A STUDY OF PHOTOPOLYMERIZATION OF VINYL MONOMERS AND THEIR GRAFT COPOLYMERIZATION ONTO SILK

A thesis submitted in partial fulfillment of
the requirements of the Degree of
Doctor of Philosophy

By

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Dedicated to my
beloved Parents

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CERTIFICATE

This is to certify that the thesis entitled **"A study of photopolymerization of vinyl monomers and their graft copolymerization onto silk"** submitted to the Tezpur University in the Department of Chemical Sciences under the School of Science & Technology in partial fulfillment for the award of the degree of Doctor of Philosophy in Chemical Sciences is a record of research work carried out by Raju Ojah under my supervision and guidance.

All helps received by him from various sources have been duly acknowledged.

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Preface

Natural silk fibres, which have been employed traditionally, can be modified to introduce more desirable properties based on different end-uses. Graft copolymerization has been acquired an apex importance amongst the techniques available for modification of the properties of the parent polymer, without disturbing its molecular architecture. In recent times, grafting has been explored as a potent method for improving textile performance properties of silk like crease recovery, dimensional stability, rub resistance, colour fastness, water and oil repellency etc.

In free radical graft copolymerization method, initiation process is a prime important step that can be brought by different initiator systems like, AIBN, BPO, cerric ammonium nitrate (CAN), Cr(VI), $KMnO_4$-oxalic acid redox system etc. The semiconductors like CdS, TiO_2, ZnO, CdSe, InP, WS_2 and GaAs are utilized in heterogeneous photocatalysis of normal chemical reactions. The heterogeneous photocatalytic reactions with various semiconductors have been studied extensively over the last few decades but these photocatalysts (based on semiconductor) have not been used for graft copolymerization.

The present work deals with the study of semiconductor-based photocatalysis where CdS is used as a photocatalyst for photopolymerization of methyl methacrylate. The application of this photocatalyst in the graft copolymerization of methyl methacrylate and acrylamide onto silk fibre is explored in the present study. The work also includes the systematic study of different reaction conditions. The different grafting parameters are also calculated and characterization of grafted products was performed with FTIR, DSC, TGA, SEM, tensile strength measurement and water retention value (WRV).

The main work has been carried out in Polymer Division, Department of Chemical Sciences, Tezpur University, Assam, India. The analyses were carried out at SINP, Kolkata, RSIC, Shillong, NCL, Pune, Jadavpur University and CEPET, Guwahati.

The result shows the potentiality of semiconductor-based photocatalyst in polymerization as well as in photograft copolymerization of selected vinyl monomers. The advanced studies in this field may open up new directions for future research and help in commercialization of research output.

Raju Ojah

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Least but not last, I offer sincere thanks to all of my friends, relatives and well-wishers for their kind support in this work.

Date: 28-Dec-2005 *Raju Ojah*

Abstract

Background

With the advent of polymer science, challenges have been made to modify natural fibres like wool, silk, cellulose, which have been employed traditionally. Out of various techniques to introduce more desirable properties to synthetic as well as natural fibre, the graft copolymerization is *the simplest technique. In this technique the polymeric side chain (to be* considered as backbone) *is connected to the surface of the fibre by chemical* processes. Graft copolymers have diverse application because of wide range of properties available when polymer chains are joined to form hybrid comb-like macromolecules.

Although, the backbone of the parent polymer remains intact during the grafting but some additional properties are added to the parent polymer system. It has been considered as one of the convenient methods to achieve better properties without disturbing of the basic nature of the parent macromolecule. It is a well-known chemical process to impart novel property or enhance the existing properties in the parent polymer backbone with minimum degradation of original properties. Stannett explained some special characteristics of graft copolymerization technique that led to their unparalleled behaviour towards the application potential in various fields. A few of them are as follows:

a) grafted products have ability to retain the properties of backbone polymer, simultaneously uploading some of properties of the side chain.
b) it also influences in the formation of microdomain structure.

Grafting is a popular technique applied to affect the textile performance of natural and synthetic fibres. Basically, modification of the properties of natural fibres through graft copolymerization of vinyl monomers has gained the interest of not only scientists but also technologists for last three decades.

The methods for synthesis of graft copolymers can be classified into three prime categories viz. '**grafting from**', '**grafting onto**' and '**grafting through**' processes. The **grafting from** is quite convenient but accurate knowledge of molecular structure of graft copolymerization is not available. The **grafting onto** method allows estimating the number of grafts per chain and average difference between two successive grafting chains. In **grafting through** process, polymerization is performed in the presence of polymer carrying pendant unsaturations that participate in the copolymerization process.

Depending upon the reaction types, graft copolymer synthesis is widely divided into three classifications,

a) Ionic polymerization methods
b) Condensation and ring opening polymerization methods
c) Radical polymerization methods

The radical polymerization has been used widely due to its limited experimental conditions. Free radical polymerization may involve through different initiator systems like anthracene, Michler's ketone, xanthane, benzophenone, bis(imidazolyl) which are popularly applied as photosensitizers. However, semiconductors like CdS, TiO_2, ZnO, CdSe, InP, WS_2 and GaAs are used in heterogeneous photocatalysis. Semiconductor-based photocatalysts have been widely utilized in areas like photochemical cell, photo electrochemical production of hydrogen, photocatalytic degradation of air/water pollutants, organic functional group transformations and metal recovery. Semiconductor based photocatalysis has become one of the major interdisciplinary research areas, attracting efforts from photochemists, photophysicists, environmental engineers and scientists in related fields.

Semiconductor-based photocatalyst is one of the modern methods for generation of radicals in photopolymerization of vinyl monomers. The efficiency of semiconductor is a function of the positions of semiconductor's conduction and valence bands relative to the redox potentials of the adsorbed substrates. To suppress the electron-hole recombination and continuously supply valence-band electron holes for an oxidative purpose, a sacrificial electron acceptor must be added to scavenge the electron in the conduction band. Considering these things, triethylamine/ethylene glycol was applied as additives along with semiconductor.

Objectives of the present work

Semiconductor-based photocatalysts are not used as initiator for graft copolymerization till now. Therefore, it has been planned to graft copolymer onto silk fibre using semiconductor-based photocatalyst along with the studies of photocatalytic behaviour of these semiconductors.

The broad objectives of this research works are mainly,

a) To find out the suitability of semiconductor as photocatalyst for photopolymerization of vinyl monomers.

b) To find out the reaction mechanisms of semiconductor based photocatalysis through UV-Visible, Fluorescence emission and Electron Paramagnetic Resonance spectrophotometers.

c) To develop a method of graft copolymerization onto silk, particularly *Bombyx mori* for modification of surface properties of the fibres through photograft copolymerization of vinyl monomers.

d) To calculate the grafting parameters, like graft yield, graft conversion, graft efficiency, homopolymer formation, total conversion etc.

e) To evaluate the changes in the physical properties, chemical resistance of grafted products.

f) To characterize the grafted products by FTIR, X-ray diffraction, DSC, TGA, UTM (universal testing machine) and SEM techniques.

Plan of work

In the present work semiconductor CdS has been chosen as initiator for polymerization of methyl methacrylate in various reaction conditions and applied as photocatalyst in graft copolymerization of vinyl monomers onto *Bombyx mori* silk fibre.

In the next phase of work semiconductor-based photocatalyst has been applied in the photografting. The photocatalyst in combination with additives (Et_3N, ethylene glycol) is showing as a promising initiator in graft copolymerization of methyl methacrylate (MMA) and acrylamide (AAm) onto silk fibres. However, variations of amount of additives and nature of additives have pronounced effect on the grafting process.

The characterization of grafted products is an important aspect of graft copolymerization for better understanding of nature of grafting, surface morphology, area of applications as end products. The structural, thermal properties and morphological structure of grafted fibres can be characterized by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TGA), scanning electron microscopy (SEM), tensile strength measurements, water absorption measurement etc. The physicochemical properties of grafted silk fibres depend on the chemical characteristics of monomer used as well as on the extent of grafting and on the reaction conditions.

The research work reported in the thesis has been divided into five chapters.

Chapter I includes an introduction of the graft copolymerization onto silk. The physico-chemical, mechanical properties and microscopic features of silk are discussed. A thorough review on graft copolymerization is described. The different initiator systems like free radical initiators, redox initiators and semiconductor-based photoinitiators have been discussed.

Chapter II deals with photopolymerization of vinyl monomer by semiconductor-based photocatalyst. The effect of eosin Y (dye) and other additives on photopolymerization of MMA has been studied. It has been observed that photopolymerization of MMA with CdS results only 2.43% of conversion of monomer to polymer whereas without CdS no polymerization was observed under the identical reaction conditions. A conversion (14.27%) has been achieved when CdS was used with electron donor like, triethylamine. A higher conversion of 22.73% has been noted when photocatalyst was used in the presence of dye. The stability of dye during exposure to light has also been explored. The mechanisms of semiconductor-assisted polymerization of MMA have been supported with EPR spectra. To optimize the reaction conditions, MMA-dye; MMA-CdS-dye; MMA-CdS-triethylamine systems were studied with variation of exposure time.

Chapter III deals with the grafting of MMA and AAm (acrylamide) using semiconductor-based photocatalyst. The grafting was carried out using CdS as a photocatalyst in the presence of the light. The graft copolymerization has been successfully completed with varying reaction time, temperature, amount of additives, and material-to-liquid ratio. The characterization of grafted products was performed by FTIR studies and grafting parameters like graft yield, graft conversion, graft efficiency, homopolymer formation and total conversion were calculated.

Chapter IV includes the characterization of physico-chemical properties of grafted products. The structural, thermal properties and morphology of grafted fibres were characterized by X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry (TGA), water absorption measurements, scanning electron microscopy (SEM), tensile strength measurements. The improvements of thermal stability and lower water retention of grafted products are observed. SEM micrographs clearly reveal that the graft copolymerization is merely a surface phenomenon.

Chapter V depicts the conclusions of the work. It is concluded that semiconductor-based photocatalyst has the potential for photopolymerization of methyl methacrylate along with other regular organic transformations.

The semiconductor-based photocatalyst in combination with additives is showing as a promising initiator in graft copolymerization of MMA and AAm onto silk fibres.

It has been observed that photocatalyst CdS along with other additives is more effective for graft copolymerization of MMA in compare with AAm in terms with graft yield, total conversion and homopolymer formation.

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Chapter II. Photopolymerization of methyl methacrylate using semiconductor-based photocatalyst

Chapter III. Graft copolymerization of methyl methacrylate and acrylamide onto *Bombyx mori* fibre initiated by semiconductor-based photocatalyst

Abbreviations

AAm	Acrylamide
AIBN	Azobis(isobutyronitrile)
CAN	Cerric ammonium nitrate
DSC	Differential Scanning Calorimetry
EPR	Electron Paramagnetic Resonance
FTIR	Fourier transform infrared spectroscopy
h	Hour
HEMA	2-Hydroxyethyl methacrylate
HOMO	Highest occupied molecular orbital
MAA	Methacrylamide
MAN	Methacrylonitrile
MMA	Methyl methacrylate
PBN	α-Phenyl-*tert*-butyl nitrone
RH	Relative humidity
SEM	Scanning electron microscopy
TGA	Thermogravimetric Analysis
WRV	Water retention value

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Chapter-I

1.1. Introduction

With the advent of polymer science, challenges have been made to modify natural fibres like wool, silk, cellulose, which have been employed traditionally. Different modification techniques have been implemented to introduce more desirable properties to synthetic as well as natural polymers so that their application spectrum can be diverged.

In comparison to star, block and dendritic polymer, graft copolymer synthesis is simple, where original backbone of polymer remains undisturbed. The graft copolymerization is a technique where the polymeric side chain (to be considered as backbone) is connected to the surface of the fibre by chemical processes. It is a well-known chemical process to impart novel property or enhances the existing properties in the parent polymer backbone with minimum degradation of original properties, where distribution of polymeric side chain grows randomly on the main chain i. e., backbone. Graft copolymers have diverse potential application because of wide range of properties available when polymer chains are joined to form hybrid comb-like macromolecules. The term graft copolymer should be reserved for the system involving polymeric graft. According to international nomenclature rules, the name of the backbone polymer should be given first and the name of the grafts second, the word graft indicating the structure of the molecules attached to main chain where a polymeric side chain is connected to the liner main chain of polymer by chemical process. Thus, poly(styrene-graft-isoprene) in short polystyrene-*g*-isoprene stands for a macromolecule that polystyrene backbone having polyisoprene grafts.

Although, the backbone of the parent polymer remains intact during the grafting but some additional properties are added to the parent polymer system. It has been considered as one of the convenient methods to achieve better properties without disturbing of the basic nature of the parent macromolecule. Stannett[1] explained some special characteristics of graft copolymerization technique that led to their unparalleled behaviour towards the application potential in various fields. A few of them are as follows:

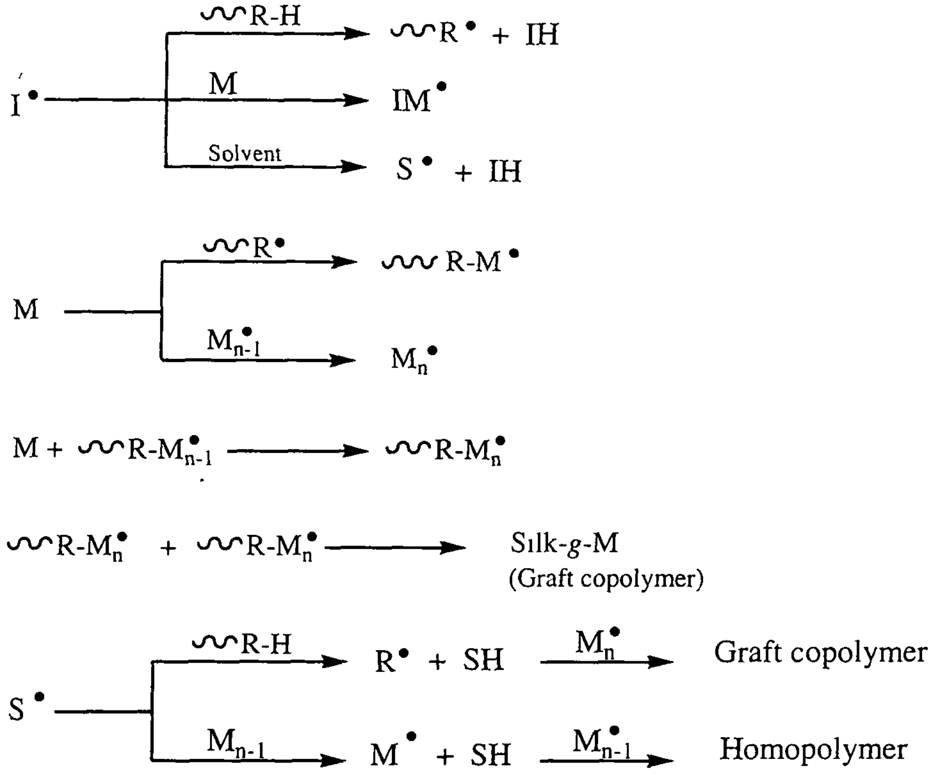
a) grafted products have ability to retain the properties of backbone polymer, simultaneously uploading some of properties of the side chain.
b) it also influences in the formation of microdomain structure.

Grafting is a popular technique applied to affect more or less expensive modification of properties and textile performance of natural and synthetic fibres.[2,3] Basically, modification of the properties of natural macromolecules through graft copolymerization of vinyl monomers has gained the interest of not only scientists but also technologists for last three decades.[4,5,6] Grafting was originally brought to increase silk weight for compensating the loss resulted from the degumming.[7] However, in recent times grafting has been explored as a promising method for improving the performance properties of silk like crease recovery, dimensional stability, rub resistance, colour fastness, water and oil repellency [2] etc. This technique was first discovered in Japan that stimulated the development of industrial treatments, currently performed on a routine basis for the production of specific textile items like necktie, yarn and fabrics, embroidery.[7] But the application on industrial scale is still confined to certain articles through the industrial grafting onto silk fibres.[8,9] Fabric comfort and soil release are affected by the graft copolymerization.[10] Improved soil release and fabric comfort can be achieved from grafted fibres with hydrophilic monomers. Moisture absorbency of cellulose fibres was increased upto 300% by radiation-induced grafting of acrylic acid from the fabric followed by cellulose decrystallization upon exposure to $ZnCl_2$.[11,12] Further, the growth of poly(ethyl acrylate) chains onto cotton fabric by means of exposure to γ-radiation showed increased resistance to abrasion.[13] Even flame retardancy of polyester and polyester/cotton-blended fabric was improved by uploading halogenated and phosphorous-based materials onto polyester and cotton by radiation-induced grafting.[14,15]

Mechanical strength of composites can be improved by graft copolymerization technique. Addition of small amount of poly(ethyl acrylate)(PEA)-*g*-poly(styrene) into PEA/PS blends increases compatibilization and result in increase of tensile strength due to increase of interfacial adhesion between PEA and PS phases.[16] Uploading of methyl methacrylate side chains onto butyl rubber graft copolymer has been performed in an endeavour to amend interfacial compatibility for possible use in elastomers and plastics.[17] The application of graft copolymer is not limited to textile or composite but it has been extensively applied in medical application where reduction in frictional forces between two dissimilar surfaces is required, like tubular devices (catheters, cytoscopes etc.).[18] In the fully hydrated state, surface grafting of poly(urethane) film with dimethyl acrylamide results in decrease of coefficient of friction.[19] Grafting of poly(dimethyl siloxane) with styrene was performed to yield derivatives with applications such as supercritical CO_2 surfactants and thermoplastic elastomers.[20] By modifying the biophysical properties of silk proteins by applying novel technique; new materials could be specially tailored for application in the biomedical field. Thus, grafting of fibres may be a powerful method to yield new polymers with multifunctional properties.[21] These examples embellished the impact of graft copolymers on improving the properties of different end-use. Graft copolymerization has been acquired an apex importance amongst the techniques available for modification of the properties of parent polymer, without disturbing its molecular architecture. The major problem encountered in graft copolymerization is the synchronous generation of homopolymer along with desired products. The major sources of homopolymer produced from syntheses, which deprive specific macroradical formation and formed the chain transfer of growing grafted chain ends. On the basis of literatures available on grafting, [22] the following reaction schemes for initiation, propagation and termination of graft copolymerization of vinyl monomers onto silk can be represented.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^{*} \longrightarrow \mathrm{I}^{\bullet}$$

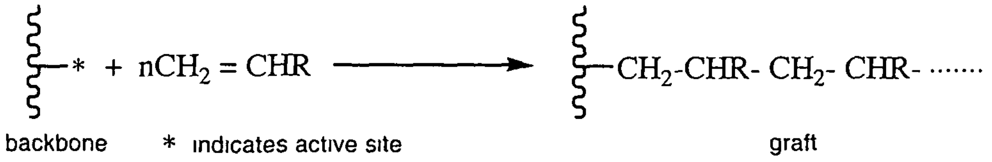
where PI is photoinitiator and $\mathrm{I}^{\bullet}$ is the radical generated during the process



In the above reactions, $\sim\sim$RH, $\sim\sim$R•, S• and M stand for silk, primary silk macroradical, solvent radical and monomer respectively. The free radical formed by the initiator interacts with respective sites on silk fibroin backbone, forming a macroradical. Carboxyl, amine and hydroxyl side groups of various amino acid residues are likely to form radicals. The silk macroradical can react with monomer, leading to the propagation of grafted polymer chain. Homopolymer can be formed by interaction of the initiating free radicals with the monomer. The coexistence of both grafted chains and homopolymer within the silk fibre matrix cannot be excluded. In respect of graft copolymer, homopolymer is a waste product, which creates difficulty in separation of grafted product from homopolymer and thus generates problem in characterizing the graft products.[22] In fact, homopolymer formation is one of the major causes for unsuitability of extensive industrial development of graft copolymers.[23]

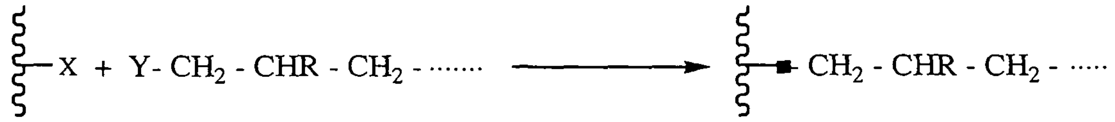
1.1.1. Principles of graft copolymer synthesis

The methods for synthesis of graft copolymers can be classified into three prime categories viz. '**grafting from**', '**grafting onto**' and '**grafting through**' processes. The **grafting from** is quite general and was used by Smets et al.[24] and Bamford et al.[25] In this method the backbone polymer chain having some active sites used to initiate the polymerization of a second monomer. The active sites created on the backbone may be of free radical, anionic, cationic or Ziegler-Natta types. Although this method is quite convenient but accurate knowledge of molecular structure of graft copolymerization is not available. This process generates a fair amount of homopolymer.



$$-* + nCH_2 = CHR \longrightarrow -CH_2\text{-}CHR\text{-}CH_2\text{-}CHR\text{-}\cdots\cdots$$

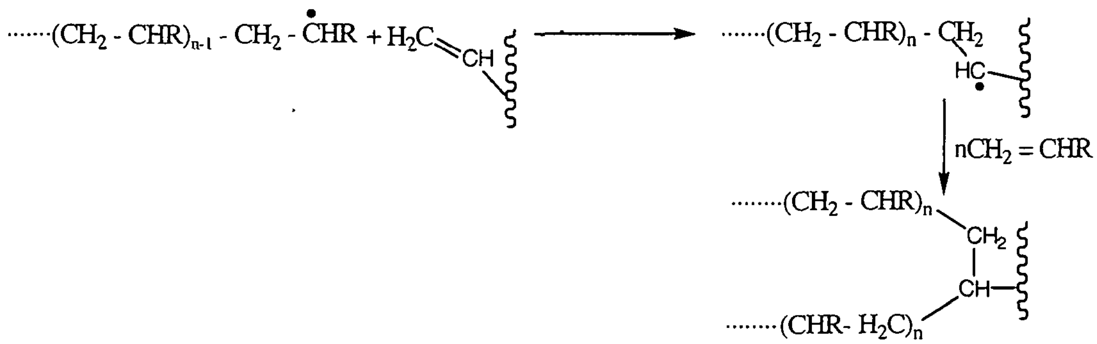
Grafting onto[26] results from the reaction between a polymer backbone having one reactive site at a chain end and another polymer with attached antagonist functions distributed at randomly along its chain. In these cases grafting does not involve a chain reaction and they are carried out in a common solvent to bring homogeneity of the reaction medium. The



$$-X + Y\text{-}CH_2\text{-}CHR\text{-}CH_2\text{-}\cdots\cdots \longrightarrow -\!\blacksquare\, CH_2\text{-}CHR\text{-}CH_2\text{-}\cdots\cdots$$

advantage of this method is that they allow estimating the number of grafts per chain and average difference between two successive grafting chains.

In **grafting through** process, polymerization of a monomer is performed in the presence of a polymer carrying pendant unsaturations that participate in the copolymerization process. Although, such reactions can involve formation of links between individual molecules, but a growing site happens to incorporate unsaturations belonging to two or more different backbone leading to the cross-linked material. Besides these, grafting can result from γ-radiation of a polymer chain in the presence of vinyl monomer,[27] which is similar as grafting from reaction. The transfer reactions [28] are also carried out in grafting processes. If polymerization is allowed in presence of a polymer having high transfer constants, radical sites are generated on the backbone. They can either initiate the polymerization to yield a graft or recombination with an incoming polymeric radical. Scanlan and Merrett [29] reported the grafting reaction involving transfer reaction where polymerization of styrene in presence of rubber with benzoyl peroxide (BPO) as initiator was successfully taken place. On the other hand no grafting was observed when azobis(isobutyronitrile) was



applied instead of BPO. This indicates the presence of highly reactive primary radical is responsible for attack on the polymer backbone.

1.1.1.1. Types of graft copolymer synthesis

Depending upon the reaction types, graft copolymer synthesis is widely divided into three classifications,

a) Ionic polymerization methods
b) Condensation and ring opening polymerization methods
c) Radical polymerization methods

Out of these, radical polymerization has found many applications with huge variety of monomers that can be polymerized and copolymerized and due to its user-friendly experimental conditions.[30] But the control over the macromolecular structure in radical polymerization is poor than in the ionic polymerization. As the possibility of controlling the molecular weight, molecular weight distribution and sequences and branching are encouraging for the synthesis of new materials; it is desirable to develop the control on macromolecular structure in radical initiation process. Improvement of poor chemoselectively of radical polymerization was challengeable task for controlling the molecular weight, polydispersity, end group branching. However, Szwarc et al.[31] attempted to reduce poor chemoselectively by establishing a dynamic equilibrium between growing radicals and dormant species, which is better known as 'controlled' radical polymerization.[32] Even though these disadvantages can be rectified up to a certain limits by anionic or cationic mechanism, their applications in polymerization processes are severely limited due to the stringent requirements on reaction condition and purity of monomer.[33-40] However, 'living free radical' [41] concept has brought better control of molecular weight, poly-dispersity index (PDI) and macromolecular structural characteristics that attracted considerable interest in graft copolymerization synthesis. The living chain growth polymerization proceeds through active propagation species which neither involved in chain nor in termination steps. The concentration of active propagating. species remains constant throughout the whole polymerization process and adding more monomers from outside may further propagate the process. The advantages on living techniques on designing macromolecular architectures make it an extremely important synthetic tool for further development of this area.[22]

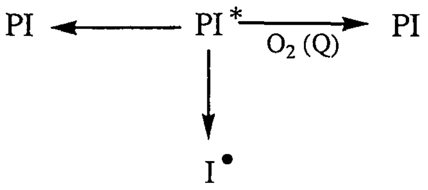
Thus, in different graft copolymerization methods, free radical induced polymerization is the easiest and widely accepted procedure. Free radical graft copolymerization is generally initiated by the different species capable of generating primary free radicals via chemical reaction or thermal dissociation. In case of free radical mechanism various initiators systems like AIBN, BPO, APS (ammonium persulphate), cerric ammonium nitrate (CAN), Cr (VI), $KMnO_4$-oxalic acid redox systems [42] have been used. In comparison with other methods, free radical process followed by light-induced initiation has the advantage due to applicability at room temperature and its user-friendly nature. Further, changing the intensity and wavelength of applied light can control the polymerization systems.

1.1.2. Photoinitiators and photopolymerization

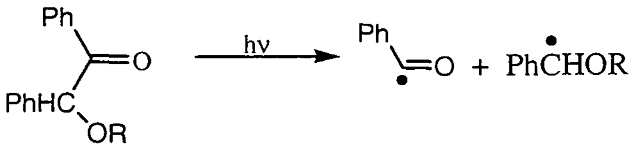
Photopolymerization of multifunctional monomers under visible light can be induced through two different processes, photoinitiation or photosensitization. Photoinitiators absorbs light energy and convert it into chemical energy in terms of reactive intermediates and subsequently initiate the polymerization. After absorption of light, the photoinitiator (PI) is raised

$$PI \xrightarrow{h\nu} PI^{*}$$

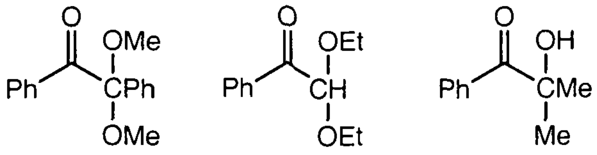
to an electronically excited state (PI^{*}) of shorter lifetime (less than 10^{-6} second). During this time, excited species may proceed through different pathways like decay back to ground state, excited state quenching by O_2 molecule or monomer or other quenching agents (Q) and chemical reaction



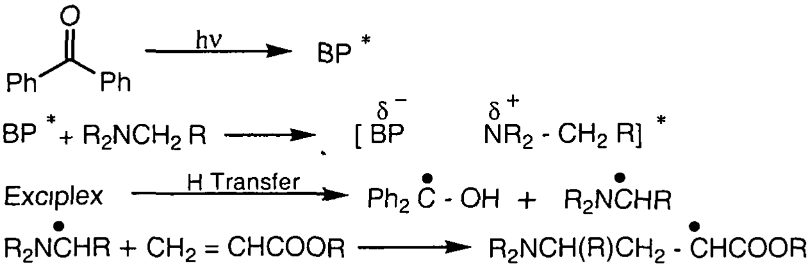
leading to species like radical or cation. Depending upon the species generated during the polymerization from photoinitiators, they are classified as radical and cationic photoinitiators for photopolymerization. The photoinitiator for radical polymerizations are photogenerated by intramolecular bond cleavage and intermolecular bond cleavage [43] through hydrogen abstractions. Aryl alkyl ketones are mostly used as initiators of



intramolecular bond cleavage type that dissociated into aryl and ether radicals. These radicals are efficient as initiators for effective polymerization of acrylate type monomers.[44] Related to aryl alkyl ketone photoinitiators also



include the **above** species, which undergo photocleavage analogously to benzoin ether. On the other hand, intermolecular hydrogen abstraction type photoinitiator include benzophenone, Michler's ketone, quinines, benzils etc. In case of benzophenone, H abstraction by excited state benzophenone(BP*) from a tertiary amine charge transfer stabilized exciplex.



$$BP^{*} + R_2NCH_2R \longrightarrow [\overset{\delta^-}{BP} \quad \overset{\delta^+}{NR_2} - CH_2R]^{*}$$

$$\text{Exciplex} \xrightarrow{\text{H Transfer}} Ph_2\overset{\bullet}{C} - OH + R_2N\overset{\bullet}{C}HR$$

$$R_2N\overset{\bullet}{C}HR + CH_2 = CHCOOR \longrightarrow R_2NCH(R)CH_2 - \overset{\bullet}{C}HCOOR$$

The exciplex generates benzophenone· ketyl radical along with α-amino radical. The low initiating reactivity of benzophenone ketyl radical, owing to their steric bulk and resonance favours α-amino radical to be more efficient towards acrylate monomers.[45] On the other hand, cationic polymerization mechanism is attractive because it can eliminate the unfavourable effects of atmospheric oxygen encountered in radical polymerization. Moreover, photoinitiators for cationic polymerization like arenediazonium salts of complex metal halides, dialkyl phenecylsulfonium salts, (η^6-benzene)(η^5-cyclopentadienyl)Fe^{II} hexafluorophosphate etc. are explored commercially for UV curing and image applications along with other studies. Photolysis of these salts generates Lewis acids that may initiate cationic polymerization

$$\text{Ar-N}_2^+\ \text{PF}_6^- \xrightarrow{h\nu} \text{Ar-F} + \text{N}_2 + \text{PF}_5$$
$$\text{PF}_5 + \text{ROH} \longrightarrow \text{H}^+\ \text{PF}_5\,(\text{OR})^-$$

of epoxy functional monomers and oligomers [46] directly and/or produce Brönsted acids by reaction with purposefully added hydroxyl substances. The cationic photo polymerizations applied for coating, printing inks, and adhesives can be conducted without the use of solvents, thus eliminating this potential source of both air and water pollution while avoiding the initial costs associated with their use and recovery. In additions to that photoinitiated cationic polymerizations have the advantage of oxygen insensitivity, which reduces both the cost and necessity of using inert atmosphere.[47]

The heterogeneous photocatalysis involves photoreaction, which occur at the surface of a catalyst. If the initial photoexiciation process occurs at the surface of an absorbate molecule, which then interacts, with the ground state of the catalyst molecule, the process is referred as catalyzed photoreaction. On the other hand, if the initial photoexcitation takes place in the catalyst substrate, the process is termed as sensitized photoreaction.[48] Usually photosensitizer is considered as an energy transfer agent that absorbs light and transfers the energy to an acceptor and reverts to its original state. Pappas et al. [44] first reported the study of mechanism of onium salts for cationic polymerization where a broader definition of photosensitization was defined, including electron transfer as well as exciplex induced bond cleavage. Anthracene, Michler's ketone, xanthane, benzophenone, bis(imidazolyl) are popularly applied as photosensitizers for cationic/radical polymerization.[43] Above all, semiconductors like CdS, TiO_2, ZnO, CdSe, InP, WS_2, and GaAs are used in heterogeneous photocatalysis that refers to semiconductor photocatalysis or semiconductor-sensitized photoreactions.[48] The advantages of semiconductors are that they are usually inexpensive and non-toxic. Semiconductor-based photocatalysis has become one of the potential interdisciplinary research areas, attracting efforts from photochemists, photophysicists, environmental engineers and scientists in related field.[49] The search for alternative energy sources due to the oil crises in early 1970s has catalyzed the development of semiconductor-based photocatalysis in laboratory as well as in industry. Later on extensive research in this field has popularized the semiconductor in photochemical cell,[50,51] photo electrochemical production of hydrogen,[52,53] photocatalytic degradation of air/water pollutants,[53,54] organic functional group transformation and metal recovery.[56-59] A better understanding of semiconductor photocatalysis is possible through different investigations.[60-63] The high efficiency of photochemical solar cell based on semiconductor has been demonstrated.[64] These types of photocatalyst have been applied for commercial treatment of air and water.[65,66]

The applications of semiconductor as photocatalyst in organic functional group transformations for organic synthesis have been studied mainly with two aims.[67-69] The first objective is to review any new photochemical reactions that are unique due to the redox microenvironment on semiconductor surfaces. The second is to find out for reactions that can assist as superior alternatives for conventional chemical processes.

1.1.3. Semiconductor photocatalysis

Semiconductor-based photocatalysis can be classified as semiconductor-mediated photocatalysis and direct photolytic transformation of substrates adsorbed on semiconductor particles.[49] Semiconductor photocatalysis corresponds with photoexcitation of semiconductor particle. On the other hand, direct photolytic reactions begin with excitation of the organic substrate. The capability of a semiconductor-mediated photocatalysis is reflected by the properties of semiconductor, type of substrate, amount of competition from the solvent, and the experimental set up. The four factors that depend on band-gap and band-edge positions of semiconductors are competitive adsorption on semiconductor surfaces, electron-hole scavenging, light sources and reactors.[48]

1.1.3.1. Band-gap and band-edge positions of semiconductor particles

Unlike metals, which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation of in the solid. By definition, a semiconductor has a band structure, roughly characterized as a series of energetically closed spaced energy levels associated with covalent bonding between atoms having the crystallite (the valence band) and a second series of spatially diffuse, energetically similar levels lying at higher energy and associated with conduction in the macromolecular crystallite (the conduction band). The empty region, which extends from the top of the filled valence band to the bottom of the vacant conduction band, is called the band gap (E_{BG}).[69] A semiconductor is usually recognized by the energy gap between its electrically populated valence band and its largely vacant conduction band.[70] Promotion of an electron from the valence band to the conduction band can be brought about by the absorption of a photon of ultra-band gap light, i.e., $h\nu \geq E_{BG}$. Figure 1.1 illustrates the fundamental electron transfer process in a semiconducting material. The band gap determines the wavelengths that

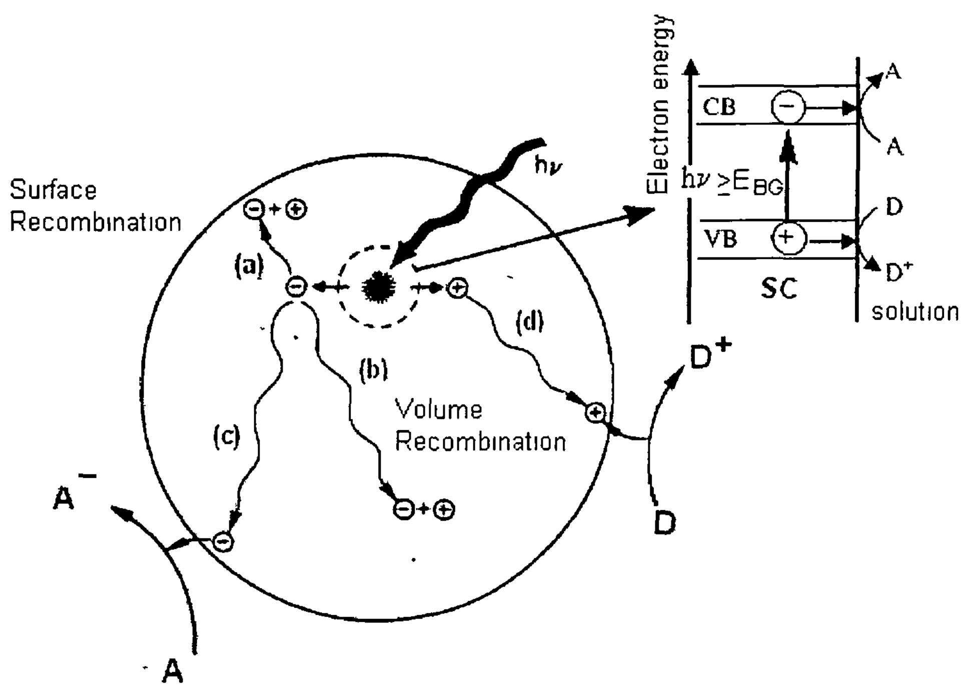


Figure 1.1: Illustration of major processes occurring on a normal semiconductor particle following electronic excitation.[71] Electron-hole recombination can occur at the surface [scheme (a) or in the bulk (b)] of the semiconductor At the surface of the particle, photogenerated electrons can reduce an electron acceptor A [scheme (c) and photogenerated hole can oxidize an electron donor (scheme (d)]. The combination of reaction (c) and (d) represents the semiconductor sensitization of the general redox reaction.

may cause excitation or charge separation in the semiconductor. After excitation, the conduction band electron (e^-) and the valence-band electron hole (h^+) may undergo either electron transfer reactions with the adsorbed substrates or recombine through deactivation processes.[60,61] If the electron hole-pair recombines, it is the only process that occurs; the semiconductor will show no photoactivity. Electron-hole recombination is promoted by defects in the semiconductor material and most amorphous semiconductor material show little photoactivity.[70] Consequently, if an electron donor (D) like ethanol, methanol, EDTA, amine [68] are present at the surface, then the photogenerated hole can react with it to generate oxidizes product, D^+. On the other hand if an electron acceptor (A) like oxygen, H_2O [71], viologen and N_2O [72] are present at the surface than the photogenerated conductance band electrons can react with it to a reduced product, A^-. Thus, hole trapping generates a stable cation, and electron trapping generates an anion. The overall reaction schemes can be represented as follows:

$$\text{Semiconductor} \xrightarrow{h\nu} e^- + h^+ \qquad (1)$$

$$h^+_{(\text{semiconductor})} + D \longrightarrow D^+$$

$$e^-_{(\text{semiconductor})} + A \longrightarrow A^-$$

$$A + D \xrightarrow[h\nu \geq E_{BG}]{\text{semiconductor}} A^+ + D^- \qquad (2)$$

These radical ions can participate in several schemes like (a) they may react chemically with themselves or other substrates, (b) they may recombine by back electron transfer to form the excited state of one of the reactant or back to ground state by nonradiative pathways, (c) they may diffuse from the semiconductor surface and participate in chemical reactions in the bulk solution. In terms of Gibbs free energy, if the equation (2) shows positive value than the overall process is termed as photosynthesis or the negative value of free energy indicates the reaction scheme as semiconductor photocatalysis. Later one is the major aspect of semiconductor photochemistry and currently undergoing heavy commercial explorations.[71]

The semiconductors are divided into two categories depending upon their ability to split water.[49] The oxidative or O-type semiconductors (like WO_3, Fe_2O_3) have enough oxidation power to oxidize water and reductive or R-type semiconductors (like TiO_2, CdS, CdSe, Si) have sufficient power to reduce water but its oxidation power is not strong enough to oxidize water. The energies for various semiconductors in aqueous electrolyte at pH=1 has shown in Figure 1.2. The figure illustrates the ability of a semiconductor to

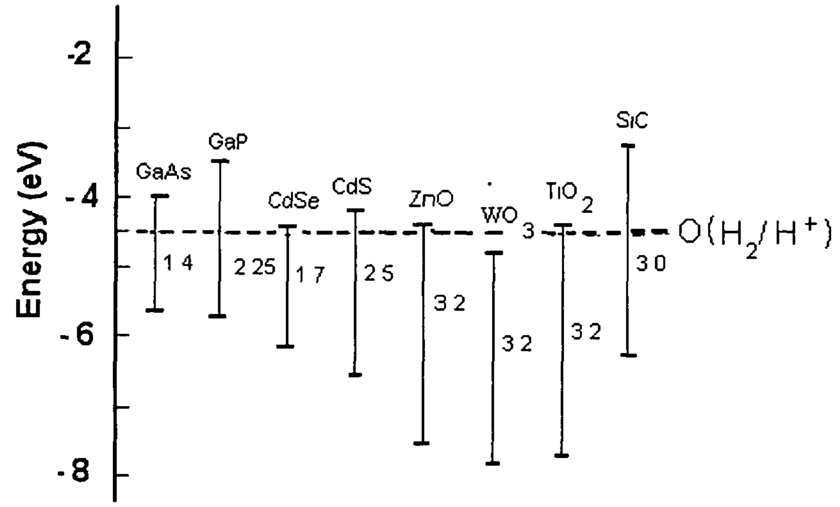


Figure 1.2: Valence and conduction band positions for various semiconductors in aqueous electrolytes at pH = 1.[70]

undergo photoinduced electron transfer to adsorbed species on its surface and it is regulated by the semiconductors and the redox potential of the adsorbate. The relevant potential level of the acceptor species is thermodynamically required to be below the conduction band potential of the semiconductor. The potential level of the donor needs to be above the valence band position of the semiconductor in order to donate an electron to the vacant hole. The pH of the electrolyte solution influences the band edge positions of various semiconductors compared to the redox potentials for the adsorbates. For example,TiO_2 has a valence band potential of +3.1V (verses saturated calomel electrode, SCE) and a conduction band potential of –0.1V (verses SCE). Many organic compounds have potentials above that of the TiO_2 valence band and therefore can be oxidized by TiO_2. Although, a few organic compounds can be reduced by TiO_2 because a smaller number has a potential below than that of the TiO_2 conduction band [72] but TiO_2 is the most common semiconductor because of its resistively to strong acids and bases and its stability under illumination.[60,61] On the other hand ZnO, the similar band gap position of TiO_2, is less applicable due to photocorrosion induced by self oxidation. CdS has limited potential for practical use, even it can be positively used in solar radiation [67] despite release of harmful Cd^{2+}.

The efficiency of a photocatalytic reaction can be estimated in terms of quantum yield.[73] Although it is defined as the number of events occurring per photon absorbed but difficult to perform exact calculation of quantum yield in case of semiconductor particle systems as light is scattered by semiconducting surface. It is assumed that all the light is absorbed and the efficiency is quoted, as an appropriate quantum yield.[70] Evidently, electron and hole recombination is the function of efficiency of a semiconductor photocatalyst. A considerable amount of efforts have been made in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the process. Efforts have been made to use the visible region of the sunlight spectra with modified particles. Modifying the surface of the semiconductor can surmount the limitations of a particular semiconductor as a photocatalyst for specific use. The three benefits of modifications to photocatalytic semiconductor systems have been reported.[70] These includes mainly inhibiting recombination by increasing the charge separation, increasing the wavelength response range and changing the selectively or yield of a particular product. Modifications of semiconductor particles include composition, metal coating, transition metal doping, dye sensitization and surface hydrophobic treatment. Coupled semiconductor photocatalyst may increase the efficiencies of photocatalytic reaction by increasing the charge separation and extending the energy range of photoexcitation. Figure 1.3 illustrates the photoexcitation process for the

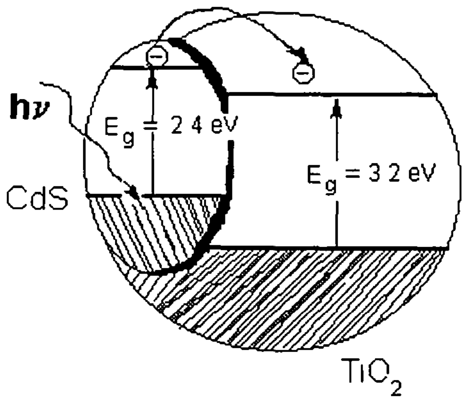


Figure 1.3: Photoexcitation in composite semiconductors system [70]

coupled semiconductor-semiconductor photocatalyst; CdS-TiO_2. Transmission electron micrograph of coupled semiconductors show the direct geometrical interaction of multiple CdS particles with the TiO_2 particle surface.[74] The energy of the excitation light is too small to directly excite the TiO_2 portion of the photocatalyst, but it is large enough to excite an electron from the valence band across the band gap of CdS (E_g=2.4eV) to the conduction band. The hole produced in the CdS valence band across the band from the excitation process remains in the CdS particle while the electron transfers to the conduction band of the TiO_2 particle. The electron transfer from CdS to TiO_2 increases the charge separation and efficiency of the photocatalytic process. The separated electron and hole are then free to undergo electron transfer and adsorbates on the surface. Thus, the quantum yield for the reduction of methylviologen drastically increased and approaches an optimum value of unity when the concentration of TiO_2 was increased in a CdS -TiO_2 system.[75]

The quantum yield of semiconductors can be affected by additions of metal as small ‘dots’ or ‘island’ on the surface of the semiconductor particles. The metal can enhance the yield of the particular product or the rate of the photocatalytic reaction. The enhancement in the reactivity was first observed for the photohydrolysis of H_2O to H_2 and O_2 using the metal-based TiO_2 system.[76] Transmission electron microscopy measurements indicated that Pt particle form clusters on the surface.[77] It was observed that 10% wt Pt covered only 6% of the semiconductor surface, leaving large surface area uncovered. After excitation the electron migrates to the metal where it becomes trapped and electron-hole recombination is suppressed. The migration of electron to the metal particles was confirmed by studied the photoconductance of semiconductor for the Pt deposited TiO_2 compared to control TiO_2.[78] The electronic modification can be performed via deposition of other noble metal also. It has been observed that the increase in production of H_2 form alcohol when silver is added to the surface of TiO_2. The increase in H_2 production for the Ag/TiO_2 photocatalysis is not great as the increase in H_2 production in H_2 production for Pt/TiO_2.[74]

Surface sensitization of a semiconductor through chemisorbed or physisorbed of dye is another efficient method to expand the wavelength range response (red shift) and prolong the electron-hole seperation.[79] The major problem associated with a dye sensitization system is the instability of the organic dye in the presence of strong oxidants and electron hole.[80] However, it has been reported that some organic dye complexes with metals are stable under redox conditions.[81] After dye sensitization, the oxidation power is determined by the highest occupied molecular orbital (HOMO) of the organic dye, which is usually less powerful as an oxidant than electron-hole.[49] The sensitization permits expansion of wavelength response of the photocatalyst, which is prime important when the photocatalyst are to be irradiated with sunlight since the chemically stable metal oxides are wide band gap semiconductors whose absorption occur in the UV spectrum.[70] Photosensitization of semiconductor by different dyes has provided valuable information of interfacial electron transfer on the semiconductor surface. Some common dyes which are used as sensitizer include erythrosin B,[82] thionine,[83] eosin [84] and analog of Ru(bpy)$_3$$^{2+}$ [85] Figure 1.4 illustrates the excitation and charge injection steps involved for the regenerative dye

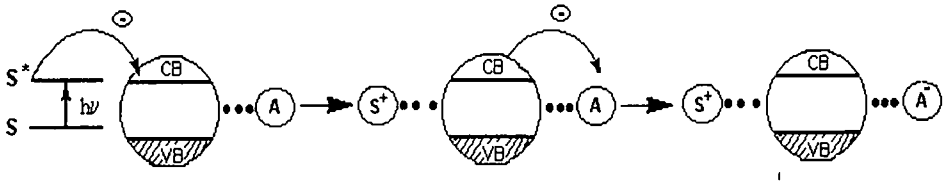


Figure 1.4: An Excitation step for dye molecule sensitizer.[70] The first steps involves the excitation of electron within the sensitizer than electron transfers to the semiconductor. Second steps involve e-transfer to acceptor and third step involves regeneration of sensitizer system.

sensitizer surface process. If the oxidative energy level of the excited state of dye molecule with respect to the conduction band energy level of the semiconductor is favourable, then the dye molecule can transfer the electron to the conduction band of the semiconductor. The surface acts as a quencher by accepting an electron from the excited dye molecule. The electron can be transferred for reducing purpose of an organic acceptor molecule adsorbed on the surface. A study of photopolymerization of methyl methacrylate (MMA) in presence of semiconductor based catalyst with dye as a sensitizer, has been successfully conducted.[84]

1.1.3.2. Effect of substrates and solvents

In the semiconductor based catalysis solvent, reaction intermediate, other nonreactive solution components other than reactant may be simultaneously adsorbed onto the semiconductor surface. Thus, there will be increasing competition between the reactant and intermediate/product for adsorption site and/or electrons or electron-hole (h^+) as well as the competition between organic substrates and semiconductor particles for protons.[86,87] Hence it decreases the quantum efficiency and product selectivity. An enhanced surface adsorption for starting material and the reactive intermediates translate to a higher reactivity for the substrate is always desirable. Strong interaction between the semiconductor particles and the starting materials, reactive intermediates and product may not be equally important. [49]

1.1.3.3. Light sources and reactors

Another important aspect of photocatalysis is the application of proper light sources. Two types of light sources are often applied in semiconductor based photocatalytic reactions [88,89] viz. medium-pressure mercury arc lamps (high photon flux and wide range of spectrum i.e.,200-800 nm) and phosphor coated (around 350 nm). This type of light sources (mercury arc lamps) can lead direct photolysis of organic substrates in presence of semiconductors. In this case reaction mechanism may be extremely complicated and intermediates can become the substrates for another. However, a phosphor-coated lamp with a narrower emission band matching the absorption spectrum of semiconductor particles is recommended for organic synthesis. Most of the organic substrates studied in a semiconductor photocatalysis absorb weakly at wavelength above 350 nm. Semiconductors like TiO_2 may shield organic substrates from receiving photons. In this case, a lamp with even narrower emission band is recommended. The concentration of organic substrate should also be low enough to avoid competition with semiconductor particles for photons.[49]

Besides these, Wilkins et al.[90] also used sunlight for waste degradation. Dolui et al.[91] have applied the sunlight for photopolymerization of methyl methacrylate using CdS as photocatalyst in view of cost effective studies. The typical complaint about sunlight is that the visible portion of the spectrum is ineffective in exciting semiconductors like TiO_2, $SrTiO_3$, WO_3 etc. However, experimental results on the degradation of organic waste in presence of sunlight have been exclusively reported.[92,93]

1.1.3.4. Size quantization effects

A size quantization effect is prominent in metal as well as in semiconductors.[94,95] It is the effect that occurs in semiconductor particles on the order of 10-100 A° in size. Semiconductor particles which exhibit quantum size effects (QSE) are often called as 'Q particles'.[96] As the size of semiconductor particle is decreased, it is expected that there will be successive transition from semiconductor properties to molecular properties. The inconsistency arises when the size of the semiconductor particles becomes comparable with the de Broglie wavelength of the charge carrier in the semiconductor. The range of size for particles experiencing quantum size effects typically lies in the range 5-25 nm. The electron and hole produced in Q-particles are confined in a potential well of small geometrical dimensions. Although, the electron and hole do not experience the electronic delocalization present in a bulk semiconductor having a conduction band and a valence band. Thus, the confinement results a quantization of discrete electronic states and increases the effective band gap of the semiconductor.[70] One of the prominent effects of quantization is an increase in E_{BG}, and hence blue shift occurs in the absorption edge with decreasing particle size. Particles larger than about 6 nm starts to absorb close to 515 nm with decreasing size, the absorption threshold shifts to shorter wavelength i. e., CdS consisting a particles below 2.2 nm is colourless. In the case of semiconductors having a band gap smaller than that of CdS, the colour changes are even more drastic. Black cadmium phosphide having band gap of 0.05 eV can be made in all colours of visible light by decreasing the particle size between 10 and 2 nm.[96] Brus [97] studied the size quantization effect in CdS in 1983. The change of band gap was observed on changing the size of the particles from cluster to materials. Figure 1.5 shows the increase in effective band gap when the size of CdS particles is decreased from d>100 A° to d~26 A°.

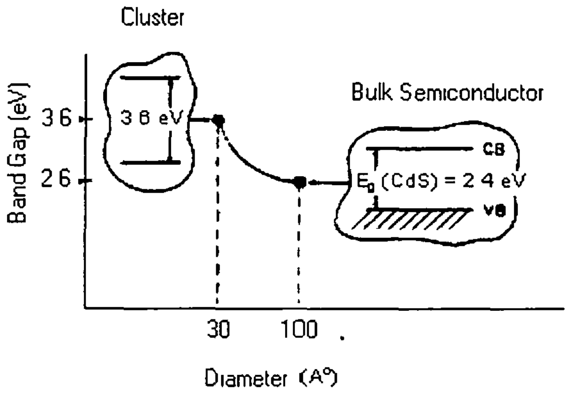


Figure 1.5: Quantum size effect on semiconductor band gap.[70]

The increase in effective band gap is observed experimentally as a blue shift in the absorption band and emission spectra for CdS.

The increase in effective band gap and consequently the blue shift in the absorption threshold can dramatically effective for bulk semiconductors with very small band gap. CdS, ZnO and PbS are the semiconductors where the shift of the absorption threshold with particle size has been explored and many review have already been published.[99]

1.1.4. Reactivity of semiconductor-based photocatalysts

A. Functional group transformations

The reaction proceed through heterogeneous semiconductor-based photocatalysis can be classified as oxidations, reductions, isomerizations, substitutions, condensations and polymerizations.

(i) Oxidations

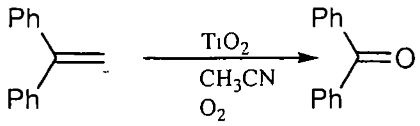
A variety of organic compounds can be oxidized with semiconductor particles[100] in presence of illumination. In the semiconductor-mediated oxidations, in addition to the electron hole, other oxidants such as oxygen, oxygen radical anion, and hydroxyl radical may also initiate the oxidations of organic substances. In case of TiO_2-mediated oxidation some active interm-

$$
\begin{aligned}
&TiO_2 \xrightarrow{h\nu} TiO_2(e^-,h^+)\\
&S \xrightarrow{h^+} S^{+\bullet}\\
&O_2 \xrightarrow{e^-} O_2^{\bullet-}\\
&H_2O \xrightarrow{h^+} H\dot{O} + H^+
\end{aligned}
$$

ediate are produced, where S indicates substrate. Virtually, every organic functional group having either a nonbonded lone pair or any π-conjugation can be available towards TiO_2 semiconductor particles. Some of them are

$$CH_3CH_2OH \xrightarrow[O_2]{TiO_2,\ h\nu} CH_3CHO$$

the gaseous anaerobic photo dehydrogenation of ethanol to the corresponding sulphoxide on TiO_2 powder suspended in aerated aqueous, nonaqueous solvent, quantitative conservation of C=C to corresponding ketone etc.

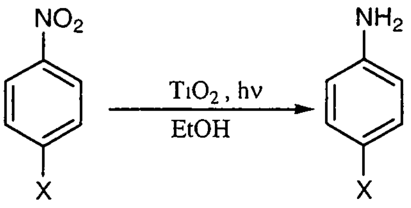


$$CH_3CO_2H \xrightarrow[H_2O \atop O_2]{TiO_2} CH_3CH_3 + CH_4$$

(ii) Reductions

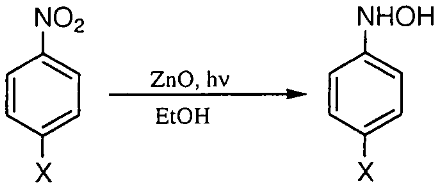
Semiconductor-catalyzed reduction involves of electron transfer, protonation and sometimes dehydration.[101] Basically, an alcohol is the source of protons as well as the electron donor to suppress electron-hole recombination. The hydrogen generated at the semiconductor-mediated reductions can be used as reducing agent. When TiO_2 is used as a catalyst in presence of light, nitro compounds are reduced to their amino derivatives.

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^-,h^+)$$
$$S \xrightarrow{e^-} S^{\dot{-}} \xrightarrow{H^+} \dot{S}H \xrightarrow{e^-} \quad \xrightarrow{H^+} SH_2$$
$$S + H_2\,(ad) \longrightarrow SH_2$$



X=H, CHO, $COCH_3$, CN, CH_3, OCH_3

On the other hand, hydroxylamino derivatives can be synthesized selectively through the photoinduced reduction of nitro compounds over ZnO.[102]



X=H ,Cl, I, NO_2, $COCH_3$, CH_3

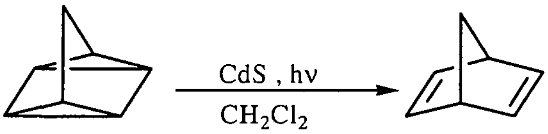
(iii) Isomerizations

It is the simplest organic conversion on semiconductor particles that involves due to single electron transfer and back electron transfer only. If the intermediate is thermally and kinetically stable enough than no net transformation occurs. Isomerizations will happen only when the intermediate is unstable. However, many isomerizations take place on irradiated semiconductor particles like CdS, TiO_2 or ZnO.[103]

$$S \xrightarrow[\text{or } e^-]{h^+} S^{\dot{+}}$$

$$S^- \xrightarrow[\text{or } h^+]{e^-} S$$

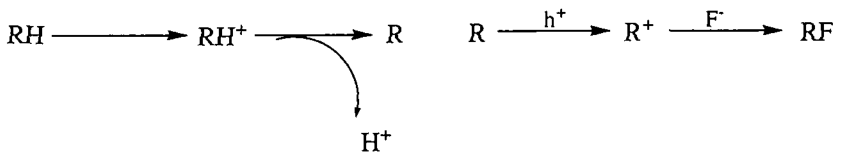
$$S \xrightarrow{h^+} S^{\dot{+}} \xrightarrow{\text{isomerization}} E^{\dot{+}} \longrightarrow E$$



(iv) Substitutions

Wang et al.[104] have reported selective fluorination of triphylmethane on irradiated TiO_2 in presence of AgF. A stable carbocation, which is formed after sequential electron transfer and proton elimination from the reactant, is the prime step for successful fluorination.

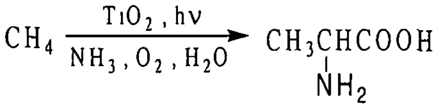
$$(C_6H_5)_3CH \xrightarrow[AgF,\ CH_3CN]{TiO_2,\ h\nu} (C_6H_5)_3CF$$



$$RH \longrightarrow RH^+ \longrightarrow R + H^+ \qquad R \xrightarrow{h^+} R^+ \xrightarrow{F^-} RF$$

(v) Condensation

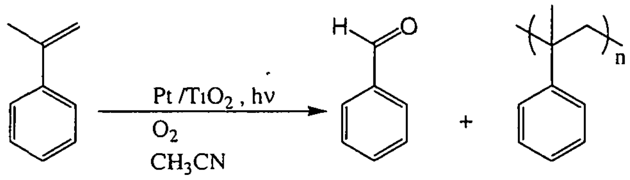
Bard and coworkers [105] have reported the production of amino acids, biologically important molecules, by illuminating near UV-irradiation of platinized TiO_2 photocatalyst in contact with $KCN/NH_3/H_2O$ mixture.

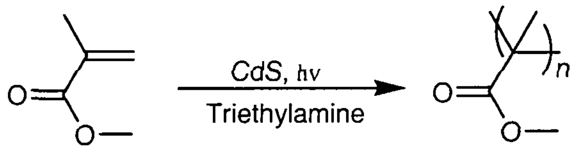


$$CH_4 \xrightarrow[NH_3,\ O_2,\ H_2O]{TiO_2,\ h\nu} CH_3CH(NH_2)COOH$$

(vi) Polymerization

Polymerization is observed only when oxygen and water are absent is heterogeneous photocatalysis system. In case of polymerization of alkenes system, semiconductor particles may generate monomer radical, which subsequently generate polymer.[84]





B. Environmental decontaminations

Semiconductor-mediated photooxidative degradation is new method for treatment of toxic and biologically persistent compounds.[54] Extensive works have been done in treatment of organic waste products through demineralization by irradiation on TiO_2 suspended in water.[106] So far, TiO_2 suspended in aerated water has proven to be the most active catalyst for this purpose, and anatase form of TiO_2 shows higher activity than rutile. A common industrial solvent, 2-ethoxyethanol can be completely decomposed by irradiating TiO_2.[107] Under same conditions, CdS and ZnO are less affective, though the same products are formed. Munner et al.[108] have successfully treated the industrial wastewater with suspended TiO_2 and over TiO_2 immobilized contaminating with methyl vinyl ketone. ZnO is also an efficient catalyst for photodecomposition of phenol,[109] but unlike TiO_2, ZnO shows accountable instability during irradiation.

Thus, semiconductor-mediated photocatalysis have shown its potential applications in different synthesis including organic functional group transformations. These transformations, operated through redox reactions, cover a wide range of organic compounds. Although, most of the transformations can be brought by conventional manner, one prime advantage of semiconductor-mediated photocatalysis is its capacity to provide an environmentally benign alternative. Literature abounds with examples of significant progress in semiconductor particle preparation and modifications to enhance surface electron-hole separation.[49] The physical difference between two electrodes is the prime difference between semiconductor photocatalysis and electrochemical processes i.e., in semiconductor-mediated reactions, both reduction and oxidation sites are on the same particle. This usually make disadvantage by charge recombination between conduction-band electrons and valence-band electron holes or back electrons transfer reaction between semiconductor particles and organic substrates. The close proximity between redox sites can also be an advantage for semiconductor-mediated photocatalysis.

There has been a wide range of semiconductor-mediated organic functional group transformations based on an oxidative step but reactions based on a reductive process are still limited. There are some excellent opportunities for new chemical transformations initiated with conduction electron transfer. Despite progress made in semiconductor particle immobilization and rector design, fundamental challenges still in the driving seat in conducting semiconductor-mediated photocatalysis at a synthetic scale. Overall, there are tremendous challenges and opportunities for research and development in the semiconductor-mediated organic synthesis.

1.1.5. Graft copolymerization onto silk

During the development of synthetic polymers, scientists and technologists have been concentrated in the modification of natural fibres and polymers through incorporation of selected monomer by graft copolymerization to make them use in specific purposes. Surface modification of fibres was always targeted to bring about the changes in their physico-chemical properties like stiffness, softness, wrinkle resistance, abrasion resistance and shrink proofing.[110] However, improvement of inferior performance properties of natural fibres such as photo yellowing, wash and wear properties, moisture absorption, crease recovery and water staining was successfully improved by different research groups.[111-113]

Narasimhan and coworkers [114] reported the graft copolymerization onto natural, formaldehyde-crosslinked cotton cellulose with methyl, ethyl and methyl methacrylate monomers. The density, birefringence and moisture regain of grafted fibres are less than those of natural cotton. Though, there is a decrease in the tensile strength of fibre but increase in elongation at break. Jute, a lignocellulosic bast fibre, faces stiff competition from .synthetic substitutes, can be improved with wider application prospects through its chemical modification including graft copolymerization of selected vinyl and related monomers.[115] Ghosh and coworkers [116] have studied the effect of graft copolymerization of mixture of acrylamide (AAm) and methyl methacrylate (MMA) on mechanical properties of jute fibres. The graft copolymerization technique offers a good scope for modification of mechanical properties depending on the degree of grafting and compositional variations of monomer mixture and multiconstituent of jute itself. Recently, Khan [117] reported UV radiation induced graft copolymerization of methacrylic acid onto jute fibre through preirradiation methods using a derivative of aromatic ketone as photoiniotiator. The study showed that the 47% graft weight has a significant effect on the mechanical and thermal properties in case of grafted jute. The mechanical properties of the jute-PMMA-grafted sample showed a decreasing trend for the breaking load and tensile strength, indicating disruption to the stronger bonds. The equilibrium water absorption showed increase in water content of jute up to 38% of graft weight. Garnett et al. [118] worked on graft copolymerization onto wool and found that the various redox systems could be successfully used for effective grafting of vinyl monomers onto wool in the presence of nitric acid and swelling solvent. Nayak and coworkers[119] reported the graft copolymerization of MMA onto wool by using hexavalent chromium ion as initiator.

Out of different fibres, silk fibres are valued for the outstanding characteristics that have been extensively used for the production of precious textile goods to household items. This fibre exhibits many outstanding properties like handle, luster, dyeability etc., which distinguish them from other synthetic and natural fibres. But, some minor textile performances viz., crease recovery, thermal stability, wash and wear characteristics need to be improved to expand silk consumption. In recent years, grafting has been regarded as a powerful tool to expand application potential. Methacrylamide (MAA), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) are currently applied for silk grafting, used either alone or in combination in the same grafting system.[113] Silk fibres, copolymerized with HEMA/MAA showed a noticeable increase in moisture content even at low graft yield [120] which took important role in improving the comfort of silk fibres. Tsukada and coworkers [7] have studied the graft copolymerization onto silk with MAA, HEMA and MMA with different free radical initiators. It is found that there is a decreasing tendency of tensile strength with increasing graft percentage. Kobayashi et al.[121] improved wrinkle recovery of grafted silk fabric through the surface modification with MMA. It was observed that the crease recovery was greatly improved by styrene grafting; especially in the weight gain range of 30-60%.[122]

Shiozaki and Tanaka [123] extensively studied the reactivity of epoxide toward silk fibre and indicated that the epoxide-grafted silk contributes significantly increase in textile properties. Tsukada [124] reported the effect of methacrylonitrile (MAN) grafting onto silk structure under the various weight gain conditions based on the result of tensile properties, DSC measurements, X-ray diffractometry, which provides valuable information about the improvement of present technique of graft copolymerizatión. The structural characteristics and physical properties of MMA-grafted *Bombyx mori* (one type of silk) fibre was determined by X-ray diffractometry, thermogravimetry and scanning electron microscopy (SEM).[125] Taking into account the X-ray diffraction patterns and increasing graft yield it is assumed that the graft chains of MMA polymer have penetrated into a weak aggregate region but not in crystalline region of fibre. The physico-chemical properties of grafted silk fibres largely depend on the chemical characteristics of vinyl monomer applied for grafting, as well as on the extent of grafting and on the reaction conditions. [119] Dolui et al. also reported the improvement of thermal stability and chemical resistance of MMA-grafted *Bombyx mori* fibre.[126]

In compare with other chemical modification processes, graft copolymerization has the advantages and drawbacks in their applications in certain end-use products. It has been observed that yellowing of silk occur during grafting.[127] To overcome this drawback, suitable post treatments are usually conducted, like bleaching, washing with suitable solvents etc. Grafting generally resulted loss of tensile strength of silk, which is reported in many lituratures.[2,7,124] The drastic changes in the surface morphology as a consequence of polymer loading, and the presence of newly generated boundary interactions between silk fibres and grafted chains, must be considered. As it is responsible for the observed drop of fibre strength, toughness induced by grafting.[7] Moreover, the extensive grafting of monomers has some negative consequences, due to the strong hydrophobic properties of the grafting polymer chains loaded inside the silk fibres and to the handle and stiffness of treated silk fabrics.

1.1.5.1. Silk microstructure

Over the decades, silk, known as 'queen of fibres' has been highly valued as a textile fibre due to its qualities of strength, elasticity, softness, absorbency and affinity for dye. In spite of synthetic fibres it has retained its supremacy in the production of luxury items and specialized articles of higher quality. However, silk apprehended the interest of scientific community more than a century ago and it was utilized as a source of protein until the early part of the twentieth century.[128]

(i) Sources of silk

Silk is produced by the larvae of variety of insects and spiders of the phylum Arthropoda. The most useful silks are from the protein secretions of the Bombycidae family. They include the domesticated moth (*Bombyx mori*), subfamily Bombycinae, Chinese tussah moth (*Antheraea pernyi*) and the Indian tussah moth (*Antheraea mylitta*) of the subfamily Saturniiae. The common varieties of the last are Tasar, Eri (*Attacus ricini*) and Muga (*Antheraea assama*). Out of these, the larvae of *Bombyx mori* are the most widely used in worldwide and most important source of silk. The amount of waste associated with the tussah and communal cocoons limits their application potential as fibres.

(ii) Physical properties of silk

The physical properties of silk are quite variable and depend widely on the source and growing environment (species and sericulture) of the silkworms.. The variations are due to the differences in amino acid composition and molecular organization. Some selected physical properties are noted in the Table 1.1.

Table 1.1. Some selected physical properties of silk (*Bombyx mori*) [129]

Property	Value
Density	1.33 gcm^{-3}
Refractive index	$n_{\parallel} = 1\ 591$
Moisture regain (65% rh, 25ºC)	10.7% (absorption)
Torsional rigidity	36×10^{12} Nm^{-2}
Specific heat of dry silk	1.38 Jg^{-1}K^{-1}

(a) Microscopic features

Bombyx mori fibres in longitudinally look like fine twisting filaments with few external marking. The average diameter of silk varies with type, variety of species, and condition of processing. The diameter of the filaments varies with the location in the cocoon, being coarser outside and finer in the inside, for example 15-25 μm for the of *Bombyx mori* and up to 65 μm for the of tussah silks. Iizuka and coworkers [129] have reported the correlations among fibre diameter and tensile strength and modulus along different filament lengths from within the same cocoon and among different species.

(b) Mechanical properties

Silk is unparallel among natural fibres because it's quite high strength and breaking extension that result in a high work to rupture. Therefore, it is highly desirable in the manufacture of textile materials where toughness is the prime consideration. Meredith [131] worked on the stress-strain curves for silk and other fibres and compared the tensile behaviour of fibres under same conditions. It was reported that both the breaking stress or tenacity and the breaking extension or strain of natural silk compare favourably with those of nylon. The Table 1.2. illustrates the typical tensile properties of some selected fibres. Tussah silks generally have a slightly lower tenacity but a much higher breaking extension than do cultivated silks. The mechanical properties, extension at break and initial modulus of silk were related to fibre fineness.[131] In common, the finer the silk, the higher is the tenacity and initial modulus and lower is the breaking extension. Similarly,

Table 1.2. Typical tensile properties of silk and other fibres[129]

Fibre*	Tenacity (N/tex)	Breaking extension (%)	Work to rupture (mN/tex)
Cotton	0.45	6.8	14.9
Viscose rayon	0.18	27.2	30.6
Silk	0.38	23.4	59.7
Nylon	0.47	26 0	76.0
Wool	0.11	42.5	30.9

* 1 cm test length, 65% rh; 20°C

finer the fibre, the higher is the Young's modulus and greater is the degree of crystanalinity.[132]

(iii) Chemical properties of silk

(a) Hydrolytic effects

Silk hydrolyzed in boiling water and stream at 100ºC. The tendering of silk by mineral acids and alkalis occurs as a result of fission of polypeptide chains of fibroin. The process is pH dependent and the least degradation occurs between pH 4 and 8. The presence of very small amount of cystine linkage is considered for higher alkali resistance.[133]

(b) Photodegradation and yellowing of silk

Silk is more susceptible to the tendering of light than any other natural fiber.[134] Photoyellowing generally accompanies photochemical degradation. These facts have serious effects, particularly for the storage, display and conservation of ancient silk fabrics and garments.

The reaction mechanisms involved in photodegradation and yellowing are complex and little understood. UV radiation is the most active component of light effecting these changes. Okamoto [135] reported that the aromatic residues, tyrosine, threonine and leucine in the amorphous regions of the fiber were most readily affected upon exposure to UV lights.

Objectives of the present study

Graft copolymerization is a well-defined technique applied for modification of properties and textile performance of fibres including natural silk. The synthesis of graft copolymerization proceeds through different methods in which radiations initiation technique is considered to be safer technique, as it causes in less deterioration of original fibre properties. In photoinduced technique photoinitiators like AIBN, BPO,1-hydroxycyclohexyl-phenyl ketone (HCAP), 2,2'-azobis(2-amidino propane), dihydrochloride (ADC) etc. are applied frequently. Semiconductors like CdS, TiO_2, ZnO are successfully applied for organic functional group transformation and environmental decontaminations. Till now these systems are not implemented for graft copolymerization. Therefore, we are planning to graft copolymerization onto silk fibre through semiconductor based photocatalyst along with the studies of photocatalytic behaviour of semiconductor.

The broad objectives of this research works are mainly,

a) To find out the suitability of semiconductor as photocatalyst for photopolymerization of vinyl monomers.

b) To find out the reaction mechanisms of semiconductor based photocatalysis through UV-Visible, Fluorescence emission and Electron Paramagnetic Resonance spectrophotometers.

c) To develop a method of graft copolymerization onto silk, particularly *Bombyx mori* for modification of surface properties of the fibres through photograft copolymerization of vinyl monomers.

d) To calculate the grafting parameters, like graft yield, graft conversion, graft efficiency, homopolymer formation, total conversion etc.

e) To evaluate the changes in the physical properties, chemical resistance of grafted products.

f) To characterize the graft copolymer by FTIR, X-ray diffraction, DSC, TGA, UTM (universal testing machine) and SEM techniques.

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Chapter-II

Photopolymerization of methyl methacrylate using semiconductor-based photocatalyst *

2.1. Introduction

In a homogeneous photocatalysis system, photoinduced molecular transformations occur at the surface of the catalyst. Based on the type of initial excitation, heterogeneous photocatalysis can be classified into two groups. If the initial excitation occurs in an adsorbate molecule that interacts with the ground state catalyst surface then the process is termed as catalyzed photoreaction. On the other hand, if the initial photoexcitation takes place in the catalyst substrate and the excited catalyst then interacts with the ground state absorbate molecule, the process is called as sensitized photoreaction.[1] However, in most cases, heterogeneous photocatalysis *refer to semiconductor photocatalysis or semiconductor-sensitized* photoreactions.

Heterogeneous dispersion of semiconductor surface expedite both a fixed environment to affect the chemical reactivity of a wide range of adsorptions and to initiate light induced redox reactivity in these weakly bounded species. On irradiating the system of specific radiation, simultaneous oxidation and reduction reaction occur. The incident light that initiate in a wavelength region absorbed by the semiconductor rather than by the substrate of interest.[2] These types of reactions are therefore involve

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photosensitization processes where indirect photoactivation of the homogeneously dispersed particles absorber take place.

The original interest of semiconductor-sensitized photoreactions was promoted by Fujishima and Honda (1972) through discovery that water could be split upon illuminating a TiO_2 single crystal electrode.[3] This observation became popular and applied as novel redox reactions of organic functional group transformations and other organic substitutions[4] could also be induced by band gap irradiation of a variety of semiconductors particles of various sizes and large single crystal.

The heterogeneous photocatalysis reactions with various semiconductors TiO_2, ZnO, CdS, ZnS etc. have been studied extensively over the last decades.[5,6] Semiconductors are used for carrying out many organic reactions. Grätzel et al.[7] reported the applicability of semiconductor particles as photocatalyst for reduction/oxidation of water and for oxidation/reduction of contaminant in water in the presence of sacrificial electron donors/acceptors. The semiconductor particle has also been used as sensitizer for organic photosynthetic processes.[8] It is also possible to introduce the alternative pathway of Kolbe's reaction for the formation of acetic acid by applying rutile TiO_2 as photoanode. Semiconductor colloids and Q particle (Q-indicates particle showing size quantization effect) has also been used by different research groups.[9,10] Hoffmann et al.[11] showed that the rate of photoinitiated polymerization of several vinyl monomers by Q-sized semiconductor particles of CdS, ZnO and TiO_2 increases with increasing particle size.

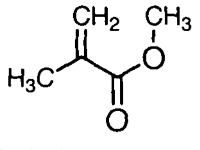
The efficiency of the electron transfer reaction governs semiconductor's ability to serve as a photocatalyst for redox reactions. The efficiency is a function of the positions of semiconductor's conduction and valence bands relative to the redox potentials of the adsorbed substrates. To suppress the electron-hole recombination and continuously supply valence-band electron holes for an oxidative purpose, a sacrificial electron acceptor must be added to scavenge the electron in the conduction band.[12] An electron donor, such as an alcohol or an amine is often used to scavenge the electron holes so that the conduction-band electrons are available for the reaction.[13] Surface sensitization of a semiconductor via chemisorbed or physisorbed is another efficient method to expand the wavelength range response and prolong the electron-hole seperation.[14] It has been reported that some organic dye complexes with metals are stable under redox conditions.[15] After dye sensitization, the oxidation power is determined by the highest occupied molecular orbital (HOMO) of the organic dye, which is usually less powerful as an oxidant than electron hole.[16] The sensitization permits expansion of wavelength response of the photocatalyst, which is prime important when the photocatalyst are to be irradiated with sunlight since the chemically stable metal oxides are wide band gap semiconductors whose absorption occur in the UV spectrum.[12] Photosensitization of semiconductor by different dyes has provided valuable information of interfacial electron transfer on the semiconductor surface.[17] Some common dyes which are used as sensitizer include erythrosin B,[18] thionine,[18] eosin [19] and analog of $Ru(bpy)_3{}^{2+}$ [20] If the oxidative energy level of the excited state of dye molecule with respect to the conduction band energy level of the semiconductor is favourable, then the dye molecule can transfer the electron to the conduction band of the semiconductor. The surface acts as a quencher by accepting an electron from the excited dye molecule. The electron can be transferred for reducing purpose of an organic acceptor molecule adsorbed on the surface.

In this study, photopolymerization of methyl methacrylate has been performed in presence of semiconductor-based photocatalyst. Among the variety of semiconductor available, CdS was considered as because it absorb in the visible region of spectrum (λ_{max} 514 nm). To increase the efficiency of semiconductor, electron scavengers like triethylamine, ethylene glycol were used. Dye like eosin (λ_{max} 524 nm) was also applied with CdS to increase the wavelength response of spectrum. The effect of dye on semiconductor assisted photopolymerization of MMA has been studied. The stability of dye during exposure to light has also been explored. The free radical polymerization of MMA has been established with EPR spectra.

2.2. Reagents and chemicals

2.2.1. Monomers

Among the different vinyl monomers, methyl methacrylate (Merck) was taken for polymerization.

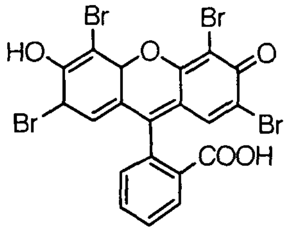


Methyl methacrylate

M.W = 100.12
M.P = 48^0C
B.P = 100^0C
Soluble in methyl ketone, tetrahydrofuran

2.2.2. Catalyst

Cadmium sulphide (CdS) of 20 nm in average size was taken as photocatalyst. Eosin Y (dye) was taken as sensitizer for semiconductor-based photocatalysis.



Eosin Y
(2',4',5',7'-tetrabromofluorescein)

2.2.3. Regents

Sodium hydroxides (CDH), acetone (Merck), petroleum ether (Merck), ethylene glycol (CDH) were used for the study.

2.2.4. Purification of monomers and additive (sensitizer)

Methyl methacrylate (MMA) was purified by repeated washing with 4% aq. NaOH solution, and then washed with distilled water to make it free from alkali. The washed monomer was dried over anhydrous BaO for 24h and distilled under nitrogen in reduced pressure.[21] The middle fraction was used for all experiments.

Eosin Y (λ_{max} 524 nm) freed from inorganic halides by repeated crystallization from butane-1-ol.[22] Acetone and petroleum ether were distilled prior to use.

Ethylene glycol (B. P. 68°/4 mm) dried with CaO and distilled under vacuum. Further, it was dried under nitrogen, refluxed and distilled. The distillate was then passed through a column of molecular sieves and finally distilled under nitrogen.[22]

Triethylamine (B. P. 89.4°C) dried with $CaSO_4$ then distilled.

2.3. Methods

2.3.1. Photopolymerization

A three-necked flask (250mL) fitted with a stirrer, a thermometer pocket and a nitrogen inlet was used for the polymerization. A known amount of purified monomer was taken in the flask and nitrogen was passed slowly through the reaction mixture (monomer and catalyst) and set up was exposed to the light source (high pressure mercury vapour lamp; 125 W, radiation intensity of 750 Wm^{-2}) with intermittent stirring. The reaction temperature was kept in the range of 35-40°C and distance between the light source and flash was maintained 10 cm in each cases. The polymer was precipitated by pouring the contents of the reaction vessel slowly in a beaker containing petroleum ether under stirring condition. Then, the polymer was filtered and washed thoroughly with acetone to make it free from the unreacted monomer. The purification was carried out by reprecipation in petroleum ether and finally the product was dried at 60°C under vacuum. The yield of the reaction was reported as percentage conversion.

2.3.2. Intensity of light source

The intensity of light source was recorded with a thermoelectric pyranometer with respect to distance between reaction vessel and light source.

2.4. Characterization of polymers

2.4.1. Gel permeation chromatography analysis

Gel permeation chromatography (GPC) was performed using GPC (Water, USA model 515) solvent delivery system at a flow rate of 1 mL/min through a set of three ultrastyregel columns. Analysis was done at controlled temperature at 45°C using HPLC grade tetrahydrofuran as eluent. Sample concentration and volume of polymer injected were 0.2% (wt/vol) and 50 μL, respectively.

2.4.2. Fluorescence spectra

The reaction mixture containing monomer and dye was exposed with light source for 2- 4 h. Then fluorescence spectra were recorded with a Sp-exFluoromax-3 Spectrofluorimeter.

2.4.3. Ultraviolet (UV) spectroscopy

The ultraviolet spectra of monomer-catalyst-additive systems were recorded in the range of 200-700 nm by using Hitachi, (U-2001) UV spectrophotometer.

2.4.4. Electron paramagnetic resonance measurement

Electron paramagnetic resonance (EPR) signals recorded in the initial stage of polymerization for the study of reaction mechanisms, on a Bruker EMX spectrometer operating in the X-band, utilizing a 100 kHz field modulation and a microwave power of 1 mW. The EPR spectrometer was coupled to a computer for data acquisition and instrument control. Monomer, additives and PBN (α-phenyl-*tert*-butyl nitrone) as a spin trapper were added to a sample tube of 3 mm outer diameter and the mixtures were purged with nitrogen gas. The sample tube was irradiated with 125 W high-pressure mercury vapour lamp for 30 minutes and EPR spectra were recorded to detect the different radicals generated in the reaction mixture.

2.5. Results and discussion

2.5.1. Effect of semiconductor based photocatalyst (SCP) and dye on polymerization of methyl methacrylate

The results of photochemical conversion of the monomer (MMA) with or without additives are reported in Table 2.1. It is found that MMA without additives is not polymerized. In presence of semiconductor particles (CdS) it shows low conversion (2.43%). A higher conversion (14.27%) has been achieved when CdS was used with electron donor like triethylamine. This is possibly due to the easy formation of radical through the oxidation of

Table 2.1: Photopolymerization of MMA using different additives

Set No.	Mixture	Yield (g)	Conversion* (%)
1	MMA	Nil	Nil
2	MMA + CdS	0.023	2.43
3	MMA + CdS + Et_3N	0.134	14.27
4	MMA + eosin	0.115	12.23
5	MMA + CdS + eosin	0.213	22.73

MMA = 1mL, CdS = 0.01g, triethylamine = 0.02 mL, eosin = 0.01g

Exposure time = 6h, temperature 35°C

* Data reported from the average of three samples

triethylamine by the hole generated in CdS. Triethylamine without CdS can also initiate the polymerization by the formation of free radicals. In presence of light, triethylamine can generate free radicals for subsequent polymerization.[16,23] Similarly, dye without CdS could also initiate the photopolymerization.[24,25] It is found that the conversion increases with

Table 2.2: Effect of exposure time on polymerization of MMA with dye as catalyst

Set No.	Mixture	Exposure time (h)	Yield (g)	Conversion* (%)
1	MMA + eosin	1	0.009	1.03
2	MMA + eosin	2	0.018	2.01
3	MMA + eosin	3	0.051	5.42
4	MMA + eosin	4	0.079	8.47
5	MMA + eosin	5	0.092	9.82
6	MMA + eosin	6	0.115	12.23

MMA = 1mL, eosin = 0.01g, temperature = 35°C

* Data reported from the average of three samples

Table 2.3: Effect of exposure time on polymerization of MMA using dye sensitized semiconductor photocatalyst

Set No.	Mixture	Exposure time (h)	Yield (g)	Conversion* (%)
1	MMA + CdS + eosin	1	0.013	1.35
2	MMA + CdS + eosin	2	0.023	2.44
3	MMA + CdS + eosin	3	0.053	5.63
4	MMA + CdS + eosin	4	0.089	9.46
5	MMA + CdS + eosin	5	0.170	18.08
6	MMA + CdS + eosin	6	0.214	22.73

MMA = 1mL, CdS = 0.01g, eosin = 0.01g, temperature = 35°C

* Data reported from the average of three samples

exposure time (Table 2.2 & 2.3) and 12.23 % conversion has been reached by 6h exposure in presence of dye as photocatalyst (Table 2.2). A conversion of 22.73% has been noted when polymerization was performed with dye-sensitized semiconductor photocatalyst (Table 2.3).

The triethylamine in presence of semiconductor can generate stable monomer free radical possibly via following mechanism.

$$\mathrm{CdS} + h\nu \longrightarrow e^-_{\,(\mathrm{CdS})} + h^+_{\,(\mathrm{CdS})}$$

$$h^+_{\,(\mathrm{CdS})} + \mathrm{Et_3N} \longrightarrow \mathrm{Et_3N}^{+\bullet} \xrightarrow{-\mathrm{H}^+} \underset{(\mathrm{R}^\bullet)}{\mathrm{CH_3\dot{C}HN(CH_2CH_3)_2}} \qquad (1)$$

$$\mathrm{R}^\bullet + \mathrm{M} \longrightarrow \mathrm{RM}^\bullet \xrightarrow{n\mathrm{M}} \text{Polymer} \quad \text{(M stands for monomer)}$$

In the reaction (1) triethylamine is oxidized by reaction with positive hole in the valence band of semiconductor and subsequently it produces stable free radical on deprotonation. This free radical subsequently generates the monomer free radical, which ultimately leads to polymer product.

The paramagnetic species generation in this case is better understood by EPR spectra of initial stage of polymerization of MMA in presence of $\mathrm{Et_3N}$ and CdS. The EPR spectra were recorded using PBN as a spin trapper to observe the generation of free radicals. The EPR spectra for this system represented in Figure 2.1 (curve c). The EPR spectrum shows signals for two different types of radical-spin trap adducts [possibly one for free radical initiator ($\mathrm{R}^\bullet$) and other for monomer or polymer radical ($\mathrm{RM}^\bullet$)].

The intensity of EPR signals is low possibly due to lower amount of *paramagnetic species generated in the system.*

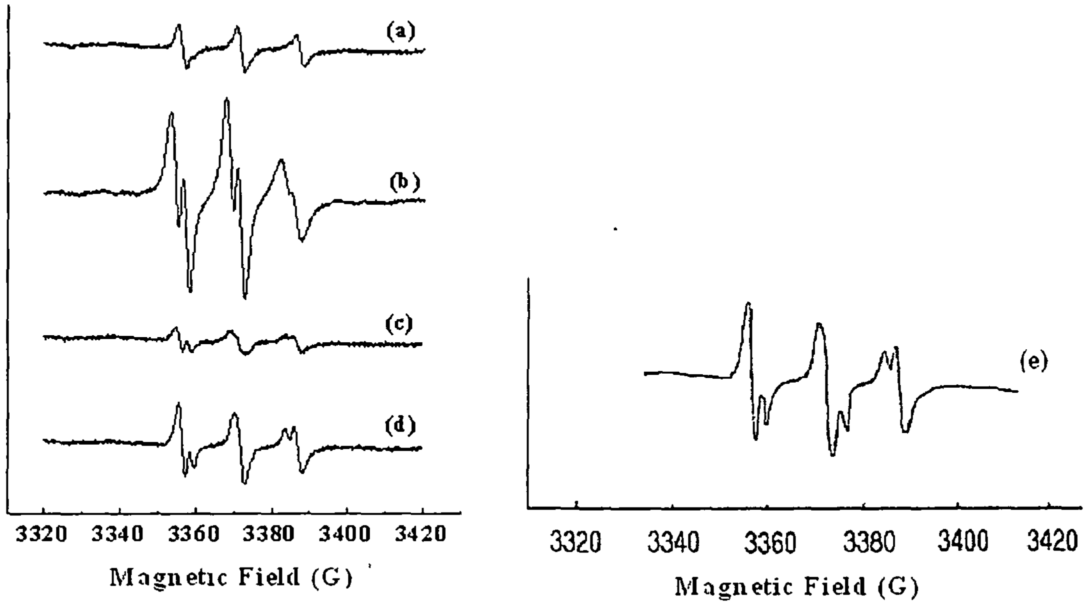


Figure 2.1: EPR spectrum of paramagnetic species observed at 25°C after 30 minutes of exposure on different systems (after 6 scans): (a) MMA-CdS-PBN, (b) MMA-CdS-dye-PBN, (c) MMA-CdS-Et_3N-PBN, (d) MMA-dye-PBN, (e) MMA-CdS-PBN (after 45 min exposure)

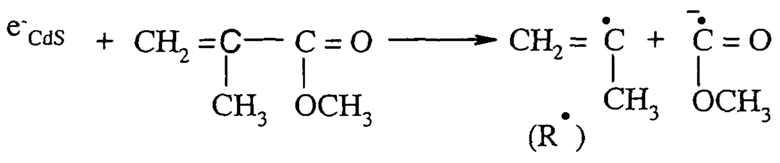
Dye-sensitized semiconductor photocatalyst can initiate photopolymerization and the possible reaction mechanism can be represented as follows.

$$D + h\nu \longrightarrow D^*$$

$$D^* + CdS \longrightarrow D^+ + e^-_{CdS} \qquad (2)$$

$$D^* \longrightarrow D \qquad (3)$$

$$D^+ + e^-_{CdS} \longrightarrow D + CdS$$

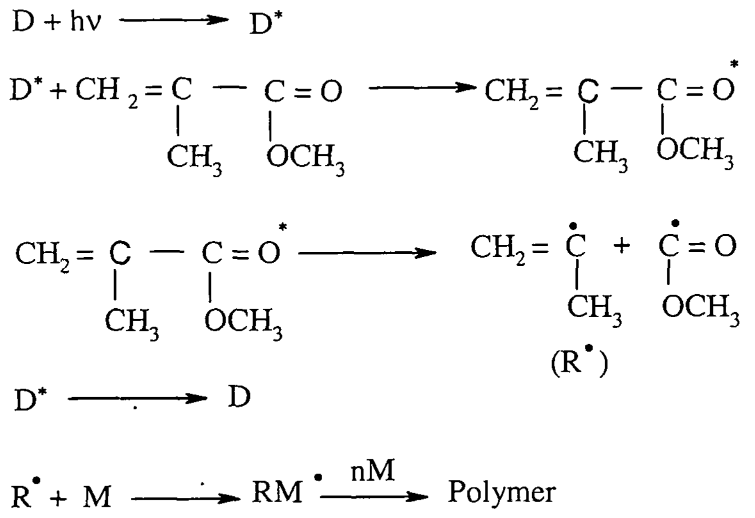


$$e^-_{CdS} + CH_2{=}C(CH_3){-}C(OCH_3){=}O \longrightarrow \underset{(R^\bullet)}{CH_2{=}\dot{C}(CH_3)} + {}^{-}\dot{C}(OCH_3){=}O \qquad (4)$$

$$R^\bullet + M \longrightarrow RM^\bullet \xrightarrow{nM} \text{Polymer}$$

The photochemical excited dye (D^*) injects the electron[16] to the conduction band of the semiconductor according to reaction (2), subsequently competing with the deactivation reaction (3). The resulting charge separated system undergoes a relaxation and a recombination process with typical time constant in the range from 10fs up to 500μs.[23] Further electron in conduction band of semiconductor may transfer it to the monomer and subsequently generates free radical (4), which is again confirmed by EPR signal represented as curve b in Figure 2.1. The intensity of EPR signal is high enough and reveals the higher concentration of paramagnetic species in the system during the initial stage of polymerization. MMA-CdS system (curve a in Fig 2.1) shows only one type of free radical-spin trap product. The non-existence of second set indicates the absence of monomer radical in the spectra. This is probably due to short time (30 minutes in all the cases) exposure, which is not sufficient to generate monomer free radical. The same system (MMA-CdS) showed two sets of EPR signal when the system was irradiated for slightly longer period of time (45 minutes) shown in Figure 2.1, curve e. Although EPR spectra with different exposure time were recorded but it was found that beyond 30 min exposure spectra were similar in nature and provides no special information (except spectra in Fig 2.1, curve e). After 1 hour exposure the solution became very viscous and solidified and EPR spectra were not well resolved.

When dye (D) is used as photocatalyst in visible light, it forms the electronically excited state (D^*) by absorption of light. Later on it transfers



$$\begin{aligned}
&D + h\nu \longrightarrow D^*\\
&D^* + CH_2{=}\underset{CH_3}{C} - \underset{OCH_3}{C}{=}O \longrightarrow CH_2{=}\underset{CH_3}{C} - \underset{OCH_3}{C}{=}O^* + D\\
&CH_2{=}\underset{CH_3}{C} - \underset{OCH_3}{C}{=}O^* \longrightarrow \underset{(R^\bullet)}{CH_2{=}\underset{CH_3}{\dot{C}}} + \underset{OCH_3}{\dot{C}}{=}O \qquad (5)\\
&D^* \longrightarrow D\\
&R^\bullet + M \longrightarrow RM^\bullet \xrightarrow{nM} \text{Polymer}
\end{aligned}$$

its energy to the acceptor (monomer) and the resulting excited state acceptor (monomer) dissociates into free radical (R$^\bullet$) by intramolecular bond cleavage [26] (5).

The generation of paramagnetic species may be supported by EPR spectra as curve d in Figure 2.1. Here again two sets of EPR spectra reveals two different paramagnetic species generated during the initial polymerization of MMA-dye system, one of which initial radical (R$^\bullet$) spin trap adduct and anther for monomer radical spin trapper. The low intensity spectrum indicates the lower concentration of initiating radical, which readily decomposes to monomer free radical and subsequently, leads the polymer product.

The fluorescence spectra were recorded at different interval of exposure with visible light (Fig 2.2). In case of dye-monomer, the fluorescence maximum was observed around 550 nm. This is an excited singlet to ground state transition for the dye, which is characteristic transition for the dye.[27] The intensity of the fluorescence maxima observed for dye exposed to 6h visible light was higher than the fluorescence maxima for the dye exposed to 2h visible light, which in turn was higher than the dye, which was not expos-

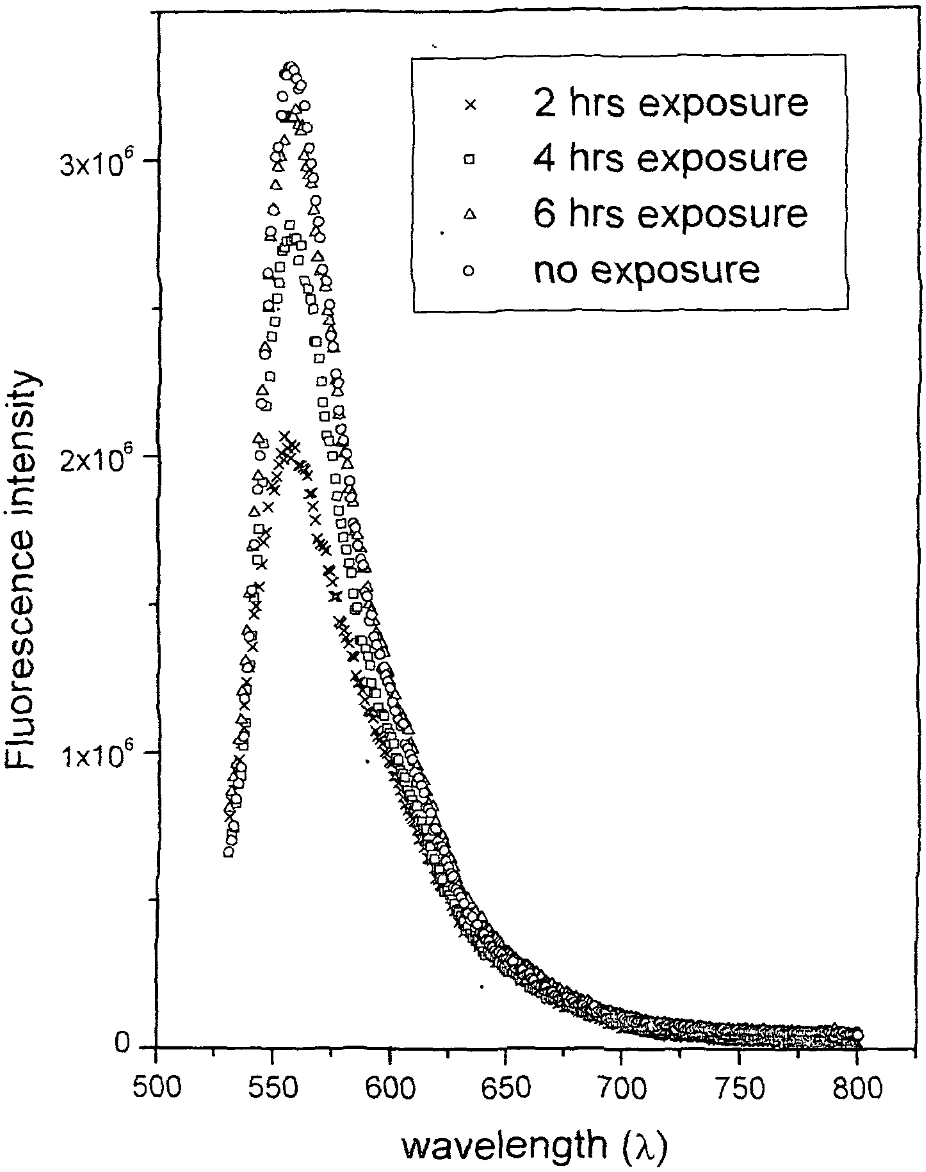


Figure 2.2 (a): Fluorescence emission spectrum of dye (eosin) and monomer (MMA). 0.001g dye in 1mL MMA.

ed to visible light at all. This is possibly due to dyes were involved various photochemical reaction i.e. excited dye molecules were trapped by the free radical generated in the systems during initial exposure.[28] As exposure time proceeds, dye became free and behaves like original dye(with no exposure).

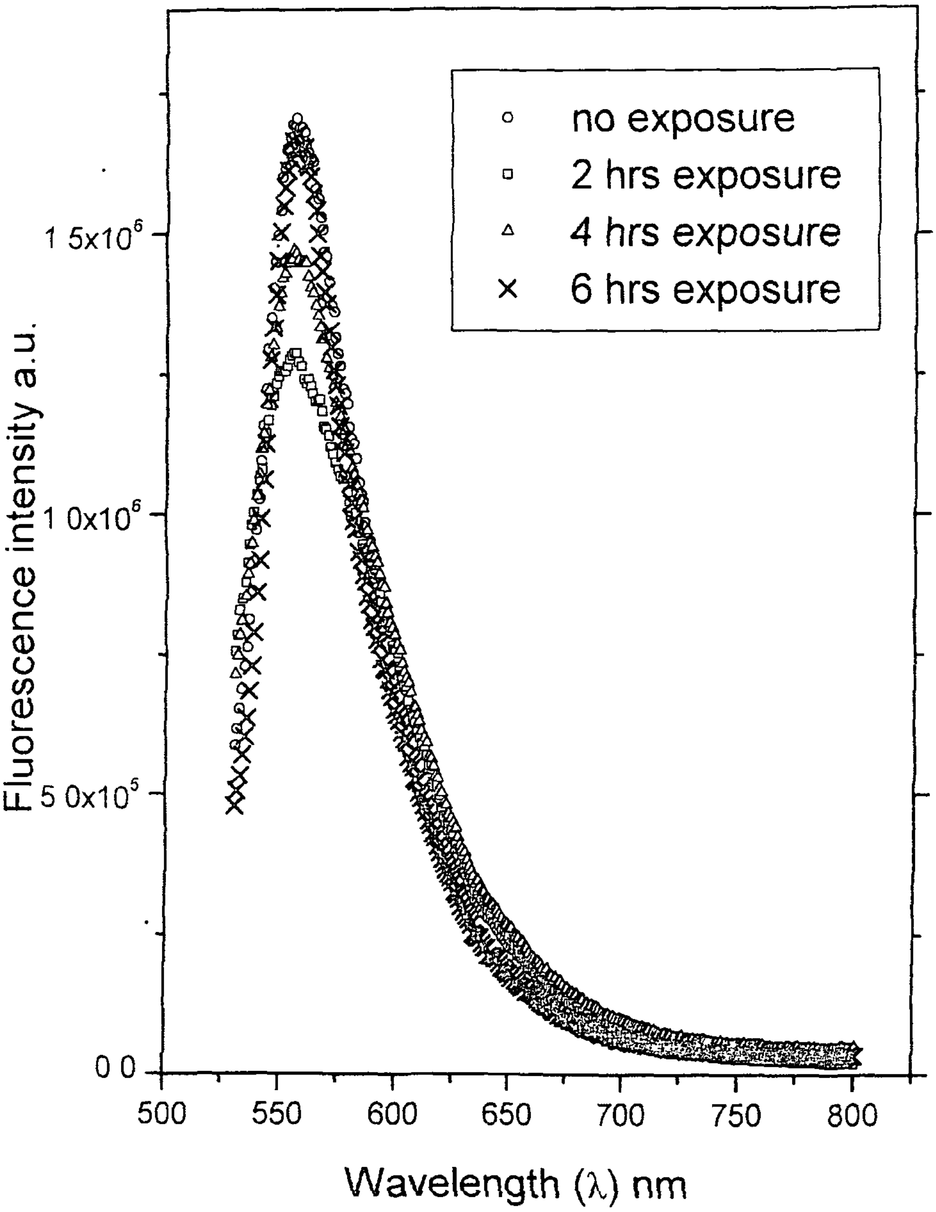


Figure 2.2 (b)·Fluorescence emission spectrum of CdS, dye and MMA. 0 001g dye and 0 001g CdS in 1mL MMA.

The fluorescence emission spectrum clearly shows the active participation of dye in the photopolymerization of MMA-dye system. The fluorescence emission spectrum of CdS-dye-monomer system was also studied [Fig 2.2. (b)] and fluorescence maxima observed at 550 nm. The intensity peaks were resolved at lower value than the due-monomer system. Except this, the nature of the absorption in different time intervals is same in each case. Similarly as exposure increases to 6 h, dye become free and behaves like original form of dye and thus it shows the active participation of dye even with the presence of semiconductor in photopolymerization of MMA.

2.5.2. Stability of dye in presence of semiconductor particles

The stability of dye exposed to visible light during photopolymerization was studied in presence of monomer and CdS. The MMA-dye and MMA-CdS-dye systems were irradiated for different time intervals and absorption spectra were recorded with Hitachi UV-Visible Spectrometer (Model 2001).

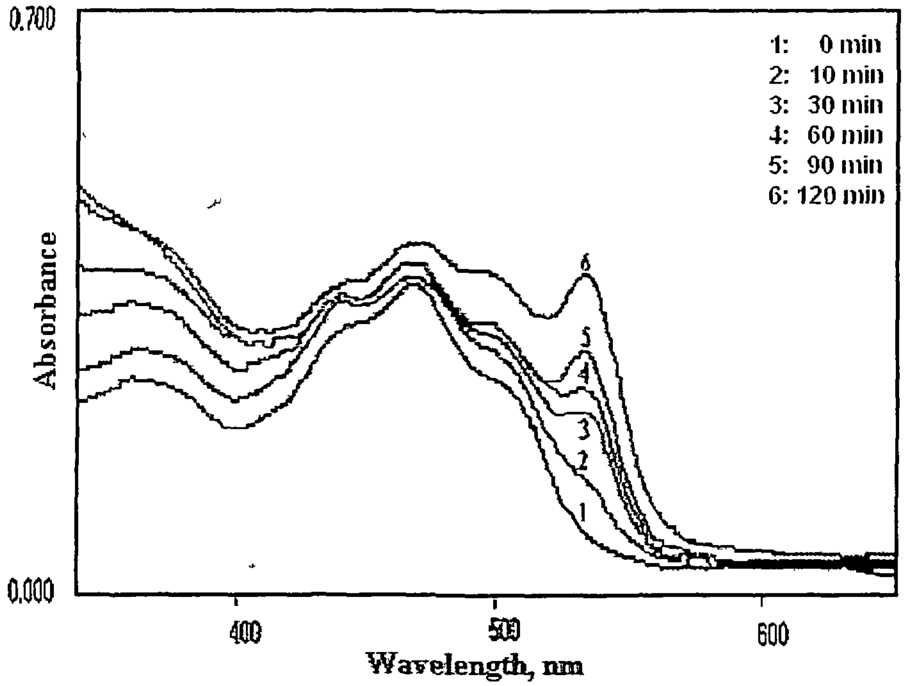


Figure 2.3: Changes in the absorption spectrum of eosin (dye)-monomer (MMA) solution with time of illumination: initial dye concentration, 0.06 g in 10 mL monomer.

In case of dye-MMA system, a new peak was observed after 30 minutes of exposure with light (Fig 2.3, curve 3). This is possibly due to the generation of new species from dye, indicating instability of dye. However dye in MMA-dye-CdS system is quite stable. There is no change of trend in absorption curve (Fig 2.4). The polymerization was going smoothly in both the cases. It indicates that dye is quite stable in MMA-CdS-dye system.

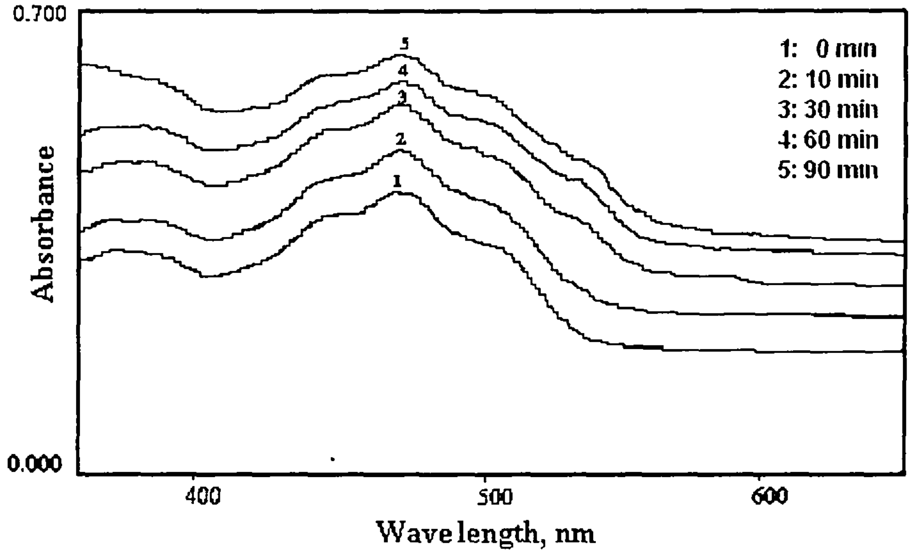


Figure 2.4: Changes in the absorption spectrum of eosin (dye)-monomer (MMA) and CdS solution with time of illumination: initial dye concentration, 0.06 g in 10 mL monomer and amount of CdS, 0.01g

2.5.3. Effect of variation of exposure time on percentage conversion

Table 2.2 shows that percentage conversion increases with exposure time for MMA-dye system. The maximum percentage conversion achieved is 12.23 after 6h of exposure. A similar trend is observed with MMA-CdS-dye system (Table 2.3). The maximum conversion of 22.75% is achieved after 6h exposure with MMA-CdS-dye. This shows efficient catalytic effect of CdS-dye system for photopolymerization of MMA.

2.5.4. Nature of polymer and molecular weight

The GPC results are given in Table 2.4. The GPC result shows higher polydispersity for CdS-eosin system than the eosin only. MMA-CdS-dye produces higher average molecular weight than MMA-dye system.

Table 2.4: Molecular weight of different PMMA by GPC (average molecular weight)

Sample	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_{z+1}$	Polydispersity
PMMA (eosin as catalyst)	12.23	26010	126050	602240	1735100	4.69
PMMA (eosin and CdS as catalyst)	22.74	61860	386580	1462320	3258700	6.25

2.6 Conclusion

The semiconductor-based photocatalyst in combination with a suitable dye has been shown to be a promising initiator for the polymerization of MMA. In the photopolymerization of MMA, CdS-dye system produces the highest conversion and higher molecular weight of polymer than dye (eosin) system. It has been observed that the semiconductor-based photopolymerization of MMA proceeds through the free radical mechanism. The generation of initiating radical in different systems follows different pathway but ultimately initiating radical combines with the monomer to start the chain reaction.

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Chapter-III

Graft copolymerization of methyl methacrylate and acrylamide onto *Bombyx mori* fibre initiated by semiconductor- based photocatalyst *

3.1. Introduction

Over the decades, silk has been highly valued as a textile fibre due to its qualities of strength, elasticity, softness, absorbency and affinity for dye. Silk apprehended the interest of scientific community more than a century ago and it was utilized as a source of protein until the early part of the twentieth century.[1] The most useful silks are from the protein secretions of the Bombycidae family. They include the domesticated moth (*Bombyx mori*), subfamily Bombycinae, The common varieties of other silk fibres are Tasar, Eri (*Attacus ricini*) and Muga (*Antheraea assama*). Out of these *Bombyx mori* are the most widely used in worldwide and most important source of silk.[2]

The physical properties of silk are quite variable and depend widely on the source and growing environment (species and sericulture) of the silkworms. The variations are due to the differences in amino acid composition and molecular organization. The different amino acids sequences available in the silk fibron were reported by Lucas et al.[3] and Lucas and Rundall.[4] The result from the selected number of amino acid analyses of fibron from *B. mori* are reported [2] in the Table 3.1

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* Part of this work is accepted for publication in Bioresource Technology, 2005 (In press).

Table 3.1: The amino acid composition of *Bombyx mori* silk fibre

Amino acids	Composition (%)
Glycine	44.60
Alanine	29.40
Serine	12.10
Tyrosine	5.17
Valine	2.20
Aspartic acid	1.30
Glutamic acid	1.02
Threonine	0.91
Phenylalanine	0.63
Isoleucine	0.66
Leucine	0.53
Arginine	0.47
Lysine	0.32
Proline	0.36
Histidine	0.14
Methionine	0.10
Triptophane	0.11
Cysteine	0.20

During the development of synthetic polymers, scientists and technologists have concentrated in the modification of natural fibre and polymer through incorporation of selected monomer by graft copolymerization process to make them use in specific purposes. Surface modification of fibre was always targeted to bring about the changes in their properties like stiffness, softness, wrinkle resistance, abrasion resistance and shrink proofing.[5] However, improvement of performance properties of natural fibres such as photoyellowing, wash and wear properties, moisture absorption, crease recovery and water staining were successfully carried out by different research groups.[6-8]

Grafting onto silk is a heterogeneous well-known process where physical structure and the state of aggregation of the silk fibre play an important role. During the grafting, chemical bonding is achieved and the synthetic polymer is associated in such a way that the uploaded polymer chains can not be separated by the usual fractionation techniques. Normally, extent of grafting depends on the incline of chemical as well as physical conditions and nature of substrate.[9] The chemical conditions include diffusion of monomer to the silk, absorption of the monomer on the silk, initiation of the active sites on the backbone, termination of active sites and homopolymer formation. On the other hand physical conditions involve swelling of silk and accessibility of silk.[10]

The silk fibre contains both amorphous and crystalline regions without having sharp boundary between the crystalline and amorphous areas. Because of their heterogeneous nature, on graft copolymerization it is expected to be affected by the pore size of the silk, the crystalline-amorphous ratio, the degree of orientation and the size of crystallite.[11]

Graft and block copolymerizations are novel methods to combine the physical and chemical properties of two or more different monomers to a single polymeric chain.[12-15] Out of different graft copolymerization methods, free radical induced polymerization is the easiest and widely accepted procedure for this purpose.[16] Free radical graft copolymerization are generally initiated by variety of species capable of generating primary free radicals via chemical reaction or thermal dissociation.

In case of free radical mechanism, various initiators systems like AIBN, BPO, APS, cerric ammonium nitrate (CAN) [17], Cr (VI) [18], $KMnO_4$-oxalic acid redox system [19] have been applied. In comparison with other grafting methods,[20] free radical process followed by light induced initiation has the advantage due to applicability at room temperature and its user-friendly nature. Further, on changing the intensity and wavelength of applied light can control the polymerization systems.[16]

Semiconductor-based photocatalyst is one of the modern methods for generation of initiating radicals in photopolymerization of vinyl monomer.[21] The heterogeneous photocatalytic reaction with various semiconductors TiO_2, ZnO, CdS, ZnS etc. have been studied extensively over the last few decades.[22] The effectiveness of these semiconductors as photocatalyst depends upon how well the radiation wavelength used corresponds to the band gap excitation energy of the semiconductor.[23] In addition to that, electron donors like ethylene glycol, glycerol, triethylamine etc. are used to scavenge the electron holes so that the conduction band electrons are available for reaction, which increase the reactivity of semiconductors.[24]

After successfully completing the photopolymerization of MMA in presence of CdS as photocatalyst (as reported in chapter II), the same system is applied for graft copolymerization of vinyl monomers (methyl methacrylate and acrylamide) onto *Bombyx mori* fibre. This chapter reports the utility of semiconductor as an initiator in free radical photografting. The effects of ethylene glycol and triethylamine with CdS on graft copolymerization have also been explored.

3.2. Experimental

3.2.1. Materials

Methyl methacrylate (MMA) was purified by repeated washing with 4% aqueous NaOH solution and then washed with distilled water to make it free from alkali. The washed monomer was dried over anhydrous BaO for 24h and distilled under nitrogen in reduced pressure.[25] The middle fraction was used for all experiments.

Acrylamide (AAm), a white solid, was recrystallized from methanol and dried *in vacuo* over silica gel.[26] Freshly prepared acrylamide aqueous solution was considered for polymerization in each case.

Cadmium Sulphide (CdS) obtained from CDH, India was used without further purification. Acetone and petroleum ether (Merck) were distilled prior to use. *Bombyx mori* fibres were supplied by a government firm of Sualkuchi, Assam, India. The excitation light source was a high pressure mercury vapour lamp (GE India Ltd., 125 W, radiation intensity of 750 Wm^{-2}). The conventional glass UV cut-off filters were employed.

3.2.2. Methods

3.2.3. Pretreatment of fibres

Silk fibre was stirred in NaOH solution (20% by weight) at room temperature for 2h and then washed with hydrochloric acid solution (1% by weight) and followed by distilled water. The sample was dried later on in the oven at 50°C.[27]

3.2.4. Graft copolymerization

A three-necked 100 mL round bottomed flask fitted with a stirrer, a thermometer pocket and a nitrogen inlet was used to carry out the reaction. The reaction mixture containing monomer, photocatalyst (CdS) and triethylamine or ethylene glycol and silk fibre were taken in the flask. The pretreated silk samples were soaked in reaction mixture for 24 h to ensure the incorporation of monomer and other additives into silk. The whole assembly was purged with the nitrogen gas and allowed to expose on visible light (500-600nm) for 1-7 h in different cases and the reactions were carried out at three different temperatures between 35-55°C. The flask was kept 10 cm apart from the light source in each case. A fan was fitted with the system to keep cool the samples during the irradiation. After the stipulated time period the silk fibres were taken out and washed with proper solvent (depending upon the monomer) for several times. For removal of monomer and homopolymer, treated silk samples along with homopolymer were precipitated in necessary solvent. For complete removals of monomer and homopolymer, silk samples were refluxed in a soxhlet apparatus using proper solvent depending upon the polymer uploaded onto fibre. The grafted fibres were dried to the constant weight and kept in desiccator for further use. The percent of grafting, homopolymer formation, grafting efficiency and total conversion were calculated. In order to optimize grafting, the experiment was repeated with different reaction mixtures.

3.2.5. Fourier transforms infrared spectroscopy (FTIR)

FTIR spectra of finely powdered grafted and ungrafted fibre samples were recorded by a Nicolet FTIR (Impact 410) spectrophotometer, using the KBr disc technique.

3.2.6. Estimation of grafting parameters

The percent grafting, grafting efficiency, homopolymer conversion and total conversion were calculated by Fernandez et. al.[28] based on increased weight of silk fibre.

The percent grafting (*G*) is the weight ratio of grafted polymer to original silk fibers.

$$G = \frac{\text{weight of grafted silk after extracting homopolymer - weight of original silk}}{\text{weight of original silk}} \times 100$$

Homopolymer conversion (C_{homo}) is the monomer fraction that affords homopolymer

$$C_{\text{homo}} = \frac{\text{weight of homopolymer}}{\text{weight of monomer}} \times 100$$

Grafting efficiency (*GE*) is the fraction of the total synthetic polymer that is grafted onto silk

$$GE = \frac{\text{weight of grafted sample after extracting homo copolymer - weight of original silk}}{\text{weight of crude polymer product- weight of original silk}} \times 100$$

Total conversion (C_t) of monomer to polymer is the monomer fraction that polymerizes

$$C_t = \frac{\text{weight of crude polymerization product - weight of original silk}}{\text{weight of monomer}} \times 100$$

3.3. Results and discussion

3.3.1. Reaction schemes for the graft copolymerization on vinyl monomers (MMA and AAm) onto silk fibres

The reaction scheme for generation of free radical on the fibre backbone and the initiation step may be represented by the following scheme, where the semiconductor in presence of light generates electron in conduction band and a positive hole is created in valence band.[29]

$$\mathrm{CdS} \xrightarrow{h\nu} e^-_{(\mathrm{CdS})} + h^+_{(\mathrm{CdS})}$$

The positive hole can easily transfer the charge to silk macromolecule by generating free radical and proton.

$$\sim\mathrm{R{-}H} \xrightarrow{h^+} \sim\mathrm{R}^\bullet + \mathrm{H}^+$$

Where, $\sim$RH and $\sim R^\bullet$ represent the silk molecule and silk monomer radical respectively. The propagation and termination steps possibly may proceed as follows where M stands for monomer.

Initiation

$$\sim\mathrm{R{-}H} \xrightarrow{h^+} \sim\mathrm{R}^\bullet + \mathrm{H}^+$$

$$\sim\mathrm{R}^\bullet + \mathrm{M} \longrightarrow \sim\mathrm{R{-}M}^\bullet$$

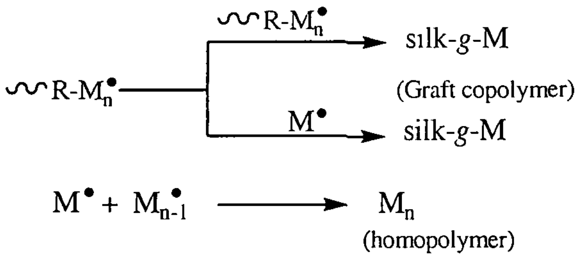
$$\mathrm{M}^\bullet + \mathrm{M} \longrightarrow \mathrm{MM}^\bullet$$

Propagation

$$\mathrm{M} + \sim\mathrm{R{-}M}^\bullet_{n-1} \longrightarrow \sim\mathrm{R{-}M}^\bullet_n$$

$$\mathrm{M}^\bullet_{n-1} + \mathrm{M} \longrightarrow \mathrm{M}^\bullet_n$$

Termination



In the above scheme monomer free radical generated during the progress of reaction, which further produced homopolymer along grafted product.

3.3.2. FTIR spectroscopy

The FTIR spectra of pure polymethylmethacrylate (PMMA), ungrafted silk and silk-*g*-MMA have been shown in the Figure 3.1. PMMA showed a characterized band at 1735 cm^{-1} for carbonyl group of ester stretching vibration [Fig 3.1(a)]. The sharp peak at 1730 cm^{-1} for grafted fibre indicated the presence of PMMA chains on *Bombyx mori* fibre, which was not prominent in case of IR spectra of ungrafted silk fibre.[29] On the other hand, the band at 2997 and 2953 cm^{-1} in Figure 3.1(c) confirmed free $-CH_3$ vibration and band at 1136 cm^{-1} for –C–C–O– stretching further confirming the formation of MMA grafted silk which was not prominent in Figure 3.1(b). The band for NH- stretching for ungrafted silk fibre was shifted from 3447 to 3411 cm^{-1} and 3295 cm^{-1} in Figure 3.1(c)

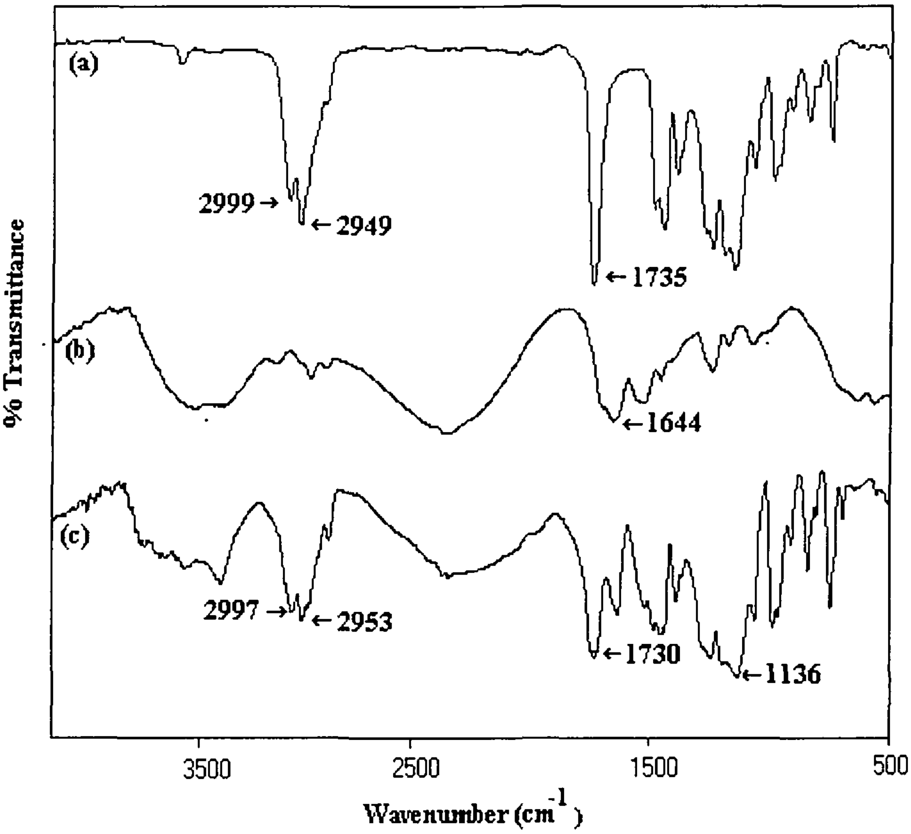


Figure 3.1: FTIR spectrum of (a) PMMA, (b) ungrafted silk, (c) 10.20 % grafted silk fibres.

Similarly IR spectra of polyacrylamide-*g*-silk was also recorded and reported in the Table 3.2. The grafted silk fibre showed the characteristics bands at 1645 cm^{-1} and 1514 cm^{-1} which might be contributed to theβ-conformation of crystalline regions. The IR spectra of grafted silk fibre was not distinguishable so far as monomer and silk having same kind of functional group i.e., -CONH-. The band at 2926 cm^{-1} for -CH_2- stretching was observed in grafted silk fibre may confirm the incorporation of polyacrylamide onto fibre.

Table 3.2: Characteristic band of IR-spectra of acrylamide grafted fibre

Frequency (cm^{-1})	Conclusion
1645	C=O stretching vibration of amide group (amide I)
1514	N-H bending vibration of amide group (amide II)
2926	$-CH_2-$ stretching vibration of $CH_2=CH-$

3.3.3. Graft copolymerization of methyl methacrylate with semi-conductor-based photocatalyst

3.3.3.1. Effect of variation of exposure time

The effect of exposure time on grafting was investigated keeping other variables like initiator, additive and temperature constant. The grafting (%) against radiation exposure time is plotted in Figure 3.2. An increasing trend was observed in the initial stage of grafting up to certain level. The increase in grafting with increase of exposure time was probably due to generation of more active sites on the backbone of fibre. The leveling off of the graft conversion after certain time period was due to predominance of

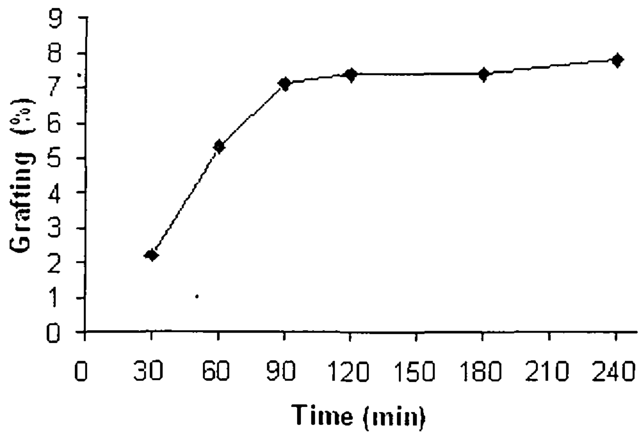


Figure 3.2: Effect of reaction time on graft copolymerization of MMA onto silk fibres Reaction conditions: MMA = 1 mL; CdS = 0.005 g; Ethylene glycol = 0.02 mL; amount of silk fibre = 0.0598 g; temperature = 35°C

homopolymerization over grafting and termination of growing grafted chains by excess primary radical formed in the reaction mixture.

3.3.3.2. Effect of additives on graft copolymerization of MMA

The graft copolymerization was carried out with different additives along with the photocatalyst. A comparative result was reported in Table 3.3. Ethylene glycol was used as hole scavenger during the copolymerization. In presence of ethylene glycol the highest amounts of grafting (10.20%) was achieved with the formation of the lowest amount of homopolymer (10.50%) with the highest grafting efficiency (16.14%) and lower the total conversion. Similarly, in presence of electron donor (Et_3N) graft copolymerization was increased (6.44%). Therefore, grafting can be increased in presence of ethylene glycol or Et_3N. This might be due to easy formation of radical on the surface of the fibre.

Table 3.3: Graft copolymerization of MMA onto *Bombyx mori* fibre. CdS = 0.01g; exposure time = 2h; temperature = 35°C; MMA = 1mL

Sl No.	Amount of silk	Ethylene glycol (mL)	Et_3N (mL)	Grafting yield (%) [a]	Grafting efficiency (%) [b]	Homopolymer formation (%) [c]	Total Conversion (%) [c]
1	0.0577	-	-	2.51	1.05	20.50	20.92
2	0.0598	0.2	-	10.20	16.14	10.50	11.61
3	0.0584	-	0.2	6.44	2.59	20.41	21.42

[a] based on weight of silk, [b] based on total conversion, [c] based on total monomer taken

3.3.3.3. Effect of variation of reaction temperature

The grafting was carried out at three different temperatures between 35-55°C and reaction time and results are shown in Table 3.4. The yield and other parameters increase with increasing temperature up to 55°C. The increase trend in rate of grafting between certain temperature ranges may be ascribed to greater activation energy. The swellability of the fibres and the diffusion rate of monomer into the fibres are influenced with increasing temperature.[30] An increasing trend in result was also observed as reaction time proceeds up to certain level. After stipulated time (7h) and reaction temperature, increasing trend was not observed as shown in earlier cases when other conditions remain as same. This is probably due to increase in viscosity of the reaction mixture, as high viscosity decreases termination more than it shows propagation. But due to extreme viscosity (viscosity increases due to increase of amount of ethylene glycol in the reaction mixture) it may traps the primary radicals in a solvent cage and causes termination to occur faster than propagation.[21]

Table 3.4: Effect of reaction temperature on grafting. MMA = 1 mL; CdS = 0.01 g; ethylene glycol = 0.2 mL; silk = 0.05 g

Reaction time (h)	Graft yield (%) [a]			Total conversion (%) [b]			Homopolymer formation (%) [b]		
	35°C	45°C	55°C	35°C	45°C	55°C	35°C	45°C	55°C
2	10.20	15.08	19.32	11.61	17.4	21.48	10.52	15.23	19.35
4	18.67	21.52	25.16	17.40	19.84	21.12	15.89	16.57	16.98
6	24.59	26.45	28.37	21.46	26.71	32.55	21.65	22.43	20.88
7	24.67	27.55	28.97	22.11	26.75	32.89	24.25	25.14	24.79

[a] Based on weight of silk, [b] Based on total monomer taken

3.3.3.4. Effect of material-to-liquid ratio

The result of grafting on variation of the material-to-liquid ratio is reported in the Table 3.5. The material-to-liquid ratio was varied by changing only the quantity of monomer and additive (swelling agent) and keeping the material amount constant. The increase in the ratio from 1:15 to 1:100 brings enhancement in grafting, whereas further increase in the monomer amount decreases the grafting with increasing homopolymer formation. Therefore, the increase in material-to-liquid ratio results in dilution of reactants. The dilution decreases the collision probability of the reaction ingredients thereby decreasing grafting.[31] Thus enhancement in grafting up to material-to-liquid ratio of 1:100 indicates that this particular liquid amount offers the most appropriate environment for collision probability among the reactants.

Table 3.5: Effect of material-to-liquid ratio on grafting. MMA = 1 - 10 mL; ethylene glycol = 0.2 - 2 mL; CdS = 0.01 g; silk = 0.05 g; temperature = 35°C

Reaction time (h)	Graft yield (%) [a]		Grafting efficiency (%) [b]		Homopolymer formation (%) [b]	
	1: 15 [c]	1: 100 [c]	1: 15 [c]	1: 100 [c]	1: 15 [c]	1: 100 [c]
2	10.20	15.77	16.14	17.50	10.52	25.45
4	18.67	37.84	19.20	22.96	15.89	41.23
6	24.59	48.45	23.26	26.28	21.65	45.27

[a] Based on weight of silk, [b] Based on total monomer taken, [c] Material to liquid ratio

3.3.3.5. Effect of ethylene glycol on grafting

Ethylene glycol along with semiconductor-based photocatalysts shown prominent effect on photopolymerization of different monomers.[21] It has been utilized in graft copolymerization of vinyl monomers onto silk fibre. The effect of amount of ethylene glycol on grafting was observed keeping the other variables like amount of initiator, monomer, silk fibre, temperature and time of exposure. The graft yield (%) against the amount of ethylene glycol has been reported as Figure 3.3. Increase of grafting was observed up

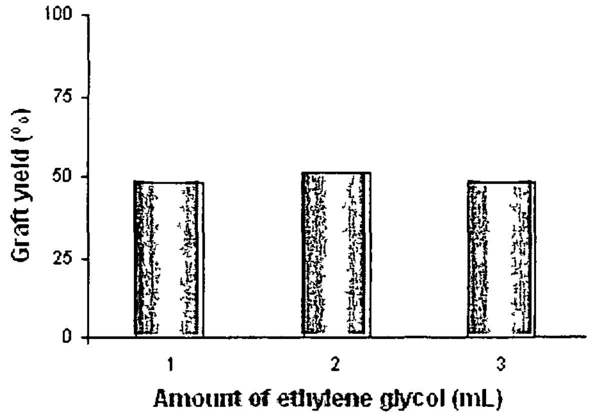


Figure 3.3: Effect of ethylene glycol on graft copolymerization of MMA onto silk fibres. Reaction conditions: MMA = 10 mL; temperature = 35°C, amount of silk fibre = 0.0598 g; time of exposure = 6h; CdS = 0 01 g

to a certain amount of ethylene glycol (2 mL in 10 mL of monomer) after that it showed decreasing trend. This is may be due to increase of viscosity of reaction mixture.[21]

3.3.3.6. Effect of amount of photocatalyst on graft conversion

The effect of amount of photocatalyst on grafting was recorded and plotted in Figure 3.4, without changing the amount of monomer, additive

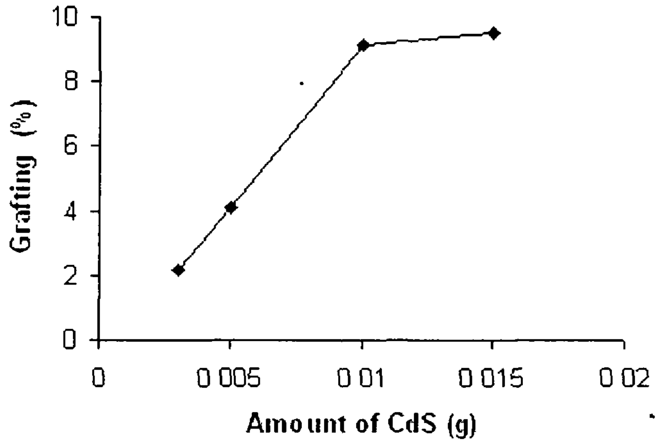


Figure 3.4: Effect of initiator amount on graft copolymerization of MMA onto silk fibres. Reaction conditions: MMA = 1 mL; Ethylene glycol = 0 02 mL, CdS = 0 005 g; amount of silk fibre = 0 0598 g; temperature = 35°C; exposure time = 2h

(ethylene glycol) and exposure time. An increasing trend of grafting is observed with increasing amount of photocatalyst (CdS). But after certain limits (1%) no increase of grafting is resulted. The retarding effect of graft conversion beyond 1% catalyst may be due to termination of growing grafted chain and the excess radicals formed in the reaction mixture.

3.3.4. Graft copolymerization of acrylamide with semiconductor-based photocatalyst

3.3.4.1. Effect of variation of exposure time

The effect of exposure time on grafting of acrylamide (AAm) onto silk fibre was investigated keeping other variables like initiator, additive and temperature constant. The graft yield, total conversion and homopolymer formation on grafting is reported in the Table 3.6. An increasing trend was observed as the reaction time proceeds up to certain level (6 hours). The increasing trend is not prominent as earlier after 6 hours of exposure time in the same conditions. The increase in grafting with increase of exposure time was probably due to generation of more active sites on the backbone of

Table 3.6: Effect of exposure time on graft copolymerization of AAm onto silk fibres. Reaction conditions: AAm = 10 mL of 1M; Ethylene glycol = 1 mL; CdS = 0.01 g; temperature = 35°C; amount of silk fibre = 0.05 g

Reaction time (h)	Graft yield (%) [a]	Total conversion (%) [b]	Homopolymer formation (%) [b]
2	11 95	13.25	24.33
4	16.23	18.10	31.21
6	26.47	29.25	40.12
7	27.54	29.98	42.57

[a] Based on weight of silk, [b] Based on total monomer taken

fibre. In comparison to the grafting process with MMA onto same silk, it was observed that acrylamide-CdS-ethylene glycol generated higher amount of homopolymer formation along with the grafted product.

3.3.4.2. Effect of ethylene glycol on grafting

It has been already reported that ethylene glycol along with semiconductor-based photocatalysts has shown the prominent effect on photopolymerization of different monomers.[21] The effect of amount of ethylene glycol on grafting was observed keeping the other variables like amount of initiator, monomer, silk fibre, temperature and time of exposure. The graft yield (%) against the amount of ethylene glycol has been reported as Figure 3.5. In case of MMA-CdS-ethylene glycol; an increasing trend is observed with increase of ethylene glycol up to certain amount (2 mL with 10 mL of monomer), after that it showed decreasing trend. A similar trend was also observed in case of graft copolymerization of AAm onto silk fibre.

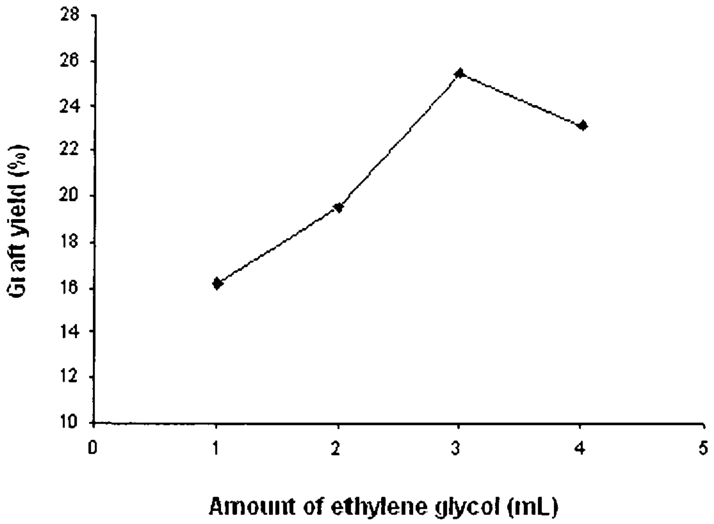


Figure 3.5: Effect of ethylene glycol on graft copolymerization of AAm onto silk fibres Reaction conditions: AAm = 10 mL of 1M; CdS = 0.01 g; temperature = 35°C; amount of silk fibre = 0.05 g; exposure time = 4 h

This is may be due to increase of viscosity of reaction mixture, as high viscosity decreases termination more than it shows propagation.[21]

3.3.4.3. Effect of amount of photocatalyst on graft conversion with AAM monomer

The effect of amount of photocatalyst on grafting was recorded without changing the amount of monomer, additive (ethylene glycol) and exposure time and represented in the Table 3.7. An increasing trend of grafting was observed with increasing amount of photocatalyst (CdS). But after certain limits (0.02 g of CdS) no prominent increase of grafting was observed. The retarding effect of graft conversion beyond 0.02 g of catalyst may be due to termination of growing grafted chain and the excess radicals formed in the reaction mixture.

Table 3.7: Effect of initiator condition on graft copolymerization of AAm onto silk fibres. Reaction conditions: AAm = 10 mL of 1M; Ethylene glycol = 0.02 mL; temperature = 35°C; amount of silk fibre = 0.050 g; exposure time = 2h

Amount of CdS (g)	Graft yield (%) [a]	Total conversion (%) [b]	Homopolymer formation (%) [b]
0.005	4.56	10.89	12.78
0.01	11.95	13.25	24.33
0.02	16.23	19.55	26.35
0.03	16.25	20.33	27.12

[a] Based on weight of silk, [b] Based on total monomer taken

3.4. Conclusion

The semiconductor based photocatalyst in combination with additives (Et_3N and ethylene glycol) is showing as promising initiator in graft copolymerization of MMA and AAm onto silk fibres. The results are quite comparable with the work performed by Tsukada et al.[33] showing increase in weight gain of fibres from 29 to 60% depending on different initiators. However, variations of amount of additives and nature of additives have pronounced effect on the grafting process. Ethylene glycol/Et_3N along with CdS have shown remarkable increase in grafting percentage in comparison with CdS alone. Although, homopolymer formation along with graft copolymer product is not encouragable but grafting with MMA has shown the moderate percentage of grafted yield with lower amount of homopolymer formation in comparison with acrylamide.

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Chapter-IV

The physico-chemical properties of grafted silk fibre *

4.1. Introduction

Graft copolymerization of vinyl monomer onto silk is one of the universal, effective and accessible methods for chemical modification of higher molecular weight compounds or for producing substantial modification of the physical, mechanical, and morphological properties of the fibres.[1-4] The characterization of grafted products is an important aspect of graft copolymerization for better understanding of nature of grafting, surface morphology, area of applications as end products. The structural, thermal properties and morphological structure of grafted fibres have been characterized by X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry, water absorption measurements, scanning electron microscopy (SEM),[5] tensile strength measurements, water absorption measurement etc. The physico-chemical properties of grafted silk fibres depend on the chemical characteristics of monomer used as well as on the extent of grafting and on the reaction conditions.[4] The study of the effect of grafting of MMA onto silk fibres are interesting from the point of exploiting the modified fibres for textile and nontextile uses.

X-ray diffraction studies usually applied to monitor the effect on crystalline nature of grafted fibres. Tsukada et al.[4] studied the X- ray diffrac-

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* Part of result is accepted for publication in Bioresource Technology, 2005 (In press).

tion intensity curves of MMA-grafted silk fibres along untreated silk sample and finally concluded that the graft copolymerization reaction that occurred inside the fibre.

DSC and TGA thermograms indicate the thermal stability of grafted products and increasing in value shows the increase of thermal stability in compare with untreated fibres.

SEM technique elaborate the changes in surface topology brought about by different chemical treatment such as dewaxing, mercerization, grafting.[1]

Water absorption measurements also contributes important conclusion in characterization of grafted fibres as moisture exerts a significant role on physical properties of hydrophilic polymers. For example, as moisture content increases from 0 to 20% by weight, *Tg* of cellulose decreased by approximately 260°C.[6]

A tensile strength measurement indicates the mechanical stability of treated fibres. Mechanical study showed that intrinsic tensile properties of silk are influenced by grafting as a result of various physico-chemical and morphological changes.[7]

4.2. Characterization methods of grafted products

4.2.1. X-ray diffraction studies

X-ray diffraction studies were performed using an X-ray source with C_uK_α radiation (λ = 1.54 A°). The conditions for X-ray measurement were followed from standard literature available.[8]

4.2.2. Thermal analysis

Thermal analysis was carried out by the Perkin Elmer differential scanning calorimeter (DSC) and DSC thermograms were recorded at the heating rate of 10°C per minutes in the nitrogen environment.

TGA analysis of ungrafted and grafted silk fibres were carried out by Perkin Elmer thermal analyzer in the temperature range of 50-800°C at the heating rate of 10°C per minutes in the nitrogen environment.

4.2.3. Scanning electron microscopy (SEM)

The surface morphology of grafted and ungrafted fibre was investigated by a scanning election microscope (Hitachi S-415 A) operating at accelerating voltage:10-15kV, image mode: secondary electron image. The samples were coated with gold in a sputter coater under vacuum with a layer of 15-20 mm thick.

4.2.4. Tensile properties

The stress-strain behaviour of the grafted and ungrafted fibres under tension was evaluated by Zwick (Z010) Tensile Testing Machine (UTM) as per ASTM D 638 standard.[9]

The fibre samples were cut into 10 cm in length and care has been taken that each specimen free from abnormalities like cut edges, creases or wrinkles. The samples were selected randomly and conditioned at 25°C and 65% relative humidity (RH).[10] The fibres were first clamped to the upper jaw, and then carefully clamped in the lower jaw. The gauge length and rate of extension were 50 mm and 10 mm/min, respectively. After carefully clamped in the both jaws load was applied to the specimen until it breaks. An average of ten samples of each silk fibre was run under same conditions.

4.2.5. Water absorption measurements

The water absorption measurements of grafted and ungrafted silk fibres were compared with standard method.[11, 12] The weight of the dry silk fibre was recorded before the sample were soaked in deionised water until an equilibrium weight was achieved at ambient environment. After that, determination of the water absorption by fibre was practiced by centrifuging the samples. The samples were placed on the strainer of a specially made centrifuge tube and centrifuged for 15 min. An arrangement was made so that the bottom of the tube to allow excess water to drain away from the sample. The centrifuge tube was sealed to ensure 100% relative humidity to prevent desorption of water by the fibres. The samples were weight and this weight was considered as wet weight of fibre and the samples were then dried in a vacuum oven at 40 ± 5°C for 24 h. The dry weight was recorded and compared with the earlier one. The water sorbency was calculated in terms water retention value and expressed as follows

$$WRV(g/g) = \frac{weight\ of\ silk\ fibre\ (wet) - weight\ of\ silk\ fibre\ (dry)}{weight\ of\ silk\ fibre\ (dry)} \times 100$$

where, WRV implies water retention value in gram of water per gram of dry sample. The average values were estimated from five replicate measurements for each specific sample, and results were reported.

4.2.6. Chemical resistance measurement

The chemical resistance of grafted and ungrafted fibres was measured using ASTM D 443-87 method. Each fibre was dipped in the respective chemical for 24 h and above (in some cases), then removed from the respective solvent and followed by washing in distilled water. The samples were weighed after drying in the oven at 40°C for 10 h and the loss/gain was calculated in terms of percentage.

4.3. Results and discussion

4.3.1. DSC thermograms

DSC thermograms of grafted (PMMA-*g*-silk, PAAm-*g*-silk) and ungrafted silk fibres are reported in Figures 4.1.(a), (b), (c). The DSC thermogram of ungrafted fibre shows one exotherm at 320°C possibly due to decomposition of fibre. The grafted product shows two exotherms at 330°C and 410°C possibly due to decomposition of grafted fibre. The shifting of initial decomposition temperature from 320°C to 330°C for grafted fibres

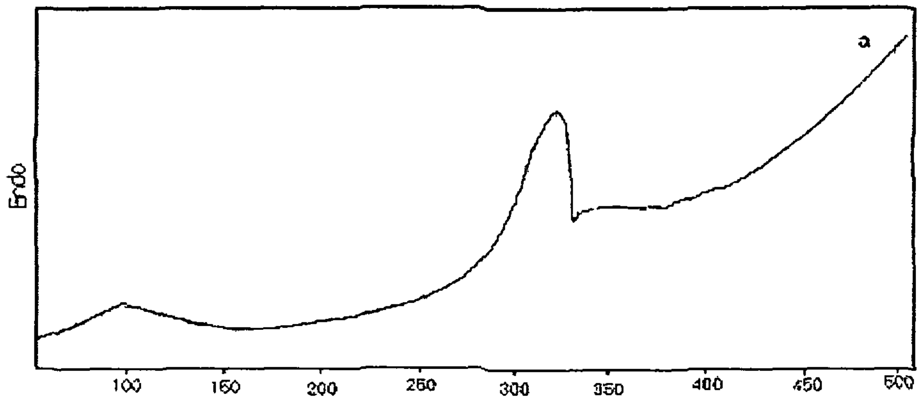

Figure 4.1. (a): DSC thermograms of ungrafted silk

indicate the increased thermal stability of grafted fibre whereas the homopolymer (PMMA) alone shows exotherm around 360-380°C due to degradation.[13] The result is similar when grafting was carried of with conventional initiator.[14]

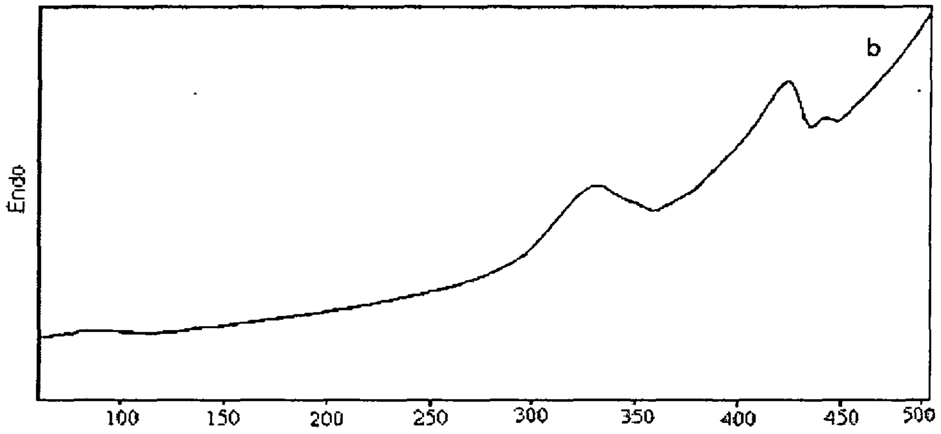

Figure 4.1. (b): DSC thermograms of 10.20 % MMA grafted silk

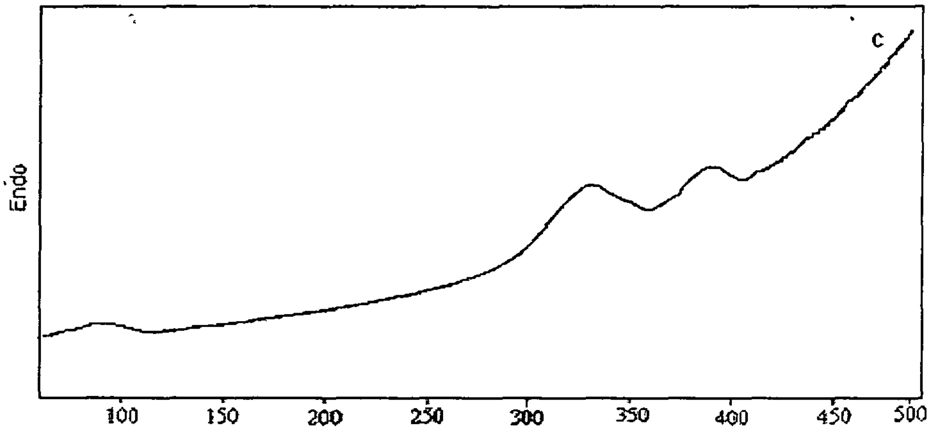

Figure 4.1. (c): DSC thermograms of 11.95 % AAm grafted silk

The DSC thermogram of grafted fibre (PAAm-*g*-silk) shows two exotherms at 330°C and 360°C. The shifting of exotherm is also observed as in the earlier case which indicates the improvement of thermal stability of grafted fibre.

4.3.2. Thermal behaviour from TGA analysis

The thermal behaviour of ungrafted and grafted silk fibres was analyzed with TGA. The TGA was performed at heating rate of 10°C per minute. TGA curves for ungrafted and grafted fibres are plotted in the Figures 4.2 (a), (b), (c).

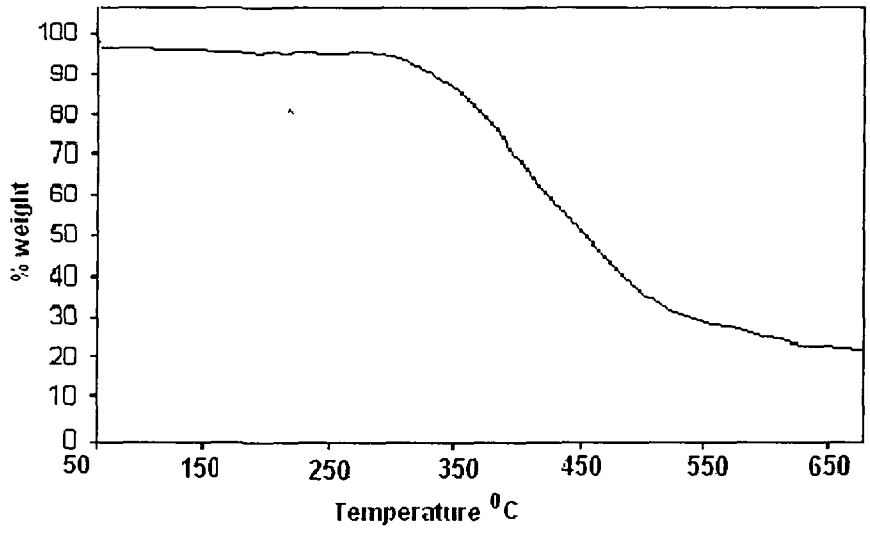

Figure 4.2 (a): TGA curves for ungrafted silk fibre

The initial decomposition temperature noted for TGA thermogram for grafted and ungrafted fibre. The initial decomposition for ungrafted fibre was 306°C whereas 350°C and 370°C for MMA grafted and AAm grafted fibre respectively. This shows higher thermal stability of the grafted fibre.

In terms of weight loss values, grafted fibre showed 10% weight loss at 370°C (MMA grafted) and 350°C (AAm grafted) in compare with 337°C for ungrafted fibre. Similar trend was observed in other values of weight loss of fibres (Table 4.1), though AAm grafted showed unusual behaviour in the first phase of heating.

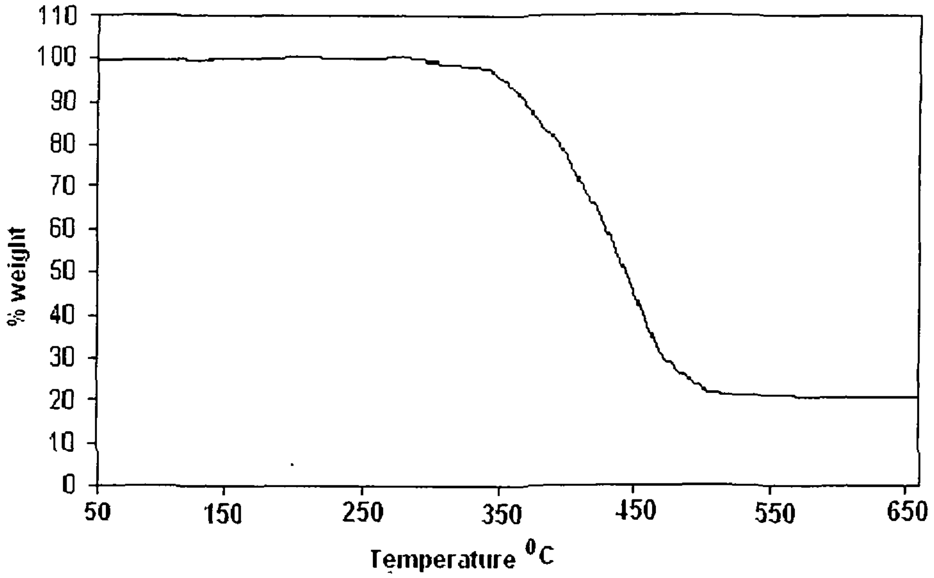

Figure 4.2 (b): TGA curves for MMA grafted silk fibre

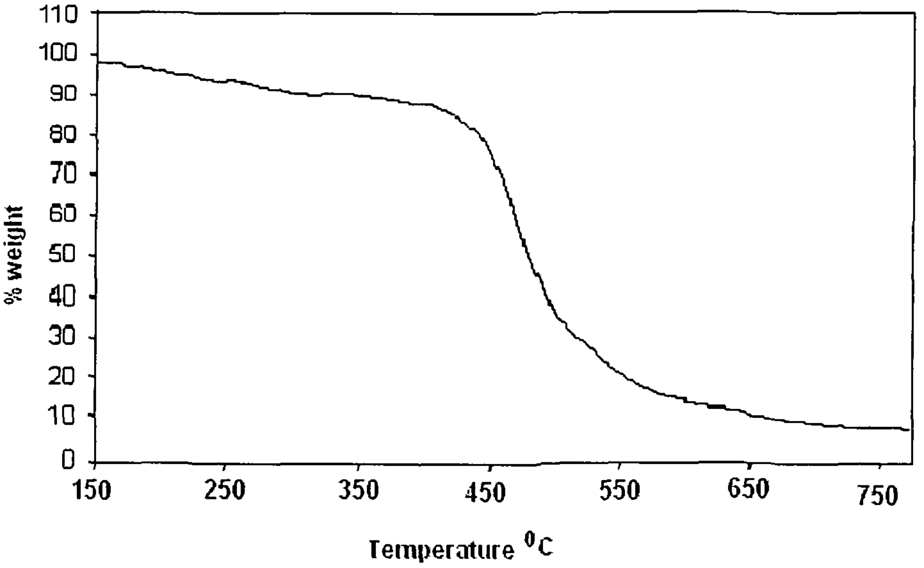

Figure 4.2 (c): TGA curves for AAm grafted silk fibre

Table 4.1: Weight losses of ungrafted and grafted silk fibres at heating rate 10°C/ minute

Nature of silk	Weight loss (%) in different temperature (°C)			
	5%	10%	15%	50%
Ungrafted	306	337	361	450
MMA grafted	350	370	379	444
AAm grafted	214	350	420	479

4.3.3. X-ray diffraction study

X-ray diffraction curves for ungrafted fibre and PMMA-grafted silk fibre with different amount of graft yield were recorded and represented in the Figure 4.3. The untreated silk fibre (curve a) showed a major X-ray diffraction peak at 20.5 degree. It has been observed from diffraction curve (curve b) of 10.20% PMMA-grafted silk that the position and intensity of the

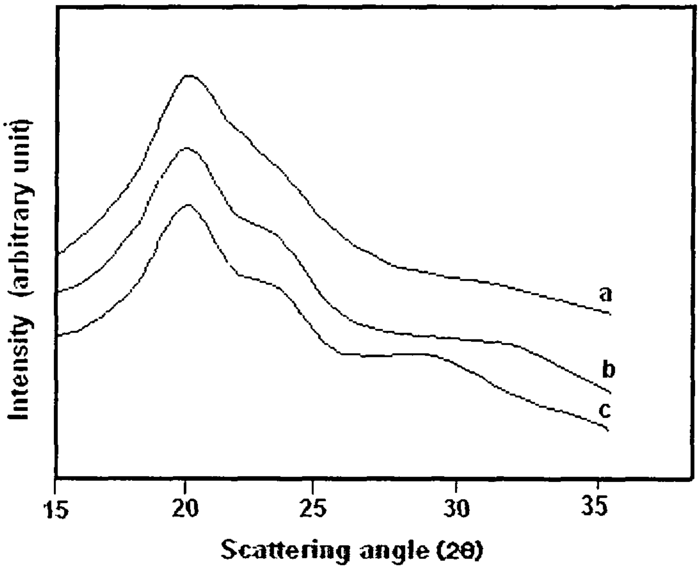

Figure 4.3: X-ray diffraction intensity curves of the grafted silk fibres with various amounts of MMA grafted yield. (a) ungrafted silk, (b) 10.20% grafted silk, (c) 18.67% grafted silk

main diffraction peak did not change. Thus it suggested that the crystalline structure of silk fibre was not altered after grafting which was also confirmed from literatures available.[5,15] Though a little change was notified in the grafted silk of higher graft yield (curve c).

4.3.4. SEM studies

The morphological studies of ungrafted and grafted silk (PMMA-*g*-silk, PAAm-*g*-silk) fibres were performed by scanning electron microscopy (SEM). The SEM micrographs of ungrafted and grafted fibre were shown in Figures 4.4 (a)-(h). As semiconductor-based photografting is likely to occur on the surface of the fibres hence grafting should leave its mark on the surface morphology of the fibres.[13] The smooth and evenness of the fibre surface was observed in the micrograph of ungrafted fibre. The change in surface morphology after grafting with monomers was clearly revealed by the SEM micrograph as grafting affected the surface of silk fibres. The unevenness of surface resulted from deposition of polymer, which formed during graft copolymerization with monomers. The cracks in the surface of ungrafted fibre [Figure 4.4 (a)] are filled up by the monomer that uploaded during the graft copolymerization in grafted fibre [Figure 4.4 (c)]. The roughness of surface of the grafted fibre increased with increasing the percent grafting.

These results are quite similar with the works by Tsukada [5] on the grafted fibres (PMMA loading silk), which demonstrating the presence of granules that appeared chemically bonded and/or physically adhered to the surface of the grafted silk fibres. However, the changes in thermal and

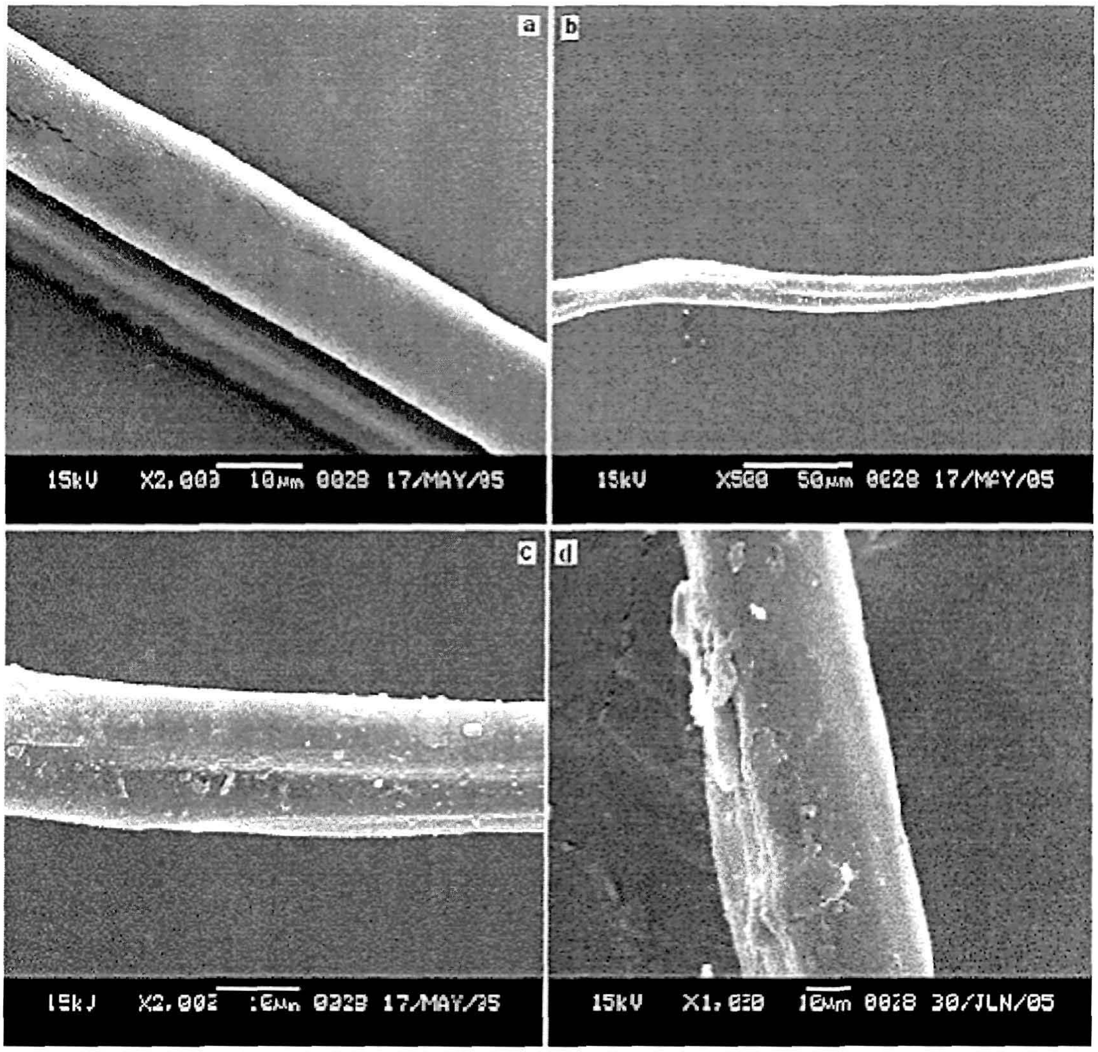

Figure 4.4 : Scanning electron micrographs of MMA grafted silk fibres. Graft yield (%): a) 0; b) 10.20; c) 18.67; d) 24.59.

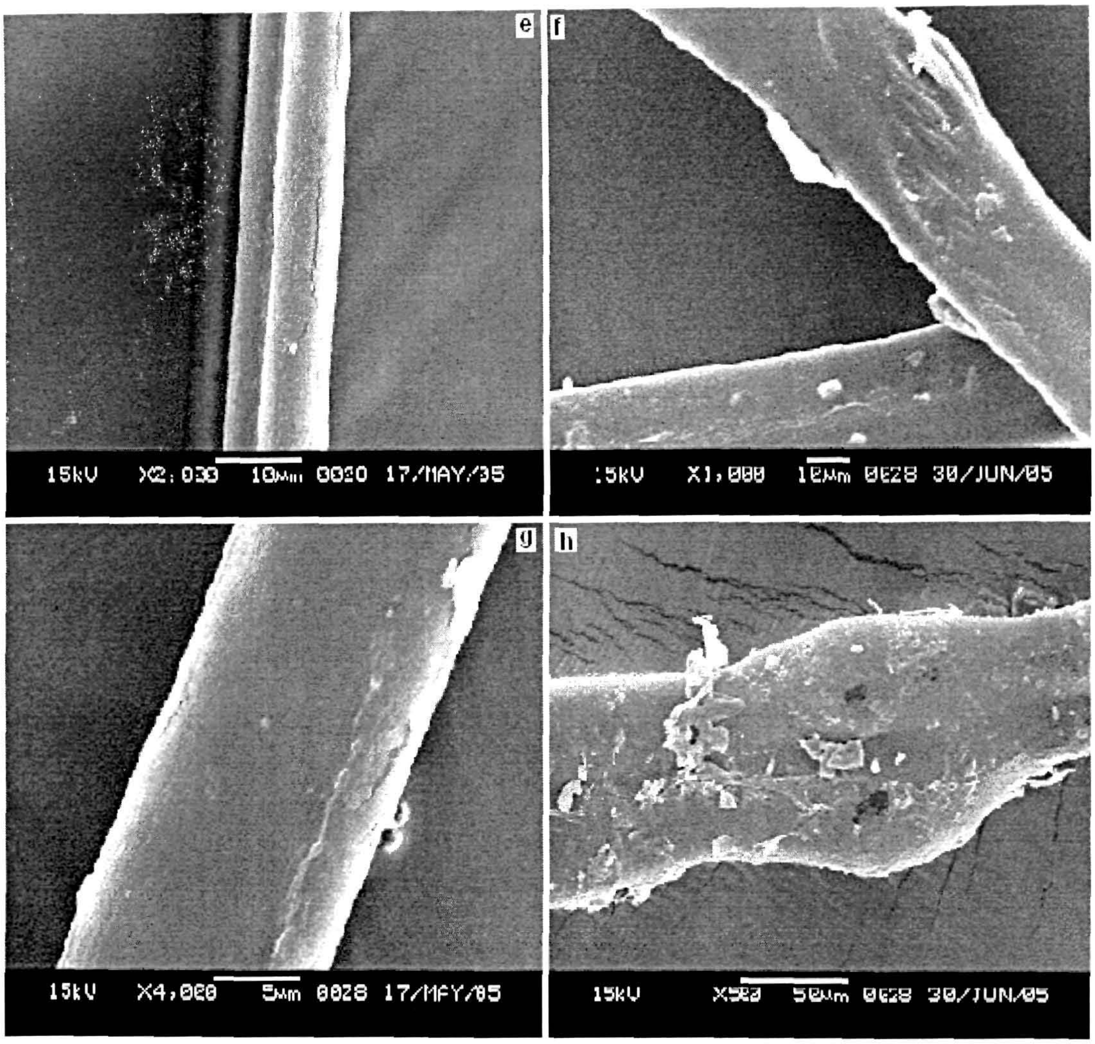

Figure 4.4: Scanning electron micrographs of AAm grafted silk fibres. Graft yield (%) : e) 11.95; f) 16.38; g) 17.25; h) 26.47.

mechanical properties (as observed in earlier results) may support that grating is not merely a surface phenomenon.

4.3.5. Tensile strength measurements

The stress-strain curves for ungrafted and grafted fibres with MMA and AAm are shown in Figure 4.5. Grafting results in increase in yield point and slope of the stress-strain curve. The percentage of elongation at break has been increased from 7% to 12% for MMA grafted fibre (curve b) and 14% for AAm grafted fibre (curve c). The decrease in yield point for grafted fibre is observed as percent of grafting increases. Similar nature is also observed for AAm grafted fibre. On the other hand MMA grafted fibre shows

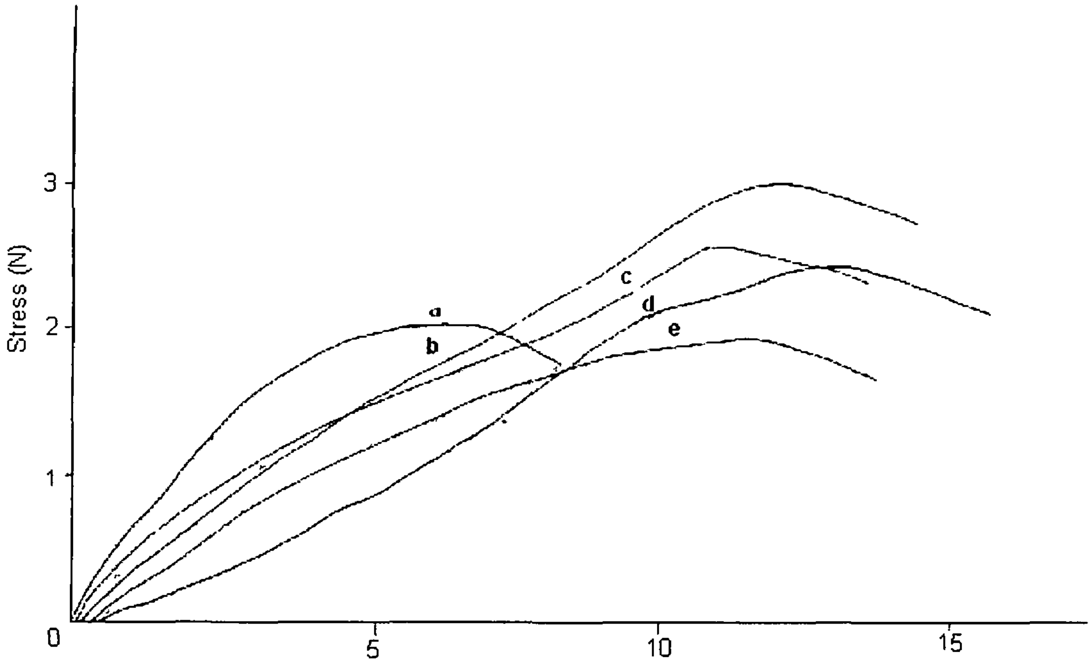

Figure 4.5· Stress-strain curves for ungrafted and grafted fibres. (a) ungrafted silk fibre, (b) MMA-*g*-silk; 37.84% grafted, (c) MMA-*g*-silk, 48.45% grafted, (d) AAm-*g*-silk; 17.38% grafted, (e) AAm-*g*-silk; 26.47% grafted

high yield value but lower elongation at break than the AAm grafted fibre. In case of MMA grafted fibres, lower elongation at break is expected since flexibility of PMMA is lower than the PAAm uploaded fibre at room temperature. The increase in elongation at break for grafted fibre indicates that due to grafting many of intermolecular forces holding the chains together are broken, facilitating the slippage of molecules.[16] Further, acrylic polymers except MMA have the T_g value below room temperature and making the grafted polymer more easily extendable. This phenomenon is also reflected while comparing the slope of stress-strain curve. With grafting, slope is gradually decreased, i.e., modulus of elasticity is decreased.

4.3.6 Chemical resistance measurements

The effect of different chemicals on ungrafted and grafted silk fibres is reported in the Table 4.2. It was observed that on treating with acetic acid, NaOH, benzene and toluene, ungrafted and grafted silk fibres (PMMA-*g*-silk, 24.59% grafting; PAAm-*g*-silk, 26.47% grafting) lose their weight to some extent. In 60% NaOH solution the ungrafted silk fibre was dissolved but both types of grafted fibre showed resistance towards the alkali. It was also found that nitric acid couldn't fully dissolve the grafted silk fibre even after 7 days.

Table 4.2: Effect of chemicals on weight of ungrafted and grafted fibres

Chemical	% weight loss in dipping for 24 h [a]		
	Ungrafted silk	PMMA-*g*-silk	PAAm-*g*-silk
Acetic acid	7.14	15.38	18.75
Conc. HCl	Dissolved	Slightly dissolved	Dissolved
60% NaOH	Dissolved	12.28	Slightly swollen
Benzene	4.95	3.47	4.61
Tolune	2.88	2.24	2.39
Conc. HNO_3	Dissolved	Slightly swollen	Partially dissolved

[a] Data reported from the average of five experiments.

On grafting overall improvement in chemical resistance was observed. The weight loss in every case was decreased in case of grafted fibres but methyl methacrylate grafted fibres showed better chemical resistance than acrylamide grafted fibres. It may be due to the nature of the hydrophobic side chains of the MMA polymer filled in the fibre.

4.3.6. Water sorbency measurements

The grafting of silk with PMMA has imparted the hydrophobic nature onto silk, which is evident from the water retention values of ungrafted and grafted silks (Table 4.3). As the grafting percentage increases, the WRV (water retention value) is decreased. The low rate of grafting (%) did not show much variation of water retention value from ungrafted silk. With the increase of grafting on silk, the surface was covered with PMMA, which made the surface more hydrophobic thereby, decreasing the water retention value.

Table 4.3: WRV of ungrafted and PMMA grafted silk fibres

Sample	Grafting (%)	WRV (g/g) [a]
Ungrafted silk	_	3.2
Grafted silk	2.51	3.1
	6.42	2.8
	10.20	2.6
	18.67	2.5
	21.52	2.4
	48.45	2.0

[a] Data reported from the average of five experiments.

A similar trend was also observed for acrylamide grafted fibre. The result showed that WRV value of grafted silk decreased with the increase of grafting (Table 4.4). The decrease in the water retention value might be due to decrease in cohesive force of the highly swollen fibre.[17,18]

Table 4.4: WRV of ungrafted and AAm grafted silk fibres

Sample	Grafting (%)	WRV (g/g) [a]
Ungrafted silk	_	3.2
Grafted silk	4.56	3.0
	11.95	2.9
	16 23	2.7
	26.23	2.3
	26.47	2.0

[a] Data reported from the average of five experiments.

4.4. Conclusion

The semiconductor-based photocatalyst in combination with additives (Et_3N and ethylene glycol) is showing as a promising initiator in graft copolymerization of methyl methacrylate and acrylamide onto silk fibres. SEM clearly illustrates the surface unevenness of grafted fibres. On grafting, increase in thermal stability is observed. Moreover, the grafted fibres have shown increase in chemical resistance, increase in elongation at break, decrease in slope of the stress-strain curve and decrease in water retention values in some extent.

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Chapter-V

Conclusions and future directions

In this work semiconductor CdS has been explored as photocatalyst for polymerization of methyl methacrylate in various reaction conditions and applied as a photocatalyst in graft copolymerization of vinyl monomers (MMA & AAm) onto *Bombyx mori* silk fibre.

The conclusions of the work may be summarized as follows.

1. The photopolymerization of methyl methacrylate has been performed in the presence of semiconductor-based photocatalyst CdS in the presence of light from high-pressure mercury vapour lamp. The effect of eosin Y (dye) and other additives on photopolymerization of MMA has been studied. It has been observed that photopolymerization of MMA with CdS results only 2.43% of conversion of monomer whereas without CdS no polymerization was observed under the identical reaction conditions. A conversion (14.27%) has been achieved when CdS was used with electron donor like, triethylamine. A higher conversion of 22.73% has been noted when photocatalyst was used in the presence of dye. To optimize the reaction conditions, MMA-dye; MMA-CdS-dye; MMA-CdS-triethylamine systems were studied with variation of exposure time.

2. It has been observed that the semiconductor based photopolymerization of MMA proceeds through the free radical mechanism which can be better understood by EPR spectroscopy.

3. The stability of dye during the photopolymerization was also monitored with help of UV spectroscopy and found that dye is quite stable in MMA-CdS-dye system.

4. It can be concluded that the semiconductor-based photocatalyst in combination with additives is showing as a promising initiator in graft copolymerization of MMA and AAm onto silk fibres. CdS along with additives have shown remarkable increase in grafting from 2% to 10% in comparison with CdS alone. Graft copolymerization has been successfully completed with two monomers separately at different reaction environment and optimized the reaction conditions. The characterization of grafted products was performed by FTIR studies and presence of some characteristic peaks indicating the uploading of particular monomer onto silk.

5. It is observed that material-to-liquid ratio dramatically influenced the entire grafting processes. It was monitored that the increase in the material-to-liquid (M:L) ratio from 1:15 to 1:100 brings enhancement in grafting, whereas further increase in M:L decreases the grafting with increasing unwanted homopolymer formation. The effect of amount of photocatalyst was recorded and noticed that increasing trend of grafting was observed with increasing amount of photocatalyst (CdS). But after certain limits (1%) no increase of grafting was observed which indicates the requirement of necessary (minimum) amount of catalyst for graft copolymerization for these systems.

6. It has been observed that photocatalyst CdS along with other additives is more effective for graft copolymerization of MMA in compare with AAm in terms with graft yield, total conversion and homopolymer formation.

7. The improvements of thermal stability and lower water retention of grafted products are observed. SEM micrographs clearly reveal that the graft copolymerization is merely a surface phenomenon. Further, the grafted fibres have shown increase in chemical resistance and elongation at break, decrease in slope of the stress-strain curve and water retention values in some extent.

Recommendation and future directions

The semiconductor-assisted photocatalyst is a promising initiator in graft copolymerization of vinyl monomers. However, detail calculation of quantum yield of photocatalyst may help for better understanding of reaction mechanism, kinetics etc. Thus, the future directions include

1. To calculate the quantum yield of semiconductor-based photocatalysis and rate of the reactions.
2. To study the behaviour of dye-semiconductor system during the progress of the reaction.
3. To calculate the frequency of side chains and end group analysis in the grafted fibre.
4. Characterization of grafted fibre should be supported by solid state spectroscopic studies like CP-MAS of 13C & 15N.

These photocatalysts may be applied for photopolymerization of vinyl monomers and it could be the potential field for commercial exploration of grafted fibre.

List of publications

A. Journals

1. *Photopolymerization of methyl methacrylate using dye-sensitized semiconductor based photocatalyst.* Raju Ojah and S. K. Dolui. J. Photochem. Photobiol. A: Chem., 2005; 172, 121.
2. *Graft copolymerization of methyl methacrylate onto Bombyx mori initiated by semiconductor-based photocatalyst.* Raju Ojah and S. K. Dolui. Bioresource Technology, 2005. (In Press)
3. *Solar radiation induced polymerization of methyl methacrylate in presence of semiconductor based photocatalyst.* Raju Ojah and S. K. Dolui. Solar Energy Materials & Solar Cells, 2005. (In Press)
4. *Graft copolymerization of vinyl monomers through CdS onto silk fibre.(Communicated to European Polymer Journal)*

B. Proceedings

1. *Photochemical conversion of methyl methacrylate monomer to polymethyl methacrylate.* R. Ojah and S. K. Dolui, in proceedings of International Conferences on Polymer Characterization. Polychar-8, 2000; University of North Texas, USA.
2. *Photopolymerization of methyl methacrylate using semiconductor-based photocatalyst.* R. Ojah and S. K. Dolui, in proceedings of National Workshop on Catalysis, CATWORK, 2002; Gauhati University, Assam, India.
3. *Graft copolymerization of methyl methacrylate onto Bombyx mori initiated by semiconductor-based photocatalyst.* R. Ojah and S. K. Dolui, in proceedings of National Conference on High Performance Polymer and Its applications, 2002; Jadavpur University, Kolkata, India.
4. *Photopolymerization of methyl methacrylate.* R. Ojah and S. K. Dolui, in proceedings of National Symposium in Chemistry, 2002; National Chemical Laboratory, Pune, India.
5. *Improvement of silk by graft copolymerization technique.* R. Ojah and S. K. Dolui, in proceedings of National Workshop on Science and Technology for Regional Development: Case for North East India, 2004; IIT, Guwahati, Assam, India.
6. *Effect of additives on semiconductor-based photocatalyst in photopolymerization of methyl methacrylate.* R. Ojah and S. K. Dolui, in proceedings of National Seminar on Current Trends in Chemical Research, 2005; Chaiduar College, Assam, India.