



A Review on Photopolymers for Polymer Nanocomposite Applications

K. Kaniappan^{1*}, S. C. Murugavel², T. Daniel Thangadurai³

¹Department of Chemistry, Chikkanna Government Arts College, Tiruppur, TN, India

²Polymer Research Laboratory, Department of Chemistry, PSG College of Technology, Coimbatore, TN, India

³Department of Nanotechnology, Sri Ramakrishna Engineering College, Coimbatore, TN, India

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Abstract

Polymer nanocomposites (PNCs) are a class of thermo or thermosetting polymers reinforced with small quantities of nano-sized particles to achieve desirable properties such as high thermal, mechanical and flame retardant properties. The present article focuses the different types of photosensitive polymers employed in the production of polymer nanocomposites for photoresist applications. Polymer nanocomposites having photoresist materials show shape dependent properties due to the presence of various photosensitive moieties which after photoirradiation and processing in the specific areas show appropriate solubility. Advanced synthetic methods geared to the needs of today's photoresist applications in fields such as photolithography, advanced microelectronics, medical fields, photo recorders, liquid crystalline displays, holographic display non-linear optical materials.

Keywords: Photosensitive polymers; Nanocomposites; Photoresists; Crosslinking.

1. INTRODUCTION

The photochemical properties of polymers containing various photoactive functional groups are well known (Reiser, 1989). Groups like cinnamoyl, coumaroyl, cyclic carbonate and stilbene derivatives are much explored for photosensitive applications. Among them chalcone containing polymers have many attractive properties, such as good thermal stability, sensitivity towards UV radiation, excellent adhesion and high resistance towards solvents after crosslinking (Rami Reddy *et al.* 1989; Rehab *et al.* 1998; Choi *et al.* 2001). Such polymers are changed by the action of ultraviolet light and this property makes them useful in the preparation of photocurable coatings, energy exchange materials and optical memory devices.

However, the drawbacks of common chalcone containing polymers are their flammability and limited solubility for processing. Modifications to the structure of these polymers have received increasing attention during the recent years in attempts to improve their resistance and solubility before processing (Balaji *et al.* 2001; Nam *et al.* 2007). Also, more attempts have been made in the recent past to

synthesize multifunctional macromolecules for their potential usage in different polymer fields (Sakthivel *et al.* 2005; Kaniappan *et al.* 2013). Remarkable advances have been made in the past two decades in photoresist technology. This article deals with the detailed literature survey on various synthetic photosensitive polymers regarding the methods of preparation, characterization, potential applications and the advantages and disadvantages associated with each method.

2. PHOTOCROSSLINKING

Photocrosslinkable polymers possess photosensitive groups or moieties which may undergo certain changes while passing light sources through them. There have been many studies conducted which evaluate the photosensitive characteristics of polymers. The irreversible transformation of photosensitive polymers by light induced crosslinking reaction into insoluble materials is very likely the most important photochemical reaction from a technical point of view. The history of photocrosslinking of polymers begins when pitch was photocrosslinked for decorative purposes (Gersheim,

*K. Kaniappan Tel.:+919976323568
Email: kaniappan_psg@yahoo.co.in

1996). The first synthetic photopolymer was developed by Louis Minsk of Eastman Kodak in 1935. The success of the process started with the well-known solid state dimerization of cinnamic acid (Fig 1).

The dimers, truxinic acid and truxillic acid, are less soluble than cinnamic acid. Incorporation of cinnamic acid as side chain in the polymer would insolubilize the polymer due to crosslinking (Reiser, 1989). In recent times, wide varieties of photocrosslinkable polymers have been developed. Most of the photocrosslinkable polymers react by a $2\pi+2\pi$ type dimerization with the formation of the cyclobutane rings (Borden, 1978; Gangadhara *et al.* 1995; Rehab *et al.* 1999; Castillo *et al.* 2004; Kaniappan and Murugavel, 2005, 2009; Devi and Murugavel, 2012). A common problem with these studies is that it is difficult to compare the results obtained from different studies because different photosensitive groups, polymer concentration levels and processing techniques have been employed.

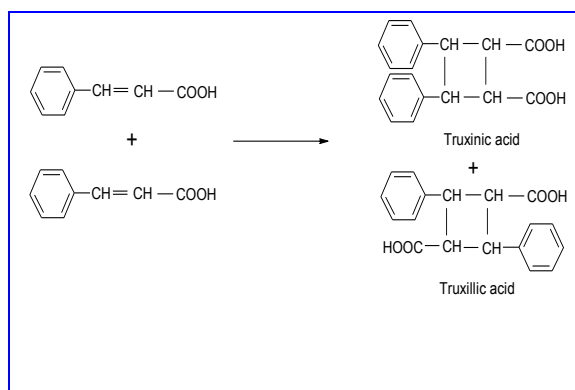


Fig. 1: Dimerization of cinnamic acid

3. POLYMERS BEARING CINNAMOYL GROUPS

Minsk and co-workers (1959) studied the photosensitive properties of crystal violet carbinol and Michler's ketone sensitized cinnamate esters of poly(vinyl alcohol) and cellulose. It was observed that varying levels of sensitivity with differently substituted cinnamate polymers through insolubilization by ultraviolet radiation. Masao Kato and co-workers (1971) prepared photocrosslinkable polymers from vinyl monomers having cinnamate ester groups. The monomers were prepared by the esterification of vinyl phenols or vinyl β -chloro ethyl ether with cinnamic acid, β -styryl acrylic acid and their homologues. Homopolymerization and copolymerization of these monomers with other monomers were investigated using radical and ionic

initiators. The results revealed that radical polymerization yield soluble polymers with low conversion. Anionic initiators failed to initiate polymerization whereas cationic polymerization produced soluble polymers with high yield.

Photosensitive poly(vinyl cinnamylidene acetate) was synthesized from poly(vinyl alcohol) and cinnamylidene acetylchloride (Tanaka *et al.* 1972). This polymer underwent dimerization of the cinnamylidene acetyl moiety to form a cyclobutane ring during photolysis reaction. The reactivity of the double bond adjacent to the carbonyl group was found to be larger than that of the double bond adjacent to the phenyl group in the chromophore.

Poly(vinyl ester)s of substituted cinnamylidene acetic acid (Fig 2) were synthesized and their photosensitivities were investigated by Hideaki Tanaka and Yoshimi Sato (1972). Poly (vinyl ester)s of planar acids reacted effectively while the poly(vinyl ester)s of twisted acids exhibited poor reactivity and photosensitive properties. Furthermore, poly(vinyl- α -cyanocinnamylidene acetate) showed good photosensitivity.

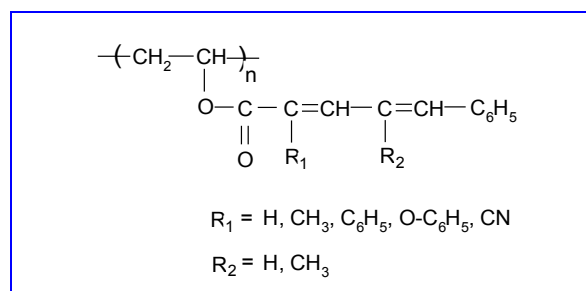


Fig. 2: Poly(vinyl ester)s

Photosensitive polymers (Fig 3) containing pendant p-(2-benzoyl vinyl) cinnamate (PBVC) were obtained by the reaction of poly (chloromethyl) styrene (PCMS) with potassium salt of p-(2-benzoylviny) cinnamate. A film was cast on a plate from THF solvent, dried and irradiated with UV light. The film became crosslinked and insoluble in the same solvent. Photosensitivity of the resulted polymer was found to be extremely high compared with those of the same chain skeleton with pendant cinnamate (CINN) and p-(2-benzoyl vinyl) benzoate (PBVB) (Nishikubo *et al.* 1981).

Polymers with pendant cinnamic ester groups (Nishikubo *et al.* 1983) have been used as photosensitive polymers for their excellent resolving power, high tensile strength, good resistance to solvents after exposure and good thermal stability.

These polymers have been used in practice with 5-10 Wt % low molecular weight photosensitizer such as N-carbamoyl-p-nitroaniline, N-carbamoyl-4-nitro-1-naphthylamine, 5-nitroacenaphthene, N-acetyl-4-nitro-1-naphthylamine and picramide (Nagamatsu and Inui, 1977).

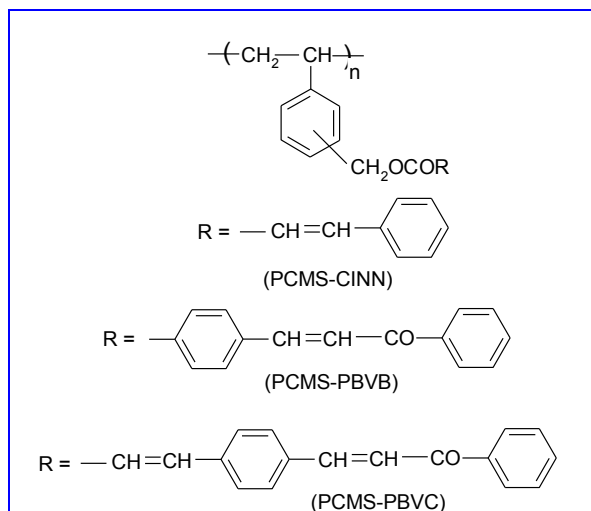


Fig. 3: Photosensitive cinnamate polymers

Photosensitive polymers containing pendant cinnamate was reported by M. Jean Farrall (1984). Soluble polystyrene was chemically modified to introduce pendant cinnamic acid, cinnamate ester, or cinnamaldehyde groups. The sensitivity of these polymers to crosslinking by ultraviolet light was studied by measuring the amount of insoluble polymer adhering to a glass plate after exposure for a given period and development in a good solvent for the unexposed film. Both the cinnamic acid and the cinnamaldehyde groups were found to crosslink more effectively than the cinnamate ester which is commonly used in photoresists.

Photopolymer chains can be preordered by the incorporation of electron donor or acceptor groups at para position of the phenyl ring of cinnamic acid to increase the photocrosslinking efficiency. Such polymers were synthesized by Lin and Reiser (1989). Photosensitive compounds with cinnamoyl units were synthesized from glycidyl cinnamate and active carboxylic acid derivatives (cinnamoyl chloride, potassium cinnamate and maleic anhydride units from styrene-maleic anhydride copolymers). Upon irradiation of synthesized compounds in solution the predominant reaction was found to be the trans-cis photoisomerization, while in film the photocrosslinking of cinnamate units occurs (Rusu *et al.* 1998). Maeshima and co-workers (1999) prepared

a series of Poly(oxyalkyleneoxy-4-[4-(2-carboxyvinylene)-phenyl carboxyloxy]cinnamate (Fig 4), with an alkyl spacer length varying between 3 to 5 methylene units and 4-[4-(2-carboxyvinylene)-phenyl carboxyloxy]cinnamate group, which has similar in structure to liquid crystal in the main chain and investigated the effect of the molecular structure on the reaction induced by linearly polarized UV light. Poly(vinyl cinnamate) and its derivatives have the ability to align the liquid crystal moieties in the direction that is perpendicular to the polarization axis of the linearly polarized ultraviolet light (Ichimura *et al.* 1997). These results indicated that the polymer with photoreactive main chain could keep the dichroism under the irradiation since unreacted sites in the polymers are difficult to react each other because of fixed movement of the polymers by dimerization.

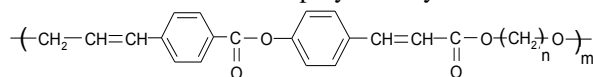


Fig. 4: Phenylcarboxyloxy cinnamate polymer

Terpolymer containing pendant cinnamic ester and cyclic carbonate groups was synthesized by the addition reaction of poly(glycidyl methacrylate-co-styrene) with CO₂ and then with cinnamoyl chloride (Park *et al.* 2003). Soluble quaternary ammonium salt catalysts showed good yield of cinnamoyl chloride addition to the glycidyl methacrylate groups. They observed that quaternary salt catalysts of longer alkyl chain length and of more nucleophilicity of counter anion offered higher yield of cinnamoyl chloride addition. Photochemical reaction experiments revealed that the terpolymer with cinnamate and cyclic carbonate groups has good photosensitivity even in the absence of photosensitizer. An integrated process has been developed for the catalytic conversion of carbon dioxide and cinnamoyl chloride to useful polymeric materials by blending of above said polymers with PMMA. It was found that the blends of the terpolymer containing cinnamoyl and carbonate groups with PMMA were miscible over the whole composition ranges. Lee *et al.* (2003) also studied the synthesis of a photopolymer bearing pendant cinnamic ester and cyclic carbonate groups in poly(glycidyl methacrylate-co-acrylonitrile).

Oriol and co-workers (2003) synthesized a new series of liquid crystalline cinnamate derivatives from 3-hydroxy and 4-hydroxycinnamic acids in order to evaluate the influence of the central core on the mesomorphic properties. The photoreactivity of some of the prepared mesomorphic and non-mesomorphic cinnamates has been studied by FT-IR, UV-Vis and NMR. A relatively low percentage of *E-Z*

isomerization was measured together with $[2\pi+2\pi]$ photocycloaddition. The resulting isomeric cyclobutane rings depend on the molecular ordering of the fluid phase. An in-depth study on the thermal and mesomorphic properties was carried out using DSC and polarized optical microscopy. Thus smectic mesomorphic ordering mainly favours a β -truxinic acid derivative but isotropic phase mainly favours a δ -truxinic acid derivative.

Polymers containing pendant photosensitive bromo-substituted cinnamoyl groups were synthesized using methacrylate monomers by free radical solution polymerization. EMK solution containing benzoyl peroxide (BPO) was used as a free radical initiator at $70\pm 1^\circ\text{C}$ (Balaji *et al.* 2003). Methacrylate monomers were prepared by reacting hydroxy chalcones with methacryloyl chloride. The photocrosslinking properties of the polymers were investigated in various solvents in the presence and absence of photosensitizers. Crosslinking was achieved via photochemical $2\pi+2\pi$ cycloaddition reactions involving chalcone units in polymers. The influence of solvent nature and concentration of polymers on the rate of photocrosslinking were also studied. It was observed that the rate of crosslinking increases with increasing concentration because of proximity of more photoactive chalcone moieties in concentrated solution.

In an effort to synthesize polymers bearing cinnamate esters from renewable resources, Esen and Kusefoglu (2003) reacted epoxidized soybean oil with cinnamic acid in presence of triphenyl phosphine catalyst yielding photocrosslinkable soya-based polymers. The reaction between the epoxidized soybean oil and cinnamic acid was highly successful; averaging over three cinnamate groups per triglyceride molecule. The mass spectra revealed that the average number of cinnamate groups per triglyceride molecule was 3.33. Esters of epoxidized soybean oil were homopolymerized into a soft and insoluble polymer by free-radical initiation and copolymerized with styrene, vinyl acetate, and methyl methacrylate.

Changag and co-workers (2004) prepared a photosensitive polymer (Fig 5) via the modification of poly(hydroxyethyl methacrylate) with α -phenyl cinnamylideneacetic acid as the pendant group of the poly(HEMA). Light irradiation upon the photosensitive poly(HEMA) film induced gel formation via dimerization between the pendant α -phenylcinnamylidene acetylates of the polymer. It was observed that the gel content of the crosslinked polymer increased with increasing irradiation time and reached 60% when irradiated for 30 minutes.

Correspondingly, the water content decreased from 27% to 18% with irradiation time increasing from 0 to 30 minutes. The crosslinked α -phenylcinnamylidene acetylated poly(HEMA) film prepared by light irradiation had much lower permeability as compared with the non-crosslinked film.

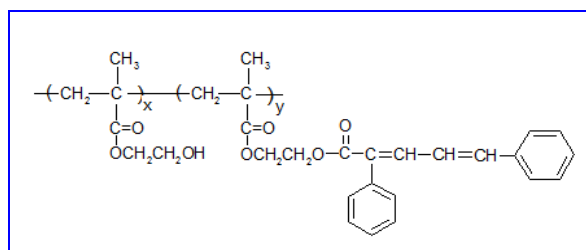


Fig. 5: α -Phenylcinnamylidene acetylated poly(HEMA)

Recently, Rachid Mahy and co-workers (2006) synthesized photosensitive polymers with cinnamate units inside position of chains by homopolymerization and copolymerization of ethyl α -cyano-4-(methacryloxy) cinnamate with methylmethacrylate. The photoreactivity test showed that the synthesized polymers can crosslink in the solid state when they are exposed to UV irradiation. The insolubility of the film at the end of the exposure to UV irradiation and the disappearance of the UV absorbance at 310 nm proved the crosslinking of the characteristic units. Various polymers containing cinnamate groups have been studied extensively by various researchers (Allcock and Cameron, 1994; Lee *et al.* 2003; Sung *et al.* 2006) to evaluate their photosensitive characteristics.

4. POLYMERS WITH PENDANT FURAN GROUPS

Minoru Tsuda (1969) prepared a new photosensitive poly(vinyl-2-furylacrylate) by the condensation of poly(vinyl alcohol) with 2-furylacrylyl chloride via aqueous alkaline process and its photosensitivity was investigated. In the presence of photosensitizers this polymer was found to crosslink at a considerably faster rate than does poly(vinyl cinnamate). The mechanism of photochemical reaction was explained through the dimerization of the furylacrylyl group.

A polymer having furan units in the side chains was synthesized by the reaction of poly(2-hydroxyethylmethacrylate) with 2-furoic chloride (Fig 6). Yusuke Tajima and co-workers (1999) demonstrated that fullerene C_{60} can be used as an effective photocrosslinking reagent for furan substituted polymers because of its high

photosensitivity and multiple functions. Tajima, Arai and Takeuchi (1999) studied the effects of singlet oxygen on photocrosslinking of poly(furfuryl methacrylate). The reactions were carried out in 1,1,2,2-tetra chloroethane solutions that contained the polymer and fullerene C₆₀. Gelation occurs when exposed to visible light in the presence of photosensitizers. The solution was turned to a gel after several hours and then solidified completely.

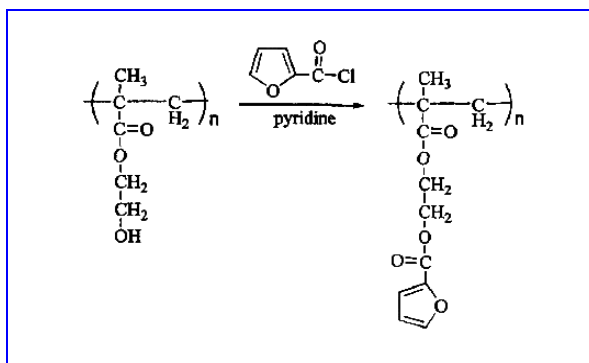


Fig. 6: Synthesis of furan containing polymer

Preparation of photocrosslinkable furan-containing polyimides was reported by Y. Tajima *et al.* (1999). It was found that the polymer crosslinks with the aid of singlet oxygen and formations of fine pattern images were observed. This was considered as clear evidence of successful photolithography in this photocurable system that uses C₆₀ as the photosensitizer. Furan substituted novolac having different molecular structures were investigated by Takeuchi and his co-workers (2001). Introduction of a 2-hydroxy-1,3-trimethylene unit between the furan ring and the phenoxy moiety of the novolac was found to be effective in enhancing its photosensitivity. In addition, the spacer had little detrimental influence on the thermal stability of the epoxy resin.

Lasseguette and co-workers (2005) proved the possibility of inserting furan chromophores in an aliphatic polyester structure by transesterification copolymerisation under mild experimental conditions. Their UV spectrum showed a maximum at 308 nm as in the case of the furan monomer. When they were irradiated with near-UV light, they followed the classical molecular photocycloaddition mechanism of cinnamic derivatives, giving insoluble networks. This makes them good candidates for negative offset plates.

5. POLYMERS WITH AZO GROUPS

The first report on photoinduced anisotropy in azo polymer was about the change of its physical

property, dichroism, under illumination with polarized light on an azo aromatic compound (Teitel *et al.* 1957). Matejka's group (1978) has reported a new reversible photochromic copolymer of maleic anhydride with styrene containing azo side groups. Upon irradiation, a reversible trans-cis photoisomerization of light-sensitive azo groups was observed with a change of refractive index. This property was employed in recording optical information in the form of phase hologram. Oskar Nuyken and Ulrich Presenz (1989) synthesized certain polycarbonates containing different amounts of thermolabile azo functions and the resulting polymeric initiators were employed to start the polymerization of methyl methacrylate. The kinetic results were explained on the basis of a high degree of termination reactions by primary radicals.

Higuchi and coworkers (1995) tailored a photoresponsive polypeptide through two α -helical poly(γ -methyl L-glutamate)s joined with an azobenzene. Monolayers of the polypeptide were formed at air-water interface and the photoresponsive behavior of the monolayer confirmed that the trans to cis photo-isomerization of the azobenzene moiety in the main chain resulted a bending structure formation of the polypeptide.

Azobenzene containing polyurethane and polymethacrylate were prepared for fabricating the diffraction gratings on the film surface (Choi *et al.* 2001). Two-beam coupling method was employed for fabricating the surface relief gratings. The dynamics of formation of the diffraction gratings was studied in terms of the variation of the diffraction efficiency. The stability of the diffraction efficiency of PU below T_g was observed to be relatively higher than that of PMA owing to the hydrogen bonds between the main chains themselves.

Rodinel Ardeleanu and co-workers (2002) synthesized several photosensitive siloxane-crown ether copolymers using polycondensation reaction of an oligosiloxane with COCl end groups and bisazo derivatives of dibenzo-18-crown-6 polyether. They also studied the photochemical behaviour of some azocrowned polysiloxanes and their corresponding complexes with metal ions. It was noticed that the complex formation favours a higher mobility of the siloxane units in the polymer chain. These studies may be helpful for molecular design and development of new sensitive cation-optical sensors. O.Nuyken and co-workers (1997) made a detailed literature survey on azo group containing polymers for use in communication technologies in one of their articles.

A photocrosslinkable amorphous polymer containing azobenzene and acrylic groups in the side chain (Fig 7) was synthesized by free-radical copolymerization followed by a substitution reaction (Takase *et al.* 2003). Surface relief gratings were inscribed by irradiating onto the film surface with an interference pattern of circularly polarized beams. Photocrosslinking with UV irradiation after inscription fixed the gratings permanently but was accompanied by some photo-degradation of the azo chromophore. In comparison with the photocrosslinked gratings, a non-crosslinked grating rapidly lost most of its shape when heated above T_g .

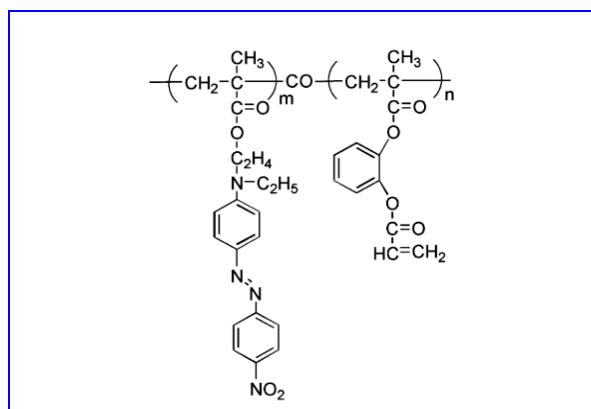


Fig. 7: Azobenzene and acrylic copolymer

6. POLYMERS WITH CHALCONE GROUPS

Photocrosslinkable chalcone containing polymer was initially synthesized by C. C. Unruh and A. C. Smith Jr (1960) of Eastman Kodak Company. Polymer containing pendant chalcone group has been synthesized by the acetylation of polystyrene followed by the condensation of the resulting poly(*p*-vinyl acetophenone) with benzaldehyde in the presence of acid catalyst. The photocrosslinking ability was investigated by ultraviolet spectroscopy. The sensitivity to light was generally higher where the aldehyde used contains electron donating substituent groups in the *para*-position.

Kato *et al.* (1971) demonstrated the synthesis and photosensitive properties of the poly[4'-(β -vinylethoxy)chalcone] and poly[4'-(β -vinyloxyethoxy)chalcone] by cationic polymerization of the corresponding vinyl monomers using BF_3 -ethyl etherate catalyst.

Pendant chalcone groups on polymers behave similarly to pendant cinnamate groups. Thus, photocrosslinkable polymer can be formed, for instance, from poly(vinyl alcohol) by a reaction with 4'-substituted-4-carboxy chalcone in homogeneous

dimethyl formamide solution using 2,4,6-trinitrochlorobenzene as the condensing agent (Watanabe *et al.* 1986). The crosslinking of the polymer was explained through the formation of biradicals derived from the double bonds of the cinnamoyl groups.

Acrylate and methacrylate monomers containing the photodimerizable α,β -unsaturated ketone moiety were prepared (Rami Reddy *et al.* 1996) and polymerized in ethyl methyl ketone using benzoyl peroxide as initiator at 70°C. These polymers showed higher rate of photocrosslinking leading to insolubilization even in the absence of photosensitizer.

Ahmed Rehab (1998) studied the preparation and characterization of photocrosslinkable homo and comethacrylate polymers containing pendant chalcone groups (Fig 8) by radical polymerization of vinyl-chalcone monomers in anhydrous toluene and tetrahydrofuran. The photocrosslinking studies revealed that the rate of disappearance of the C=C bond depends on several factors such as, spacer units between the sensitive moieties and the backbone of polymers, copolymer ratios and concentration. The rate was fast in the first few minutes followed by a slow rate. They also noticed that the copolymer types and the solvent used in the photocrosslinking process have no significant effect on the rate of dimerization of the C=C bond.

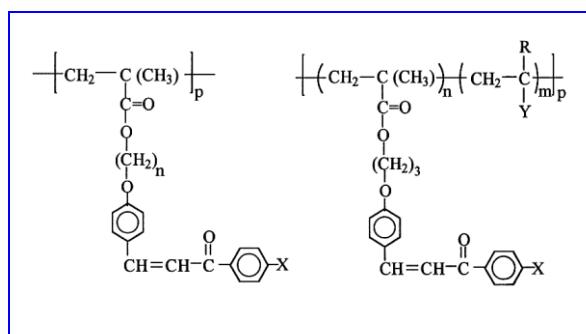


Fig. 8: Homo and comethacrylate chalcone polymers

Ahmed Rehab and Nehal Salahuddin (1999) also reported that complete crosslinking cannot be achieved even after a long irradiation time (150 min). This might be due to chain fragmentation reactions which accompany the photocrosslinking process and reduce the yield of crosslinking. Further, intramolecular crosslinks can be formed by the dimerization of adjacent chalcone groups. Intramolecular links do not contribute to network formation and will also lower the yield of crosslinking.

Choi and co-workers (2001) synthesized a new photochemically bifunctional chalcone-epoxy compound by the reaction of 4,4'-dihydroxychalcone and epichlorohydrin. They observed that the chalcone-epoxy compound undergoes photodimerization by UV irradiation. They also indicated that the chalcone-epoxy compound can be photopolymerized with a trace amount of onium salt. The UV cured chalcone-epoxy compound showed an excellent thermal stability as compared to the conventional UV-cured bisphenol-A type epoxy compound.

Balaji and Nanjundan (2001) investigated the polymerization of 4-methacryloyl oxyphenyl-3'-methylstyryl ketone (MPMSK) containing pendant chalcone moiety using ethyl methyl ketone solution and benzoyl peroxide as a free radical initiator. The TGA results of this study indicated that poly(MPMSK) had very good thermal stability as required for negative photoresists. The high T_g value of the polymer was due to the presence of bulky and rigid pendant chalcone units and the short side chains which facilitated chain entanglement. The rate of photocrosslinking of the poly(MPMSK) in chloroform solution was very fast even in the absence of photosensitizer due to free movement of pendant phenyl unit.

Dong Hoon Choi and Young Kwan Cha (2002) synthesized photocrosslinkable chalcone-epoxy compound comprising of 1,3-bis-(4-hydroxyphenyl) propenone (Fig 9) and studied optically induced anisotropy of the thin films. Chalcone group was introduced into the main chain of the epoxy oligomer and they observed the photodimerization behaviour of the compound by irradiation using UV light. In another study, Choi and Cha (2002) prepared modified epoxy compound to evaluate the photosensitive properties. Linearly polarized UV irradiation on the chalcone-epoxy films with cationic photo initiator induced optical anisotropy of the film and the resultant film showed the property of low molecular weight nematic liquid crystals.

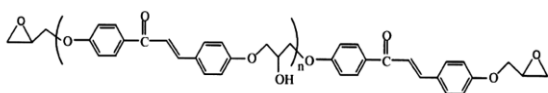


Fig. 9: Chalcone-epoxy compound

Photochemically bifunctional epoxy and dimethacrylate compounds have been synthesised by the same research group. The chalcone epoxy

oligomer derived from 4,4'-dihydroxy chalcone and epichlorohydrin was modified by end-capping method. The photosensitivity and photodimerisation was studied by UV radiation. Density of the polymeric matrix of dimethacrylate compound increased due to the UV irradiation.

Song *et al.* (2002) synthesized certain chalcone derivatives and introduced them as a side chain unit in the backbone of polyimide for photo-alignment layers. The photo-alignment properties of chalcone monomers and the attached polyimide films treated by polarized UV light were investigated as a function of the exposure dose. They studied the effect of the length of alkyl chain in chalcone derivatives and found that the alignment properties were very much dependent on the chain length.

Jae Hong Kim and coworkers (2003) studied copolymers bearing photochromic spiropyran dye in the side chain to evaluate the dynamic properties of their photochromism. The dynamic processes of colorization and decolorization under an excitation light were investigated using the two copolymers. To improve the stability of the colored species of photochromic spiropyran, they synthesized a new bifunctional copolymer having both photochromic spiropyran and photo-crosslinkable chalcone moieties. The rate control of ring closure reactions of spiropyran dye in copolymer was successfully achieved by $2\pi+2\pi$ photocycloaddition between the chalcone units which is expected to control the free volume surrounding photochromic moiety.

Cibin and co-workers (2003) proved that intramolecular photocycloaddition of chalcones to give cyclobutanes was fast and convenient method to shrink a cyclophane ring to a tricyclic system to prepare potential ditropic receptors. X-Ray results confirmed the structure for the cyclobutanes in which the cyclization occurs by a head-to-head syn ring closure. Priyarega *et al.* (2003) synthesized photosensitive polyesters containing photoreactive chalcone moieties in the main chain from 1,3-bis(4-hydroxyphenyl) propenone and 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxy phenyl)propenone with adipoylchloride by an interfacial polycondensation technique. The use of phase-transfer catalysts influenced the reaction rate and yield.

Lee and coworkers (2004) studied rate control of decolorization of photochromic chalcone containing polymers with spiropyran dye successfully by $2\pi+2\pi$ photocycloaddition between the chalcone units. The chalcone-epoxy polymer system proved to

retard the decaying behavior of photochromism most effectively resulting from the steric hindrance after UV irradiation. Chalcone epoxy system and that with cationic photoinitiator showed quite effective retardation of decolorization significantly by virtue of photocrosslink and photopolymerization.

In recent years, photochromic and thermochromic spiropyrans and spiroxazines have been receiving considerable attention due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics. The effect of photocrosslinked chalcone moiety on the stability of photochromism was investigated intensively by Choi and his team. New spiroxazine polymer containing chalcone moiety was prepared and its photochromic behaviour had been investigated (Kim *et al.* 2005). This polymer showed effective retardation of decolouration by virtue of photocrosslinking.

Acrylamide based photocrosslinkable polymers were prepared by polymerizing 4-acrylamidophenyl-2',3'-benzostyryl ketone or 4-acrylamidophenyl-4'-N,N'-dimethylstyryl ketone in ethyl methyl ketone using benzoyl peroxide as the initiator (Selvam *et al.* 2005). Thermal stability, effect of different solvents and concentration of polymers on the rate of photocrosslinking were also assessed for using the polymers as negative photoresist materials.

Nam and co-workers (2007) prepared a series of linear ester compounds having two chalcone units connected to a benzene ring through ester linkages and studied their reactivity with different number of alkyloxy tail carbons. All linear ester compounds showed enantiotropic liquid crystalline phases. Upon UV irradiation, polymerization proceeded through the $2\pi+2\pi$ addition reaction between chalcone units in a stepwise manner.

7. POLYMERS WITH ACETYLENE MOIETY

Photosensitive poly(acetylenes) (Fig 10) were prepared by oxidative coupling of bis(propargyl ether)s of various bisphenols (Hay *et al.* 1970). The thin film of the base polymers underwent crosslinking when irradiated with medium pressure mercury lamp.

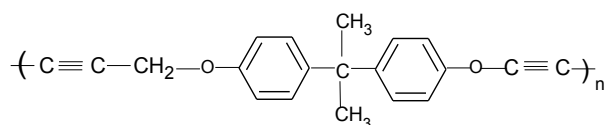


Fig. 10: Photosensitive poly(acetylenes)

Polyimide block copolymers with diacetylene functionality were prepared in two stage process. The first step involved the oligomeric imide formation terminated with 1-amino-3-ethynylbenzene. In the second step, the oxidative coupling of *m*-diethynylbenzene and bispropargyl ether of bisphenol-A formed block copolymers. The resulting copolymers were crosslinked with UV-irradiation (Chao *et al.* 1990). Gao *et al.* (1996) synthesized poly(ether imide) containing diphenyl acetylene moiety from dianhydride with acetylene group by solution polycondensation. This polymer possessed thermal crosslinkability when heated above 350°C. Yanming Hu *et al.* (2007) synthesized poly(diphenylacetylene) containing siloxy and halogen / methyl groups. These siloxy group containing polymer membranes were studied for their gas permeability.

8. POLYMERS WITH STILBENE MOIETY

Ichimura and Watanabe (1980) synthesized polymers containing photosensitive stilbazolium group from poly(2-chloroethylvinyl ether) and γ -stilbazole. They were used for immobilization of enzymes due to their water solubility and photosensitivity. The photocrosslinking reactions take place via $2\pi+2\pi$ cycloaddition reaction (Fig 11).

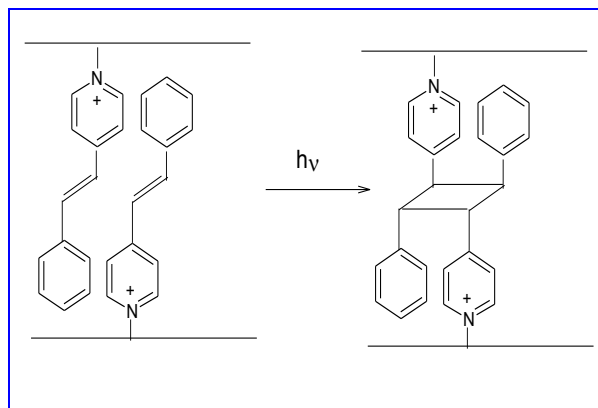


Fig. 11: Photocrosslinking of stilbazolium polymers

Yun Chen and Cherng-Jing Tsay (1995) synthesized polyesters from trans-2,2-dihydroxystilbene with aliphatic diacid chloride by interfacial polycondensation. The monomer 2,2-dihydroxystilbene was prepared via asymmetric photocleavage of coumarin dimer acid. They were semicrystalline with melting temperature of 39-192°C. The photoreactive stilbene chromophore present in the main chain dimerized to form cyclobutane under UV-irradiation.

9. POLYMERS WITH AZIDES MOIETY

Merrill and Unrush (1963) synthesized polymers containing photosensitive pendant azide group by the reaction of poly(vinylalcohol) with azidophthalic anhydride. The photocrosslinkability depended on the photochemical decomposition of the azide group with evolution of nitrogen producing imine radicals which reacted rapidly in three different ways: which coupling with another imine radical forming an azo group or inserting into the C-H bond of the polymer chain or abstracting hydrogen atom from the environment and changed into $-NH_2$. The first two processes led to crosslinking.

Poly(vinyl-p-azidocinnamate)s (Fig 12) were synthesized by the aqueous alkaline process. The polymer coatings were obtained from 2 % (W/V) solution in a 1:2 mixture of ethyl methyl ketone and cyclohexanone (Yabe *et al.* 1971)

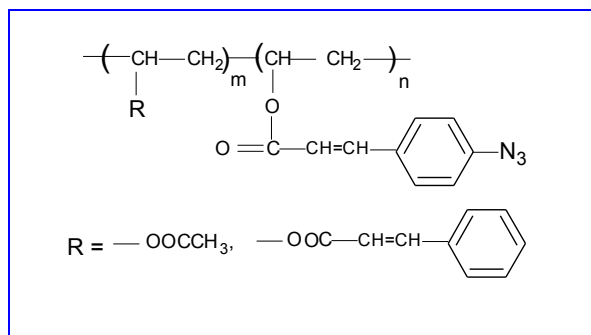


Fig. 12: Poly(vinyl-p-azidocinnamate)s

Nishikubo *et al.* (1981) described the synthesis of poly-2(2'-azido-5-nitrobenzyloxy) ethyl methacrylate and poly-2(4-azido-3-nitrobenzyloxy)ethyl methacrylate from the reactions of 2-hydroxy ethyl methacrylate with 2-chloro-5-nitrobenzoic acid and 4-chloro-3-nitrobenzoic acid respectively by solution reactions of sodium azide with corresponding chloronitrobenzoyl group. The degradation reaction of the 2-azido-5-nitrobenzoyl group and the transformation of the 4-azido-3-nitrobenzoyl group to 5-carboxyl benzofurazane-1-oxide ring by the irradiation of ultra violet light were investigated.

The applications of polyesters, polycarbonates and polyimides containing the photolabile triazene group ($Ph-N=N-NR_2$) in photoreists and XeCl excimer laser ablation were studied by Ch. Hahn *et al.* (1998).

10. POLYMERS WITH OTHER PHOTSENSITIVE GROUPS

Eastman Kodak company developed a light sensitive coating material consisting of polycarbonate derived from divinylall cyclopentanone and phosgene. This polycarbonate containing arylidene moiety in the main chain underwent crosslinking on exposure to UV light. A series of photosensitive polysulfonate copolymers with arylidene group were synthesized from bisphenols and aromatic disulphonyl chlorides. These bisphenols contain the light sensitive strylyketone group. These polymers showed good photosensitivity and readily underwent crosslinking to give alkali and acid resistant materials. They were found to be useful in photoresist application (Arcesi *et al.* 1971).

Deboer (1973) synthesized polymers containing 1,2-diphenylcyclopropane-3-carboxylate group by the reaction of poly(vinyl alcohol) with 1,2-diphenyl cyclopropane-3-carboxylchloride in pyridine medium. This photofunctional group was also introduced into poly(styrene) by chloromethylation of poly(styrene) followed by the reaction with 1,2-diphenyl cyclopropane-3-carboxylic acid in the presence of trimethylamine.

Theocharis (1987) described by the synthesis of coordination polymers containing 2,5-dibenzylidene cyclopentanone (Fig 13) segments, capable of forming metal complexes as well as possessing photocrosslinking properties.

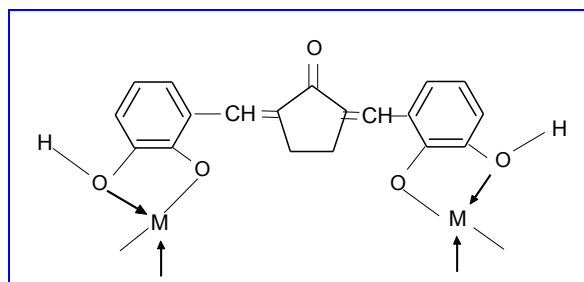


Fig. 13: 2,5-Dibenzylidene cyclopentanone polymer

Unsaturated polyamides and imides were prepared by condensing 2,6-bis(amino benzylidene)cyclohexanone with terephthaloyl chloride, pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, maleic anhydride and nadic anhydride to yield a bismaleimide and

bisnadimide which were utilized as new polymer precursors (Mikroyannidis *et al.* 1992).

Everelt *et al.* (1995) modified simple cresol epoxy novolac resin with hydrophilic chain producing surfactant-modified epoxy resins. They were modified with photoacid generator and solvent, subsequently exposed to deep UV light. They behaved as a conventional chemically amplified negative resist material. Crivello and Shim (1995) synthesized the copolymer di-tert-butylfumarate with either allyltrimethyl silane or styrene which showed photosensitivity behaviour with poor dry etch resistant.

Photosensitive polysiloxanes containing perfluorinated pendant group and acrylated groups linked with urethane moiety were studied. The synthesis involved the copolycondensation of α,ω -dihydroxy dimethylsiloxane and dichlorosilane bearing fluorine as well as acetoxy group (Boutevin *et al.* 1995). Oberski *et al.* (1995) prepared liquid crystalline polymers containing photosensitive arylene vinylene segments in the main chain for their structure property relationship study and light-emitting applications.

Manjunath Kamath *et al.* (1996) investigated the properties of interpenetrating polymer networks of photocrosslinkable cellulose derivatives. Masse *et al.* (1996) prepared epoxy based photocrosslinkable polymers and studied their second order nonlinear optical properties. Xiang-Qian Liu *et al.* (1998) synthesized acrylic polymers having phenothiazine oxide moieties and studied their photochemical properties. Ying-Hung So *et al.* (2000) reported aryl cyclic sulphonium zwitterions which on ring opening photo polymerization gave non ionic polymers.

Polymers with pendant anthracene moiety were investigated by Chae and Jang (2002). These polymers undergo [4+4] cycloaddition on exposure to light and acts as negative photoresists. Kamal I Aly *et al.* (2003) synthesized polyketones containing diarylidene cyclohexanone by Freidel Crafts polymerization with aromatic diacid chlorides. Raghu *et al.* (2007) synthesized polyurethanes (Fig 14) containing 2,6-bis(4-hydroxybenzylidene) cyclohexanone segments and studied thermal and acoustic properties. The experimental results demonstrated that the mesogenic transition and isotropization temperature gradually decreases with increase in even number of methylene spacer of the polymer chain.

Balakrishnan and Murugavel (2008) developed a photosensitive epoxy resin from bis(4-

hydroxy-3-methoxy benzylidene) acetone and epichlorohydrin using solution polycondensation method. The results indicated that the photocrosslinking of the epoxy polymers was influenced by photoinitiators and photosensitizers. Malgorzata Sierant *et al.* (2013) synthesized a highly fluorescent coumarinated polymer to develop photosensitive nanocapsules for molecular imaging devices. These polymeric nanocapsules can also be used for the fluorescent labelling of membranes.

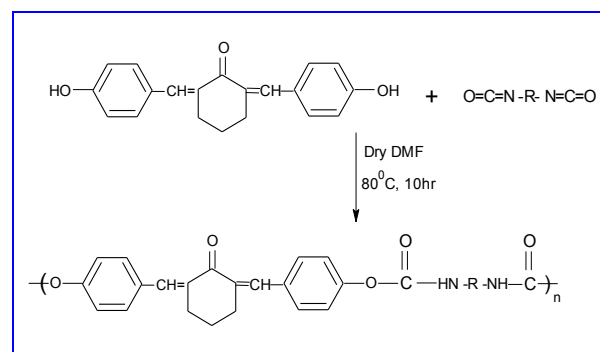


Fig. 14: 2,6-Bis(4-hydroxybenzylidene) cyclohexanone polyurethane polymer

11. CONCLUSION

This review paper has attempted the compilation of several photosensitive polymers, their characteristics, applications and limitations. These photosensitive polymers can be exploited to prepare different kinds of polymer nanocomposites which may find advanced photoresist applications. Polymers with different photosensitive groups can be employed to make photoresists with high chemical resistance, better thermal stability and good resolution capability. Photosensitive polymers particularly having outstanding physical properties are compatible with existing semiconductor processing techniques. The conclusion from this literature review has opened up new avenues for further research to be explored.

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