CHAPTER 1

INTRODUCTION

The synthesis of functionalized polymers has attained considerable technological interest as reactive materials. Many polymers with definite functional groups are now being synthesized, tested and used. Some functional groups may give polymers with chemical reactivity, photothermal, biological or medicinal approach to a subsequent modification of the polymer for required applications. Functional polymers in the crosslinked form are useful in a number of applications such as column materials in chromatography, combinatorial synthesis and neural networks (Liz et al 2001). Generally synthetic functional polymers have wide applications in medicine, protective chemical reactions, electrical and electronic devices, information storage and optical materials (Trout et al 1998).

1.1 PHOTO RESIST POLYMERS

During the last two decades, the synthesis and applications of photosensitive polymers has developed into a widespread research area. These photosensitive materials have technological applications in the field of macro- and micro-lithography (Chen and Yin 2004, Fang et al 2002), non-linear optics (Arun and Reddy 2004, Harry and Charles 1994), liquid crystals (Sakthivel and Kannan 2004, Jackson et al 2001), tissue engineering (Schmedlen et al 2002), biosensors (Tsafack et al 2000), UV-curing adhesive (Choi et al 2001), hole transporting material in organic light emitting diodes (Braig et al 2000), optical anisotrophy (Choi and Cha 2002), electrographic

Photosensitivity, photosensitization, solubility and thermal stability are important to the practical use of a photosensitive polymer. Photopolymers or photoresists are polymer carrying photosensitive groups, which easily bring about a change in the molecular structure by photoirradiation. These structural changes provide variation in the physical properties such as solubility, absorbability of light, elasticity etc. of the polymer.

Photoresists are of two types. viz., (i) Negative photoresist and (ii) Positive photoresist. The exposed areas of (i) are insoluble in a solvent and the unexposed areas are soluble in solvent and the unexposed areas are soluble while the exposed areas of (ii) latter become more soluble and it gives a resists image on developing in a suitable solvent. The swelling of the unexposed areas of positive photoresists is less than those of negative photoresists in a developing solvent. However, in contrast to a positive photoresist, a negative photoresist can apply more readily to various applications because of structural variety of photofunctional groups as well as polymer backbones (Ichimura and Nishio 1987).

Most of these systems are based on cinnamate derivatives of polymer. Esterification is the most commonly employed method for the attachment of cinnamoyl group onto polymers having hydroxyl groups. Cellulose, polycondensation products of epichlorohydrin and 2,2’(4,4’-dihydroxydiphenyl)propane, polyesters from glycerol and phalic anhydride and poly(vinyl alcohol) are the most frequently used polymers. Polymers with pendant cinnamic ester groups (Kato et al 1971), have been used as
photosensitive polymers for their excellent thermal stability, resolving power, high tensile strength, good resistance to solvents and photosensitivity.

These polymers have been used in practice with 5-10 wt% of photosensitizers because the photosensitivity of the cinnamic ester group is not enough. Polymers with pendant chalcone (Unruh and Smith 1960), α-Cyanocinnamic ester (Nishikubo et al 1974) and Styryl pyridinium (Borden and Williams 1977) have high photosensitivity but cannot be sensitized.

1.2 PHOTOCROSSLINKABLE POLYMERS

Photoresist in combination with multiple-imaging devices have enabled engineers to produce microcircuits and thereby considerably reducing the size of digital computers. α,β-unsaturated carbonyl compounds are well known photocrosslinkable units. These moieties are present in the polymer backbone as they undergo photocrosslinking upon UV irradiation.

The widely used photoresists are based on various photoactive groups such as cinnamate esters, coumarin, stilbene, arylidene, benzylidene and vanillylidene. The schematic representation of photocrosslinkable mechanism was shown in Figure 1.1.

![Figure 1.1 Schematic representation of photocrosslinkable mechanism](image)
1.3 REVIEW OF LITERATURE

Minsk et al (1959) investigated the photosensitivity of cinnamic acid ester of poly(vinyl alcohol) and cellulose and studied the effect of substitution on the photosensitivity. Unruh and Smith (1960) prepared styryl ketone polymer with photosensitive group by the condensation of poly(vinyl acetophenone) with benzaldehyde. Tsuda (1964) synthesized photocrosslinkable polymers having pendant cinnamoyl groups by reacting poly(vinyl alcohol) with cinnamoyl chloride. Kato et al (1971) reported the polymers having pendant cinnamic ester groups and this have been used as negative type photoresists for their high photosensitivity. Tanaka et al (1972) studied the synthesis of poly(vinyl cinnamylidene acetate) from poly(vinyl alcohol) and cinnamylidene acetyl chloride.

Nishikubo et al (1974) reported the photosensitivity and rate of photocrosslinking of poly(vinylcyanocinnamoxoy acetate) and poly(vinyl cyan cinnamate). Polymers with α-cyanocinnamic ester (Nishikubo et al 1974) and α-phenyl maleimide (Ichimura et al 1976) cannot be sensitized but have high photosensitivity. Azuma et al (1980) reported the preparation and properties of photosensitive rubbers having cinnamoyl groups. Roucoux et al (1981) studied the photosensitivity of the polymer obtained from cyanocinnamylidene acetic acid and poly (4-vinyl pyridine). Nishikubo et al (1981) reported the photochemical and thermochemical reaction of polymers having azidonitrobenzoyl groups. Watanabe and Ichimura (1982) adopted a new method for the improvement of photosensitivity by mixing two different polymers having substituted cinnamoyl groups for the selective intermolecular photocrosslinking of poly (vinyl cinnamate) derivatives. Nishikubo et al (1983) synthesized novel photosensitive polymers with pendant photosensitive group such as cinnamic ester and photosensitizer groups such as N'-Carbamoyl-p'-nitroaniline and N'-Carbamoyl-4-nitro-1-napthylamine by radical copolymerization of (2-cinnamoyloxy)ethyl...
methacrylate with photosensitive monomers or by the copolymerization of 2-hydroxyethylmethacrylate with the same photosensitizer monomers.

Iizawa et al (1983) studied the photochemical reactions of polymers obtained by the reaction of poly(chloromethyl styrene) with the potassium salts of photoactive compounds such as crotonic acid, cinnamic acid or 2-cyano-3-(styryl)acrylic acid. Sierocka et al (1984) reported the synthesis of photoresponsive polymers containing pendant cinnamic acid moieties. The synthesis and photocrosslinkable properties of poly(2-vinylxy ethyl cinnamate) was studied by Watanabe and Kato (1984). Nishikubo et al (1985) synthesized the self-sensitized photopolymer by addition reaction of poly(glycidyl methacrylate) with nitroarylcinnamate and its photosensitivity was evaluated.

Watanabe et al (1986) reported photosensitive polymers having pendant chalcone groups obtained by reacting 4'-substituted-4-carboxy chalcone with poly (vinyl alcohol) using 2,4,6-trinitro chlorobenzene as a condensing agent. Lamaitre et al (1987) reported the synthesis and photocrosslinking properties of UV-sensitive liquid polysiloxanes having cinnamic groups. The synthesis and photosensitive property of vinyl polymer p-phenylineadiacrylate side chain was reported by Ichimura and Nishio (1987).


Sinsermsuksakul and Bualek (1995) reported synthesis and characterization of polysiloxane containing different cinnamic ester groups and different length of alkyl ring group in order to investigate their effects on the kinetics of hydrosilation reaction of polysiloxane and on the photoreactivity of the polymer films. Jegal and Blumstein (1998) studied liquid crystalline thermotropic main chain polyesters and copolyesters based on 4,4'-dihydroxy-α-methylstilbene (mesogen) and azeloylchloride (fluoride) and 10,12-docosadiynedioxy chloride (Ultra violet crosslinkable moiety) were synthesized by interfacial polymerization. UV crosslinking of the LC polymers containing UV-sensitive diacetylenic groups was attempted, and crosslinked LC polymer films were obtained. Photocrosslinkable side chain liquid crystalline copolymers comprising of photoreactive 4-(2-cinnamoyl ethoxy) biphenyl group have been synthesized by Kawatsuki et al (1998). The
effects of copolymer composition and irradiation temperature on the photoinduced alignment behaviour was investigated in detail.


Vargas et al (2000) have worked on photocrosslinkable copolyester poly(alkylene terephthalate-co-1,4-phenylene bisacrylate). The phenylene bisacrylate structural units undergo rapid photochemical reaction in the solid state to form crosslinks. Kawatsuki et al (2000) did photoreaction of methacrylate polymer films comprising of 2-cinnamoyloxybiphenyl mesogenic side group using a linearly polarized ultraviolet light and determined the alignment behaviour of liquid crystal on the resultant films. When the film was irradiated near the clearing temperature of the polymer, photoinduced thermal orientation process of the mesogenic groups was generated along the photocrosslinked mesogenic groups that were parallel to the electric vector of the incident LPUV light. Zhang et al (2000) synthesized epoxy-p-nitroaniline cinnamyl [EPNAC], a photocrosslinkable side-chain second order nonlinear optical polymer. It has bisphenol-A as polymer backbone, p-nitroaniline as the chromophore and cinnamyl group as the photosensitizer.
The crosslinked polymer showed high glass transition temperature (160°C) and improved chromophore orientation stability. Kamal and Ahmed (2000) synthesized the main chain liquid crystalline poly(acrylidene ether)s containing cyclopentanone polymers. Anisotropic properties of all polymers were exhibited at higher temperature under polarized optical microscope and showed nematic textures. The electronic spectra showed absorption band and also small bathochromic shifting with $\lambda_{\text{max}}$ near 273-285 nm due to the $\pi-\pi^*$ excitation of $\text{-C=C-}$ group present in the polymer backbone. Tamai et al (2000) did work on photochemical oxygenation and crosslinking of poly(4-trimethylsilylmethylstyrrene) thin film by UV irradiation. The irradiated film surface became hydrophilic owing to the formation of carboxylic acid group and the photocrosslinking caused the insolubilization of the film imide.

Tsafack et al (2000) designed a novel sensing layer based on the non-covalent immobilization of enzymes on derivatized sepharose beads subsequently entrapped in PVA-SBQ photopolymer. Iiojiu et al (2000) synthesized polydimethylsiloxanes containing benzyl acrylate groups. Differential scanning calorimetry was used to study the crosslinking behaviour of the functional polydimethylsiloxanes in the presence of different photoinitiators. Mateo et al (2000) determined styrene-butadiene-styrene block copolymer system, which on exposure to UV irradiation in the presence of unimolecular and bimolecular photoinitiators, a crosslinked polymer was obtained. The crosslinking densities of the SBS block copolymer irradiated were relatively low. Fu and Hsieh (2000) has done copolymerization of 3-hydroxy-3-methacrylate for reactive ion etching resistance and lithographic applications. Laschewsky and Rekai (2000) reported the synthesis of cinnamoylated poly(N-2-hydroxypropyl methacrylamide). The presence of cinnamate chromophore induces not only lower critical solution temperature but also photoresponsive.
Copolyacrylates containing the side groups presented by the two types of photosensitive fragments such as cyanoazobenzene and benzylidene-p-menthane-3-one groups were synthesized by Bobrovsky et al (2001). Mitsuishi et al (2001) synthesized the copolymer of 9-anthrylmethylmethacrylate with neo-pentyl methaacrylamide by free radical polymerization. Kim et al (2001) reported the synthesis of poly(vinyl benzyl abietate) by the polymer reaction of poly (vinyl benzyl chloride) with sodium abietate in chlorobenzene poly (vinyl benzyl abietate) in film state was found to be crosslinkable via photodimerization of the conjugated carbon-carbon double bonds of the abietic acid moieties. Wu and Gonsalves (2001) did work on photoacid generating monomer containing a sulfonium group and its polymerization behaviour was investigated by conduction homopolymerization with various methacrylates. Their imaging properties were investigated by exposure to 248 nm deep Ultraviolet radiation.

Zhi et al (2002) reported a series of novel thermotropic side chain liquid crystalline polymers by grafting copolymerization of mesogenic monomer cholesteryl undecylate and photochromic monomer 4-allyloxy-4-nitroazobenze on polymethylhydrosiloxane. Wu and Qu (2002) investigated a new benzophenone derivative with a long carbon chain and two chromophoric groups di(4-hydroxyl benzophenone)sebacate as a photoinitiator in the photocrosslinking of polyethylene.

Kaczmarek et al (2002) synthesized five different multifunctional acrylic monomers trimethylolpropane triacrylate, trimethylol propane trimethacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate and dipentaerythritol pentacrylate and it was photopolymerized by the usage of poly(vinyl chloride) with 2,2-dimethyl-2-hydroxyacetophenone as a photoinitiator. The crosslinked polymerization of pure monomers was much faster than that in the presence of PVC. Jameela et al (2002) prepared 1-
chloro-2-hydroxy-3-azidopropyl by reacting epichlorohydrin (1-choro-2,3-epoxy propane) with sodium azide in presence of phase transfer catalyst. It was then coupled onto chitosan to prepare photocrosslinkable derivative of a biopolymer. Callau et al (2002) synthesized methyl 4’-(5-hexenoxy)-4-biphenyl carboxylate and methyl 4’-(10-undecenoxy)-4-biphenylcarboxylate and used them as reactive diluents in the crosslinking of vinyl terminated side chain liquid crystal polyepichlorohydrin derivatives.


Photocrosslinkable co- and ter-polymers of N-isopropyl acrylamide-2-(dimethylmaleimide)-N-ethylacrylamide and N,N-dimethylacrylamide were prepared by free radical polymerization. Aqueous solution of the co- and ter-polymers showed lower critical solution temperature (Kuckling et al 2002). A novel methacrylate monomer 4’-(4-methoxy cinnamoyl)-4-phenyl phenoxy alkyl methacrylate was synthesized by Kawatsuki et al (2002). It was then polymerized by free radical solution polymerization. Irradiation with LPUV light induces negative optical anisotropy of the films as a result of an axis-selective photoreactivity of the side groups. Choi and Cha (2002) synthesized chalcone epoxy compound comprising 1,3-bis-(4-hydroxyphenyl)-propenone for studying the optically induced anisotropy of thin films.
Fisher et al (2003) investigated the mechanism involved in the photoinitiated crosslinking of the polyester poly(propylene fumarate) using the initiator bis-(2,4,6-trimethylbenzoyl)phenylphosphine oxide. By polycondensation reactions, starting from α, ω-bis(chloromethyl) polydimethylsiloxanes with different molecular weights and 2,6-bis(4-hydroxy benzylidene) cyclohexanone, new acrylidene-siloxane polyethers were obtained (Racles et al 2003).

Colomines et al (2003) synthesized photocrosslinkable fluorinated polydimethylsiloxane through direct hydrosilation of allyl-2-(perfluorohexyl)ethyl ether with copoly(dimethyl-methyl hydrosiloxane). Formulations containing fluorinated PDMS were ultra violet cured and their ultra violet transparency was investigated. Decker and Bianchi (2003) has done crosslinking of polymethacrylate bearing pendent maleimide group by UV irradiation of the photoinitiator-free functionalized polymer. Photocrosslinkable co- and ter-polymers of N-isopropylacrylamide, 2-(dimethylmaleimido)-N-ethyl-acrylamide as the photosensitive component and 3-acryloylaminopropionic acid or N-(2-dimethylamido)ethyl)acrylamide as ionizable comonomers were prepared by free radical polymerization (Harmon et al 2003).


Frank et al (2005) studied the formation of a cyclobutane via photodimerization of two phenylene moieties in poly [styrene-co-2-(4-vinylphenyl)indene]. The polymers were prepared by copolymerization of styrene and 2-(4-vinyl phenyl) indene. Kim et al (2005) investigated new spiroxazine polymer containing chalcone moiety. The visible range absorption increased gradually by the UV, which is ascribed to the generation of the open mesocyanine from the closed spiro-oxazone form. Rehab (2005) synthesized photocrosslinkable copolymers of nonbornene-co-styrene-maleic anhydride with different mole ratios as a polymer matrix for UV photoresists.

1.4 ANALYSES OF COPOLYMERS

Copolymerization of vinyl monomers can be carried out in bulk, solution, suspension and emulsion using free radical initiators. Among these free radical initiated copolymerization in solution has been investigated by a number of workers.

Mayo and Lewis (1944) and Alfrey and Goldfringer (1944) proposed the mechanism of copolymerization with an equation for
determining the reactivity ratio of the monomers in the copolymers. Later the monomer reactivity ratios were determined by the application of conventional linearization methods such as Finemann-Ross (1950), Kelen-Tüdös (1975) and extended Kelen-Tüdös (1977). The accurate estimation of copolymer composition and reactivity ratios is significant for tailor-making copolymers with physico-chemical properties and in evaluating the end application of copolymers. Though chemical methods have been employed for copolymer composition analysis, physical techniques have gained importance in recent years because of its inherent sensitivity, simplicity and rapidity (Brame 1978). Among the physical techniques, $^1$H-NMR spectroscopic technique is well established as a simple, rapid and accurate method for its determination of copolymer composition (Duc and Petit 1999, Brar and Dutta 1998 and Fernandez-Garcia et al 2000).

Synthesis of copolymers of acrylic (or) methacrylic monomers with MMA or GMA and determination of monomer reactivity ratio using $^1$H-NMR analysis have been reported by some of the researchers. Dhal (1986) adopted spectroscopic methods for the determination of monomer reactivity ratios in glycidyl methacrylate-styrene copolymerization. Le et al (1989) reported the kinetics of free radical polymerization of methyl methacrylate with ethylene glycol dimethacrylate. Pitchumani et al (1982) reported the determination of reactivity ratio of ethyl acrylate-n-butyl methacrylate and N-vinyl-2-pyrroldione-phenyl methacrylate copolymer system by $^1$H-NMR analysis. Patel et al (1986) reported the determination of reactivity ratios of 2-hydroxy-4-acroyloxybenzophenone methyl methacrylate copolymers. Shaban et al (1989) estimated the reactivity ratios of the copolymer systems of N-acryloyloxy phalimide-MA/MMA/AN by $^1$H-NMR analysis.

The synthesis of glycidyl methacrylate-styrene copolymers and the evaluation of the reactivity ratios by Kelen-Tüdös method have been reported

Subramanian et al (2001) described the synthesis and characterization of cinnamoyl group containing copolymers and determined monomer reactivity ratios by Fineman-Ross and Kelen-Tüdös-Tüdös methods. Synthesis and determination of reactivity ratios for the copolymers of 4-chlorophenyl acrylate with glycidyl methacrylate was studied by Vijayaraghavan and Reddy (1999) and its adhesive property was also investigated. Andreej and Pawel (1997) studied the reactivity ratios in the styrene-methyl methacrylate copolymer system.