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ABSTRACT

Methyl methacrylate was grafted onto bleached kraft pulp using the ceric ion initiation method. It was observed that the lower the oxygen content of the reaction mixture and atmosphere, the less drastic the effect of the stirrer rpm was on the reaction conversions. Stirring rate was found to have no appreciable effect on the grafting efficiencies of the reactions when these reactions were carried out with the same level of oxygen impurity. However, lower conversions and grafting efficiencies were observed at higher oxygen concentrations.

ACKNOWLEDGEMENTS

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INTRODUCTION

1.1 Historical background:

Grafting has been used as an important technique for modifying physical and chemical properties of polymers for quite a long time. The technique can be applied to the modification of pre-existing polymers. This becomes of particular importance when applied to natural polymers such as cellulose. Ideally certain properties can be imparted to the substrate without significantly altering others. For example, by grafting various monomers onto cellulose it is possible to attain many different properties, such as elasticity, sorbancy, ion exchange capabilities, and resistance to micro-biological attack (1).

Interest in cellulose modification reactions has been going through cycles. The interest reached a peak in the early 1950's, this was followed by a lengthy stagnation period when a lot of research activities shifted towards petrochemical-based polymers. Cheap source of monomer, and relatively stable political climates in petroleum-producing countries helped to advance research activities in the field of synthetic polymers. However, significant political and economic events in the early 1970's (particularly the 1973 Arab-Israeli war) instituted a change in attitude. The changes in political climates and fear of impending shortages or embargos of petrochemicals pronounced an end to the era of cheap and abundant monomer sources. Those events forced a rethinking of important research directions in polymer science. Again, an appreciable shift in research emphasis toward the most abundant polymer in the world, cellulose, started to take place. However, in spite of the renewed research activities in the field of grafting cellulose, there has been relatively little large-scale commercialization of grafting processes. The reason for this is partly economical and partly because many aspects of this field are still not well known, and many technical challenges are still facing researchers.

1.2 Basis and Scope of the present study:

In 1982 V. Hornof and T. Graczyk (2) published the first of a series of papers on the results of their studies (carried out at the University of Ottawa, Ottawa, Ontario) on the effects of stirring on the graft copolymerization of certain monomers onto cellulose. The first paper dealt with the grafting of 2-Dimethylaminoethyl methacrylate (DMAEM) onto dissolving pulp by the Xanthate initiation method. They reported that conversions to both copolymer and homopolymer were dependent on the rpm of the stirrer used in the reactor system. They also carried out further studies using monomers ranging from hydrophilic (DMAEM) to hydrophobic (styrene). The results of these studies were published in subsequent papers (3,4,5). In all the new studies, the dependence of conversion on the stirrer rpm was appreciable, although it differed for different monomers. A sample of the results obtained by V. Hornof and T. Graczyk is presented in figures (1) through (12). In 1985, another paper on the subject was published by the same authors. This time the influence of the purity of the reaction atmosphere was investigated (6). Part of their experimental results is shown in figure (12). These results indicated that almost no conversion took place under pure oxygen, while air slowed down the reaction. However, the dependency of the reaction conversion on the stirrer rpm was still present and pronounced.

The main objectives of our study were to investigate further the effect of stirring, and to try to find out whether or not there is any correlation between the amount of oxygen present in the reaction system, and the effect of the stirrer speed. It was decided, however, to carry out the new study by the ceric ion initiation method because of its relative simplicity in comparison to other initiation methods.

Figure 1: Effect of Agitator Speed on the Conversion of DMAEM

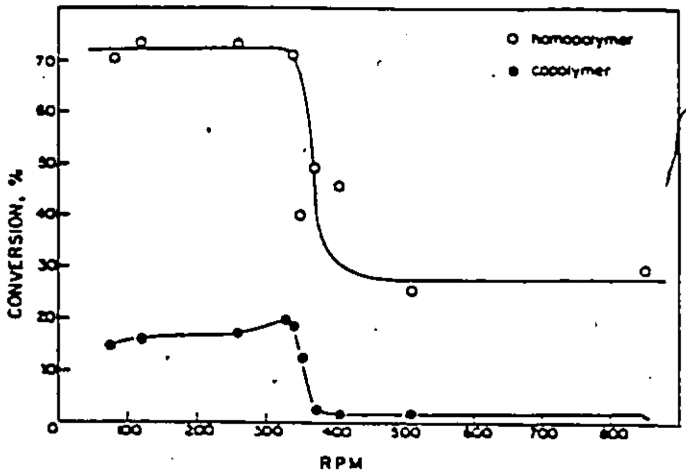
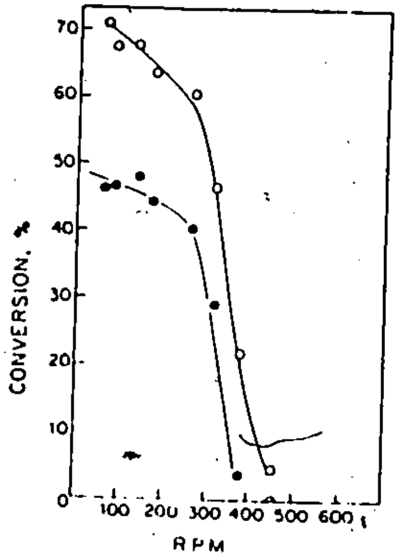


Figure 2: Conversion of An as a function of agitator speed



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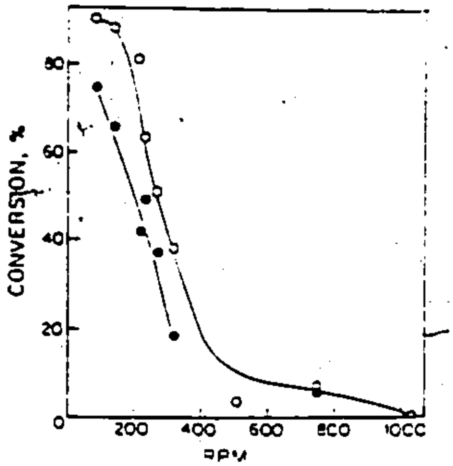

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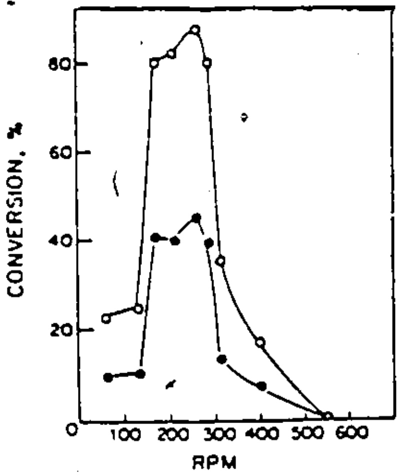

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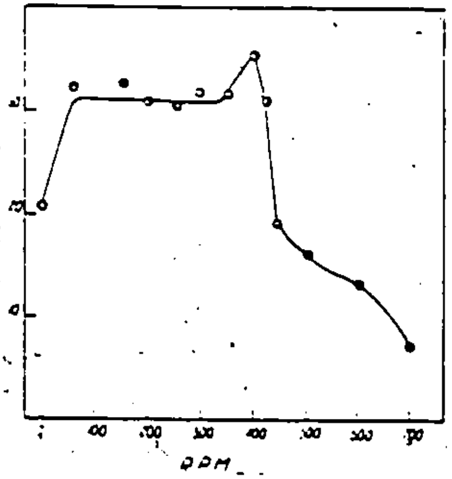

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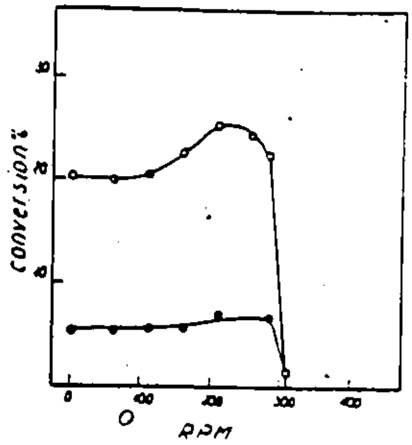

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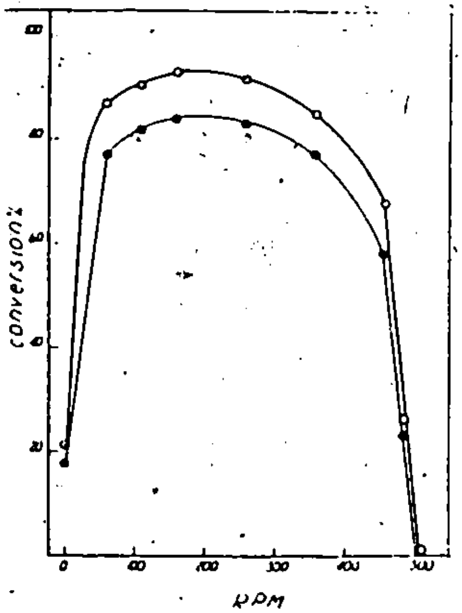

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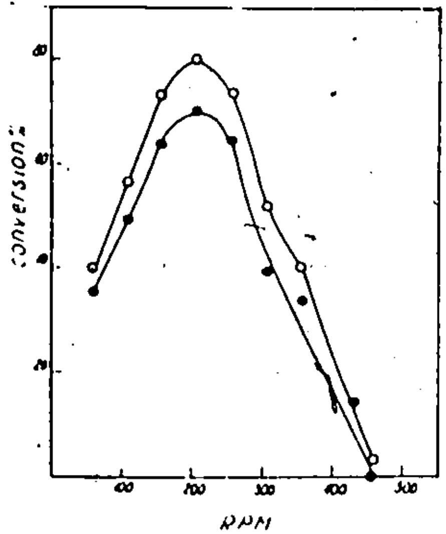

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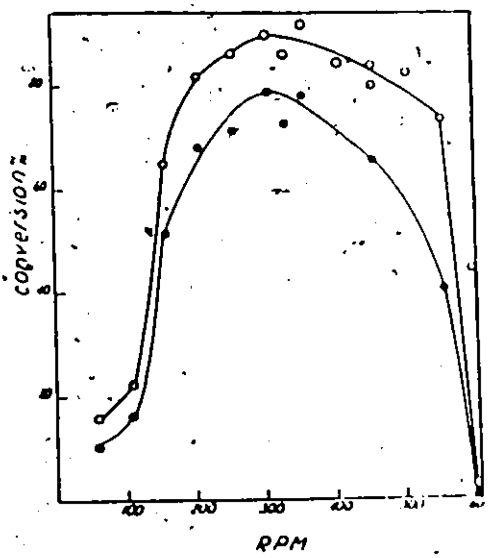

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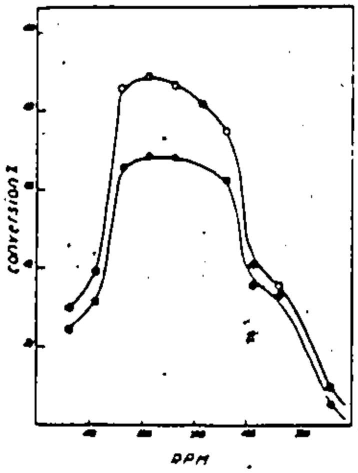

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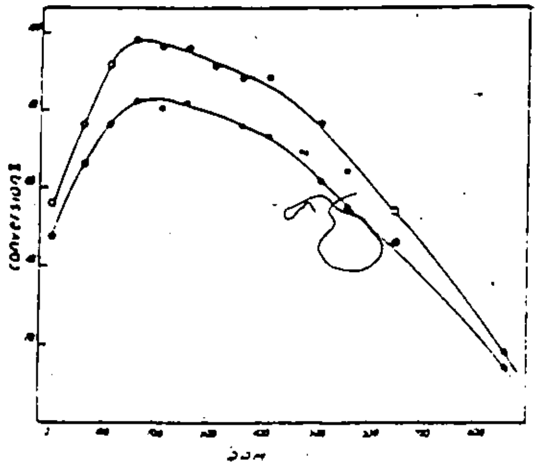

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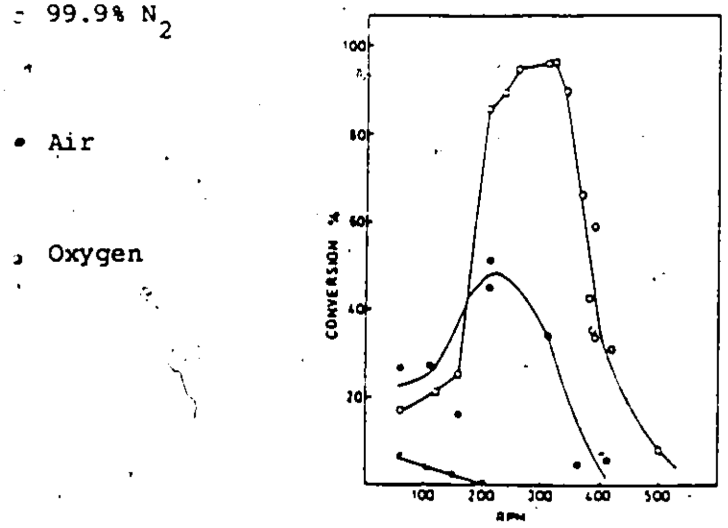


Chapter II

THEORY

Before discussing the theoretical basis of the graft copolymerization of cellulose, one needs to define some frequently used terms.

HOMOPOLYMER:

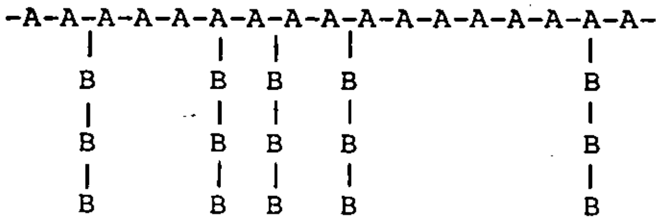
The term Homopolymer describes a polymeric chain derived from a single monomer.

COPOLYMER:

A copolymer is defined as a polymer having at least two different monomers incorporated into one polymeric chain.

GRAFT COPOLYMER:

In a graft copolymer, sequences of one monomer are "attached" onto the backbone of a polymer made from a different monomer. In the illustration shown below, one can imagine the "A"'s sequence as being the cellulose backbone, and the "B"'s as being methyl methacrylate.



2.1 Grafting:

In general there are two principal techniques for grafting side chains onto cellulose substrate molecules. These are grafting by free radical polymerization and grafting by condensation. Only the free radical method will be discussed here.

The free radical copolymerization methods use either initiation by chemically formed radicals or by those created by irradiation. A few cases are known where grafting is initiated by radicals formed by mechanical treatments, such as milling (7). Only the method of initiation by chemically formed free radicals will be presented here.

The chemical methods for grafting polymer side chains onto cellulose backbone make use of the following chemical mechanisms:

(a) Chain transfer during radical polymerization of vinyl monomers.

(b) Activity of radical producing or polymerizable substituents introduced prior to grafting, to the cellulose molecule.

(c) Initiation by interaction with redox systems.

In making such a subdivision one has to be aware of the fact that in some cases it is almost impossible to assign the reaction leading to grafting to only one of these mechanisms or methods. This is particularly the case with the grafting initiated by certain redox systems, where uncertainty exists if the grafting is caused by direct action with the cellulose structure or if the attachment of side chains originates from chain transfer with the activated monomer or growing living polymer. However, such subdivision seems useful and follows the treatment given in reviews by a number of authors.

2.1.1 Grafting by chain transfer reaction:

The most generally and widely used method for grafting is based on the well known phenomena that free radicals, such as the radicals arising from the decomposition of a polymerization initiator, or an activated monomer molecule, or a growing polymer chain, are capable of extracting hydrogen or other labile atoms from certain atomic groupings in organic compounds, e.g. in a polymer molecule. This process leading to a radical of the organic compound or the polymer is called "chain transfer" and may be written in a more general form as follows:

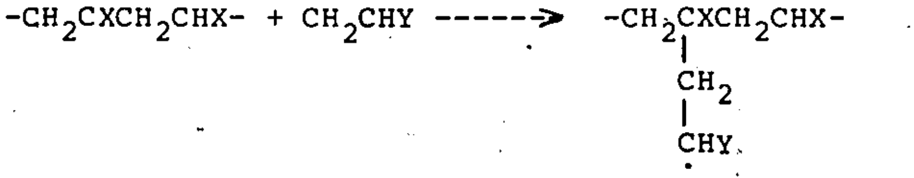
$$\dot{R} + X\text{-}H \xrightarrow{\hspace{3em}} R\text{-}H + \dot{X}. \qquad (1)$$

In cases where polymerization of a monomer ($CH_2{=\!=}CHY$) is performed in the presence of an initiator (R) and an already formed polymer ($-CH_2CHXCH_2\dot{C}HX-$) such chain transfer reactions will lead to grafting of $-CH_2CHYCH_2CHY-$ side chains onto the $-CH_2CHXCH_2CHX-$ backbone molecule. The reaction leading to this attachment of side chains to a polymer backbone are presented in the following scheme:

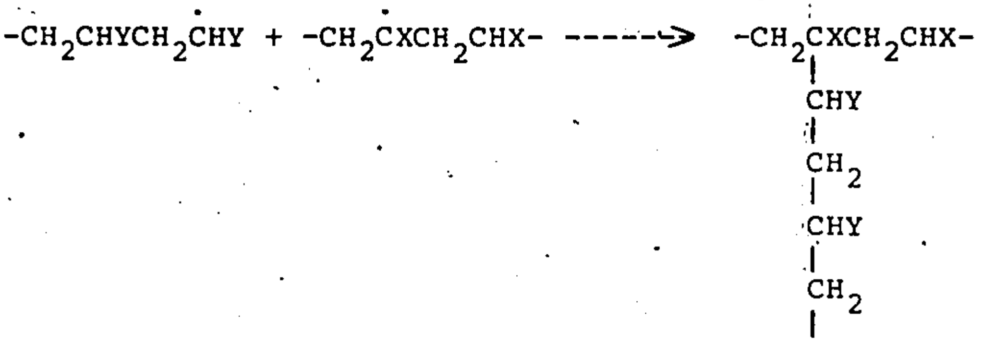
$$\dot{R} + -CH_2CHXCH_2CHX- \xrightarrow{\hspace{2em}} RH + -CH_2\dot{C}XCH_2CHX- \qquad (2)$$

$$RCH_2\dot{C}HY + -CH_2CHXCH_2CHX- \xrightarrow{\hspace{2em}} RCH_2CH_2Y + -CH_2\dot{C}XCH_2CHX- \qquad (3)$$

$$-CH_2CHYCH_2\dot{C}HY + -CH_2CHXCH_2CHX- \xrightarrow{\hspace{2em}} -CH_2CHYCH_2CHY + -CH_2\dot{C}XCH_2CHX- \qquad (4)$$



$$-CH_2CXCH_2CHX- + CH_2CHY \xrightarrow{\hspace{2em}} -CH_2\underset{\substack{|\\ CH_2\\ |\\ CHY\\ \bullet}}{C}XCH_2CHX- \qquad (5)$$



$$-CH_2CHYCH_2\dot{C}HY + -CH_2\dot{C}XCH_2CHX- \xrightarrow{\hspace{2em}} -CH_2\underset{\substack{|\\ CHY\\ |\\ CH_2\\ |\\ CHY\\ |\\ CH_2\\ |}}{C}XCH_2CHX- \qquad (6)$$

The possible chain transfer reactions between the initiator radical, the activated monomer, and a growing chain of the monomer applied on the one hand and the preformed polymer on the other are given under equation (2). The graft copolymer initiates either from addition of the monomer applied to the polymer radical formed by chain transfer (reaction 5) or from recombination of two polymer radicals (reaction 6), the latter one being less probable (7).

It has been shown by extensive grafting work on widely different systems of various initiators, monomers, and preformed polymer used as substrates that a large number of factors can influence the grafting reaction. These include relative reactivities of the primary radicals for transfer and propagation, the competition between substrate polymer and monomer for the radical, and the reactivities of the polymer radicals. The presence of labile atoms enhancing chain transfer in the substrate polymer, and the possible participation of other ingredients in the reaction medium, such as solvents and dissolved oxygen, can play a decisive role.

2.1.2 Initiation on radical producing or polymerizable substituents:

The most simple modification of cellulose leading to the formation of radical producing groups is ionization. The action of ionized oxygen creates hyperoxide sites which at elevated temperature split into radicals initiating grafting and homopolymerization.

Already in 1955 Polymer Corporation (8) had applied for a patent on a process of treating naturally occurring polymeric substances or their derivatives with ozone containing inert gases and subsequently contacting the ozonized substrates with polymerizable monomers. In the presence of redox activators butadiene, acrylonitrile, and styrene were grafted onto cellulose, starch, casein, gelatin, and rubber (7).

Kargin, Usmanov, and Aikhodzhaev (9) used a similar technique of ozonation to introduce hyperoxide groups into cellulose substrates. They observed grafting of styrene to ozonized viscose tire cord even without the presence of any other initiating system imparting improved rubber-adhesion to the rayon tire cord. In a later report, Usmanov, Aikhodzhaev, and Azizov (10) described the grafting of acrylonitrile, methyl methacrylate, methylvinylpyridine, and of vinyl acetate onto ozonized cellulose.

A vapor phase grafting process based on the ozonation of polymer films and fabrics followed by a treatment with vapors, such as acrylonitrile, dichloroethylene, and vinyl acetate, has been patented by PolyPlastic (11). Also cotton fabrics can be used as substrates.

Vasiliu, Feldman, and Simionescu grafted acrylonitrile onto cotton and poplar fluff cellulose which were ozonized before the grafting reaction. The authors characterized the graft copolymer by nitrogen analysis and by infrared spectroscopy and studied their behaviour towards acids, bases and swelling agents.

The graft copolymerization of styrene onto regenerated celluloses, such as viscose rayon and cellophane, and onto cellulose acetate has been investigated by Pikler, Suta, and Alfoeldi (12) and by Alfoeldi and Pasteka (13). In both studies the authors used ozonized substrate for initiating the graft copolymerization.

2.1.3 Grafting by interactions with redox systems:

Kolthoff, and Miller (14) have shown that persulphate ions decompose when heated in aqueous solution forming sulphate radicals. The sulphate radicals may react further with water to form hydroxyl radicals. Polymerization by persulphate may thus be initiated either by sulphate radicals or by hydroxyl radicals:

$$S_2O_8^{--} \longrightarrow 2\ SO_4^{-\cdot} \qquad (6)$$

$$SO_4^{-\cdot} + 2\ H_2O \longrightarrow H_2\ SO_4^{-} + 2\ HO^{\cdot} \qquad (8)$$

As early as 1903 Marie and Bunel (16) have shown that alcohols accelerate the persulphate decomposition. Kolthoff, Meehan, and Carr (61) confirmed this and proved that this reaction is not between the sulphate ion and the alcohol:

$$SO_4^{\cdot-} + CH_3OH \dashrightarrow HSO_4^{-} + {}^{\cdot}CH_2OH \qquad (9)$$

$${}^{\cdot}CH_2OH + S_2O_8^{--} \dashrightarrow HCHO + HSO_4^{-} + SO_4^{-\cdot} \qquad (10)$$

This is proved by the observation that the rate of decomposition of persulphate drops to the same low value as when allyl acetate is added in the absence of alcohol. On addition of allyl acetate, the sulphate ion radicals react with the allyl monomer rather than with the alcohol, so that no alcohol radicals are formed in the absence of allyl acetate. It should be noted that Bartlet and Nozaki (15) could not confirm these observations.

It is obvious that should cellulose react in the same manner as methanol in the experiments of Kolthoff, Meehan, and Carr (16) the chance for grafting in the persulphate initiated polymerization of vinyl monomers would be low. However, since grafting has been observed by several scientists, one has to assume that there exist differences in the behaviour of different monomers and alcohols during such reactions. As expressed by Hermans (17) the initiation of grafting in accordance with the reaction mechanisms discussed above will depend on the relative reaction rates of the monomer and the alcohol groupings in the substrate polymer in their competing reaction with the sulphate ion radical. If cellulose is present in excess, which may be the case inside swollen film or fiber, substantial amounts of sulphate ion radicals may actually interact with cellulose forming radical sites. However, so far no proof has been presented to show that the primary action of the sulphate ion radical with the cellulose or chain transfer reactions are initiating the grafting step.

A well-known example of an oxidation-reduction reaction leading to the formation of radicals is the decomposition of hydrogen peroxide by ferrous ions. Haber and Weiss (18) formulated this decomposition as follows:

$$H_2O_2 + Fe^{2+} \longrightarrow HO^{\cdot} + HO^{-} + Fe^{3+} \qquad (11)$$

$$HO^{\cdot} + Fe^{2+} \longrightarrow HO^{-} + Fe^{3+} \qquad (12)$$

The hydroxyl radicals decompose further hydrogen peroxide in a chain reaction, when H_2O_2 is present in large excess over ferrous ions (7):

$$HO^{\cdot} + H_2O_2 \longrightarrow H_2O + HOO^{\cdot} \qquad (13)$$

$$HOO^{\cdot} + H_2O_2 \longrightarrow HO^{\cdot} + H_2O + O_2 \qquad (14)$$

Baxendale et al. (19) demonstrated that the hydroxyl radicals produced by reaction (11) initiate polymerization. With increased monomer concentration reaction (12) is more and more suppressed until, finally at high monomer concentration all hydroxyl radicals are used for initiating polymerization.

Kolthoff and Medalia (21) showed that hydroxyl radicals from hydrogen peroxide are capable of oxidizing ethanol in accordance with the following chain reaction scheme:

$$HO^{\cdot} + CH_3CH_2OH \longrightarrow CH_3{}^{\cdot}CHOH + H_2O \tag{15}$$

$$CH_3CHOH + H_2O_2 \longrightarrow CH_2CHO + H_2O + HO^{\cdot} \tag{16}$$

In the presence of monomers, such as acrylonitrile, reactions (12) and (15) are suppressed, since all hydroxyl radicals are captured by the monomer.

It is assumed by some authors that hydroxyl radicals formed from hydrogen peroxide and ferrous ions react with cellulose in a similar manner to ethanol in reaction (15) and that radical formation caused by such hydrogen abstraction leads to active sites from which graft copolymerization can start:

$$\text{Cell-H} + HO^{\cdot} \longrightarrow \text{Cell}^{\cdot} + H_2O \tag{17}$$

However, from the suppression of the hydrogen abstraction from the alcohol mentioned above one has to conclude, as Hermans did, that cellulose will have to compete with the monomer, while at the same time, for grafting to occur, the cellulosic radical formed must be able to react with the monomer at a reasonable rate.

2.2 The Ceric Ion Initiation Method:

The Cerium (IV) initiation method has also been used quite extensively for the graft copolymerization of vinyl monomers to all kinds of cellulose substrates. In the present study, the ceric ion initiation method was used to graft methyl methacrylate monomer onto bleached kraft pulp.

American Cyanamid Company (21), starting in 1956, applied for a number of patents on the graft polymerization of vinyl monomers, especially esters of acrylic acid, with a cellulose substrate using cerium (IV) ions as catalysts. The original inventors, Mino and Kaizerman (21-23) have published a number of papers on this method, especially on the mechanisms of initiation.

The precise kinetics and mechanism governing the grafting of vinyl monomers onto cellulose are difficult to determine since the reaction is heterogeneous. Therefore a great deal of work has been performed on alcohols and other model compounds (1).

Duke and coworkers (24,25) examined the kinetics of ceric ion oxidation of glycols. Since tetravalent cerium has a coordination number of six, the formtion of mono-, di-, and triglycolated intermediates are possible:

$$CeX_6 + A \rightleftharpoons CeAX_4 + 2X \tag{18}$$

$$CeAX_4 + A \rightleftharpoons CeA_2X_2 + 2X \tag{19}$$

$$CeAX_2 + A \longrightarrow CeA_3 + 2X \qquad (20)$$

where A is a glycol, Ce is tetravalent cerium and X the groups co-ordinated with tetravalent cerium, e.g. OH^- .NO_3^- and H_2O .

It is generally assumed, as originally shown by Duke from his kinetic data (24) that only monoglycolated intermediates are formed to any appreciable extent. This intermediate then dissociates forming a free radical which is rapidly oxidized by another ceric ion as follows:

$$Ce(IV) + A \rightleftharpoons B \rightleftharpoons Ce(III) + A\cdot + H^+ \qquad (21)$$

$$Ce(IV) + A \longrightarrow \text{Products} + Ce(III) + H^+ \qquad (22)$$

where B is the complex formed.

Evidence of complex formulation between cerium (IV) and cellulose has been studied by several investigators (26-31). Kurlyankina and coworkers (26,27) observed spectroscopically that the ceric-cellulose complex had a characteristic absorption maximum at 320 mu. Others have proposed complex formation on the basis that the initial absorption of cerium (IV) was rapid and the amount absorbed was much greater than the carbonyl content of the cellulose (28-30).

From evidence available on the oxidation of cellulose, an intermediate complex appears to be formed between the ceric ion and the cellulose. This is followed by disproportionation of the complex to form a radical on the cellulose molecule (1).

The copolymerization of vinyl monomers initiated by free radicals, formed with ceric oxidized alcohols is expected to proceed according to the following reaction scheme (32):

INITIATION:

$$\mathrm{Ce(IV)} + A \rightleftharpoons B \longrightarrow A\cdot + \mathrm{Ce(III)} + H^+ \qquad (23)$$

$$A\cdot + M \longrightarrow M \qquad (24)$$

$$\mathrm{Ce(IV)} + M \longrightarrow M\cdot + \mathrm{Ce(III)} + H^+ \qquad (25)$$

PROPAGATION:

$$M\cdot_n + M \longrightarrow \dot{M}_{n+1} \qquad (26)$$

TERMINATION:

$$\dot{M}_n + \mathrm{Ce(IV)} \longrightarrow M_n + \mathrm{Ce(III)} + H^+ \qquad (27)$$

$$A\cdot + \mathrm{Ce(IV)} \longrightarrow \text{Oxidation products} + \mathrm{Ce(III)} + H^+ \qquad (28)$$

where A is the alcohol, M is the monomer and B is the ceric-alcohol complex.

A similar reaction scheme for the grafting of cellulose by the ceric ion method has been proposed by Ogiwara et al. (33), as shown below:

INITIATION:

$$\mathrm{Ce(IV)} + \mathrm{Cell{-}H} \rightleftharpoons \mathrm{Complex} \longrightarrow \mathrm{Cell}^{\cdot} + \mathrm{Ce(III)} + \mathrm{H}^{+} \quad (29)$$

$$\mathrm{Cell}^{\cdot} + \mathrm{M} \longrightarrow \mathrm{Cell{-}M}. \quad (30)$$

$$\mathrm{Ce(IV)} + \mathrm{M} \longrightarrow \mathrm{M}^{\cdot} + \mathrm{Ce(III)} + \mathrm{H}^{+} \quad (31)$$

PROPAGATION:

$$\mathrm{Cell{-}M}_n^{\cdot} + \mathrm{M} \longrightarrow \mathrm{Cell{-}M}_{n+1}^{\cdot} \quad (32)$$

$$\mathrm{Mm}^{\cdot} + \mathrm{M} \longrightarrow \mathrm{Mm}^{\cdot} +1 \quad (33)$$

TERMINATION:

$$\mathrm{Cell{-}M}_n^{\cdot} + \mathrm{Ce(IV)} \longrightarrow \mathrm{Cell{-}M}_n + \mathrm{Ce(III)} + \mathrm{H}^{+} \quad (34)$$

$$\mathrm{M}_m^{\cdot} + \mathrm{Ce(IV)} \longrightarrow \mathrm{M}_m + \mathrm{Ce(III)} + \mathrm{H}^{+} \quad (35)$$

$$\mathrm{Cell{-}Mn}^{\cdot} + \mathrm{Cell}^{\cdot} \longrightarrow \text{Stabilization} \quad (36)$$

$$\mathrm{Cell}^{\cdot} + \mathrm{Ce(IV)} \longrightarrow \text{Oxidation products} + \mathrm{Ce(III)} + \mathrm{H}^{+} \quad (37)$$

A similar reaction scheme has been proposed by other workers for the grafting of cellulosics (33-38).

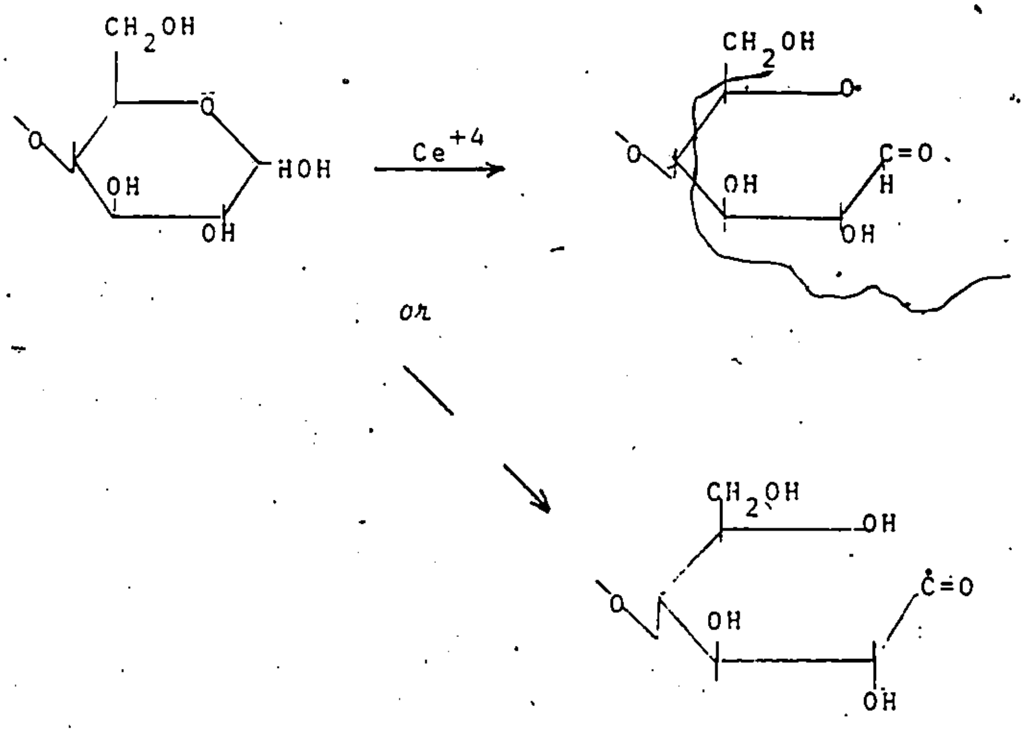
The cellulose molecule contains several possible sites for oxidation by ceric salts; The hydroxyl at the C_6 position, the glycol group at the C_2-C_3 position and the hydroxyl at the end of the cellulose chain. Many authors have examined model compounds to elucidate relative rates of oxidation of these sites. For example, Iwakura and coworkers (39) examined the polymerization of styrene initiated by free radicals formed on various alcohols by ceric ions. Since primary alcohols and

1,2-glycols were found most effective (1) it was concluded that polymerization onto cellulose would occur at the C_6 or C_2-C_3 positions.

Bergam et al. (40) found evidence of oxidation at the C_6 position since paper treated with NO_2, which preferentially attacks the C_6 carbon, failed to graft. It was noted that NO_2 oxidation is not totally selective and grafting at the C_2-C_3 position was also possible. Support for grafting at the C_2-C_3 glycol group with cleavage of the C_2-C_3 bond was obtained by others (24,40,41). The relative rates of oxidation of the C_6 hydroxyl and the C_2-C_3 glycol were examined by Hintz and Johnson (43). They used model compounds such as cyclohexane-methyl alcohol and tetrahydropyran-2-methyl alcohol for the C_6 hydroxyl, and trans-1,2 cyclohexanediol for the C_2-C_3 glycol. It was found that oxidation of cellulose with ceric ions will occur mainly at the C_2-C_3 glycol group and not the C_6 position. This increased reactivity of α-glycol groups was also observed by others (44,45).

Oxidation at the hemiacetal unit was also investigated. For example, model compounds containing a hemiacetal unit, such as glucose, were more readily oxidized than compounds in which this group was blocked, suchas α-methyl glucoside (28,41,46). It was found that vinyl polymerization also proceeded more rapidly when initiated by compounds containing hemiacetal units (47-51).

To further examine the most likely site of grafting, several polymers containing glucose residues were grafted with methyl methacrylate (51). Reduced reaction rates were noticed only for the polymers in which the site of glucose attachement to the polymer chain was the C_1 position. On the basis of these results, Imai, Masuhara, and Iwakura (51) proposed that the oxidation of cellulose by ceric ions occurred primarily at the hemiacetal unit, as illustrated below. They found the carbonyl radical (B) to be the most likely radical formed.



(38)

(39)

Pottenger and Johnson also found support for the rapid oxidation of the hemiacetal unit, i.e. reducing end group, using model compounds for cellulose (52). Other investigators have also noted the importance of the hemiacetal units in the ceric oxidation of cellulose (31,33,53-55).

In conclusion, it seems most likely that the oxidation and grafting of cellulose takes place predominantly at the reducing end group and the glycol units as opposed to the C_6 group.

O.Y. Mansour and A. Nagaty (36) carried out extensive studies on the graft copolymerization of vinyl monomers onto cellulose by use of tetravalent cerium. They concluded that in these grafting reactions, growing polymer radicals are produced mainly through the transfer of radicals formed at the cellulose backbone to the monomer where propagation takes place. The growing polymer radicals either recombine with active sites on the cellulose leading to grafting or react with each other through coupling and/or are oxidized with ceric ions to give homopolymer.

Chapter III

EXPERIMENTAL

In this chapter, the reactants, equipment and procedures used to carry out the experiments are described in detail.

3.1 Reactants:

Never-dry Hardwood bleached Kraft pulp supplied by THURSO PULP & PAPER (Thurso, Quebec) was used as the reaction substrate. The pulp was stored in a freezer before use. The Methyl Methacrylate monomer used came from two sources: Fisher Scientific (Nepean, Ontario) and Scientific Polymer Products Inc. (Ontario, New York). Both batches were inhibited with Hydroquinone. The first batch, from Fisher Scientific, was purified by vacuum distillation. The second batch was purified by passing the monomer, drop-wise, through a molecular sieve column packed with HR-4 (the columns and instructions were supplied by Scientific Polymer Products Inc.). Ceric Ammonium Nitrate used as the initiator was supplied by Fisher Scientific (Reagent Grade). Nitrogen gas cylinders with different oxygen concentrations were used. These were made-to-order mixtures of oxygen and nitrogen supplied by Air Products & Chemicals Inc. (Nepean, Ontario).

Oxygen, of 99.99% purity, was used to prepare different oxygen-in-nitrogen mixtures (1%, 5%, 10%, and 30% mixtures). The oxygen cylinders were also supplied by Air Products & Chemicals Inc. Hydroquinone (Reagent Grade) was used, as supplied by J.T. Baker Chemical Co. (Phillisburg, N.J.), to terminate the copolymerization reaction. Acetone (FCC specifications) was used, as supplied by Fisher Scientific, in extraction of the homopolymer from the reaction products.

3.2 EQUIPMENT

The reaction was carried out in a 2-litre Pyrex resin kettle equipped with a Teflon stirrer driven by a variable-speed electric motor. The configurations and dimensions of the reactor system are shown in figure (13).

The reactor was placed in a constant-temperature bath equipped with heating and cooling coils. The temperature of the bath was controlled by a Precision Temperature Controller (Model 245) made and supplied by Baley Instrument Company (Danville, California). This controller was able to keep the actual temperature within +/- 0.5° C of the set temperature (45°C). The speed of the stirrer was measured with a General Radio 1538-A STROBOTAC strobe light. The measurement of oxygen

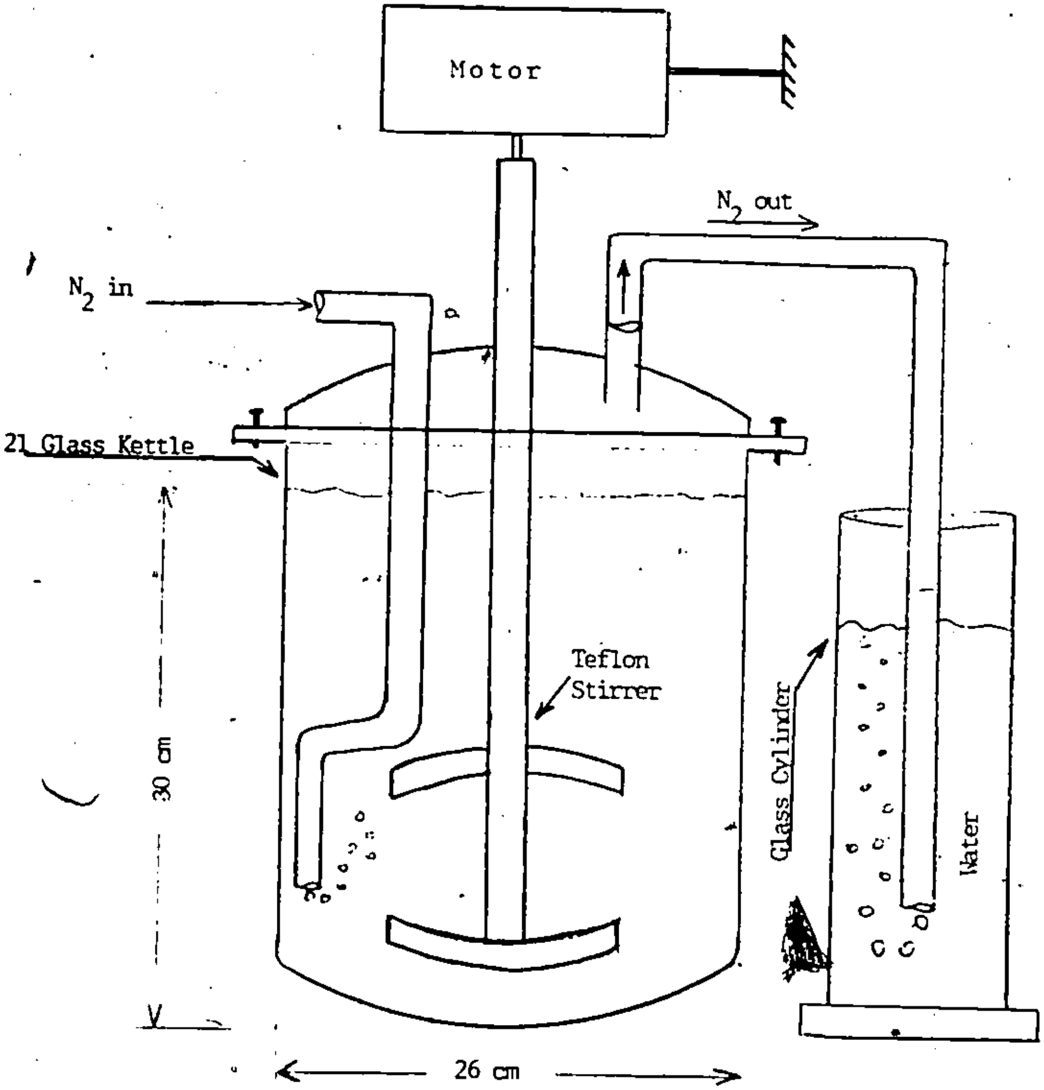


Figure 13: Reactor system

dissolved in the reaction mixture was taken with a YSI Model 54ARC oxygen meter made and supplied by Yellow Springs Instrument Co. (Yellow Springs, Ohio). The extraction of homopolymer from the reaction products was carried out by Soxhlet Extraction. The extraction unit used is illustrated in figure (14). The cellulose thimble used was supplied by Fisher Scientific. The drying of pulp samples and reaction products was carried out in an ISOTEMP vacuum oven (Model 281) supplied by Fisher Scientific.

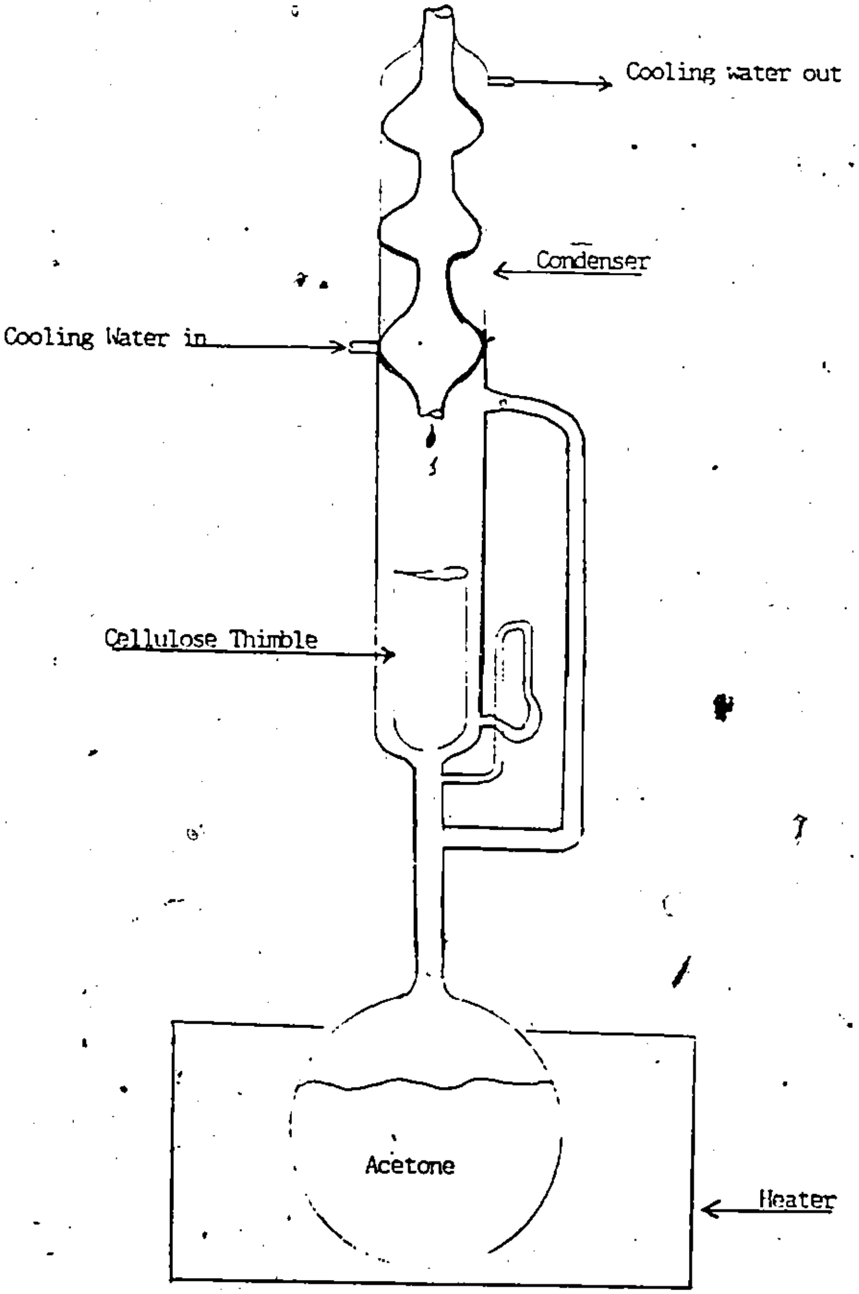


Figure 14: Soxhlet Extraction Unit

3.3 PROCEDURES

3.3.1 Determination of pulp consistency:

The consistency, or dryness, of the pulp used in the graft copolymerization was determined by taking a sample of frozen pulp (about 60 grams), thawing it, and drying it at about 110°C in the ISOTEMP vacuum oven for 24 hours. The dry sample was then cooled in a dessicator containing Silica gel for about one hour, then the sample was quickly weighed. The same procedure was repeated until constant weight was achieved. The consistency of the pulp was then calculated as follows:

% consistency = 100 x (dry wt. of sample)/(wet wt. of sample)

3.3.2 Reaction:

An amount of wet pulp having a dry weight of about 20 grams was charged in the reactor with distilled water. A nitrogen-oxygen mixture of desired ration was then bubbled in the reaction mixture, under continuous stirring, for about four hours. At the end of the Nitrogen-bubbling period, the concentration of dissolved oxygen was measured with the oxygen meter. A solution of about 6.07 g of Ceric Ammonium Nitrate in distilled water was then charged into the reactor. One minute later, about 25.66 g of Methyl Methacrylate monomer was also injected into the reactor. The reaction was assumed to have started at the moment the monomer was injected. The reaction was then allowed to proceed, at 45°C and constant stirring rate, for one hour; it was then terminated by injecting a solution of distilled water and about 1.7 grams of Hydroquinone.

3.3.3 Determination of Conversion and Grafting Efficiency

After the reaction was terminated, the products were filtered in a funnel with ordinary filter paper and thoroughly washed with distilled water. The reaction products were then dried, at about 100°C, in the vacuum oven, and weighed in a manner similar to the one described in section (2.3.1). The conversion to total polymer (or polymer yield) was calculated as follows:

$$\%\ \text{conversion to polymer} = 100 \times (D-B)/C$$

The homopolymer in the reaction products was then removed by Soxhlet Extraction (with Acetone as a solvent) for about 48 hours. The conversion to copolymer and the grafting efficiency were then calculated as follows:

$$\%\ \text{conversion to copolymer} = 100 \times (A-B)/C$$

$$\text{Grafting efficiency } (\%) = 100 \times (A-B)/(D-B)$$

where A is the dry wt. of the products after reaction and extraction, B is the dry wt. of pulp charged into the reactor, C is the wt. of the monomer charged into the reactor, D is the wt. of products after reaction and filtration.

Chapter IV

EXPERIMENTAL RESULTS

As was already mentioned, the main objectives of this study were to investigate the effects of the stirring rate (i.e. rpm of stirrer) and oxygen on the yield of the graft copolymerization of cellulose. In order to achieve that, experiments were carried out in sets consisting of four to five reactions each. Within each set, all reaction conditions, including the oxygen content in the nitrogen flow, were kept constant except for the stirrer rpm. The stirrer rpm was varied from ~~as~~ low as 10 rpm to as high as 1000 rpm in some cases. For each set of experiments, a different nitrogen-oxygen mixture was used. The experimental conditions of a typical experiment are shown in table (1).

In the first set of experiments, nitrogen with less than 1 ppm oxygen concentration was used. The oxygen dissolved in the reaction mixture was found to be 0.5 ppm (this was probably due to oxygen originally present in the solution and/or the frozen pulp). The experimental results of the first set are shown graphically in figure (15). These results show an initial increase of conversion as the stirrer rpm increases up to about 350 rpm. Both conversions then attain a constant level above this stirrer speed.

Table 1: Conditions of a typical experiment

Weight of wet pulp	119.80 g	+/- 0.01
Dry weight of pulp	20.00 g	+/- 0.01
Total reactor volume	2 litres	
Temperature	45.0°C	+/- 0.5
Weight of monomer	25.66 g	+/- 0.01
Weight of initiator	6.07 g	+/- 0.01
Stirrer rpm	Varies within each set	
Dissolved oxygen	Constant within each set	
Reaction time	1 hour	
Weight of Hydroquinone	1.70 g	+/- 0.01

Table (2) shows that the grafting efficiencies for the first set of experiments did not show any appreciable dependence on stirring rate. The grafting efficiencies, in this case, were found to be about 80%.

The second set of experiments was carried out with a higher purity nitrogen. For this set, the nitrogen grade used in set #1 was purified further by passing it through a heated column (450°C) packed with copper shavings. Furthermore, the monomer and initiator solution were deoxygenized by bubbling the purified nitrogen through them for about two hours prior to

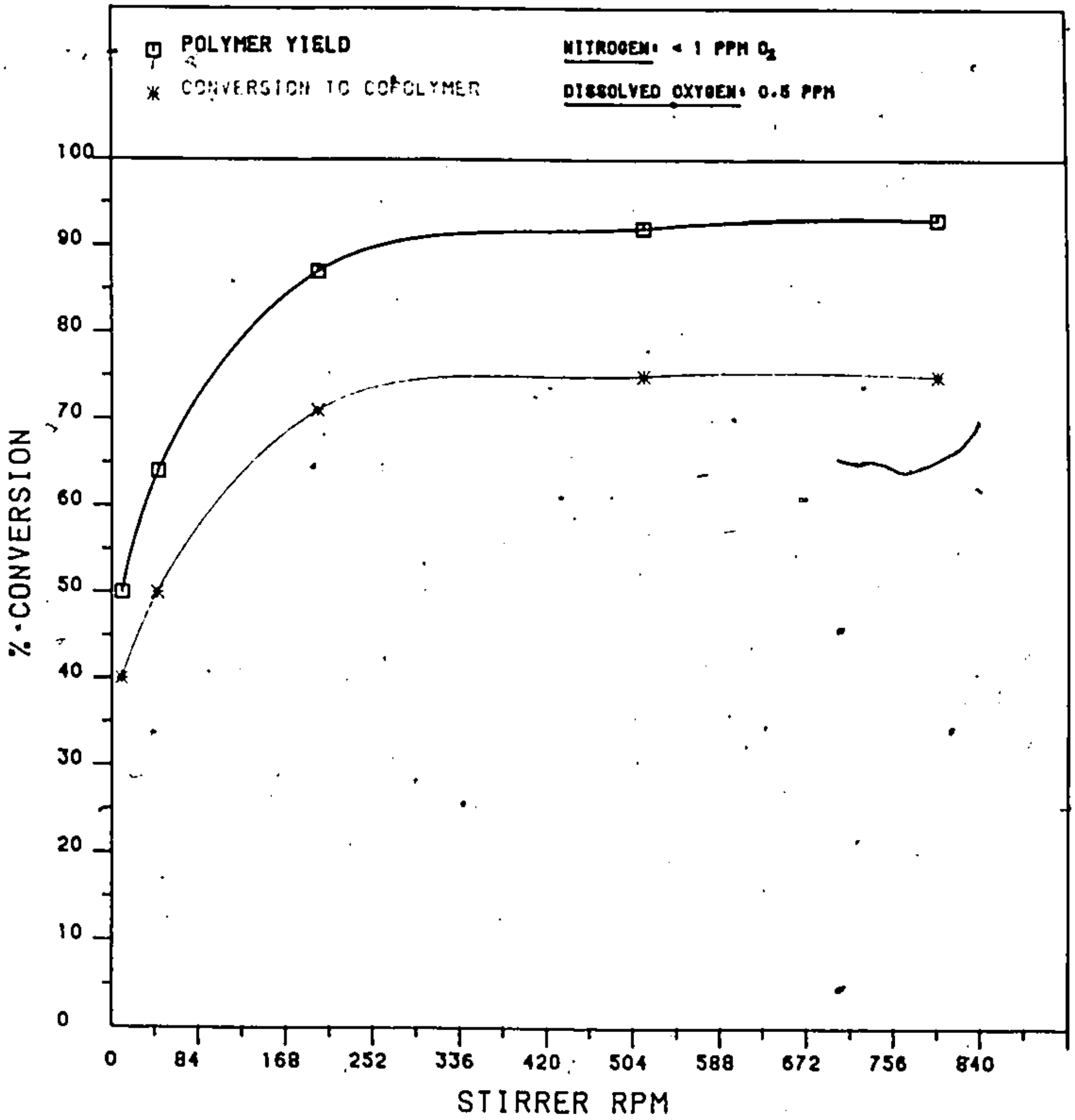


FIGURE 15

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Table 2: Grafting efficiency vs. stirrer rpm for set #1

STIRRER RPM	GRAFTING EFFICIENCY (%)
10	80.0
45	78.1
200	81.6
515	81.5
800	80.7

the reaction. The amount of dissolved oxygen was undetectable by the oxygen meter used in this study. The results of set #2 are shown in figure (16). The behaviour of the conversion vs. rpm curves for this set are similar to that of the first set except that the maximum conversion level attained is higher.

Table (3) shows the grafting efficiency vs. stirrer rpm for set #2. Here again, no appreciable dependency on stirring rate was observed. The values of the grafting efficiency ranged from 79 to 82%.

In the third set of experiments a mixture of 1% pure oxygen and 99% nitrogen (molar percentage) was used. The nitrogen

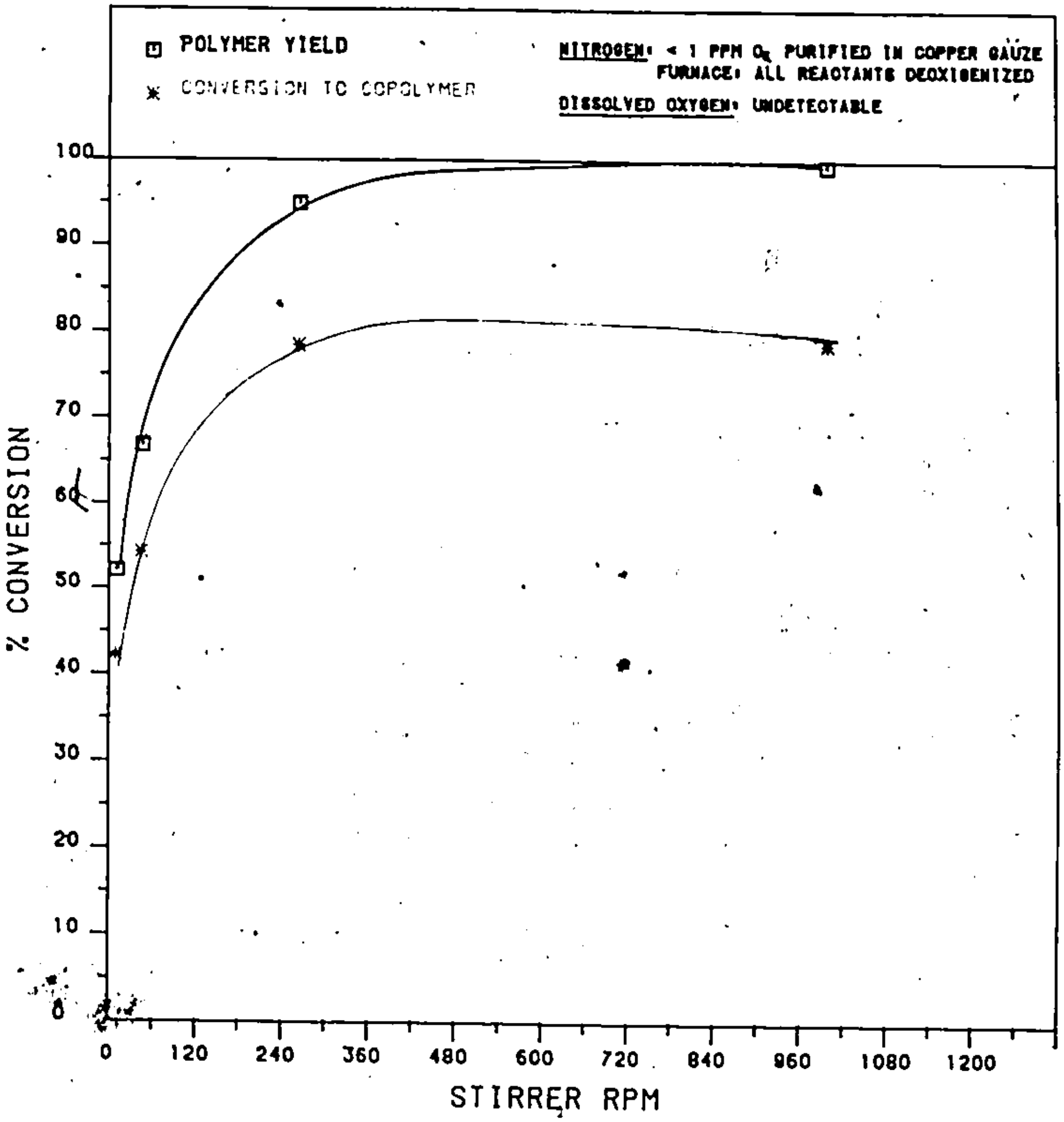


FIGURE 16

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Table 3: Grafting efficiency vs. stirrer rpm for set #2

STIRRER RPM	GRAFTING EFFICIENCY (%)
10	81.2
45	81.3
265	82.7
1000	79.2

used here was of the same grade used in the first set. The oxygen was of 99.99% purity. The mixture of oxygen and nitrogen was prepared using two pre-calibrated rotameters. The dissolved oxygen in the reaction mixture was found to be 0.6 ppm. The results of set #3 are shown in figure (17). A different behaviour of the conversion vs. rpm curves was obtained. A slight drop in conversions was observed at about 400 rpm.

The grafting efficiencies for set #3 are shown in table (4). Here again, no dependency on stirring rate was apparent.

The fourth set of experiments was carried out with a 5%-oxygen and 95%-nitrogen gas mixture. The dissolved oxygen was found to be 3 ppm. The results of this set are shown in

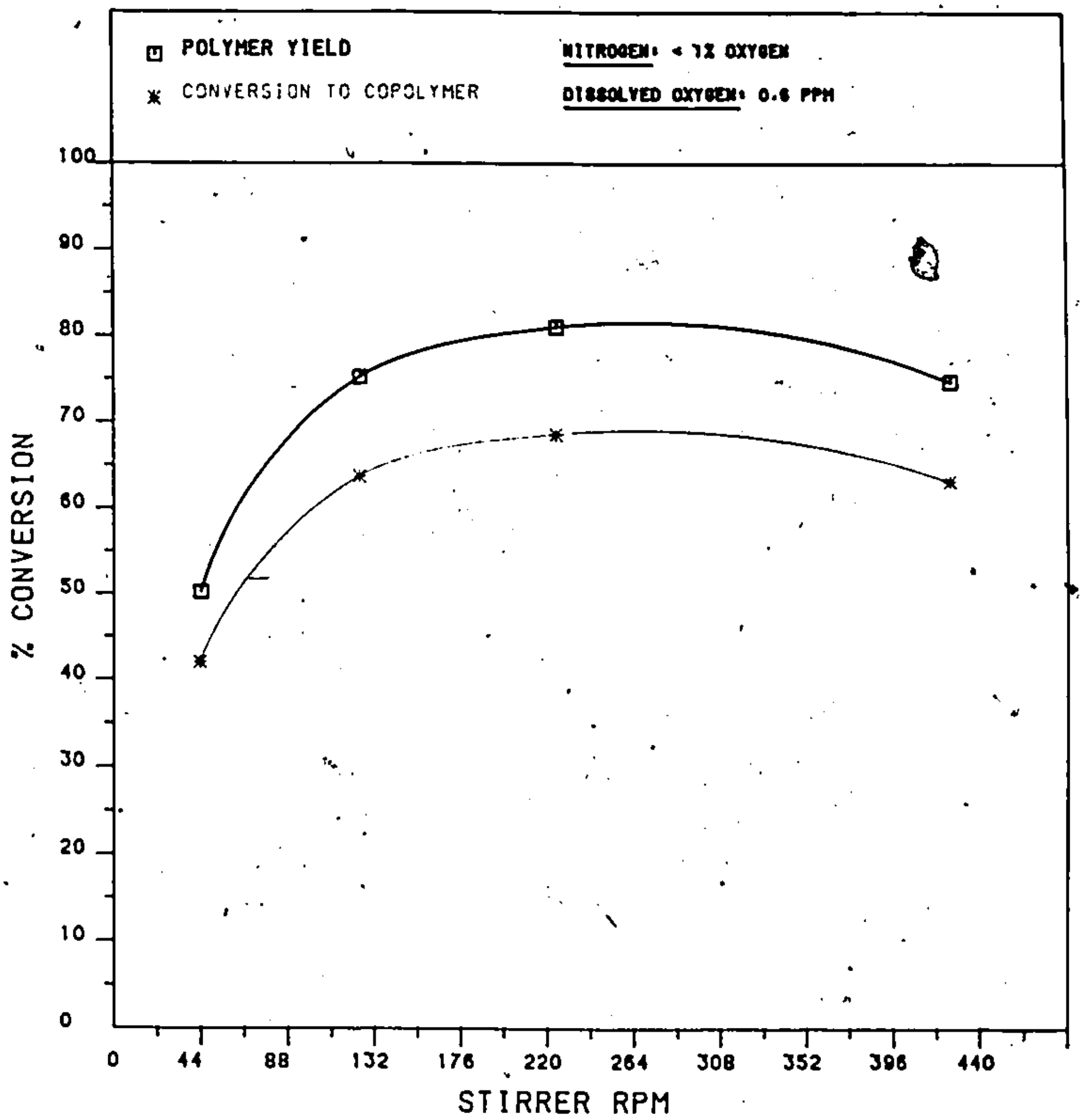


FIGURE 17

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Table 4: Grafting efficiency vs. stirrer rpm for set #3

STIRRER RPM	GRAFTING EFFICIENCY (%)
44	83.7
125	84.7
225	84.7
425	84.6

figure (18). In this set of experiments a new trend started to develop : An initial increase of conversion with an increase of rpm up to a certain maximum, followed by a gradual drop in conversions at higher stirrer rpm.

The values of the grafting efficiency for set #4 are shown in table (5). Although the grafting efficiencies for this set of experiments are lower than previous ones, they do not show strong dependence on stirring rate.

The results of the fourth set of experiments were indicating a significant and interesting effect of oxygen on the conversions of the graft copolymerization. It was then decided to try to increase the oxygen content in the oxygen-nitrogen mixture even further. A fifth set of experiments was carried out with 10%-oxygen and 90%-nitrogen. The dissolved

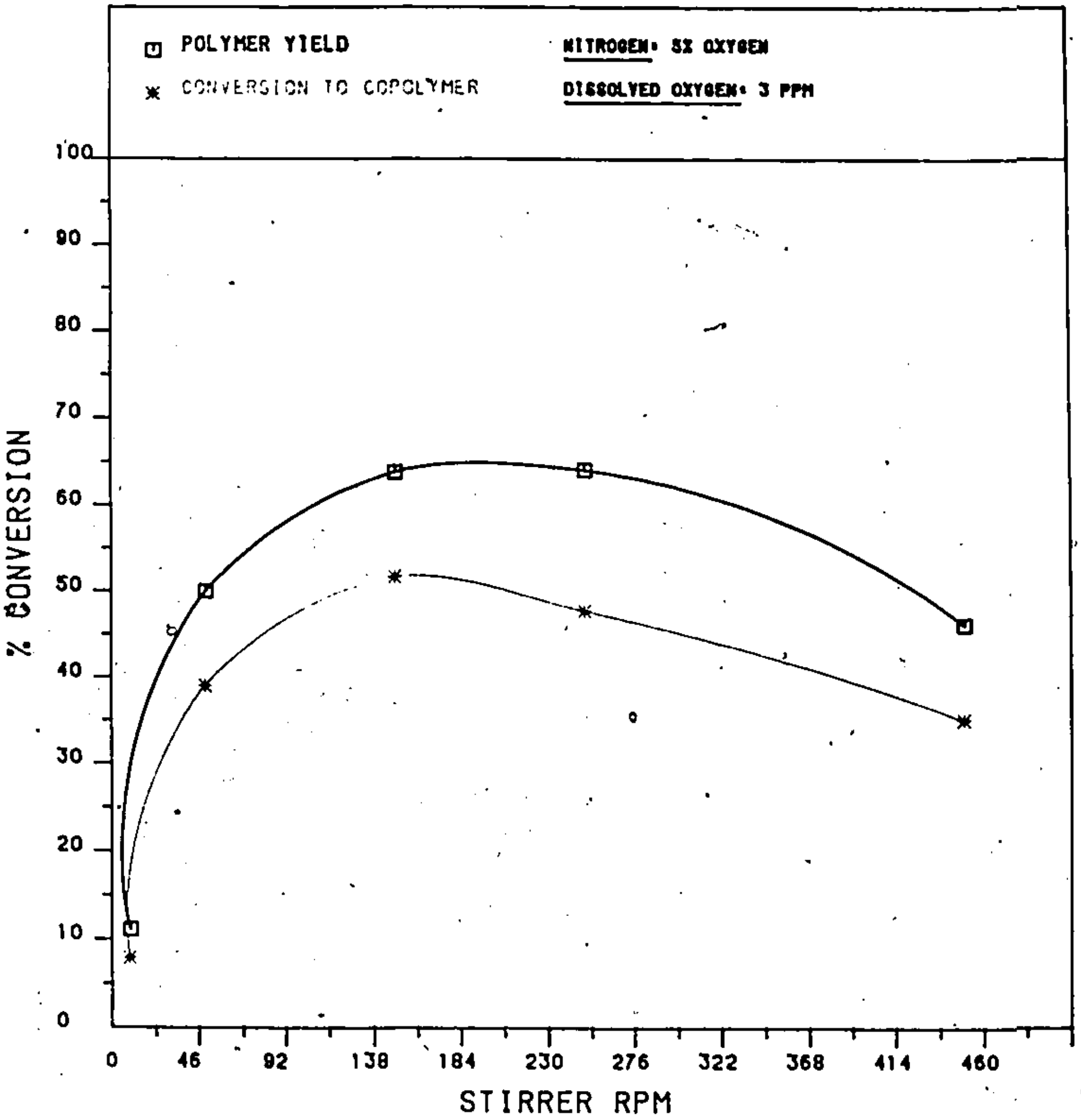


FIGURE 18

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Table 5: Grafting efficiency vs. stirrer rpm for set #4

STIRRER RPM	GRAFTING EFFICIENCY (%)
10	62.4
50	69.4
600	71.1
970	76.9

oxygen was found to be 5.5 ppm. The results of this set are shown in figure (19). The behaviour of the conversions vs. stirrer rp curves showed a drastic change from that of the first three sets. At lower stirrer rpm, an increase in conversions as the rpm is increased was observed. The conversions then reached well defined maximas followed by a quick drop as the stirrer rpm was increased. The conversions even reached zero at an rpm as low as 300. The maximum conversion reached in this set of experiments was about 48% (far below the maximum conversions obtained in the first four sets).

Table (6) shows that the grafting efficiency for this set of experiments started to show an appreciable dependency on the stirrer rpm. Figure (21-23) graphically presents the grafting efficiencies vs. stirrer rpm for sets #4, #5, and #6.

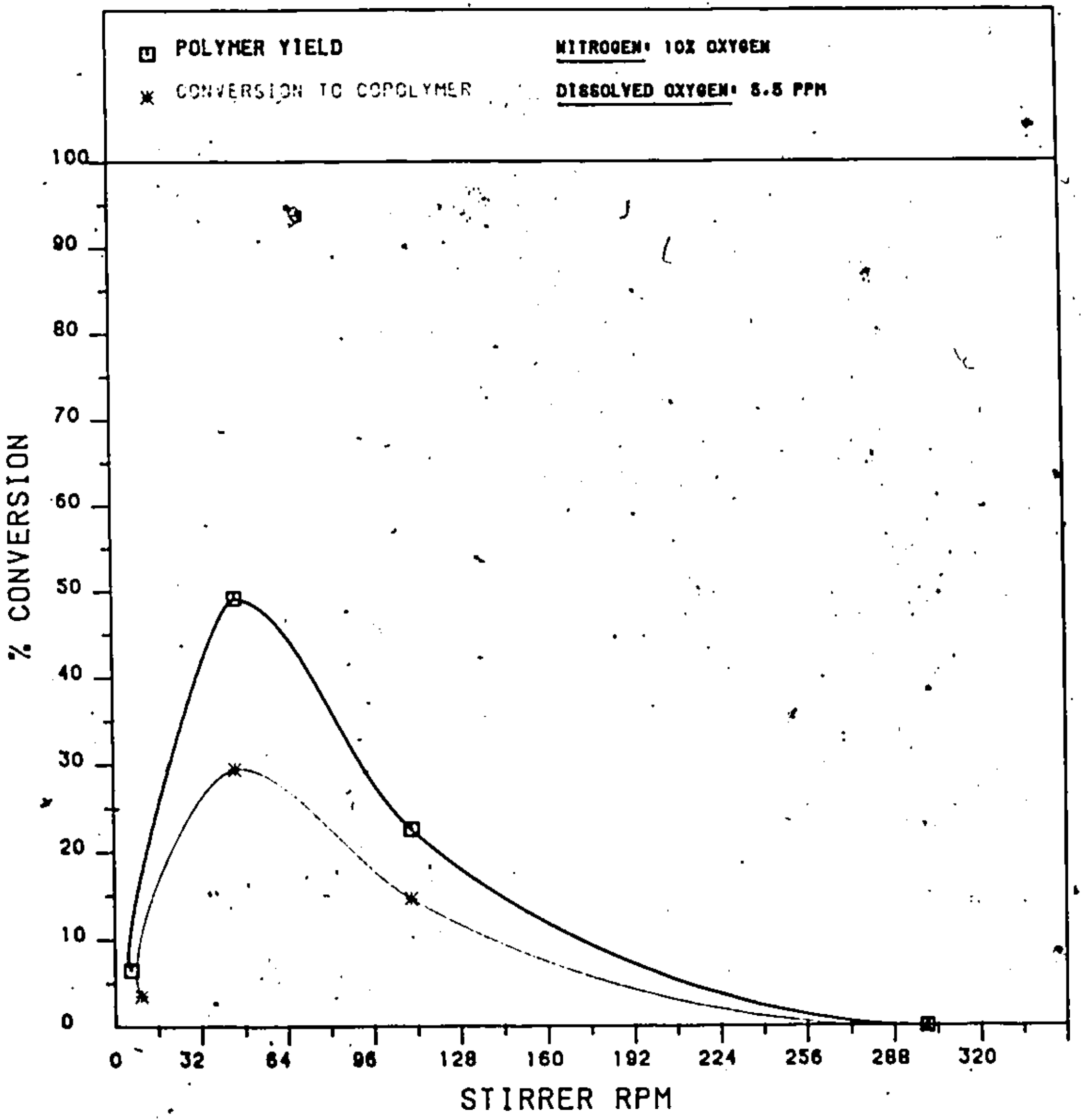


FIGURE 19

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Tabcap.Grafting efficiency vs. stirrer rpm for set #5

STIRRER RPM	GRAFTING EFFICIENCY (%)
10	53.8
45	60.0
110	65.0
250	----

A sixth set of experiments was carried out with a mixture of 30%-oxygen and 70%-nitrogen. The results of this set are shown in figure (20). The behaviour of the conversions vs. stirrer rpm curves were similar to that observed in the previous set, except that an even lower maximum conversion was observed.

Table (6) shows that the grafting efficiency for this set of experiments was significantly affected by the stirrer rpm.

A seventh set of experiments was carried out with nitrogen containing less than 1 ppm oxygen. The nitrogen was purified further by passing it through the heated copper column. The new aspect of this set was the use of a Stainless Steel stirrer instead of the Teflon stirrer. This set was carried

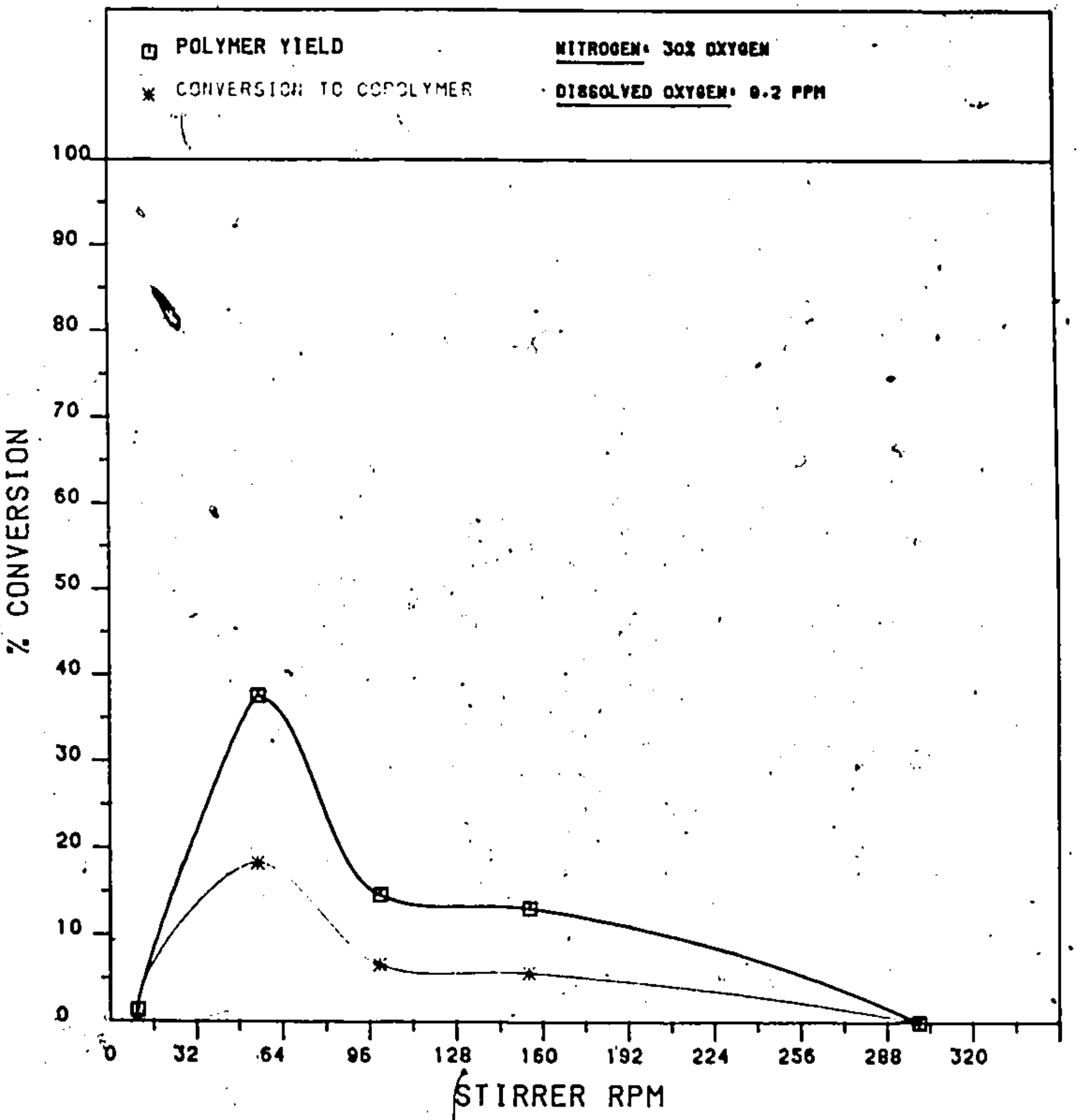


FIGURE 20

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Table 6: Grafting efficiency vs. stirrer rpm for set #6

STIRRER RPM	GRAFTING EFFICIENCY (%)
19	38.5
55	48.7
100	45.2
155	43.5

out in order to verify reports of a decrease in conversion when the graft copolymerization of cellulose was carried out in Stainless Steel vessels (36). The results of this set are shown in figure (24). These results showed conversions lower than those of the first set of experiments, although the dissolved oxygen in the last set of experiments was 0.3 ppm compared to 0.5 for the first set. The shape of the conversions vs. rpm curves was also found to be different.

An analysis of the significance of the results shown in the previous six figures will be presented in the next chapter.

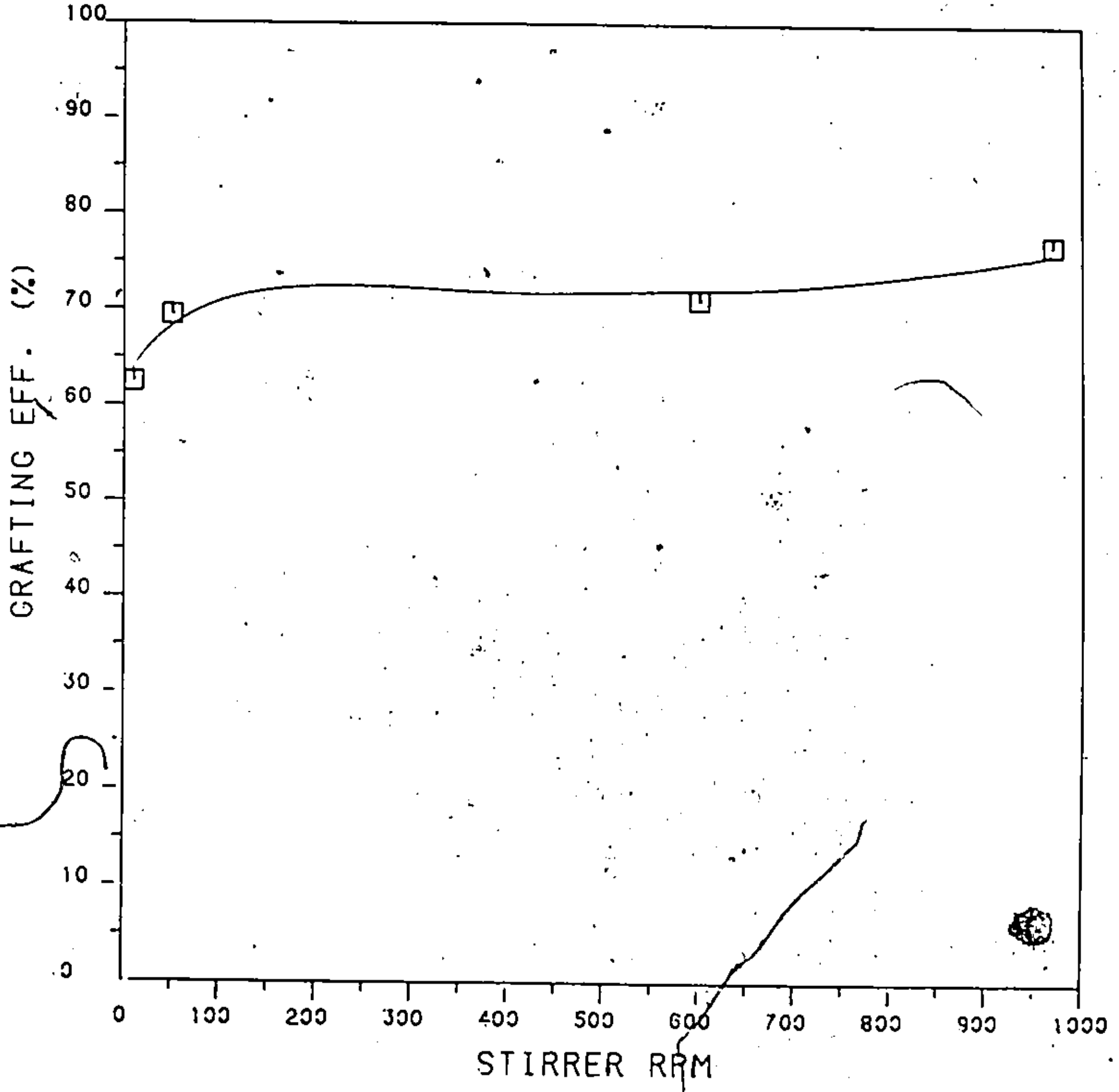


FIGURE 21

GRAFTING EFFICIENCY VS. STIRRER RPM

(set #4)

(Dissolved O_2 = 3.0 ppm)

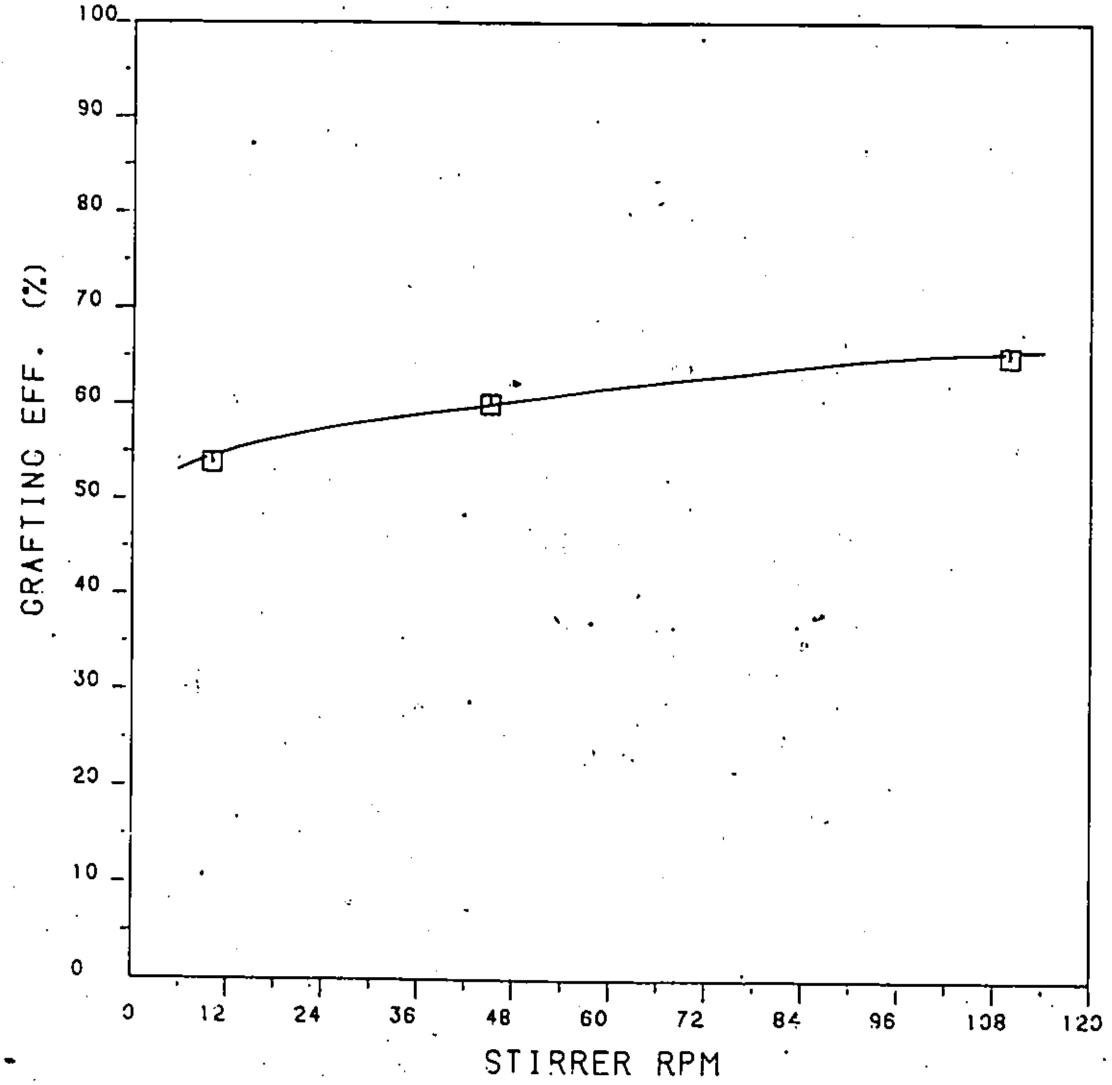


FIGURE 22

GRAFTING EFFICIENCY VS. STIRRER RPM

(set #5)

(Dissolved O_2 = 5.2 ppm)

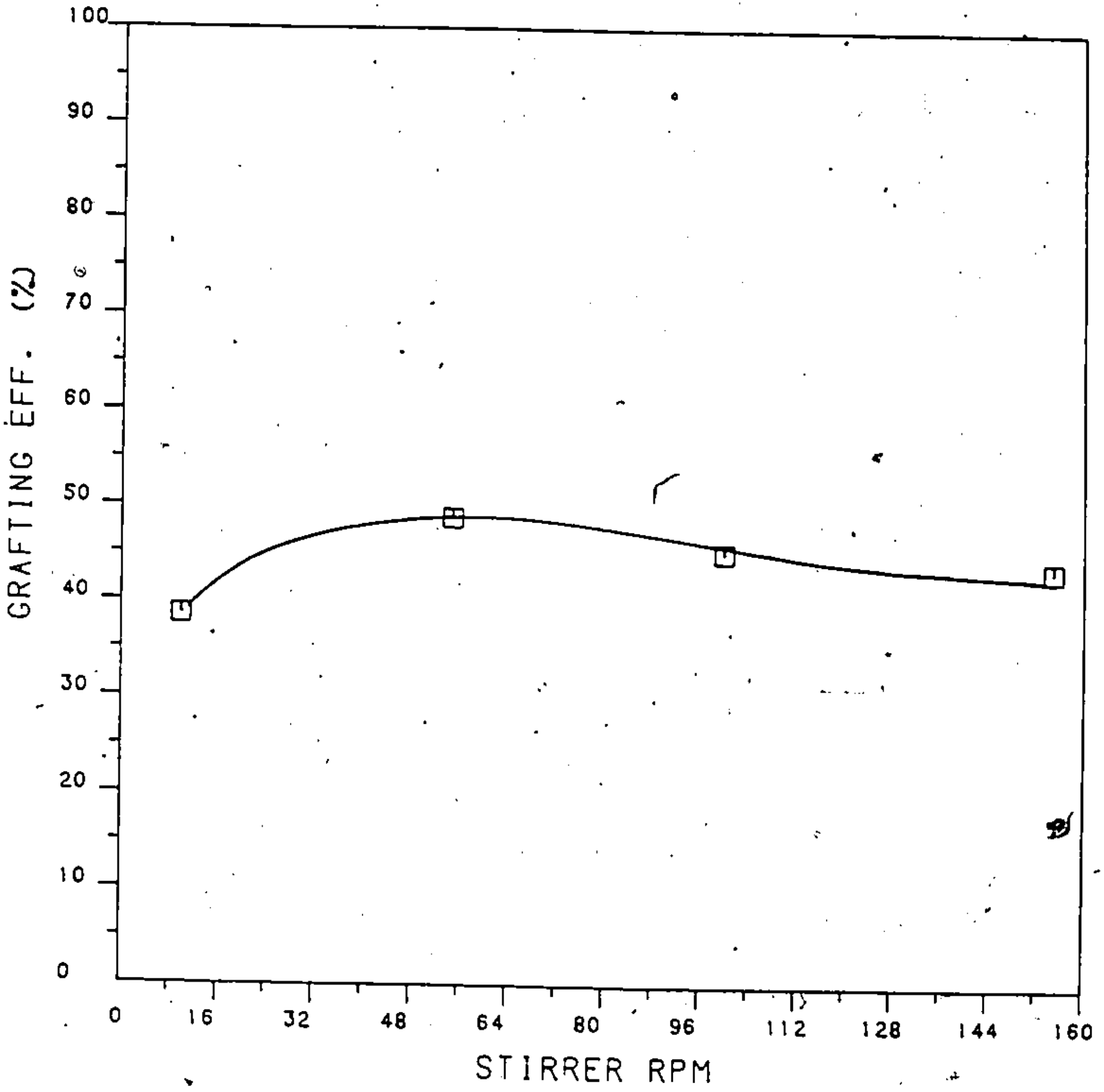


FIGURE 23

GRAFTING EFFICIENCY VS. STIRRER RPM

(set #6)

(Dissolved O_2 = 9.2 ppm)

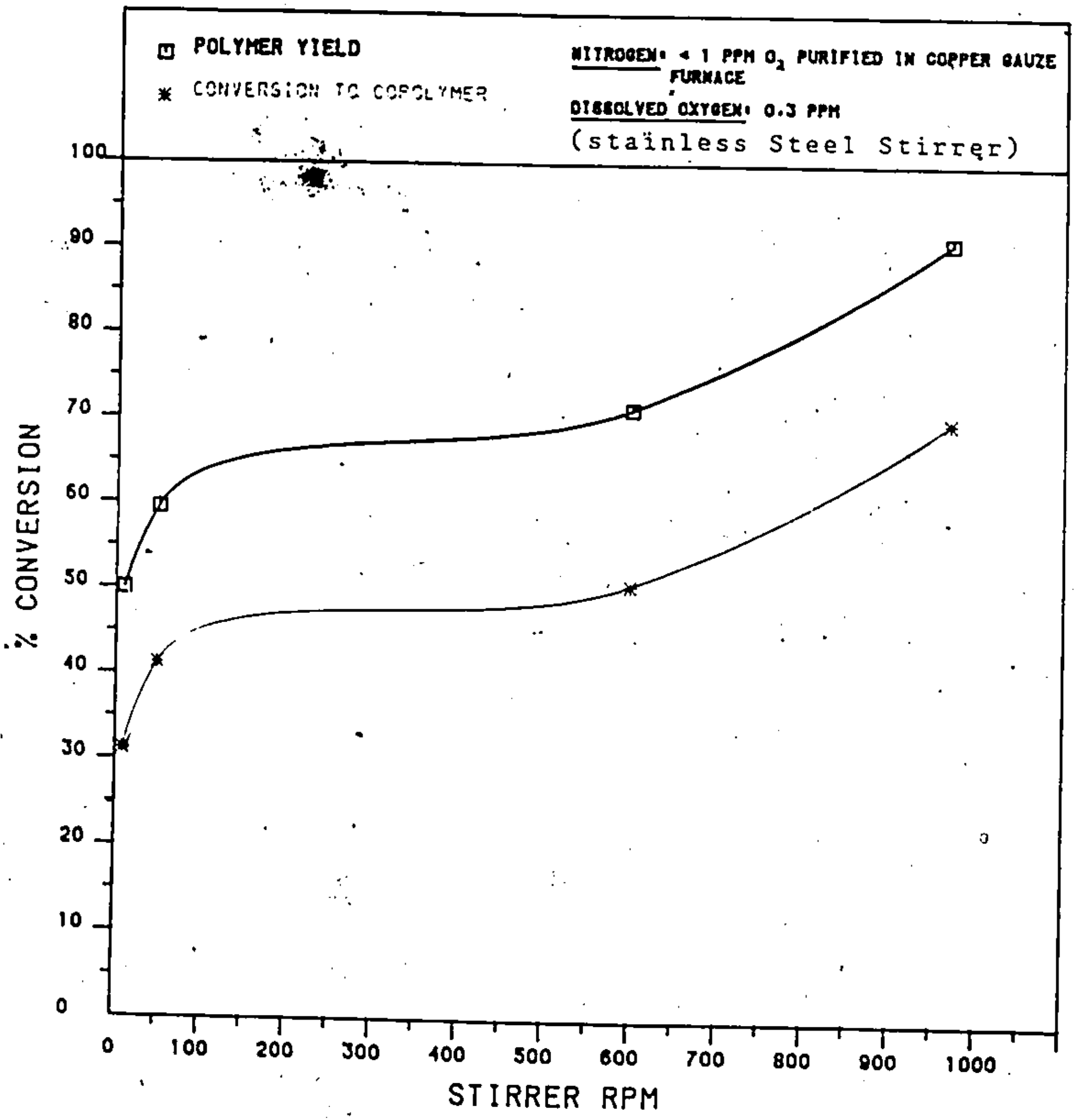


FIGURE 24

CONVERSION VS. STIRRER RPM
FOR THE GRAFT COPOLYMERIZATION
OF METHYL METHACRYLATE MONOMER
ONTO CELLULOSE BY CERIC IONS

Chapter V

DATA ANALYSIS AND DISCUSSION

All the experimental data obtained in this study tend to indicate that the dependencies of conversion on the stirring rate reported by Graczyk and Hornof (2-6) were probably due, mostly, to residual oxygen that might have been present in the reaction system at the start of the polymerization reaction or introduced in the course of the reaction by flushing the system with nitrogen containing small amounts of oxygen as an impurity.

Our data showed that when the reaction atmosphere and mixture were highly deoxygenized, the effect of stirring rate was confined to an initial increase of conversion with increased stirrer rpm, followed by a levelling-off of the conversion vs. rpm curve. The initial increase of conversion can be attributed to the enhanced mixing associated with an increase in stirrer rpm. Enhanced mixing is particularly important here because the reaction system is heterogeneous and the monomer is only partially soluble in water. The solubility of methyl methacrylate in water at 40°C was measured by simple titration and was found to be about 11.8 grams per litre of water. The actual concentration of methyl methacrylate at the onset of the reaction was 14.8 grams per litre of water. No drop in conversion was observed even at very high stirrer rpm. Thus, the assumption that the decrease of conversion obtained by Graczyk and Hornof (5) at high stirrer rpm was due to the instability of cellulose-initiator association complex due to high shear rate may be quetionable in the present system.

The observed increase, followed by a decrease of the conversion vs. stirrer rpm curves for systems with high oxygen contents could be easily explained. The initial increase of conversion with increased stirrer rpm is due to enhanced mixing, i.e. enhanced mass transport.

As the stirrer rpm is increased further, oxygen is transported from the reaction atmosphere into the reaction mixture at a higher rate, and a point is reached where the enhanced mixing brought about by the increase in stirrer rpm is offset and then outweighed by the inhibition of retardation effects of the oxygen being transported into the reaction mixture.

The experimental data obtained in this study were replotted as %-conversion vs. dissolved oxygen at constant stirrer rpm. The new curves are shown in figures (25) and (26). The effect of oxygen on the yield of the reaction now becomes quite obvious. It can be seen that increasing the dissolved oxygen level leads to lower conversions. Figure (26) shows that at very high oxygen contents a high stirring rate leads to very low conversions. This seems to support the explanations given above.

The grafting efficiencies were also plotted against the level of dissolved oxygen in figures (27) and (28). These figures clearly show a decrease in grafting efficiency with an increase in the level of dissolved oxygen.

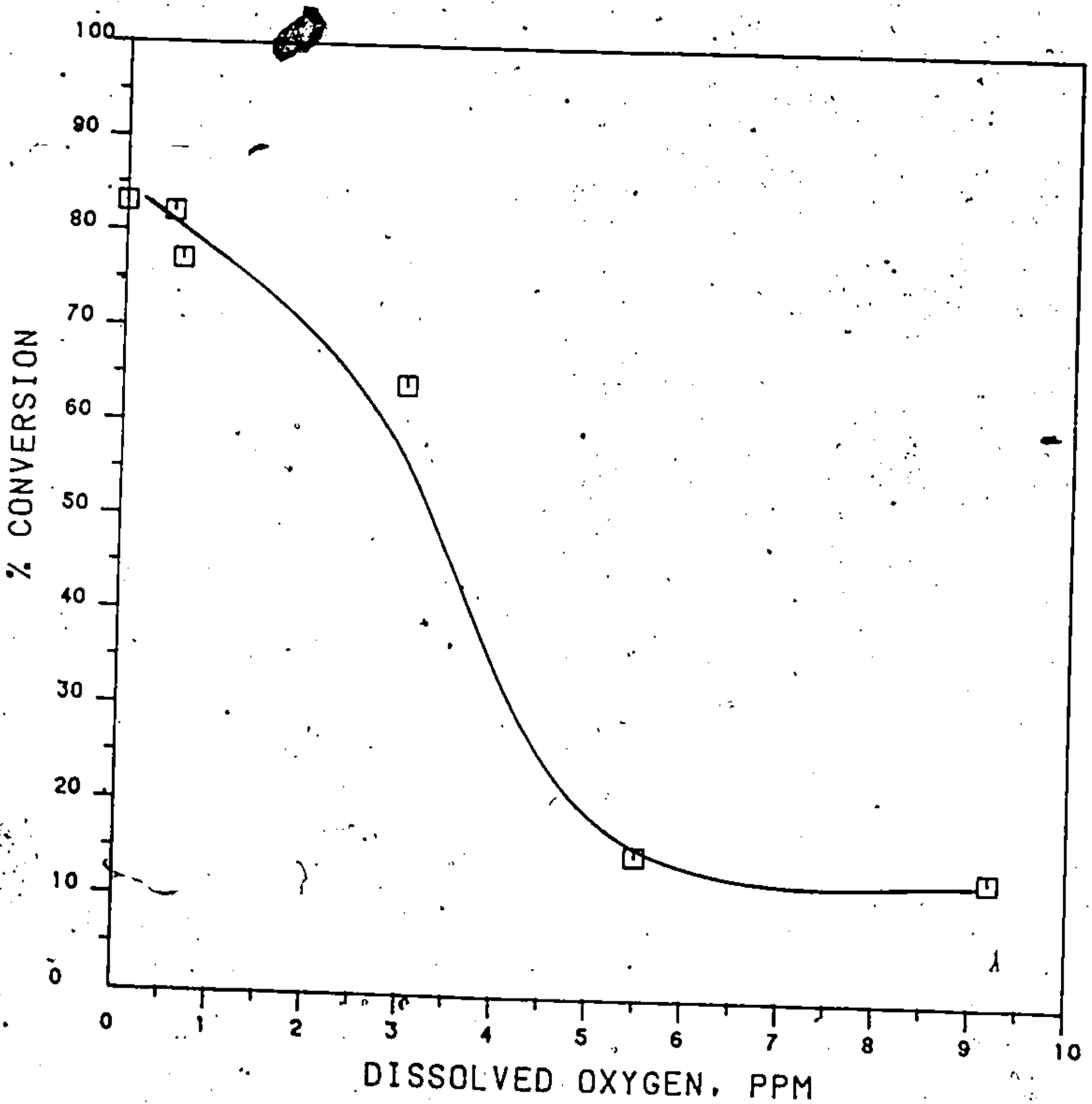


FIGURE 25

CONVERSION VS. DISSOLVED OXYGEN
STIRRER RPM = 150

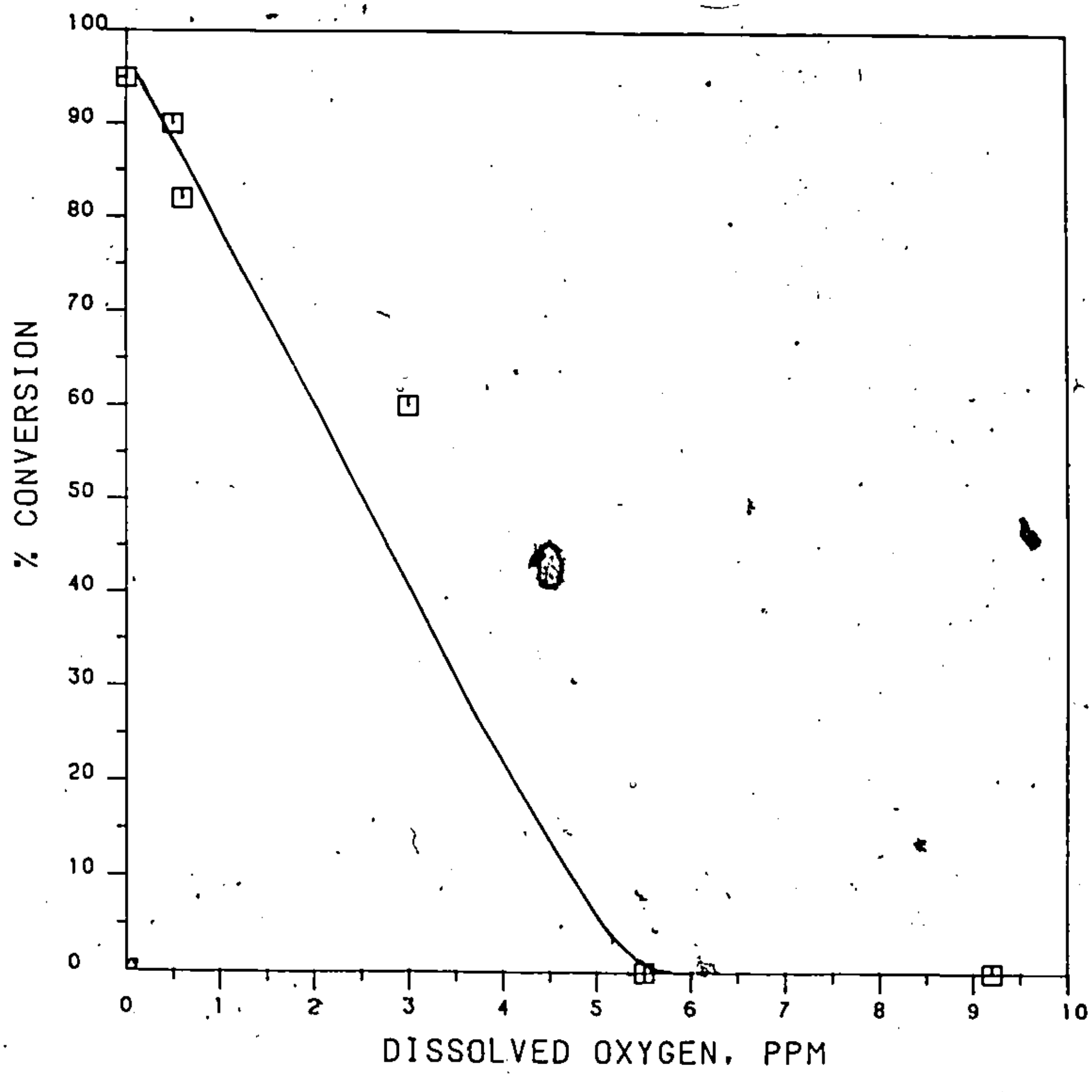


FIGURE 26

CONVERSION VS. DISSOLVED OXYGEN
STIRRER RPM = 300

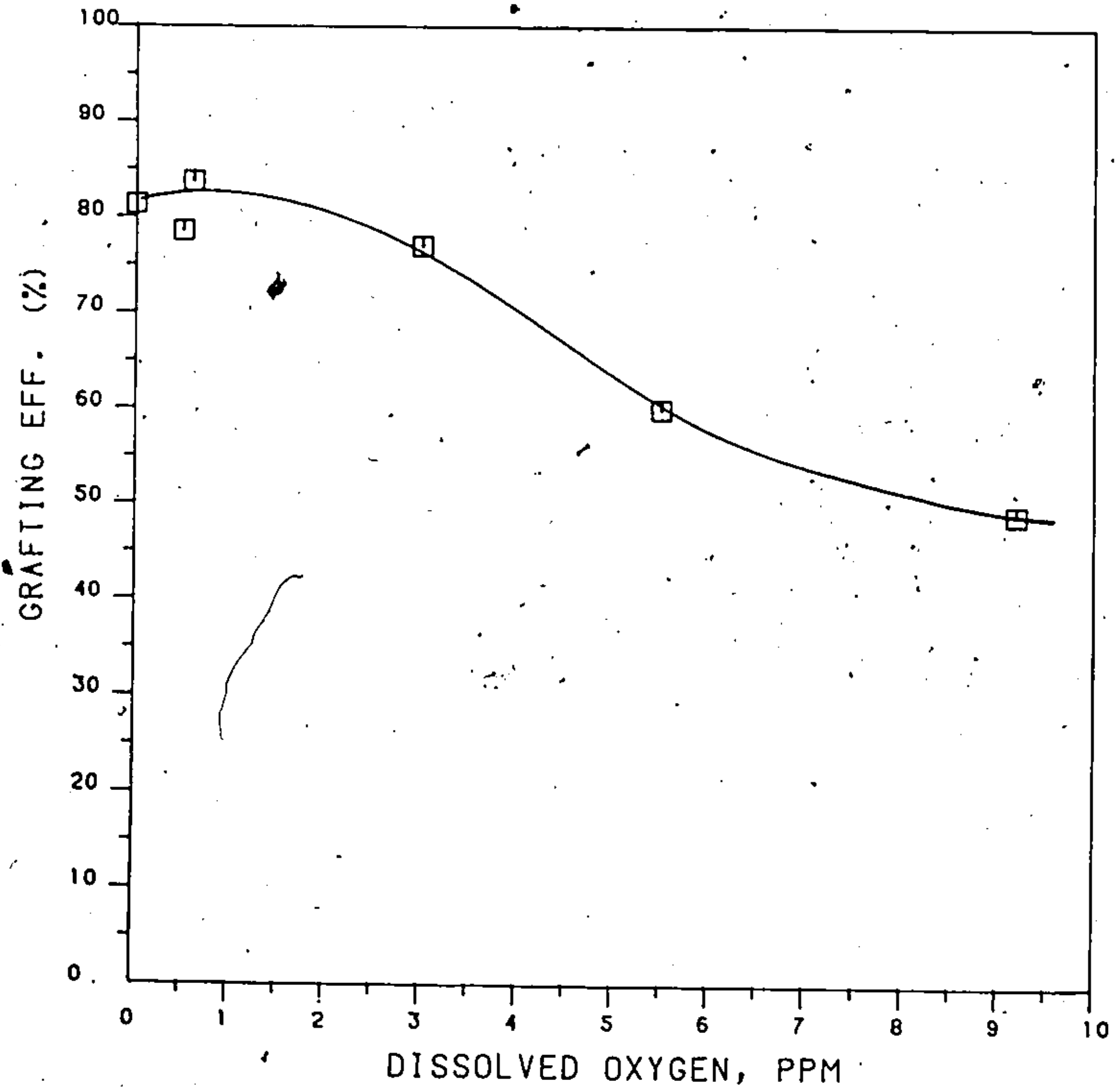


FIGURE 27

GRAFTING EFFICIENCY VS. DISSOLVED OXYGEN
STIRRER RPM = 50

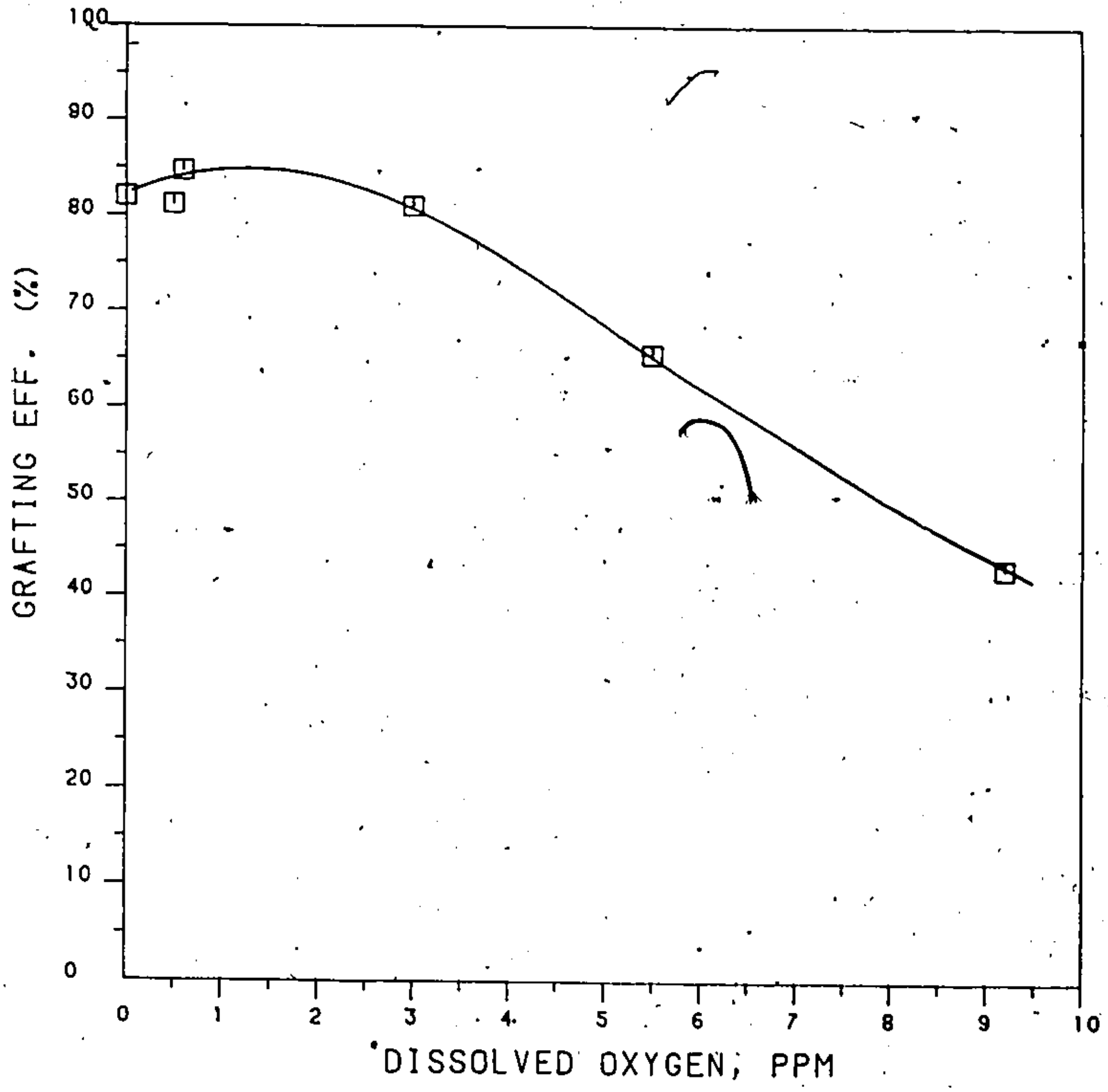


FIGURE 28

GRAFTING EFFICIENCY VS. DISSOLVED OXYGEN
STIRRER RPM = 150

The effect of oxygen and stirring rate on the graft copolymerization of styrene onto dissolving pulp by the Xanthate-Fe^{3+}- H_2O_2 system was studied by Graczyk and Hornof in a more recent paper (6). Their data clearly confirm that at high oxygen content (i.e. in air) the conversions were lower. When they used nitrogen instead of air, the conversions increased, but they were still able to observe a drop in conversion at high stirrer rpm. This could be due either to a different effect of oxygen in their reaction system, or to the presence of some oxygen impurities in the nitrogen (the quality of their nitrogen and the method of purification were not specified).

Other workers referred to the effects of oxygen and/or stirring. While some workers confirmed the importance of oxygen impurities, others stated that oxygen had no appreciable effects on the graft copolymerization.

In a paper published in 1972 Mamoru Namoura, Makota Harada, Wataru Eguchi and Shinji Nagata (56) discussed the effects of stirring on the emulsion polymerization of styrene. In their study they used different grades of nitrogen (i.e. N with different oxygen contents). They plotted their data as %-Conversion vs. reaction time, with the stirrer rpm being a parameter. In order to compare the results obtained by this group of researchers with the results obtained in the present study, their data was re- plotted as %-Conversion vs. stirrer rpm at constant reaction times. The new plots are shown in figure (29). Curve "A" represents data obtained when the reaction was carried out under a nitrogen of 99.9% purity passed through an alkaline pyrogallol solution. Curve "B", on the other hand, represents data obtained with the same grade of nitrogen that was passed through an alkaline pyrogallol solution then through an electric furnace containing copper gauze. The dependence of conversion on the stirrer rpm is obvious and it is more pronounced when the oxygen content in the reaction mixture is higher (i.e. curve "A"). Although their reaction system was very different from ours, the resemblance of the results in both studies is striking.

O.Y. Mansour and A. Nagaty (36) reported oxygen effects on the graft copolymerization of vinyl monomers onto cellulose by the tetravalent cerium initiation method. They observed that grafting yield and efficiency decreased when the reaction was carried out under unpurified nitrogen. The decrease was found to be greater on carrying out the grafting without a continuous stream of nitrogen. They concluded that the occluded air partially inhibited the graft copolymerization reaction. They also stated that this may indicate the free-radical nature of the reaction.

S. Kaizerman, G. Mino and L.F. Meinhold (57) stated, in a paper on the polymerization of vinyl monomers in cellulosic

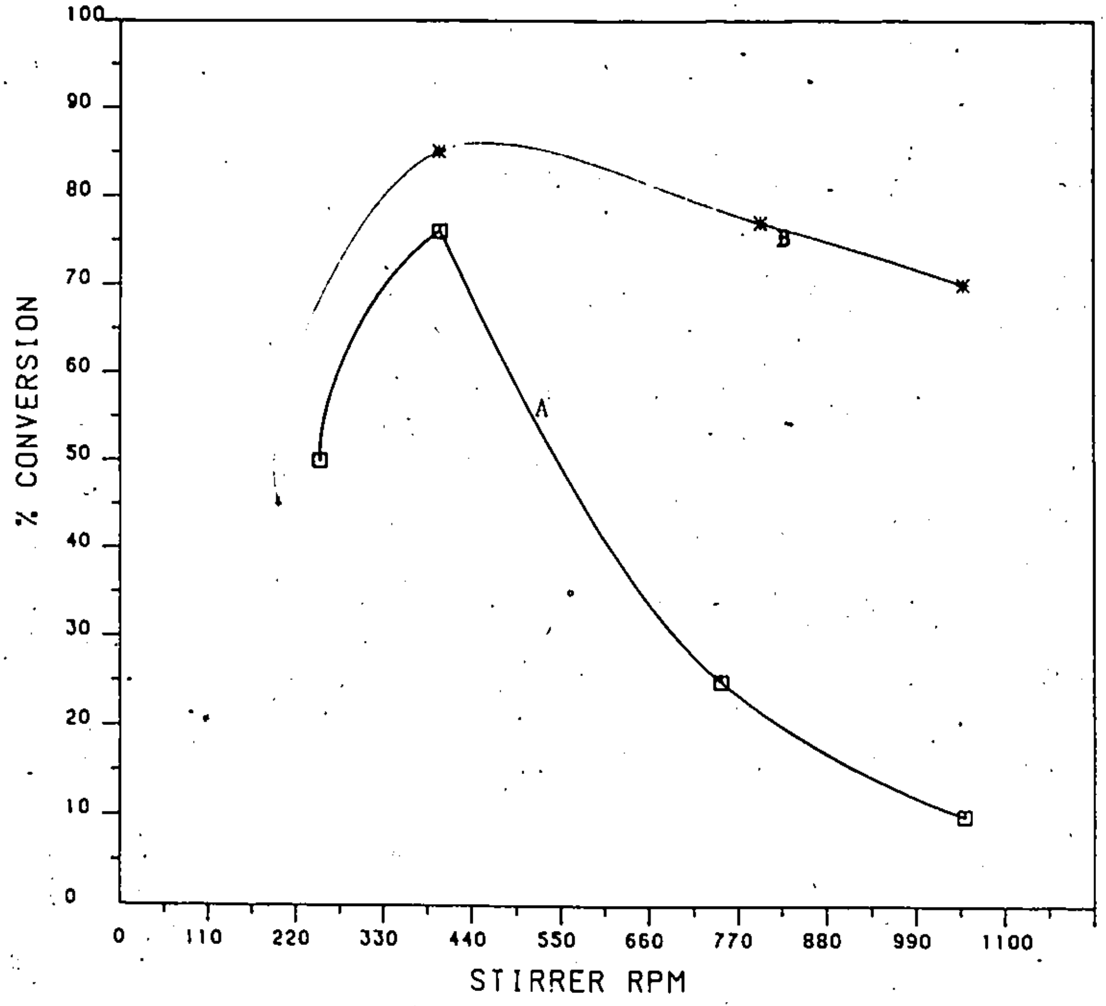


FIGURE 29

Conversion vs. Stirrer rpm for the Emulsion Polymerization of Styrene.

fibres by the ceric ion method, that displacing the air in the system by flushing with an inert gas such as nitrogen or carbon dioxide served to reduce the induction period of the reaction and to assure the prompt onset of polymerization within the fibres. However, they also indicated that homopolymerization in the reaction solution could be eliminated by including some air in the system. This last statement implies that the grafting efficiency would be improved by including some air in the reaction system. Our experimental data, as shown in figures (28) and (29), sharply contradict this statement.

In a paper on the preparation of highly branched graft copolymers by the ceric ion method, Y. Iwakura, Y. Imai and K. Yagi (48) indicated that they have bubbled nitrogen through the reaction solution for 30 minutes prior to the start of the grafting of methyl methacrylate onto poly (6-methacrylolyl-D-galactose). However, the quality of the nitrogen and the purification method were not specified. Many other workers mentioned the use of nitrogen instead of air, but very few of them elaborated on this aspect of their experiments.

E. Schwab, V. Stannett, D.H. Rakowitz and J.K. Magrane (58) studied the effect of nitrogen purge on the grafting of paper with vinyl monomers by the ceric ion method. They found that failure to purge the reaction system with nitrogen reduced the amount of graft obtained by almost 90% in the case of methyl methacrylate and by about 80% in the case of acrylonitrile. However, they did not report the quality of nitrogen they used.

On the other hand, in a paper on the effect of grafting on the dimensional stability of paper, Y. Ogiwara, H. Kubota, H. Murayama and A. Sakamoto (59) indicated that they carried out the graft copolymerization of methyl methacrylate and acrylonitrile onto paper in the presence of air. Also, A. Hebeish and P.C. Mehta (60) carried out a study on the cerium initiated grafting of acrylonitrile onto cellulosic materials and concluded that any traces of oxygen that may be occluded in the system did not inhibit grafting.

In a review paper on the grafting of vinyl monomers to cellulose by the ceric ion method, D.J. McKowall, B.S. Gupta and V.T. Stannett (1) stated that a decrease in grafting with increases in the intensity of agitation might result from the incorporation of oxygen into the reaction system.

The mechanism of the oxygen inhibition or retardation of the graft copolymerization of methyl methacrylate, or other vinyl monomers, onto cellulose is not well known. In fact, an extensive computer search for publications dealing with this topic was not successful.

One possible scheme for the effect of oxygen on the grafting reaction may be simplified as follows:

$$\text{Cell-H} + \text{Ce(IV)} \longrightarrow \text{Cell}^{\cdot} + \text{Ce(III)} + \text{H}^{+} \qquad (40)$$

$$\text{Cell}^{\cdot} + \text{M} \longrightarrow \text{Cell-M}^{\cdot} \qquad (41)$$

$$\text{Cell-M}^{\cdot} + (n-1)\text{M} \longrightarrow \text{Cell(M)}^{\cdot}\text{n} \qquad (42)$$

$$\text{Cell(M)}^{\cdot}\text{n} + \text{O}_2 \longrightarrow \text{Cell(M)nO-O.} \qquad (43)$$

The Cell (M)nO-O$^{\cdot}$ would be expected to be a low reactivity radical. It is important to note here that this scheme is a speculative one, and that we have no solid data to support it. More kinetic data is required in order to make reasonable assumptions about the ways in which oxygen affect the reaction.

Chapter VI

CONCLUSIONS

It was observed that the extent of the influence of the stirrer rpm on the conversions of the copolymerization reaction was dictated by the amount of oxygen present in the reaction mixture and atmosphere. At extremely low oxygen concentrations, the conversions (to both copolymer and homopolymer) increased initially with the increase of the stirrer rpm, then these conversions reached steady levels and did not drop even at very high stirrer rpm. At high oxygen concentrations (higher than 1%), the conversion-vs.-rpm curves showed an initial increase up to well defined maximum, followed by a sharp decrease as the stirrer rpm was increased. It was concluded that the drop in conversions at high stirrer rpm was due to the fact that increased stirring caused more oxygen to be transported from the reaction atmosphere to the reaction sites. This oxygen was believed to have inhibited or retarded the reaction.

The experimental data also showed that the grafting efficiencies did not depend on the stirrer rpm (at constant oxygen content). This was believed to be due to the fact that oxygen inhibited both the copolymerization and the homopolymerization reactions at approximately the same rate. However, lower grafting efficiencies were obtained when the oxygen content of the reaction system was raised.

Chapter VII

RECOMMENDATIONS FOR FUTURE STUDIES

More studies are needed in order to understand better the mechanism in which the oxygen affects the reaction. In the present study, the reaction time was fixed at one hour for all experiments. Thus, no time-vs.-conversion data is available at the present time. Such data could have helped improve our understanding of the phenomena observed in this study. Thus, we recommend that more experiments be carried out at different reaction times. We further recommend a study of the consumption rate of the initiator under different levels of oxygen in the reaction atmosphere.

REFERENCES

1. D.J. McDowal, B.S. Gupta and V. Stannett Grafting of Vinyl Monomers to Cellulose by Ceric Ion Initiation. Prog. Polym. Sc., 10, 1-50 (1984).
2. V. Hornof and T. Graczyk Influences of Stirring on the Efficiency of Grafting onto Cellulose. Polym. Prep., 23 (2), 124-125 (1982).
3. V. Hornof and T. Graczyk Effect of Stirring on Cellulose Graft Copolymerization. J. Appl. Polym. Sc., 28, 1371-1378 (1983).
4. V. Hornof and T. Graczyk Effect of Stirring on Cellulose Graft Copolymerization. J. Appl. Polym. Sc., 29, 4247-4255 (1984).
5. V. Hornof and T. Graczyk Effect of Stirring on Cellulose Graft Copolymerization: Grafting of Styrene by Initiation Systems Involving Potassium Persulfate. J. Appl. Polym. Sc., Polym. Chem. Ed., 23, 851-857 (1985).
6. V. Hornof and T. Graczyk Effect of Stirring on Cellulose Graft Copolymerization: Influence of Reaction Parameters. J. Appl. Polym. Sc., 30, 4175-4186 (1985).
7. H.A. Krassig and V. Stannett Graft Copolymerization to Cellulose and its Derivatives. J. Poly. Sc., 4, 157-235 (1965).

8. J. Borunsky Grafting Polymerizable Compounds onto Preformed Naturally Occurring Polymers. Can. Patent 549110 (Nov. 19, 1957).

9. V.A. Kargin, K.U. Usmanov, and B.I. Aikhodzhaev The Formation of Graft Polymers by Ozonation of Cellulose. Vyskomolekul. Soedin., No. 1, 149-151 (1959).

10. K.U. Usmanov, B.I. Aikhodzhaev, and U. Azizov Modification of the Properties of Cellulose by Means of Grafting. J. Polym. Sci., 53, 86 (1961).

11. Y. Landler, and P. Lebel Dutch Patent 1100286 (Feb. 23, 1961).

12. A. Fikler, S. Suta, and A. Alfoldi Preparation of Graft Copolymers from Regenerated Cellulose. C.A. 59, 12965 (1963).

13. J. Alfoldi, and M. Pasteka Grafting of Cellulose Acetate with Styrene. Chemicky prmysl, 13, No. 10, 554 (1963); C.A. 60, 7017 (1964).

14. I.M. Kolthoff and I.K. Miller The Chemistry of Persulfate. III. The reaction of persulfate with mercaptan solubilized in sodium laurate solution in the presence of unsaturated compounds. J. Am. Chem. Soc., 74, 4419 (1952).

15. P.D. Bartlett, and K. Nozaki Polymerization of allyl compounds. IV. Emulsion polymerization of allyl acetate. J. Polym. Sc., 3, 216 (1948).

16. I.M. Kolthoff, E.J. Meehan, and E.M. Carr Mechanism of initiation of emulsion polymerization by persulfate. J. Am. Chem. Soc., 75, 1439 (1953).

17. J. J. Hermans Chemical mechanisms in the grating of cellulose. Pure and Appl. Chem., 5, 154-155 (1962).

18. F. Haber, and J. Weiss The catalytic decomposition of hydrogen peroxide by iron salts. Proc. Roy. Soc. (London) a 147, 332, (1934).

19. J.H. Baxendale, M.G. Evans, and G.S. Park The mechanisms and kinetics of the initiation of polymerization by systems containing hydrogen peroxide. Trans. Faraday Soc., 42, 155 (1946).

20. I.M. Kolthoff, and A.I. Medalia Reaction between ferrous iron and peroxides. I. Reaction with hydrogen peroxide in the absence of oxygen. J. Am. Chem. Soc., 71, 3777 (1949).

21. G. Mino, and S. Kaizerman American Cyanamid Company: Process for polymerization of a vinylidene monomer in the presence of a ceric salt and an organic reducing agent. U.S. Patent 2,922,768 (Jan. 26, 1960).

22. G. Mino, S. Kaizerman, and E. Rasmussen Oxidation of pinacol by ceric sulfate. J. Am. Chem. Soc., 81, 1494, (1959).

23. G. Mino, and S. Kaizerman A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox systems. J. Polym. Sc., 31, 242 (1958).

24. F.R. Duke, and A.A. Forist The theory and kinetics of specific oxidation. III. J. Am. Chem. Soc., 71, 2790-2792 (1943).

25. F.R. Duke, and R.F. Bremer The theory and kinetics of specific oxidation. IV. J. Am. Chem. Soc., 73, 5179-5181 (1951).

26. V.I. Kurlyankina, V.A. Molotkov, O.P. Koz'mina, A.K. Khripunov and I.N. Shtennikova On the mechanism of grafting chains of synthetic polymers to cellulose using salts of transition metals. Eur. Polym. J., Suppl. 1969, 441-445 (1969).

27. V.I. Kurlyankina, O.P. Koz'mina, A.K. Khripunov, V.A. Molotkov, and T.D. Novoselova Complexing of cerium with cellulose and other hydroxyl-containing compounds. Dokl. Akad. Nuak. SSSR 172, 341-344 (CA 66:669 06U).

28. A.Y. Kulkarni, and P.C. Mehta Ceric ion-induced redox polymerization of acrylonitrile on cellulose. J. Appl. Polym. Sc., 12, 1321-1342 (1968).

29. A.Y. Kulkarni, and P.C. Mehta Oxidation of cellulose by ceric ion. J. Polym. Sc., part B, 5, 209-215 (1967).

30. Y.O. Ogiwara, Y.U. Ogiwara, and H. Kubota The mechanisms of consumption of ceric salt with cellulosic materials. J. Polym. Sc., part Ab-1, 6, 1489-1499.

31. I. Terasaki, and M. Matsuki Studies on oxidation of cellulose by ceric salts and graft copolymerization. Sen-i Gakkaishi 18, 147-152 (CA 56:14505h) (1962).

32. A.A. Katai, V.K. Kulshrestha, and R.H. Marchessault *Ceric ion-initiated polymerization of Acrylonitrile in the presence of alcohols.* J. Polym. Sc., Part C, 2, 403-414 (1963).

33. Y.O. Ogiwara, Y.U. Ogiwara, and H. Kubota *Effects of carbonyl and aldehyde groups in the graft copolymerization of methyl methacrylate on cellulose with a ceric salt.* J. Polym. Sc., Part A-1, 5, 2791-2805 (1967).

34. M.M. Huque, M. Habibuddowla, A.J. Mahmood, and A. Jabber Mian *Graft copolymerization onto Jute fibre: Ceric ion-initiated graft copolymerization of methyl methacrylate.* J. Polym. Sc., Poly. Chem. Ed., 18, 1447-1458 (1980).

35. I.M. Trivedi, and P.C. Mehta *Grafting of Acrylonitrile onto Jute fibres with ceric-ion initiation.* Cellulose Chem. Technol., 7, 401-416 (1973).

36. O.U. Mansour, and A. Nagaty *Some aspects of graft polymerization of vinyl monomers onto cellulose by use of tetravalent cerium. IV.* J. Polym. Sc., Chem. Ed., 12, 141-152 (1974).

37. H. Narita, U. Uchino, and S. Machida *Modification of textile fibres by graft copolymerization. I.* Sen-i Gakkaishi, 19, 225-229 (CA 62:13293g) (1963).

38. H. Kamogawa, and T. Sekiya *Graft polymerization of Acrylamide onto cotton fabric for further treatment.* Text. Res. J., 31, 585-591 (1961).

39. Y. Iwakura, T. Kurasaki, K. Uno, and Y. Imai *Reactive Fibre. II.* J. Polym. Sc., Part C, 4, 673-698 (1963).

40. F.R. Duke *The theory and kinetics of specific oxidation. I.* J. Am. Chem. Soc., 69, 2885-2888 (1947).

41. R.J.E. Cumberbirch, and J.R. Holker *Cerium-initiated polymerization of some vinyl compounds in cellulose fibres.* J. Soc. Dyers Colour., 82(2), 59-63 (1966).

42. N.V. Sarana, and V.I. Kurlyankina *Oxidation mechanism of hydroxyl-containing compounds by cerium (IV).* Trudy leningr. tekhnol. Inst. Tselklyul-Bum. Prom. 27, 235-242 (CA 77:90257f) (1970).

43. H.L. Hintz, and D.C. Johnson *The Mechanism of oxidation of cylic alcohols by cerium (IV).* J. Org. Chem., 32, 556-564 (1967).

44. G. Mino, S. Kaizerman, and E. Rasmussen *The oxidation of Polyvinyl alcohol by ceric ion.* J. Polym. Sc., 39, 523-529 (1959).

45. A.A. Il'In, L.S. Gal'Braikh, and B.P. Morin *Effect of the structure of Polysaccharide on their oxidation by cerium (IV).* Cellulose Chem. Technol. 14,327-338 (CA 94:84402j) (1980).

46. N.V. Sarana, V.I. Kurlyankina, and O.P. Koz'mina *Mechanism of initiation of graft polymerization on cellulose.* Khimiya Tekhnol. Proizvod. Tsellyul. 1971, 307-309 (CA 78:73818t) (1971).

47. Y. Iwakura, T. Kurosaki, and Y. Imai Graft copolymerization onto cellulose by the ceric ion method. J. Polym. Sc., Part A, 3, 1185-1193 (1965).

48. Y. Iwakura, Y. Imai, and K. Yagi Preparation of highly branched graft copolymers by the ceric ion method. J. Polym. Sc., Part A-1, 6, 801-807 (1968).

49. K. Matsuzaki, and T. Miyata Graft polymerization onto cellulose. Kami-pa Gikyoskhi 19, 575-583 (CA 64:8471d) (1965).

50. A. Ishizu, R. Lin, A. Sawatari, and T. Takashima Grafting of methyl methacrylate onto cellulose pretreated with Periodate by ceric ion method. Mokuzai Gakkaishi 17, 237-242 (CA 76:35369y) (1971).

51. Y. Imai, E. Masuhara[illegible]nd Y. Iwakura Initiation mechanism of cerium-initiated grafting onto cellulosic materials. J. Polym. Sc., Part B, 8, 75-79.

52. C.R. Pottenger, and D.C. Johnson Mechanism of cerium (IV) oxidation of glucose and cellulose. J. Polym. Sc., Part A-1, 8, 301-318 (1970).

53. A. Takahashi, and S. Takahashi Graft copolymerization on cellulose derivatives. 2. Kobunshi Kagaku 30, 239-243 (CA 79:55105z) (1973).

54. T. Sun, A. Chang, S. Huang, C. Chin, and P. Ch'Ien Chemical modification of cellulose. XV. ko Fen Tzu T'ang Hsun 8, 28-40 (CA 65:13939g) (1966).

55. Y.O. Ogiwara, Y.U. Ogiwara, and H. Kubota Graft polymerization of methyl methacrylate on pulp with ceric salt. Kogyo Kagaku Zasshi 70, 103-108 (CA 67:55272d) (1967).

56. M. Nomura, M. Harada, W. Egushi, and S. Nagata Effect of stirring on the emulsion polymerization of styrene. J. Poly. Sc., 16, 835-847 (1972).

57. S. Kaizerman, G. Mino, and L.F. Meinhold The polymerization of vinyl monomers in cellulosic fibres Textile Research Journal, pp. 136-140 (Feb. 1962).

58. E. Schwab, V. Stannett, D.H. Rakowtiz, and T.K. Magrane Paper grafted with vinyl monomers using the ceric ion method. Tappi, 45 (#5), 390-400 (1962).

59. Y. Ogiwara, H. Kubota, H. Murayana, and A. Sakomoto Effects of graft copolymerization on the dimensional stability of paper. Tappi, 53 (#9), 1685-1689 (1970).

60. A. Hebeish, and P.C. Mehta Cerium-initiated grafting of Acrylonitrile onto cellulosic materials. J. Appl. Polym. Sc., 12, 1625-1647 (1968).

61. C. Marie, and J. Bunel Sur le dosage des persulfates. Bull. Soc. Chim. France, 29, 930 (1903).

Appendix

SUMMARY OF EXPERIMENTAL DATA

Table 7: RAW DATA FOR SET #1

Weight of wet pulp	(g)	119.77
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	0.5
Temperature	(C)	40.0
Reaction time	(min.)	50.0
EXTRACTION:		
Dry weight of sample	(g)	7.28
Dry wt. after extraction	(g)	6.67
CALCULATIONS:		
% Conversion to polymer		50.8
% Conversion to copolymer		40.1
% grafting Efficiency		78.9

Table 8: RAW DATA FOR SET #1

Weight of wet pulp (g)	119.86
Dry weight of pulp (g)	20.02
Weight of monomer (g)	25.94
Weight of initiator (g)	6.10
Stirrer rpm	45
Dissolved oxygen (ppm)	0.5
Temperature (C)	40.0
Reaction time (min.)	60.0
EXTRACTION:	
Dry weight of sample (g)	8.10
Dry wt. after extraction (g)	7.32
CALCULATIONS:	
% Conversion to polymer	64.2
% Conversion to copolymer	50.7
% grafting Efficiency	79.0

Table 9 RAW DATA FOR SET #1

Weight of wet pulp	(g)	119.86
Dry weight of pulp	(g)	20.02
Weight of monomer	(g)	25.94
Weight of initiator	(g)	6.10
Stirrer rpm		200
Dissolved oxygen	(ppm)	0.5
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	8.31
Dry wt. after extraction	(g)	7.49
CALCULATIONS:		
% Conversion to polymer		87.4
% Conversion to copolymer		71.1
% grafting Efficiency		81.4

Table 10: RAW DATA FOR SET #1

Weight of wet pulp	(g)	119.77
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.94
Weight of initiator	(g)	6.10
Stirrer rpm		515
Dissolved oxygen	(ppm)	0.5
Temperature	(.C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	10.12
Dry wt. after extraction	(g)	9.07
CALCULATIONS:		
% Conversion to polymer		92.6
% Conversion to copolymer		75.0
% grafting Efficiency		81.0

Table 11: RAW DATA FOR SET #1

Weight of wet pulp	(g)	119.77
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.94
Weight of initiator	(g)	6.10
Stirrer rpm		800
Dissolved oxygen	(ppm)	0.5
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	9.53
Dry wt. after extraction	(g)	8.55

CALCULATIONS:

% Conversion to polymer	93.2
% Conversion to copolymer	75.7
% grafting Efficiency	81.2

Table 12: RAW DATA FOR SET #2

Weight of wet pulp	(g)	110.38
Dry weight of pulp	(g)	20.20
Weight of monomer	(g)	26.00
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	Undetectable
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.11
Dry wt. after extraction	(g)	6.57
CALCULATIONS:		
% Conversion to polymer		52.1
% Conversion to copolymer		42.3
% grafting Efficiency		81.2

Table 13: RAW DATA FOR SET #2

Weight of wet pulp	(g)	110.37
Dry weight of pulp	(g)	20.20
Weight of monomer	(g)	26.00
Weight of initiator	(g)	6.10
Stirrer rpm		45
Dissolved oxygen	(ppm)	Undetectable
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	8.02
Dry wt. after extraction	(g)	7.32

CALCULATIONS:

% Conversion to polymer	66.8
% Conversion to c[illegible]lymer	54.3
% grafting Efficiency	81.3

Table 14: RAW DATA FOR SET #2

Weight of wet pulp	(g)	110.64
Dry weight of pulp	(g)	20.25
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		265
Dissolved oxygen	(ppm)	Undetectable
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.01
Dry wt. after extraction	(g)	6.35
CALCULATIONS:		
% Conversion to polymer		94.9
% Conversion to copolymer		78.5
% grafting Efficiency		82.3

Table 15: RAW DATA FOR SET #2

Weight of wet pulp	(g)	110.38
Dry weight of pulp	(g)	20.20
Weight of monomer	(g)	26.00
Weight of initiator	(g)	6.10
Stirrer rpm		1000
Dissolved oxygen	(ppm)	Undetectable
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	6.78
Dry wt. after extraction	(g)	5.98
CALCULATIONS:		
% Conversion to polymer		99.4
% Conversion to copolymer		78.7
% grafting Efficiency		79.2

Table 16: RAW DATA FOR SET #3

Weight of wet pulp (g)	120.50
Dry weight of pulp (g)	20.00
Weight of monomer (g)	25.92
Weight of initiator (g)	6.10
Stirrer rpm	44
Dissolved oxygen (ppm)	0.6
Temperature (C)	40.0
Reaction time (min.)	60.0
EXTRACTION:	
Dry weight of sample (g)	7.15
Dry wt. after extraction (g)	6.69
CALCULATIONS:	
% Conversion to polymer	50.2
% Conversion to copolymer	42.0
% grafting Efficiency	83.7

Table 17: RAW DATA FOR SET #3

Weight of wet pulp	(g)	120.52
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		125
Dissolved oxygen	(ppm)	0.6
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	8.02
Dry wt. after extraction	(g)	7.41
CALCULATIONS:		
% Conversion to polymer		75.2
% Conversion to copolymer		63.7
% grafting Efficiency		84.7

Table 18: RAW DATA FOR SET #3

Weight of wet pulp	(g)	120.51
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		225
Dissolved oxygen	(ppm)	0.6
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	6.20
Dry wt. after extraction	(g)	5.71
CALCULATIONS:		
% Conversion to polymer		81.0
% Conversion to copolymer		68.6
% grafting Efficiency		84.7

Table 19: RAW DATA FOR SET #3

Weight of wet pulp (g)	120.50
Dry weight of pulp (g)	20.00
Weight of monomer (g)	25.92
Weight of initiator (g)	6.10
Stirrer:rpm	425
Dissolved oxygen (ppm)	0.6
Temperature (°C)	40.0
Reaction time (min.)	60.0
EXTRACTION:	
Dry weight of sample (g)	7.15
Dry wt. after extraction (g)	6.61
CALCULATIONS:	
% Conversion to polymer	74.7
% Conversion to copolymer	63.2
% grafting Efficiency	84.6

Table 20: RAW DATA FOR SET #4

Weight of wet pulp	(g)	120.51
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	3.0
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	6.73
Dry wt. after extraction	(g)	6.49
CALCULATIONS:		
% Conversion to polymer		11.1
% Conversion to copolymer		7.9
% grafting Efficiency		71.2

Table 21: RAW DATA FOR SET #4

Weight of wet pulp	(g)	120.50
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		50
Dissolved oxygen	(ppm)	3.0
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	7.42
Dry wt. after extraction	(g)	6.77

CALCULATIONS:

% Conversion to polymer	50.0
% Conversion to copolymer	39.0
% grafting Efficiency	78.0

Table 22: RAW DATA FOR SET #4

Weight of wet pulp	(g)	120.50
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		150
Dissolved oxygen	(ppm)	3.0
Temperature	(° C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	6.46
Dry wt. after extraction	(g)	5.91
CALCULATIONS:		
% Conversion to polymer		63.8
% Conversion to copolymer		51.7
% grafting Efficiency		81.0

Table 23: RAW DATA FOR SET #4

Weight of wet pulp	(g)	120.50
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		250
Dissolved oxygen	(ppm)	3.0
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.12
Dry wt. after extraction	(g)	6.30
CALCULATIONS:		
% Conversion to polymer		64.1
% Conversion to copolymer		47.8
% grafting Efficiency		74.6

Table 24: RAW DATA FOR SET #4

Weight of wet pulp	(g)	120.50
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		450
Dissolved oxygen	(ppm)	3.0
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.51
Dry wt. after extraction	(g)	6.84
CALCULATIONS:		
% Conversion to polymer		46.2
% Conversion to copolymer		35.2
% grafting Efficiency		76.2

Table 25: RAW DATA FOR SET #5

Weight of wet pulp	(g)	120.51
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	5.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	6.40
Dry wt. after extraction	(g)	6.17

CALCULATIONS:

% Conversion to polymer	6.5
% Conversion to copolymer	3.5
% grafting Efficiency	53.8

Table 26: RAW DATA FOR SET #5

Weight of wet pulp	(g)	120.50
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		45
Dissolved oxygen	(ppm)	5.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	6.36
Dry wt. after extraction	(g)	5.37

CALCULATIONS:

% Conversion to polymer	49.2
% Conversion to copolymer	29.5
% grafting Efficiency	60.0

Table 27: RAW DATA FOR SET #5

Weight of wet pulp	(g)	120.62
Dry weight of pulp	(g)	20.02
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		110
Dissolved oxygen	(ppm)	5.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.82
Dry wt. after extraction	(g)	7.20
CALCULATIONS:		
% Conversion to polymer		22.6
% Conversion to copolymer		14.7
% grafting Efficiency		65.0

Table 28: RAW DATA FOR SET #5

Weight of wet pulp (g)	120.50
Dry weight of pulp (g)	20.00
Weight of monomer (g)	25.92
Weight of initiator (g)	6.10
Stirrer rpm	300
Dissolved oxygen (ppm)	5.2
Temperature (C)	40.0
Reaction time (min.)	60.0

EXTRACTION:

Dry weight of sample (g)	7.13
Dry wt. after extraction (g)	7.13

CALCULATIONS:

% Conversion to polymer	~~0.0~~
% Conversion to copolymer	0.0
% grafting Efficiency	---

Table 29: RAW DATA FOR SET #6

Weight of wet pulp	(g)	120.13
Dry weight of pulp	(g)	19.94
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	9.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	6.12
Dry wt. after extraction	(g)	6.05

CALCULATIONS:

% Conversion to polymer	1.3
% Conversion to copolymer	0.5
% grafting Efficiency	38.5

Table 30: RAW DATA FOR SET #6

Weight of wet pulp	(g)	145.46
Dry weight of pulp	(g)	20.07
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		55
Dissolved oxygen	(ppm)	9.2
Temperature	(C).	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	6.02
Dry wt. after extraction	(g)	5.12

CALCULATIONS:

% Conversion to polymer	37.6
% Conversion to copolymer	18.3
% grafting Efficiency	48.67

Table 31: RAW DATA FOR SET #6

Weight of wet pulp	(g)	108.34
Dry weight of pulp	(g)	19.83
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		100
Dissolved oxygen	(ppm)	9.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	7.31
Dry wt. after extraction	(g)	6.22

CALCULATIONS:

% Conversion to polymer	14.6
% Conversion to copolymer	6.6
% grafting Efficiency	45.2

Table 32: RAW DATA FOR SET #6

Weight of wet pulp	(g)	109.33
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		155
Dissolved oxygen	(ppm)	9.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.74
Dry wt. after extraction	(g)	7.06
CALCULATIONS:		
% Conversion to polymer		13.1
% Conversion to copolymer		5.7
% grafting Efficiency		43.5

Table 33: RAW DATA FOR SET #6

Weight of wet pulp	(g)	109.72
Dry weight of pulp	(g)	20.08
Weight of monomer	(g)	25.92
Weight of initiator	(g)	6.10
Stirrer rpm		300
Dissolved oxygen	(ppm)	9.2
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	7.13
Dry wt. after extraction	(g)	7.13
CALCULATIONS:		
% Conversion to polymer		0.0
% Conversion to copolymer		0.0
% grafting Efficiency		---

Table 34: RAW DATA FOR SET #7

Weight of wet pulp	(g)	119.76
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.66
Weight of initiator	(g)	6.10
Stirrer rpm		10
Dissolved oxygen	(ppm)	0.3
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	5.17
Dry wt. after extraction	(g)	4.41
CALCULATIONS:		
% Conversion to polymer		50.0
% Conversion to copolymer		31.2
% grafting Efficiency		62.4

Table 35: RAW DATA FOR SET #7

Weight of wet pulp	(g)	119.80
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.66
Weight of initiator	(g)	6.10
Stirrer rpm		50
Dissolved oxygen	(ppm)	0.3
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	7.87
Dry wt. after extraction	(g)	6.83

CALCULATIONS:

% Conversion to polymer	59.5
% Conversion to copolymer	41.3
% grafting Efficiency	69.4

Table 36: RAW DATA FOR SET #7

Weight of wet pulp	(g)	119.77
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.66
Weight of initiator	(g)	6.10
Stirrer rpm		600
Dissolved oxygen	(ppm)	0.3
Temperature	(C)	40.0
Reaction time	(min.)	60.0

EXTRACTION:

Dry weight of sample	(g)	5.16
Dry wt. after extraction	(g)	4.45

CALCULATIONS:

% Conversion to polymer	71.3
% Conversion to copolymer	50.7
% grafting Efficiency	71.1

Table 37: RAW DATA FOR SET #7

Weight of wet pulp	(g)	119.76
Dry weight of pulp	(g)	20.00
Weight of monomer	(g)	25.66
Weight of initiator	(g)	6.10
Stirrer rpm		970
Dissolved oxygen	(ppm)	0.3
Temperature	(C)	40.0
Reaction time	(min.)	60.0
EXTRACTION:		
Dry weight of sample	(g)	4.60
Dry wt. after extraction	(g)	3.87
CALCULATIONS:		
% Conversion to polymer		91.0
% Conversion to copolymer		64.3
% grafting Efficiency		70.7