO_4^- + SO_4^{-\cdot} + O_2$$

$$St - OH + R^{\cdot} \longrightarrow St - O^{\cdot} + RH$$

where St - OH= starch; $R^{\cdot} = SO_4^{-\cdot}$, $HO^{\cdot}$ or $HO_2^{\cdot}$

Scheme 13. Persulfate iniation.

If a starch is soaked in $KMnO_4$ solution, MnO_2 is deposited on it. In the presence of an acid, primary radical species will be formed as a result of the acid reaction on the deposited MnO_2. The radical produced depends on the type and nature of the acid.

In the case of oxalic acid, the production of primary radical species are as described in Scheme 14.

$$Mn^{4+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{3+} + CO_2 + {}^{\cdot}COO^-$$

$$Mn^{4+} + {}^{\cdot}COO^- \xrightarrow{\text{rapid}} Mn^{3+} + CO_2$$

$$Mn^{3+} + 2C_2O_4^{2-} \xrightarrow{\text{rapid}} [Mn(C_2O_4)_2]^-$$

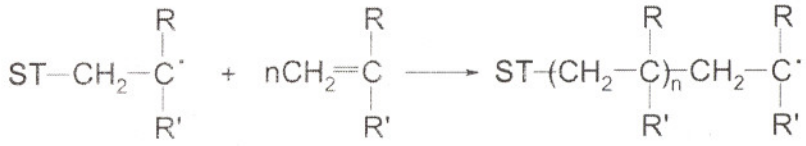
$$Mn^{3+} + C_2O_4^{--} \xrightarrow{\text{measurable}} M^{2+} + {}^{\cdot}COO + CO_2$$

$$Mn^{3+} + {}^{\cdot}COO^- \xrightarrow{\text{rapid}} Mn^{2+} + CO_2$$

Scheme 14. Formation of primary radical species from Mno_2 and H_2CO_4.

Once of the free-radical species (R.) are created, starch macroradicals are produced via direct abstraction of hydrogen ion from hydroxyl groups of the starch molecules. In the presence of a vinyl monomer, the starch macro radical is added to the double bond of the vinyl monomer, resulting the formation of an active center. Subsequent addition of the monomer propagates the graft copolymerization onto the starch (Scheme 15).

Propagation:



Scheme 15. Propagation reaction of vinyl monomer onto starch macro radical.

Based on this proposed mechanism, a rate equation for the polymerization was derived. The equation for the rate of polymerization of grafting methyl acrylate or acrylonitrile onto sago starch using ceric ammonium nitrate as an initiator is a first order dependence of the monomer concentration and the square root of the initiator concentration [Lutfor *et. al.*, 2001d, Lutfor *et. al.*, 2000e].

Several analytical techniques were used to study the formation and properties of graft copolymer. Infrared spectroscopy is used to determine the presence of characteristic peaks of the products. For example, the presence of the absorption peak at 1741cm^{-1} (Figure 12) indicates the existence of a C=O group which confirms that poly(methyl acrylate) is successfully grafted onto the starch and the sharp absorption peak at 2244 cm-1 in purified poly(acrylonitrile) grafted sago starch FTIR spectrum (Figure 13) supports the gravimetric analysis which suggests that acrylonitrile is copolymerized onto the starch.

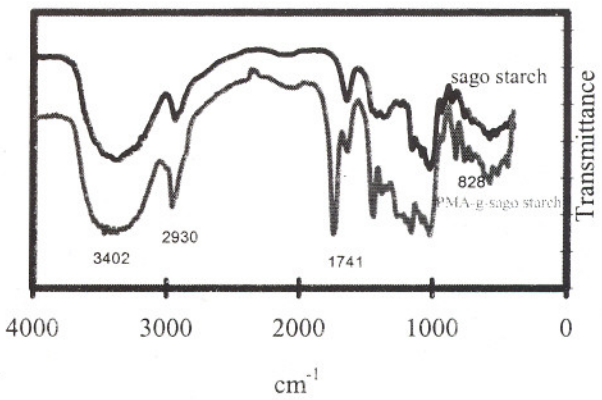


Figure 12. IR spectra of sago starch and PMA-g-sago starch

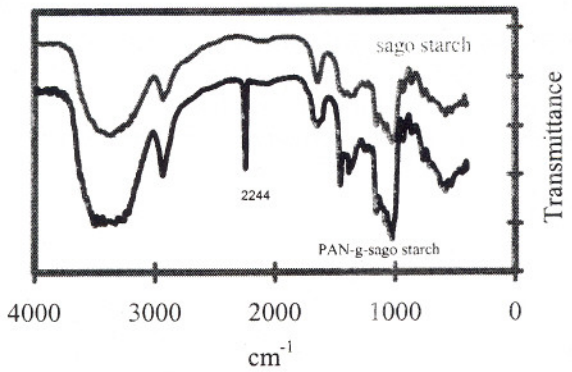


Figure 13. IR spectra of sago starch and PAN-g-sago starch

Surface morphology of the starch and its modified products is studied by scanning electron microscopy. Sago starch particles are smooth oval granules but the granular structure is destroyed after gelatinization (Figure 14). The compact surface of the gelatinized starch may be due to crystallization. Surface morphology of poly(2-hydroxy methacrylate) is similar to that of the gelatinised starch (Figure 15) which suggests that this polymer is homogenously grafted onto the starch and has a good compatibility with the backbone polymer.

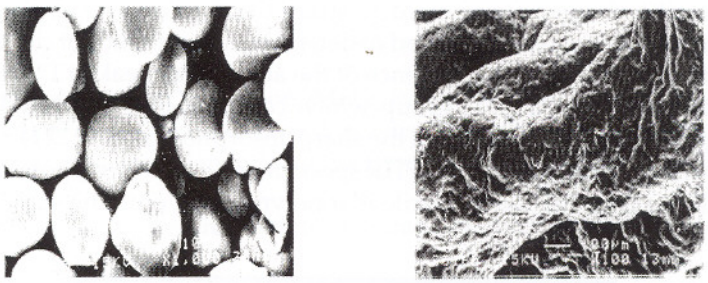


Figure 14. SEM photographs of sago and gelatinized sago starch

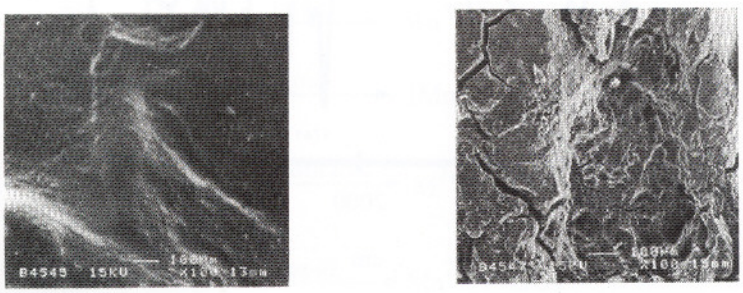


Figure 15. SEM photographs of Pg=90% and Pg=30% of sago starch of -g-poly (HEMA)

Figures 16 and 17 show the thermal behaviour of sago starch and poly(2-hydroxy ethyl methacrylate), respectively, studied by thermogravimetric analysis. Sago starch shows a characteristic two-step thermogram (Figure 16) where the first weight loss is due to water evaporation and second weight loss which occurs between 264-399°C is owing to the decomposition of sago starch. Figure 17 shows the thermal stability of poly(2-hydroxy ethyl methacrylate) grafted sago starch. The presence of the synthetic component in the composite is indicated by the third peak of weight loss.

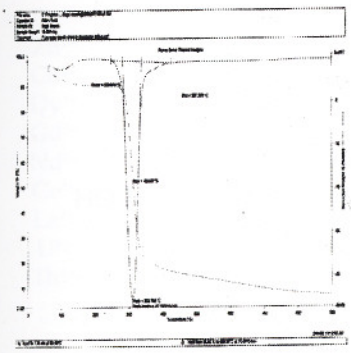


Figure 16. TGA and DTG Thermograms of Sago

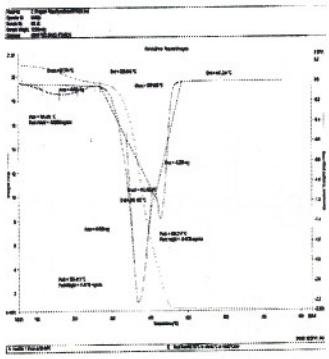


Figure 17. TGA and DTG Thermograms of 81% Starch-g-Poly(HEMA)(%G)

Grafting of hydrophilic polymer onto the starch drastically increase the water sorption capacity. The degree of sorbency does not only depend on the type of polymer grafted onto the starch but also on the degree of grafting. For example, for poly(2-hydroxy ethyl methacrylate) grafted sago starch, the percentage of swelling increases with the increase of percentage of grafting (Figure 18).

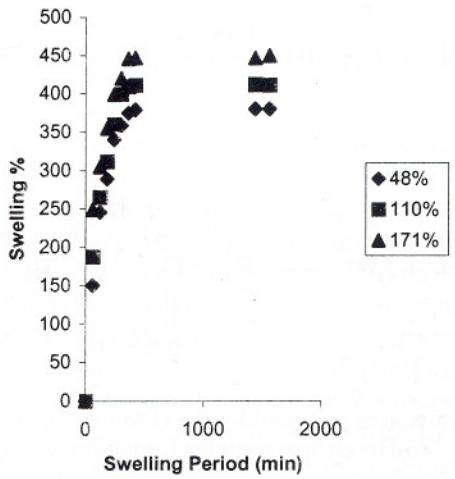
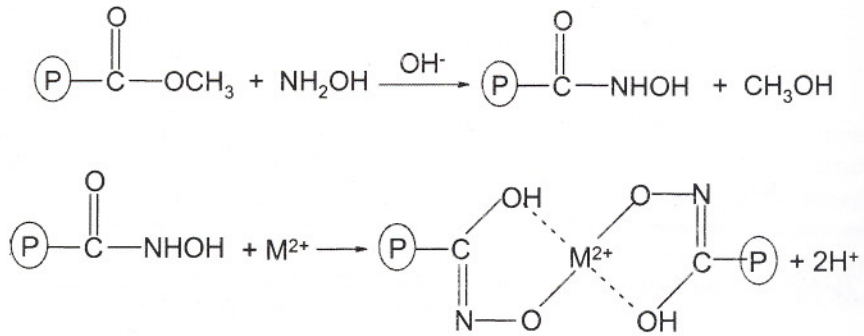
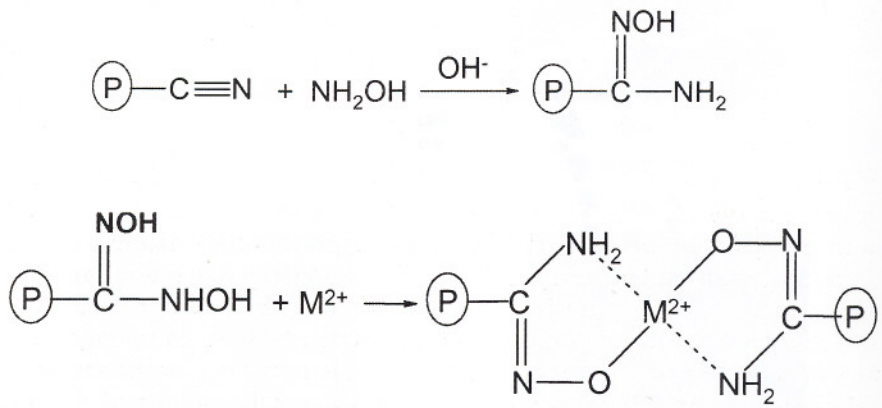


Figure 18. Percentage of swelling as a function of swelling period

Another potential application of vinyl monomer grafted sago starch is as matrices for ion exchanger resins. Functional groups can be introduced onto the copolymers by treating these starting materials with suitable chemicals. We have, using both poly(methyl acrylate) and poly(acrylonitrile) grafted sago starches as starting materials, successfully prepared poly(hydroxamic acid)[Lutfor et. al., 2001b, 2001c] and poly(amidoxime) [Lutfor *et. al.*, 2000b] resins respectively. The conversion of these starting materials into the resins is a simple (one-step reaction) (Scheme 16 and 17) but produces resin having very high capacity (Table 7 and 8) and good kinetics of extraction.



Scheme 16. Preparation of poly(hydroxamic acid) from PMA-g-copolymer and chelate complex formation



Scheme 17. Preparation reaction of poly(amidoxime) from poly(acrylonitrile)-g-sago-starch and its chelate complex formation.

Table 7. Metal Ion Capacity of Poly(hydroxamic acid) Resin

Metal Ions	Metal ions capacity / mmolg^{-1} PH				
	2	3	4	5	6
Cu^{2+}	1.25	1.42	2.08	2.83	3.46
Fe^{3+}	1.40	1.53	1.93	2.47	2.49
Cr^{3+}	0.56	0.71	1.56	2.23	2.43
Ni^{2+}	0.51	0.88	1.18	1.86	2.34
Co^{2+}	0.42	0.45	0.99	1.77	1.86
Zn^{2+}	0.35	0.51	1.10	1.79	1.71
Cd^{2+}	0.17	0.56	0.85	1.18	1.26
Dy^{3+}	0.85	1.33	1.39	2.01	2.24
Gd^{3+}	0.67	0.94	1.20	1.91	2.20
Nd^{3+}	0.58	0.78	1.12	1.68	2.04
Ce^{3+}	0.42	0.70	1.11	1.13	1.87
La^{3+}	0.40	0.64	0.82	1.21	1.77
U^{6+}	0.59	0.89	1.56	2.04	2.15
Th^{4+}	0.29	0.46	1.12	1.26	1.45

Table 8. Metal Ion Capacity of Poly(amidoxime) Resin

Metal Ions	Metal ions capacity / mmolg^{-1} PH				
	2	3	4	5	6
Cu^{2+}	0.89	1.12	1.59	2.72	3.00
Fe^{3+}	0.68	0.88	1.01	1.61	2.18
Zn^{2+}	0.55	0.71	1.56	1.58	1.99
As^{3+}	0.19	0.55	0.75	0.81	1.00
La^{3+}	0.78	0.89	0.99	1.05	1.28
Gd^{3+}	0.59	0.89	0.88	0.85	1.12
Nd^{3+}	0.39	0.65	0.76	0.91	1.07
Ce^{3+}	0.52	0.61	0.75	0.81	1.00
U^{6+}	0.68	1.03	1.12	1.19	1.35
Th^{4+}	0.31	0.52	0.83	0.82	1.00

In summary, it can be said that various vinyl monomers such as methyl methacrylate, methyl acrylate, acrylonitrile, styrene, acrylic acid and 2-hydroxyethyl methacrylate, were successfully grafted onto sago starch by free radical graft copolymerization. The optimum yield of grafting, grafting efficiency and rate of graft copolymerization are dependent upon the the type and amount of the initiator, the amount of the monomer and sago starch in the reaction mixture as well as the reaction temperature and period. A new rate equation for the polymerization was derived from the proposed reaction mechanism. A new kinetic model for graft fraction was also proposed and the validity of the model was satisfactorily supported by the experimental results up to a certain concentration of the monomer. Characterization of the copolymers produced could be carried out using thermogravimetric analysis, scanning electron microscopy, FTIR spectroscopy and differential scanning calorimetry. Further investigations indicated that some of the copolymers produced were suitable for use as hydrogels and matrices for chelating ion exchange resins.

CONCLUSION

Chemical modification of polymers has been one the most active fields of research in polymer sciences for the past several decades. Chemical modification enables us to introduce functional or reactive groups into polymers, to alter the polymer surfaces, to provide side chain substituents, etc. Therefore this research field is very wide and covers many topics. Current applications such as polymeric reagents and catalysts, separation on functionalized polymers, polymeric supports for active groups, conductive polymers and polymeric stabilizers, focus mainly on chemical properties of the products. It is expected that polymer modification will still be a major component of polymer science research but future emphasis of the research will also focus on physico-mechanical properties and biodegradable polymeric materials.

REFERENCES

Ab. Rahman, M.Z., M.R. Lutfor, S. Silong, W.M.Z. Wan Yunus, M. Ahmad and M.J. Haron (2000). Separation of copper iron, cobalt and cadmium using poly (hydroxamic acid) chelating resin. *Oriental J. Chem.* 16: 47-52.

Ab Rahman, M. Z., Md. Lutfor Rahman, Md Jelas Haron, Sidik Silong, Wan Md Zin Wan Yunus and Mansor Ahmad, 2001a. Preliminary study on application of sago starch based poly)hydroxamic acid) resin for extraction of lanthanide group elements from aqueous media, *Malay. J. Anal. Sci.* 7(2):448-457.

Ab. Rahman, M.Z., Lutfor Rahman, Sidik Silong, Wan Md. Zin Wan Yunus, Mansor Ahmad and Md. Jelas Haron 2001b. Poly(amidoxime) chelating resin used for separation of metal ions in aqueous media. *Oriental J. Chem.* 17(2):205-208.

Akelah, A. and A. Moet. 1990. *Functionalized polymers and their applications.* London: Chapman Hall,

Ampon, K., A.B. Salleh, A. Teoh, W.M.Z. Wan Yunus, C.N.A. Razak and M. Basri. 1991a. Sugar esterification catalysed by alkylated trypsin in dimethylformamide. *Biotech. Lett.* 13: 25-30.

Ampon, K., A.B. Salleh, F. Salam, W.M.Z. Wan Yunus, C.N.A. Razak and M. Basri. 1991b. Reductive alkylation of lipase. *Enzyme Microbiol. Technol.* 13: 597-601.

Ampon, K., M. Basri, C.N. A. Razak, W.M.Z. Wan Yunus and A.B. Salleh. 1992. The effect of attachment of hydrophibic modifiers on the catalytic activities of lipase and trypsin. *Biocatalysis in Non-Conventional Media.* edited by J. Tramper et al. Amsterdam: Elsevier Sci. p. 331-338.

Ampon, K., A.B. Salleh, E. Anthony, M. Basri, W.M.Z. Wan Yunus and C.N.A. Razak. 1993a. Relationship of the sugar esterificaiton activity of alkylated trypsin with surface hydrophobicity determined by hydrophobic chromatography. *Asia-Pacific J. Mol. Biol. Biotechnol.* 1(1): 51-56.

Ampon, A.B. Salleh, M. Basri, W.M.Z. WanYunus, C.N.A. Razak and J.R. Whitaker. 1993b. Relationship of surface hydrophobicity to the sugar esterification activity of alkylated trypsin. *J. Biosci.* 4: 154-160.

Ampon, K., M. Basri, A.B. Salleh, W.M.Z. Wan Yunus and C.N.A. Razak. 1994. Immobilisation by adsorption of hydrophobic lipase derivatives to porous polymer beads for use in ester synthesis. Biocatalysis 10: 241-251.

Ampon, K., A.B. Salleh, M. Akon, M. Basri, W.M.Z. Wan Yunus and C.N.A. Razak. 1997. Hydrophobicity determined by a fluorescence probe method and its correlation with esterification and hydrolytic activities of alkylated lipases. *Pertanika J. Sci. Technol.* 5(2): 1-11.

Awang, R., W.M.Z. Wan Yunus, M.J. Haron and A. Yahaya. 1995a. Preparation and characteristic of poly(N-phenyl hydroxamic acid) chelating ion exchange resin from poly(methyl acrylate). *Malays. J. Anal. Sci.* 1(2): 287-293.

Awang, R. 1995b. Preparation and characteristic of (*N*-phenyl hydroxamic acid) from poly(methyl acrylate-divinyl benzene). M.S. Thesis, UPM.

Basri, M., A.B. Salleh, K. Ampon, F. Salam, W.M.Z. Wan Yunus and C.N.A. Razak. 1991. Modification of lipase by polyethylene glycol. *Biocatalysis* 4: 313-317.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A. Razak and A.B. Salleh 1992a. Catalytic activity of lipase modified with hydrophobic imidoesters. *Annals N. Y. Acad. Sci.* 672: 577-579.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A Razak and A.B. Salleh. 1992b. Amidation of lipase with hydrophobic imidoesters. *JAOCS* 69(6): 579-583.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A. Razak and A.B. Salleh. 1993. Immobilizaiton of hydrophobic lipase derivatives onto organic polymer beads. *J. Chem. Technol. Biotechnol.* 59: 37-44.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A. Razak and A. B. Salleh. 1994. Stability of hydrophobic lipase derivatives immobilised on organic polymer beads. *Appl. Biochem. Biotechnol.* 48: 173-183.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A. Razak and A.B. Salleh. 1995. Enzymic synthesis of fatty esters by hydrophobic lipase derivatives immobilized on organic polymer beads. *JAOCS* 72: 407-411.

Basri, M., W.M.Z. Wan Yunus, W.S. Yoong, K. Ampon, C.N.A. Razak and A.B. Salleh. 1996. Immobilization of lipase from Candida rugosa on polymer beads for use in the synthesis of fatty esters. *J. Chem. Tech. Biotechnol.* 66: 169-173.

Basri, M., A.C Heng, C.N.A. Razak, W.M.Z. Wan Yunus, M. Ahmad, R.N.A. Rahman, K. Ampon and A.B. Salleh. 1997a. Alcoholysis of palm oil mid fraction by lipase Rhizopus rhizopdiformis. JAOCS 74: 113-116.

Basri, M., K. Ampon, W.M.Z. Wan Yunus, C.N.A. Razak and A.B. Salleh. 1997b. Enzymatic synthesis of fatty esters by alkylated lipase. *J. Molecular Catalysis B: Enzymatic* 3: 1171-176.

Bin, Y.C. 1995. Preparation and characterization of sago starch-graft-poly (acrylic acid) and sago starch-graft-poly(methyl acrylate). M.S. Thesis, UPM.

Beauvais, R.A. and S.D. Alexandratos. 1998. Polymer supported reagents for selective complexation of metal ions: an overview. *Reactive and Functional Polymers* 36: 113-123.

Esa, N.M., W.M.Z. Wan Yunus, M.B. Ahmad, M. Basri, C.N.A.Razak and A.B.Salleh (1998). Water activity efffect of lipase immobilised onto different compositions of poly(HEMA-MMA). *Annals. New York Acad. Sci.* 864:489-493.

Fakhru'l -Razi, A., Isam Y.M. Qudsieh, Wan Md Zin Wan Yunus, Mansor b. Ahmad and Mohamad Zaki Ab. Rahman 2001. Graft Copolymerization of Methyl Methacrylate Onto Sago Starch Using Ceric Ammonium Nitrate and Potassium Persulfate as Redox Initiator Systems. *J. Appl. Polym. Sci.* 82:1375-1381.

Haron, M.J., W.M.Z. Wan Yunus, M.Z. Desa and A. Kassim. 1994. Synthesis and properties of poly(hydroxamic acid) from crosslinked poly(methacrylate). *Talanta* 41(5): 805-807.

Haron, M.J., W.M.Z. Wan Yunus, S.A. Wasay, A. Uchiumi and S. Tokunaga. 1995. Sorption of fluoride ion from aqueous solutions by yittrium-loaded poly(hydroxamic acid) resin. *Intern. J. Environ.* Studies 48: 245-255.

Haron, M.J., W.M.Z. Wan Yunus, M.A. Sukari, L.T.Wum and S. Tokunaga. 1997. Removal of arsenic(V) by cerium(III) complexed ion exchanger. *Malays. J. Anal.* Sci. 3(1): 193-204.

Haron, M.J., W.M.Z. Wan Yunus, N.I. Yong and S. Tokunaga (1999). Sorption of arsenate and arsenate ions by iron(III)-poly(hydroxamic acid) complex, *Chemosphere* 39(14), 2459-2466.

Haron, M J., S. Balci, W.M.Z. Wan Yunus, S. Silong, M.Z.A. Rahman, M. Ahmad and M.Y.M. Sulaiman 2000. Preparation and characteristion of poly(N-methylhydroxamic acid) resin from poly(Methyl acrylate-divinyl benzene) beads. *Sci. Int. (Lahore)* 12: 53-55.

Haron, M.J, W.M.Z. Wan Yunus, S. Tokunaga, S.A. Wasay. 2001. Removal of arsenic(V) ion from aqueous solutions by basic lanthanum carbonate. Malays. J. Anal. Sci. 7(1): 173-176.

Haron, M.J. and W.M.Z. Wan Yunus. 2001a. Removal of fluoride ion aqueous solution by a cerium-poly(hydroxamic acid) resin complex. *J. Environ. Sci. & Health - Part A* 36(5):727-734.

Haron, M.J., S. Balci, W.M.Z.Wan Yunus, Sidik Silong, M Z Ab Rahman and Mansor Ahmad and M.Y.M.Sulaiman. 2001b. Preparation and use of poly(N-methyl hydroxamic acid) resin for separation of rare earth metal ions.*Ultra Scientists*, 13(1):16-19.

Haron, M.J., W.M.Z. Wan Yunus, P.C. Yap, M.A. Sukari and M.Y. Sulaiman. 2001c. Separation of yttrium and uranium from from xenotime using poly(hydroxamic acid) chelating ion exchange resin, *Oriental J. of Chem.* 17(2):173-176.

Holmes, L.B.(1996) Hydroxamic acid: a potentia human teratogen that could be recommended to treat ureoplasma. *Teratology* 53, 227-229.

Janarthanan, P. 1999. Preparation and characterization of styrene grafted sago starch. M.S. Thesis, UPM.

Kassim, A., Hamdan Suhaimi, W.M.Z. Wan Yunus, dan Md. Jelas Haron. 1992. Zinc ion selective electrode using active zinc(11) complex compound membrane of poly(hydroxamic acid). *Sains Malaysiana* 21(2): 47-58.

Kurzak,B., H. Kozlowzki and E. Parkas .1992. Hydroxamic and aminihydroxamic acids and their compolxes with metal ions. *Coord. Chem.Rev.*114,169-200.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.J. Haron, M.Z. Ab Rahman, M.J.Haron and M.B. Ahmad. 2000a. Modification of sago starch by graft copolymerization: Effect of reaction condition on grafting parameters. *Intern. J. of Polym.* Materials, 1-13.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab Rahman, M.B. Ahmad and M.J. Haron. 2000b. Metal ions binding by chelating ligands from new polymer bearing amidoxime fuctional groups *J. Chem. Res.* (S), 52-53.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab. Rahman, M. Ahmad and M.J. Haron. 2000c. Graft copolymerization of methyl acrylate onto sago starch using ceric ammonium nitrate as an initiator. *J. Appl. Polym. Scie.*761(4):516-523.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab. Rahman, M. Ahmad and M.J. Haron. 2000d. Kinetics and mechanism of free radical grafting of methyl acrylate onto sago starch. *J. Appl. Polym. Sci.* 77(6):784-791.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab. Rahman, M. Ahmad and M.J. Haron. 2000e. Preparation and characterization of poly(amidoxime) chelating resin from poly(acrylonitrile) grafted sago starch. *Euro. Polym. J.* 36: 2105-2113.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab Rahman, M.B. Ahmad and M.J. Haron. 2001a. Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate. *Design Monomers and Polym.* 4: 253-260.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab Rahman, M.B. Ahmad and M.J. Haron. 2001b. Synthesis And Characterization of Poly(hydroxamic acid) Chelating Resin From Poly(methyl acrylate) Grafted Sago Starch, *J. Appl. Polym. Sci.* 79:1256-1264.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z.A. Rahman, M. Ahmad and J. Haron. 2001c. New polymer bearing hydroxamic acid chelating resin for binding of heavy metal ions, *J. Chem. Res.* (S), 450-451.

Lutfor, M.R., S. Silong, W.M.Z. Wan Yunus, M.Z. Ab. Rahman, M. Ahmad and M.J. Haron. 2001d. Preparation and swelling of a polymeric absorbent containing hydroxamic acid group from polymer grafted sago starch. *Carbohydrate Polym.* 45:95-100.

Mohd, D.H., A. B. Salleh, C.N.A. Razak, M. Hamenudin, K. Ampon, W.M.Z. Wan Yunus and M.Basri. 1991. Cell immobilization by radiation polymerization - A comparative study. *Sains Nuklear Malaysia* 9(1): 37-45.

Mulder, K. F. 1998. Sustainable consumption and production of plastic. *Technological Forecasting and Social Change* 58: 105-124.

Najjar, A.M.K., W.M.Z. Wan Yunus, M. Ahmad and M.Z. Ab. Rahman (2000). Preparation and characterization of poly(2-acrylamido-2-methyl propane-sulforic grafted chitosan using potassium persulfate as redox initiator. *Journal of Applied Science* 77(10): 2314-2318.

Najjar, A.M.K. 2002. Preparation of hydrogels by free radical copolymerization of sago starch / chitosan and hydrophilic vinyl monomers and their characterization. Ph.D. Thesis. UPM.

Phillip, R.J. and J.S. Fritz (1980). Synthesis and analytical properties of N-phenyl hydroxamic acid resin. Anal. Chim. Acta, 121:225-232

Razak, C.N.A., Z. Zakaria, A.B. Salleh, K. Ampon, W.M.Z. Wan Yunus, M. Basri and D. Mohd. 1996. Parameters affecting lipase production by HEMA-immobilised bacteria. *Annals N. Y. Acad Sci.* 799: 157-163.

Salleh, A.B., W.M.Z. Wan Yunus, C. Pau, K. Ampon, C.N.A. Razak and M. Basri. 1988. Poly(ethylacrylate-divinylbenzene) Polymer as a Matrix for Immobilization of Lipase. *Proc. 7th Federation of Asian and Oceanian Biochemistry Congress.*

Salleh, A.B., K. Ampon, F. Faridah, W.M.Z. Wan Yunus, C.N.A. Razak and M. Basri. 1990. Modification of lipase for reactions in organic solvents. *Annals N. Y. Acad. Sci.* 613: 521-522.

Salleh, A.B., W.M.Z. Wan Yunus, K. Ampon, C.N.A. Razak and M. Basri. 1991. Lipase immobilised onto Amberlite XAD-7 for hydrolysis of oil. *Asean J. Sci. Technol. Develop.* 8(2): 87-93.

Salleh, A.B., M. Taib, M. Basri, K. Ampon, W.M.Z. Wan Yunus and C.N.A. Razak. 1996. The effect of water activity on modified lipase during estrification. *Annals N. Y. Acad Sci.* 799: 328-331.

Salleh, A.B., C.N.A. Razak, M. Basri, W.M.Z. Wan Yunus and K. Ampon. 1997. Polyurethane as a matrix for immobilization of lipolytic cells. *J. Biosci.* 8: 15-21.

Vernon, F. and T.W. Kyffin. 1977. Chelating ion-exchanger containing N-substituted hydroxylamine functional groups. Part VI. Iron, copper and uranium separation on Duolite 346 Resin. Anal. Chim. Acta 94:317-322.

Vernon, F. and Wan Md. Zin Wan Yunus. 1981. Chelating ion exchangers containing N-substituted hydroxyl-amine functional groups part 6: Sorbtion and separation of gold and silver by a poly(hydroxamic acid). *Anal. Chem. Acta* 123: 309-313.

Wan Yunus, W.M.Z.. 1980. Synthesis, optimizaiton and application of a poly(hydroxamic acid) ion-exchanger resin. Ph.D Thesis, University of Salford.

Wan Yunus, W.M.Z. and Zaharuddin Ahmad. 1988a. Preparation of a poly(hydroxamic acid) ion-exchange resin from poly(ethyl acrylate-divinyl benzene) beads and its properties. *Pertanika* 11(2): 225-229.

Wan Yunus, W. M. Z. and Md. Jelas Haron. 1988b. Extraction of tin by a poly(hydroxamic acid) resin. *Proc. Malaysian Chemical Conference*. Johor Bahru.

Wan Yunus, W.M.Z, M. J. Haron and T. L. Heong. 1990a. Extraction and separation of gold, silver, iron, copper, cobalt and zinc by poly(hydroxamic acid). *Proc. Fourth Malays. Anal. Chem. Symp.* UPM.

Wan Yunus, W.M.Z., A.B. Salleh, A. Ismail, K. Ampon, C.N.A. Razak and M. Basri. 1992. Poly(methyl methacrylate) as matrix for immobilization of lipase. *J. App. Biochem. Biotech.* 36: 97 - 105.

Wan Yunus, W.M.Z, A.B. Salleh, M. Basri, C.N.A. Razak and K. Ampon. 1995a. Poly(methylacrylate-methyl methacrylate-divinyl benzene) beads for immobilization lipase. *Annals N.Y. Acad. Sci.* 750: 246-249.

Wan Yunus, W.M.Z, M.J. Haron and A. Yahaya. 1995b. Effect of cyanide ion of extraction of Fe(III), Pb(II), Au(III), Cu(II), Cr(III) and Ni(II) with poly(hydroxamic acid) resin. Malays. J. Anal. Sci. 1(1): 165-169.

Wan Yunus, W.M.Z. and M.J. Haron. 1996. Speciation of iron ions by a poly(hydroxamic acid) resin. *J. Sains Malaysiana* 25(2): 35-39.

Wan Yunus, W.M.Z., A.B. Salleh, M. Basri, K. Ampon and C.N.A. Razak. 1996a. Preparation and immobilization of lipase onto poly(methylacrylate-methylmethacrylate-divinyl benzene) beads for lipid hydrolysis. *Biotechnol. Appl. Biochem.* 24: 19-23.

Wan Yunus, W.M.Z., M. Basri, C.N.A Razak and A.B. Salleh. 1996b. Immobilisation of lipase onto poly(methylacrylate-methyl methacrylate) beads. *10th Intern. Biotechnol. Symp.* Sydney, Australia.

Wan Yunus, W.M.Z., M.J. Haron and T.L.Heong. 1996c. Separation of gold from nickel, cobalt and zinc by a poly(hydroxamic acid) ion exchange resin. *Pertanika J. Sci. Technol.* 4(2): 149-155.

Wan Yunus, W.M.Z.,R. Awang and M.J. Haron. 1996d. Extraction of gold(111) chloride by poly(*N*-phenyl hydroxamic acid) resin. *Malays. J. Anal. Sci.* 2(2): 223-228.

Wan Yunus, W.M.Z, R. Awang, M.J. Haron and A. Yahya. 1997. Synthesis and some properties of poly (N-phenyl hydroxamic acid) ion exchange resin from crosslinked poly(methacrylate). *36th IUPAC Congress.* Geneva, Switzerland.

Wan Yunus, W.M.Z, Awang1,R., Haron,M.J. and Yahya, A.. Separation Of Nickel And Cobalt From Iron, Lead, Chromium And Copper By Poly(N-Phenyl Hydroxamic Acid) Chelating Ion Exchange Resin. *World Chemistry Congress,* Brisbane, Australia, 1-6 July 2001.

Zakaria, Z., C.N.A. Razak, K. Ampon, M. Basri, W.M.Z. Wan Yunus, Y. Shirai, A.B. Salleh and K. Hashimoto. 1992. Optimun conditions for the production of lipase by alginate-immobilized bacteria. *J. Gen. Appl. Microbiol.* 38: 429-438.

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