CHAPTER 1

INTRODUCTION

The radiation has grown from a subject of esoteric research specialities into major industrial developments and is now a field of central importance in polymer science and technology.

Radiation process is a relatively sophisticated industrial technique that can be economically substituted for conventional, thermal and chemical processes. There are indications that radiation process is attaining prominence as many companies recognize the special benefits that radiation process can provide. These benefits have come from the improved product and energy saving characteristics. Active research on radiation curing has been in progress since the1980’s in India. The development of new photoinitiators and prepolymers enhances the use of photocrosslinkable polymers in the field of radiation technology based particularly on ultraviolet (UV) radiation.

The photocrosslinking polymerization is a rapidly growing, vigorously expanding discipline that utilizes relatively less hazardous raw materials and leads to useful products. It is a well-accepted fact that the rapid development, during the last decade, of high-performance UV-curable systems should find a growing number of applications in various industries. With an estimated world consumption of UV-curable products that corresponds roughly to a billion dollar market, that the growth rate should get boosted in the coming years. The design of new reactive monomers and oligomers, improved photoinitiators will presumably accompany the market growth. The pressure for the development of green technologies such as UV-curing (because of the drastic rules and regulations enforced for the control of air pollution) will induce new
efforts and new applications in the field of UV-curing of photocrosslinkable polymers.

The photochemistry of synthetic polymer substrates has attracted considerable interest for many years (Ranby & Rabek 1975, Ranby & Rabek 1977). Pure polymers which contain single bond between carbon, hydrogen, oxygen, nitrogen, chlorine and fluorine, do not absorb light of the higher wavelength that are highly stable. Polymers that absorb light with longer wavelength show poor photostability. Such polymers undergo photopolymerization producing crosslinked polymers.

Photoinitiated polymerization reaction (Rabek 1987, Hoyle & Kinstle 1990, Pappas 1992, Fouassier & Rabek 1993) is a chain reaction where the initiation step involves a photochemical process. In this curing process, the liquid monomer containing more than one reactive function is converted into a crosslinked solid polymer.

The photochemistry of commercial synthetic polymers is complex in nature (Arthur & Allen 1980, Needles & Alger 1975, Ogiwara et al 1975, Tsunooka et al 1974). The properties of the polymers are affected by external impurities, additives and, internal UV-absorbing chromophores. The chromophores may be present in the monomers or formed during their preparation. These photoinitiated reactions are primarily oxidative in nature and lead to the formation of carbonyl groups and hydroperoxides (Ranby & Rabek 1975). The photochemical reactions can be carried out by either radical or cationic mechanisms employing different initiators.

1.1 APPLICATIONS OF UV-CROSSLINKED POLYMERS

UV-curing technology is widely used today in microlithography printing to produce, through negative working photoresists, high-resolution relief
images which are needed for the fabrication of integrated circuits or printing plates. In the coating industry, fast drying UV-curable varnishes, inks or paints are employed to improve the surface properties of all kinds of materials (Pappas 1985, Randell 1987, Roffey 1982) such as metals, plastics, papers, woods, and textiles (Fouassier 1995, Fouassier et al 1993, Holman & Oldring 1988). In optics and microelectronics (Thompson et al 1994), they are used for optical fiber coating, protective coatings for compact discs, holographic relief image protection, layers of printed circuits, inks and organic polymeric conductive materials. The development of powerful and versatile laser sources open a new area in the application such as laser writing of complex patterns (Fouassier & Rabek 1990, Thompson et al 1984) and the recording and storage of information. In decorative coatings, it is particularly used in posters, embossed vinyl flooring, coating for wood panels, leather, textile and plastics. In protective coatings, it is used in abrasion-resistant coatings for polycarbonate sheets, protective coatings for plastic lenses, heat-resistant coatings, corrosion protection weather-resistant coatings and protection finish for colour prints and films.

Summary of applications: Photocurable epoxy acrylate and polyurethane acrylate is used to produce high-temperature oil resistance; Water-dispersible urethane acrylate oligomers for photocurable inks and coatings. A urethane methacrylate resin composition for UV-curable light transmittable screens for lenses and their cured products.

The synthesis of functionalized polymers as reactive materials has attained considerable technological interest (Akelah and Moet 1990). Recently the synthesis and application of radiation sensitive polymers have progressed into a wide active research area. Radiation sensitive polymers are applied to (i) microlithography (Reichmanis & Thompson 1989, Thompson et al 1994), (ii) printing materials (Tazuke 1982), (iii) liquid crystalline (Whitcombe et al

1.2 PHOTOINITIATORS

A photoinitiator is responsible for the initiation step in a photopolymerization reaction. The initiator, by absorbing radiation, breaks into the primary reactive species called free radicals.

A polymerizable compound consists of a photopolymerizable vehicle and a light-sensitive functional group (chromophores). The chromophores absorb light energy and undergo reaction with the binder to polymerize to give a hard solid mass.

The increased demand for improved photopolymerizable initiators for coating technology can be met only by improving our knowledge concerning the mode of action of the photoinitiators under various conditions. This will facilitate the development of more efficient photoinitiators for specialized applications. The choice of photoinitiators for specific requirements depends upon the relationship between the macromolecular structure and properties of the initiators (Dietliker et al 1993, Allen et al 1998a).

The Efficient photoinitiation depends upon an appropriate light source and other following factors are (i) suitable absorption coefficient and wavelength sensitive to the initiator molecule and (ii) important initiation quantum yields. It is must for the initiator molecule or any of its photofragments should not function as chain transfer agents or termination agents.
Most of the photopolymerization processes require the addition of the initiators; it may be either free radical or cationic photoinitiators (Fouassier 1989, Hageman 1989, Paul 1996). In photopolymerization reactions, the photoinitiators are classified as Fragmentation reactions, hydrogen abstraction reactions and ionic initiation reactions.

These fragmentation reactions are of the following types:

Norrish-I-type: The bond dissociation energy of carbon-carbon bonds adjacent to a carbonyl group is comparatively small and consequently, photochemical excitation of ketones usually results in the homolytic fission in the α-carbon-carbon bond (Crivello 1978).

Norrish-II type: This is an intramolecular non-radical process leading to the creation of six-membered cyclic intermediates; this subsequently decomposes by hydrogen abstraction from α-carbon to yield an olefin and an alcohol/aldehyde. An intramolecular process within a long chain segment may occur with polymers. Carbonyl n-π* triplet states react easily by hydrogen abstraction reaction with high quantum yields.

Norrish-III type: This is another intramolecular non-radical process, which involves a β-hydrogen atom transfer. This leads to the formation of an aldehyde and an olefin in a carbon-carbon bond scission adjacent to the carbonyl.

Reactive monomers and efficient photoinitiators have synthesized largely in number and are available commercially. Among the many requirements for the practical uses of such polymerization systems, the curing speed is an important factor. Surface curing by radical polymerization in an air requires the high rate of radical polymerization not only to consume surface...
oxygen but also to compete with the surface. Improved photoinitiator systems, which exhibit faster-curing speed and superior to photosensitivity are required (Tomioka 1997).

In a photochemical reaction, the primary process involves the excitation of the UV-radical photoinitiator; the generation of radicals is primarily in their triplet state. Photoinitiators sensitive to UV-radiation are usually built on the benzoyl chromospheres, which exhibit a good absorption in the specified wavelength range and a good photochemical reactivity. Biacetyl in methanol gives an $\alpha$-substituted alkanone, a very effective photoinitiator for vinyl pyrrolidone and vinyl acetate (Encinas et al 1985).

1.3 FREE-RADICAL POLYMERIZATION

Free-radical photopolymerization (UV-curing) is a well-established polymerization technique which takes place at room temperature under UV-light. Upon irradiation, a liquid poly functional monomer containing a proper photo-initiator forms a solid highly crosslinked film. A typical formulation may consist of more than one monomer and oligomer, but is solvent-free. The irradiation time ranges from a few seconds or few minutes and light are the only energy source for building up the polymeric thermo-set matrix. The process is well known for being fast and environmentally friendly, as the energy consumption is low and no emission of volatile organic compounds.

Photoinitiator contains bonds that have lower dissociation energies compared to an excitation energy of the reactive excited states and high sufficient to provide thermal stability. However, since fragmentation is a unimolecular process, the most common type of these photoinitiators produces benzoyl radicals, which react with olefinic double bonds of vinyl monomers.
The unimolecular fragmentation (Norrish-I type, $\alpha$-cleavage) of ketones into two radicals under UV-radiation forms the chemical basis of photoinitiators for photocuring applications. The hydrogen abstraction (Norrish-II type) of ketones from a macromolecular hydrogen donor under UV-radiation forms the chemical basis for the photoinitiation of free radical grafting polymerization. Accompanying the growing interest in commercial UV-curable systems, extensive efforts and studies have made into the photografting ketone initiators for more photochemical processes and for developing new and effective photoinitiators (Hageman 1989).

Allen et al (1999) have studied the curing behaviour of Norrish-I and II photoinitiators and from their study, Norrish-I photoinitiators have found superior to effective systems in clear coatings.

$\alpha$-Cleavage photoinitiators are the most important Norrish-I type photoinitiators have found to be their high reactivity and thermal stability. Some applications of $\alpha$-cleavage photoinitiators which are used include clear coatings, circuit boards, laminates, printing inks, printing plates and white lacquers.

Four novel benzophenone containing photoinitiators (monomers PI-1 and PI-2 and their polymers PPI-1 and PPI-2) have been prepared from alkyl $\alpha$-hydroxy methacrylates. PI-1 has been synthesized from the reaction of tert-butyl $\alpha$-bromomethacrylate and 4-hydroxybenzophenone followed by cleavage of tert-butyl groups using trifluoroacetic acid. PI-2 has been synthesized from the reaction of ethyl $\alpha$-bromomethacrylate and 3-benzoylbenzoic acid. All of the photoinitiators are given phosphorescence emissions from their n–$\pi^*$ states. Polymeric photoinitiators have found to have higher efficiencies than benzophenone and monomeric ones (Balta et al 2015).
A novel polymeric photoinitiator, poly (glycidyl benzophenone ether) (PGBE) with a side-chain benzophenone (BP) group have synthesized from poly (epichlorohydrin) and 4-hydroxybenzophenone (Wang et al 2014). The structure of PGBE has characterized by IR and $^1$H-NMR. The light absorption of PGBE has detected by UV-spectrophotometer with the maximum absorption wavelength of 283 nm in acetonitrile solvent, red-shift compare to BP. The photopolymerization of tripropylene glycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA) initiated by PGBE and BP/EDAB have studied by real-time FTIR. The polymeric initiator has found in higher efficiency than BP/EDAB.

Recently acylphosphine oxides have developed as a new class of photoinitiators. Laser flash photolysis of 2,4,6-trimethyl benzoyl diphenyl phosphineoxide (TMDPO) in dilute solutions of benzene, methanol and dichloromethane has studied by Sumiyoshi et al (1984). They have concluded that the radicals produced from the TMDPO are of relatively high reactivity towards compounds having olefinic double bonds. TMDPO has suitable for the initiators of photopolymerization of TiO$_2$-pigmented coatings and of thick-walled glass fiber-reinforced polymers.

New polymeric photoinitiator bearing side-chain benzoyl phenyl phosphine oxide moieties have used in clear coatings. Polymeric photoinitiator contains side-chain benzoyl diphenyl phosphineoxide moieties have prepared by reacting poly(4-vinylbenzoic acid) or 4-vinylbenzoic acid/methyl methacrylate copolymers with thionyl chloride followed by methoxy diphenylphosphine (Angiolini et al 1994).

When the photoinitiator, xanthen dye, rose bengal (RB) or eosin (EO) photopolymerization, rates increase when irradiated with visible light in the presence of aromatic carbonyl compounds. Burget et al (1999) have synthesized
a new eosin and rose Bengal ester with an O-benzoyl-α-oxooxime group (EOAO & RBAO) as a visible light photoinitiator for polymerization. They have found that the presence of an amine as a co-initiator, the dyes EOAO and RBAO have shown good photoinitiators. The rate of photopolymerization (Rp) values is higher than the physical mixtures of dye/acyloxime or than corresponding to the pure dyes. The photochemical and photopolymerization properties of arylsuberone have been reported and shown an efficient photoinitiator for the radical polymerization of acrylic monomers (Almeida et al 1996). The newly developed trans-10,11-dibromodi-benzosuberone is a very efficient photoinitiator for the radical polymerization of multifunctional acrylates and oligomers.

N-aliphatic maleimides have been used as the photoinitiators for the photopolymerization of diacrylate monomers (Clark et al 1999). The reactivity of diacrylate thin films increased continuously as the concentration of N-aliphatic maleimides increased from 0.1 to 30 mol %.

Carlini et al (1997) have prepared polymeric photoinitiators with pendant α-aminoacetophenone moieties present in the homopolymers, 1-(4-morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-methacryloyloxyphenyl)]amino-propane-1-one and 1-(4-morpholinophenyl)-2-benzyl-N-methyl-N-[3-methacryloyloxy propyl)]aminobutan-1-one and fully characterized.

Hu & Shi (2011) have synthesized acrylic resin containing organic-inorganic hybrid nanocomposites and initiated by trimethoxysilane-modified 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one as a hybrid photoinitiator. This hybrid photoinitiator has been obtained by the esterification of 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone with thioglycolic acid, then reacted with 3-(2,3-epoxypropoxy)propyltrimethoxy-silane. The chemical structure has been characterized by Fourier transform
infrared spectroscopy and proton nuclear magnetic spectroscopy. The trimethoxy silane-modified, 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one as a hybrid photoinitiator has been investigated by photo-differential scanning analysis. To compare the UV-cured pure polymer and cured films obtained from hybrid photoinitiator have shown that the high thermal stability and mechanical properties.

Wang et al (2014) have synthesized poly (glycidyl benzophenone ether) photoinitiator (PGBE) with a side-chain benzophenone (BP) group of poly(epichlorohydrin) and 4-hydroxybenzophenone. The structure of PGBE has characterized by IR and $^1$H-NMR. The light absorption of PGBE has detected by UV-spectrophotometer at the maximum absorption wavelength of 283 nm in acetonitrile solvent.

Type-II photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (co-initiator) generate free radicals. The visible light photoinitiators belong almost exclusively to the type-II class of photoinitiators. In recent years, there has extensive interest in aromatic ketone systems containing carbon-sulphur bonds (Fouassier et al 1995). Laser flash photolysis has used to study the triplet-state reactivity of $\alpha$-sulphonyloxy ketone photoinitiators (Fouassier and Burr 1990). They have found that an electron donating substituents at the $\alpha$-position in acetophenone derivatives decreases the triplet lifetime.

4-methylthio derivative of benzophenone has increased photocuring activity over that of benzophenone which is associated with its red-shifted absorption and lower triplet state activity towards the monomer (Rahlmann & Fouassier 1991).
Novel photoinitiators based on a phenazine scaffold have used as initiator for the ring opening polymerization of epoxy monomers and the free radical polymerization of (meth)acrylates. The initiation mechanisms have investigated by fluorescence, cyclic voltammetry, steady state photolysis and electron spin resonance experiments (Tehfe et al 2010).

Fouassier et al (1995) have studied the photolysis of aryl-alkyl sulphoxide by time-resolved spectroscopy. They have concluded that the singlet state cleaved at the sulphur-alkyl bond. The triplet state generated aryl and alkyl sulphinyl radical.

A new α-sulphonyl acetophenone has proved recently to be particularly suitable for the curing of thin layer coatings (Fouassier et al 1997). They have found that their \( \varepsilon_{\text{max}} \) is high, only small quantities of compounds have needed to initiate photochemical reactions. The physical and practical characterization of new photoinitiators, α-sulphonyl acetophenone have been investigated by Lemee et al (1999). They have concluded that the triplet state energy levels greatly depended on the substituent present in the compound.

A new photoinitiator, bis-2-sulphonyl ketone derivative (DKS) belongs to the 2-sulphonyl ketone derivative. The photochemical behaviour and the excited-state processes of the DKS have studied using time-resolved laser spectroscopy and steady-state photolysis technique (Fouassier et al 1997). The spectroscopy investigations have shown that the triplet state of DKS is quite a long species, which cleaves in the \( \beta \)-position as with other compounds used by the same family (Rahlmann & Fouassier 1993). To compare the thioxanthone, it is widely used in industry, it has the advantages of colourless when dissolved and can also be used in UV-curable coatings.
The perylene derivatives combined with an iodonium salt or an amine has been used as photoinitiating systems to initiate the cationic polymerization of epoxide. The free radical polymerization of acrylates/thiol-ene polymerization in trithiol-divinylether mixture in the presence of perylene derivative and iodonium salt is also used as photoinitiator under various irradiation sources. (Xiao et al 2014).

The photochemical reactivity and polymerization activity of a novel radical photoinitiator belongs to the class of bifunctional ketosulphone/benzophenone has shown an efficient in curing of pigmented coatings. They have been found that not to show any unpleasant smell in curing of coatings and exhibit an excellent safety in use in polymerization (Visconti et al 2000).

Allen et al (1998) has studied the photochemistry and photopolymerization activities of novel alkylthiobenzophenone photoinitiators. Significant transient absorption in the region at 300-400 nm shows side chain scission of the phenyl-sulphur bond to produce an alkylthio and aryl radical species, while the sulphoxide group is prone to scission at the alkyl-sulphur bond, generating a sulphoxide radical species. Both these species are likely contenders as initiators of free radical polymerization.

The photochemistry and photoinduced polymerization activities of several novel phenyl thiobenzophenone and diphenyl thiophene photoinitiators have been determined and compared to that of benzophenone using real-time infrared and pencil hardness methods (Allen et al 1998a). All the phenylthio derivatives exhibited higher activity than that of benzophenone. The dibenzo-thiophenes have exhibited lower activities than the phenylthio derivatives, but remained somewhat greater than that of the phenylthio derivatives associated
with their higher molar extinction coefficients and long wavelength absorption in the near ultraviolet region above 300 nm.

The search for the development of new photoinitiators have exhibited the specific properties, an enhanced and red-shifted absorption, water solubility, hydrophilicity, compatibility and the low odour remains the fascinating challenge. Many studies have been devoted to the investigation of the excited state processes occurring in a great number of compounds working in radical, cationic or anionic photopolymerization reactions under UV or visible light. All these works led to superior to understand the mechanisms involved. The structure-properties relationship shows a way to develop even more efficient photoinitiation systems (Fouassier 1995, Pappas 1992, Holman & Oldring 1990, Allen et al 1995, Fouassier & Rabek 1993, Scranton et al 1997). Structure-properties relationship of a novel bifunctional photoinitiator BP-SK based on ketophone-benzophenone has been studied by Allonas et al (2001). Preliminary toxicological studies support the safety of BP-SK. This photoinitiator is also very useful when added to a mixture based on isopropylthioxanthone and amine, for curing of thin coatings used as inks.

The photochemistry of new substituted benzyl benzoin benzyl ether photoinitiator has been investigated by Lemee et al (2000). Their polymerization activity has been evaluated by using steady-state photolysis and mass spectroscopy. The excited state processes have studied with time-resolved laser spectroscopy. The photochemistry is widely dependent on the substituent present at the β-methylene group. They have concluded that the benzoin ethers contain benzene, dichlorobenzene, and benzoyl chloride cleave is usually in the α-position to provide products, which then undergo a rearrangement. They are very efficient initiators but, as the parent compounds of this family, they have unfortunately poor molar extinction coefficients in the near UV-Visible range.
The other compounds contain a pyrene or naphthalene group which exhibit a higher absorption are very stable under irradiation.

Alkyl phenyl glyoxalate has found to an efficient photoinitiator for acrylate polymerization. Benzoyl and phenyl radicals derived from intermolecular hydrogen abstraction are the initiating species. A negative photo image system has developed based on this observation.

The photolysis of safranine-T in triethanolamine has been used as a source of free radicals in the polymerization of methacrylate in aqueous solution (Encinas et al 1996). Flash photolysis studies of safranine-T in basic aqueous solutions have indicated that the photoinitiation proceeded by the amine radicals in the interaction of the unprotonated form of the dye triplet with the hydroxylamine. Primary radical termination does not play a significant role.

As recently many articles have been published on the design of new, efficient photoinitiators of polymerization (Schnabel 1990). The development of systems based on three components have been accomplished for visible laser light induced radical polymerization reactions of eosin-amine-onium salts (Fouassier & Rabek 1990), keto coumarin-amine- onium salts or dye-amine-onium salts (Fouassier 1989). Fouassier et al (1993) have studied the excited state processes in a three component system based on a new ketone-amine-onium salt combination studied by time-resolved laser spectroscopy. They have concluded that the addition of an onium salt to the usual ketone-amine system mostly resulted in a decrease of the termination reaction of the growing macromolecular chains, allowing an increase in the rate of polymerization.

The excited state interactions occur when a photoinitiation system based on thioxanthone derived dye TXD-amine-additive has subjected to visible
light radiation. Eraddalance et al (1996) have studied the efficiency and excited state processes in a system based on TXD/amine/additive by time-resolved absorption spectroscopy, spectrofluorometry and photolysis. They have concluded that the reactivity of the triplet state of the dye is very low. The ketyl radicals that arise from the interaction of the singlet state of the dye have quenched by the additives, CBr$_4$ or the onium salts.

Fouassier et al (1997a) have studied the role of the dye/iron arene complex/amine system as a photoinitiator for free radical polymerization. Their activities have studied by fluorescence-quenching experiments, and time-resolved laser spectroscopy. They have found that the efficiency of this system in radical polymerization reactions is higher by a factor of three to four than that of the dye/amine system.

A new photoinitiating system based on isopropylthioxanthone (ITX), amine (AH), and bifunctional benzophenone-ketosulphone (BP-SK) photoinitiator is capable of initiates the radical polymerization reactions. Radical polymerization activity and mechanistic approach in this new photoinitiator system have been investigated by Fouassier et al (2000). Additions of ITX to BP-SK-AH have shown to enhance the efficiency of the photoinitiation of clear or pigmented coatings.

A new system consists of xanthenes dye, ferrocenium salt, hydro peroxide, and an amine is capable photoinitiate the radical polymerization of thick films. Simonin & Fouassier (2001) have studied the radical polymerization activity and the mechanistic approach of this system. They have concluded that that dye-amine interaction and dye-ferrocenium salt interaction could occur with charge transfer, the latter one presumably the most efficient.
Several coumarin or keto coumarin-additives combined (bisimidazole derivative, mercapto benzoxazole, titanocene oximeester) has been used to initiate radical polymerization reactions (Allonas et al 2001). They found that the coumarin produce a free radical by an electron transfer reaction between an additives and coumarin leads to an energy transfer with the bisimidazole. The hydrogenabstractions from the benzoxazole derivative produce free radical.

The design of an efficient photosensitizer/photoinitiator combination is best to understand the excited state process involved. Excited state properties of a new photoinitiation system based on the thiopyrylium salt as the photosensitizer and of a tetra per ester of benzopenone as initiator used in laser imaging system applications have been investigated by Savary et al (1994). They have found that the triplet state lifetimes have found that 1 ns in acrylonitrile.

Ajayghosh et al (1993) have synthesized new sulfur-contains photoinitiator, S-benzoyl-O-ethylxanthate and examined the photoinitiated property by conventional polymerization methods and nanosecond laser flash photolysis studies. This study has revealed that the primary photoprocess involves the cleavage of a carbon-sulphur bond adjacent to the carbonyl group to generate benzoyl radical, which initiated the polymerization reaction.

The photoinitiation of methyl methacrylate has been initiated by substituting thioxanthone in the presence of an amine (Corrales et al 2000). They have found that the polymerization rate depended on amine concentration, photoinitiator efficiency and ketone structure.

Thioxanthone and keto-coumarin have been shown an efficient photoinitiator invisible laser light induced polymerization reactions.
The excited state reactivity of this photoinitiators has been studied by Fouassier & Wu (1992). They have found that those compounds undergo the fast electron transfer reaction in the presence of amines and onium salts.

The excited state characteristics of novel 1-chloro-4-oxy/acyloxy-derivatives of thioxanthone have been determined by micro, nano, and picoseconds flash photolysis (Allen et al 1999). All the initiators have exhibited high polymerization activity except the 4-hydroxy model a 2-methyl-4n-propoxy derivatives. The triplet energies have found fairly intensive to solvent polarity with an observed spectral broad from non-polar to polar solvents.

Angiolini et al (1997) have studied copolymer systems bearing side-chain thioxanthone and α-aminoacetophenone moieties as a photoinitiator for ultraviolet pigmented coatings and these have structurally characterized.

Photosensitizer/photoinitiator interactions in copolymeric systems bearing side-chain thioxanthone and α-morpholino acetophenone moieties have been studied by Angiolini et al (1995). Photophysical and photoinitiation polymerization data have suggested that the sensitized process occurs through an energy transfer than an electron transfer mechanism favours the two photosensitive moieties which attached to the same macromolecule.

The spectroscopic properties, absorption, fluorescence and phosphorescence of 2-acryloxythioxanthone (ACOTXA) have been examined in various solvents. Photoreduction study has carried out in benzene and acetonitrile solution using 2-diethyl amino ethanol as hydrogen donor (Catalina et al 1992). A lower photo-reduction, quantum yield has found to thioxanthone (TXA) in benzene compared to that of the model compound ACOTXA. A notable decrease in the photoreduction quantum yield of ACOTX has found to increase the concentration of methyl acrylate, confirming the
intermolecular interaction between the triplet state of the thioxanthone carbonyl and the acrylic double bond

One major deficiency with thioxanthone initiators is the requirements of a tertiary amine co-synergist, when aside from the additional cost can cause unacceptable smelly and formation yellow product problems. Many new derivatives of thioxanthone have developed in recent years not to circumvent such problems but also to provide an enhanced speed of cure and synergism with other photoinitiators. The 1-chloro-4-propoxy derivative of thioxanthone exhibits photoinitiation lacking of tertiary amine co-synergist (Dietliker 1993). Allen et al (1997) have studied the effect of 4-oxy substituted groups of the photochemical and photoinitiator properties of 1-chloro-thioxanthone. They have found that 4-oxy derivatives exhibit much higher photoinitiation activity than other initiators.

More recently the potential of photochemical crosslinking of thermoplastics have attracted interest for improving certain desirable properties, mechanical performance and flame retardant. Allen et al (1993) have developed effective photoinitiator for the crosslinking of fiber forming nylon 6,6 polymers based on the 2-substituted amino anthraquinone where the addition of an acrylate monomer or prepolymer is unnecessary. The photophysical and photoinduced polymerization activities of 2-acrylamido-2-(2-ethylhexyl) amino and 2-acryloxyanthraquinone have studied by Allen et al (1995). They have concluded that the initiated properties of 2-substituted anthraquinone molecules show a high degree of activity for the amide group in 2-acrylamido-anthraquinone exhibit the highest activity result from a long-lived active and low-lying excited triplet state.

Allen et al (1995a) have studied photochemistry and photoinitiator properties of 2-substituted anthraquinone by RTIR spectroscopy and
photocalorimetry. The relative order of photoinitiator efficiency has found to highly dependent upon the method used, the light source, amine co-synergist and the monomer used.

Pullen et al (1996) have studied the photophysical, photochemical and photopolymerization properties of 2-substituted anthraquinone. They have found that the polymer activity is dependent on the triplet excited state configuration of the molecule.

The performance of the photoinitiated system has related to high absorptivity of the photoinitiators in the spectral region. It corresponds to the irradiating lamp emission, high-efficiency, high quantum yield and high reactivity, good solubility, low odor and toxicity. A possible way to do most of the above mentioned requirements represented by the uses of polymeric photoinitiators having the photosensitive moieties present in the side chain, as they give several advantages connected to their macromolecular structure (Carlini & Angiolini 1993).

Novel polymeric photoinitiators bearing side chain photosensitive camphorquinone moiety are suitable to the radical polymerization and crosslinking of multifunctional (meth) acrylic monomers under irradiation with visible light. Angiolini et al (2000) have synthesized novel polymethacrylic photoinitiator from the corresponding methacrylic monomer and copolymerized with a methacrylic comonomer bearing a pendant tertiary amine group has acted as co-initiator.

α-diketones have been used as a visible photoinitiator for the photocrosslinking of waterborne latex paints. The efficiency of several α-diketones as visible light photoinitiators for crosslinking of water-borne latex dispersions in the presence of acrylic monomers have been evaluated by
Among the eight α-diketones studied, camphorquinone allows the fastest curing speed and curing of acrylic waterborne coatings are not affected by the presence of oxygen. The properties of the sunlight cured volatile organic compound (VOC) free pigmented paints prepared from the waterborne latex have better than the equivalent conventional paint contains VOCs.

The use of UV-radiation-induced chain polymerization of acrylic monomers have been studied by Pappas (1978). The efficiency of the reaction is depending on the photochemical reactivity of the initiators. The potential use in photopolymerization conducted in aqueous media, water-soluble photoinitiators have developed by introducing ionic groups into oil-soluble structures, which known to exhibit high activity in non-polar solvents.

In the last few years, considerable interests have stimulated by the developments of water-soluble photoinitiators, capable of starting radical polymerization of unsaturated monomers under UV-light exposure. The activities of water-soluble photoinitiators derived from thioxanthone, benzophenone, and benzil have been studied by Lognot & Fouassier (1988). They have concluded that the photophysics and photochemistry of the upper excited states of the benzophenone-derived ketyl radical have been shown that the reactivity of the radical is highly reactive.

The photochemistry of five novel water-soluble $p$-substituted benzophenone derivatives has examined in water and 2-propanol by absorption, luminescence, and conventional flash photolysis techniques (Allen et al 1988). The photopolymerization has found to occur effectively only without oxygen and the presence of a secondary or tertiary amine. On flash photolysis, the lowest excited triplet state of the initiator has abstracted an electron from the amine via an excited triplet exciplex followed by hydrogen abstraction to give the ketyl radical.
Fouassier et al (1991) have studied the excited state processes ($\alpha$-cleavage, electron transfer, monomer quenching) of water soluble photoinitiators by time-resolved laser spectroscopy. They have concluded that the substitution at the $p$-position of the phenyl ring changes the reactivity, when combine these photoinitiators with thioxanthone derivatives.

Catalina et al (1998) have studied the synthesis, photochemical and photoinitiation activity of water-soluble copolymers with pendant benzil chromophores. The copolymers have exhibited higher polymerization rates and quantum yields similar to low molecular weight model compounds.

Novel water soluble anthraquinone copolymers have synthesized by copolymerize with 2-acryloxy and 2-acrylamido anthraquinone monomers at 1-2% w/w concentration with three water-soluble co-monomers, acrylamide, 2-acrylamido-2-methylpropane sulphonic acid and 2-acryloxyethyltrimethyl-ammonium iodide. The proton and the iodide have replaced on corresponds obtained copolymers by sodium and chloride ions using ion exchange resins (Catalina et al 2001).

Xiao et al (2014) have studied the perylene derivatives (PTCTE) combined with an iodonium salt in the presence an amine use as photoinitiator for the epoxide. It initiates the cationic polymerization of epoxide. The free radical polymerization (FRP) of acrylates or the thiol-ene polymerization of a trithiol/divinyl ether mixture has exposed to halogen lamp/laser diodes at 473 nm to 457 nm (blue light). Upon a blue light exposure, the PTCTE based systems have found very efficient in the cationic polymerization of FRP is superior to the camphorquinone based reference systems. They have studied the photochemical mechanisms by steady state photolysis, fluorescence, cyclic voltammetry, laser flash photolysis, electron spin resonance and spin trap techniques.
1.3.1 Ionic Photoinitiators

Ionic initiators can generate via the photon from reactions involving electron or charge transfer. These are electron donor/acceptor complex formed in solution by dissociation of the ground state complex into radical cations by the absorption of light (Tazuke & Okamura 1968). The excited states produced from ground state interactions leads to the forms of the ionic species.

1.3.2 Anionic Polymerization

Tertiary amines have been used in anionic polymerization (Paul 1996). Metal alkoxides found limited applications because of their slow curing rate.

1.3.3 Photoinitiated Cationic Polymerization

The compound must possess chromophores, which permit the absorption of UV or visible light and, as a result, undergoes some photochemical transformation, which generates a species capable of initiating cationic polymerization. Before photolysis, the ideal photoinitiator should be indefinitely stable when irradiated, it should generate the initiated species with quantum efficiency and without the simultaneous liberation of by-products, which inhibit or retard polymerization. A number of examples of the sulphonium salt photoinitiated polymerization of epoxide, vinyl ethers, olefins and cyclic acetals are given together with a discussion of the dependence of their polymerization rates on the structure of the photoinitiator (Crivello & Allen 1981).

Photoinitiated cationic polymerizations have the important commercial advantage that they are not inhibited by oxygen and thus may carry out in the air without the need for blanketing with an inert atmosphere to achieve
rapid and complete polymerization (Crivello 1978a). Cationic polymerization is widely applicable for both vinyl and ring-opening polymerization.

Dialkyl phenacyl sulphonium salts have been used as photoinitiators for the cationic polymerization. Various dialkyl pencil sulphonium salts with various unions have been prepared from phenacyl bromide, appropriate dialkyl-sulfide, and appropriate sodium anions (Crivello & Lam 1979a).

Diaryliodonium and triaryl sulphonium salts have been used for photoinitiated crosslinking reactions. Onium salt photoinitiated cationic polymerizations have found use in the multitude practical applications, coatings, stereolithography, micro electronics, holographic recording, composites and photoresists (Crivello 1999).

The Synthesis, reactivity and properties of new diaryliodonium tetrakis (pentafluorophenyl) borate salts have been studied by Castellanos et al (1996). They have concluded that the diaryliodonium tetrakis-(pentafluorophenyl)borate salts are more reactive than other known diaryliodonium salt in this family.

Triaryl sulphonium salts with complex metal halide anions have been used as a highly efficient photoinitiators for the cationic polymerization of an epoxide. Triarylsulphonium salts with complex metal halide anions have been synthesized from the corresponding sulphonium salts. Mechanistic studies have been shown that when these compounds have irradiated at wavelengths of 190-365 nm carbon-sulphur bond cleavage occurs to form radical fragments. At the same time strong Bronsted acid is the active initiator of cationic polymerization (Crivello & Lam 1979).

Cationic radicals of phenothiazine salts used as cationic initiators for the polymerization of N-vinyl carbazole, cyclohexene oxide, and
tetrahydrofuran. Cationic radicals of phenothiazine, N-ethylphenothiazines having the counter ion antimony hexafluoride anion have been synthesized by the oxidation of substituted phenothiazine using tri(p-bromophenylamine)-hexafluoroantimonate (Abu-abdoun & Landwith 1997). They have found that the rate of polymerization depends on the salt structure and light wavelength.

A new system contains camphorquinone, benzil, 2-isopropylthioxanthone and 2-ethylanthraquinone have irradiated in the presence of a monomer can serve as a hydrogen donor. The resulting monomer-bound radical rapidly reduces a diaryliodonium salt or a dialkyl phenacyl sulphonium salt. These monomers-centred cations have been initiated the polymerizations of epoxides, vinyl ethers, and heterocyclic compounds (Crivello & Sangermano 2001). An onium salts with a high reduction potential, do not undergo sensitization by this new system.

2-chlorothioxanthone-onium salts are efficient photoinitiator for the cationic polymerization. The interaction of iodonium, selenium, sulphonium, phosphonium, arsonium, and heterocyclic nitrogen salts with the triplet state of 2-chlorothioxanthone have been studied by Manivanan et al (1992). They have calculated the bimolecular quenching rate and a charge transfer quantum yield.

A series of cationic polymerizable mono and difunctional alkoxyallene monomers have been prepared by the base catalyzed isomerization of the corresponding propargyl ethers (Crivello et al 1995). These monomers have exhibited highest reactivity in photocationic polymerization.

A series of difunctional 1-propenyl ether monomers bearing ether, ester, carbonate and urethane groups have been prepared from trimethylolpropane diallyl ether (Crivello & Lohden 1996). The reactivity
depends on the basicity of the functional group, which have presented in the molecule.

A novel series of mono, di, and multifunctional propenyl ether monomers have been prepared in good for excellent yields by the catalytic isomerization of correspond to allyl ethers (Crivello & Bi 1993). Propenyl ether monomers have found that very less reactive as compared to vinyl ethers in photoinitiated cationic polymerization and more reactive than epoxide monomers with related structures (Crivello & Jo 1993).

The effect of photoinitiator structure and variations in the experimental parameters on the rate and extent of photoinitiated cationic polymerization of propenyl ether monomers have been studied by Crivello & Jo (1993). They have demonstrated that the photoinitiated cationic polymerization of propenyl ether monomers in the presence of iodonium and certain sulphonium salt photoinitiator is accompanied by a process of involving the free radical-assisted decomposition of the photoinitiator. The chain carriers are ether radicals, which function as a reducing agent for the photoinitiator. This addition favoured decomposition mechanism contributes to an increased efficiency of acid generation and results in increase efficiency in the photopolymerization of these monomers.

Cationic photopolymerizable multifunctional 1-butenyl ether monomers have been prepared in good yields by ruthenium catalyzed isomerization of the corresponding crotyl(2-butenyl)ethers (Crivello & Yang 1995). Cationic polymerization rate studies have found that this monomer exhibits comparable reactivity to vinyl and 1-propenyl ether analogues.

Aryl-1-propenyl ethers are used for the photoinduced cationic polymerization studies. A series of aryl-1-propenyl ethers have been prepared by
the isomerization of the corresponding allyl aryl ethers (Crivello & Kong 1999). These compounds have found to much lower reactivity in cationic/vinyl photopolymerization as compared to their alkyl analogues are due to Friedel-crafts alkylation, side reactions take place.

Crivello et al (1999) have synthesized new cationic photopolymerizable alkyl and aryl-1-propenyl ether monomers from good to excellent yields by the isomerization of alkyl and aryl allyl ethers in a basic ethanolic solution containing pentacarbonyl iron used as a catalyst.

The use of poly (3,4-epoxy-1-butene) (Poly-EPB) in photoinduced free radical polymerizations have found in several beneficial effects. In combination with aromatic ketones, poly-EPB functions as a hydrogen donor to form a highly effective photoinitiator for the polymerization of acrylate monomer. At the same time, poly-EPB can undergo fast auto-oxidation, serves to mitigate inhibition effects due to oxygen during free radical photopolymerizations (Sangermano et al 2002). Poly-EPB has found that an effective chain transfer agent increases both the rate of polymerization and conversion (%) in photoinduced crosslinking polymerization of the multifunctional prepolymer. Poly-EPB functions as a matrix-modifying agent, which incorporated into the resin matrix during photopolymerization due to photoinduced grafting reactions (Sangermano et al 2002a).

Crivello & Ortiz (2001) have synthesized a series of novel cationic photocrosslinkable epoxidized prepolymer contain benzyl, allyl and propargyl acetal and ether groups. These prepolymer have found to enhanced reactivity in cationic photopolymerization in the presence of an onium salt used as a photoinitiator.
Epoxy alcohol monomers have been found that reactive monomers in photocationic polymerization (Crivello & Liu 2000). The rate of photopolymerization ( Rp) has enhanced by the presence of the hydroxyl group. They have observed that the rate of polymerization accelerates, when the novel monomers contains mono and multifunctional epoxide.

The multifunctional oligomer containing cationic photopolymerizable enolether groups at the terminal positions along with backbone has been synthesized by the etherification of 2-butene-1,4-diol with α,ω-dibromo alkenes or an alkyl ether linking group followed by reaction with allyl bromide. The base catalyzed isomerization of allylic double bonds has carried out afford the desired enol ether oligomers (Crivello & Sangermano 2001a). The rate of polymerization has found that depending on the character of linking group.

The reactivity of the cyclo aliphatic epoxide, 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexane carboxylate in cationic polymerization has been studied by Crivello & Varlemann (1995). They found that the presence of the ester group retarded the rate of polymerization of this bis epoxide.

A large variety of cationic initiators have been using the polymerization of 1, 3-dioxepane under various conditions. Vuluga et al (1999) have studied the photoinitiated cationic polymerization of 1,3-dioxepane by a mixture of triaryl sulphonium salt, 4,4′-bis-(diphenylsulphonio)diphenyl sulphide hexafluoroantimonate and 4-diphenylsulphoniodiphenylsulphide hexafluoroantimonate in the temperature range of 30-60 °C. They have found that the enthalpy of polymerization and final monomer conversion dependant on the temperature used.

The two monomers, nopol ether epoxide and nopol-1-propenyl ether epoxide have been prepared from nopol[(R)-(−)-2-(2′-hydroxyethyl-6,6-
dimethyloxaytricyclo[3.1.1.1]octane] (Crivello & Liu 1999). The rates of ring-opening polymerization of both monomers have enhanced to compare the analogue model compounds.

3,4-epoxy-1-butene has been used as a reactive monomer in the photopolymerization of multifunctional epoxide. Sangermano et al (2001) have observed that the rate of polymerization accelerates, when less reactive epoxy monomers used as diluent. To compare the epoxide monomers, 3,4-epoxy-1-butene is very reactive and those ascribed to stabilization of the growing cationic chain end by the double bond during the ring-opening polymerization.

A series of α-hydrogen-ω-epoxy silane and siloxane compounds have been prepared in good yields by using rhodium and platinum catalyzed region selective hydrosilation. These intermediates have been further condensed with vinyltrimethoxysilane in subsequent hydrosilation reactions to prepare an interesting new class of ambifunctional monomers containing both epoxy and trimethoxy silane groups (Crivello & Bi 1993).

The photopolymerization of methyl methacrylate (MMA) has been performed using different photoinitiating systems based on isopropyl thioxanthone ethyl-4-(dimethylamino) benzoate leads to full conversion. The mechanistic investigation of the photoinitiating process and identification of the reactive species have shown that the molecular weight of the photopolymerized PMMA can modulate. The addition of a triazine derivative leads to the disappearance of the isopropyl thioxanthone ketyl radicals, which act as terminating agents. The molecular weight of the final polymer increases. This new opportunity has been used to perform an efficient photopolymerization of thermoplastics like MMA (Charlot et al 2014).
1.4 LIGHT SOURCES

The commonly used light sources must fulfill the following requirements: high intensity in the desired spectral region, long life, stability of output, ease of operation, proper physical dimensions of the process under consideration and the minimum amount of auxiliary equipments. Mercury arc lamps meet the best of all, these requirements. Among low pressure, medium pressure and high pressure lamps, the characteristic features of which have been reviewed earlier by Paul (1985), medium pressure lamps were chiefly used. The latest developments in the lamps concern power rating. Earlier lamps had power of 100W/cm$^2$, whereas nowadays lamps with power between 100 and 160 W/cm$^2$ can be selected. With properly designed UV-curable systems, high powered lamps are useful to obtain through curing of pigmented and thick coatings (Paul 1996).

The photons emitted by mercury vapour lamp correspond to transitions between the excited levels (produced by an electrical discharge in the Hg vapour) and the ground state of mercury. Particular lines are delivered by such a lamp; their intensities are dependent on the Hg pressure. Low pressure mercury lamps give photons centered on 254 nm. Typical commercial medium-pressure Hg lamps have an electrical power of 80-120 W/cm$^2$.

The photopolymerization is a process in which a formulated reactive liquid (monomer and prepolymer) which is transformed into a 100% solid (polymer network) upon exposure to light. The solid is referred to as the cured material and the light source can be a conventional polychromatic lamp or a laser.
Benefits of light-curable coatings: The benefits and advantages of UV-curing technologies are rapid cure, non-polluting and solvent-free systems, application versatility, enhanced product durability, low-energy requirements, low-temperature operation, small space requirements (Fouassier 1995).

1.5 PREPOLYMERS/Oligomers

An oligomer or a functional polymer in UV-cured coatings have termed to have a molecular weight of greater than 250 g/mol, which contains at least two reactive groups such as vinyl, acrylate, methacrylate and epoxy. The physical and chemical properties of the cured coatings will strictly depend on the nature and structure of the oligomer (Fouassier 1995).

The major types of vinyl-based oligomer have been used in the coatings and inks industries have divided into the following groups (Paul 1996). i) Unsaturated polyesters ii) acrylate oligomers iv) an epoxide v) Other oligomers.

1.5.1 Unsaturated Polyesters

Unsaturated polyesters are typically manufactured from the unsaturated acids (maleic or fumaric) or reaction of saturated acid (phthalic acid) and dihydric alcohols. The limited solubility in various solvents, UV-curable systems based on unsaturated polyester have sensitive from a formulation point of view.

1.5.2 Acrylic Oligomers

Acrylic oligomers are mainly obtained by attaching an acrylic group either as a terminal or pendant group to the chemical types including
epoxides, urethanes, polyesters and, silicones. The basic differences among the various acrylic oligomer types can summarize as in Table 1.1 (Blair 1995).

Polydimethylsiloxane epoxy acrylate as a special family of inorganic backbone polymers. UV-curable polydimethylsiloxane epoxy acrylate has been synthesized by hydro silation of allyl glycidyl ether with the hydrogen-containing poly dimethyl siloxane to give polydimethylsiloxane-type epoxy resin, which modified with acrylic acid (Wang 2003, Gea et al 2014). Siloxane-based networks have been used in metal coating and protection of glass or optical fibers. The important properties of polydimethylsiloxane have found that lower glass transition, low solubility, low dielectric constant, transparent to visible and UV-light, very resistant to ozone, and stable against atmospheric oxygen even oxygen plasma.

Abdulah et al (2002) have synthesized the photocrosslinkable polysiloxane containing alkyl fluorinates groups either by modification of commercially available polysiloxanes bearing vinyl groups reacted with 2-mercaptopoethanol followed by addition of \( p \)-(chloro ethyl) styrene or by polycondensation of \( \omega,\omega \)-dihydroxy polydimethyl siloxanes and dichloro silanes and contain acetoxy group and dichlorosilanes bearing fluorinated groups. The introduction of styrene groups has achieved by reaction with \( p \)-(chloromethyl) styrene. They have crosslinked by UV-curing in the presence of a cationic photoinitiator. They have found that the copolymers contain a fluorinated group enhances the thermal properties.
Table 1.1  General differences between the performances of conventional acrylic prepolymers

<table>
<thead>
<tr>
<th></th>
<th>Properties</th>
<th>Epoxy Acrylate</th>
<th>Urethane Acrylate</th>
<th>Polyester Acrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Viscosity</td>
<td>High</td>
<td>Variable</td>
<td>Easy</td>
</tr>
<tr>
<td>2.</td>
<td>Dilution with monomers</td>
<td>Easy</td>
<td>Easy</td>
<td>Easy</td>
</tr>
<tr>
<td>3.</td>
<td>Viscosity cutback</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>4.</td>
<td>Cure speed</td>
<td>Very fast</td>
<td>Variable</td>
<td>Variable</td>
</tr>
<tr>
<td>5.</td>
<td>Flexibility</td>
<td>Poor</td>
<td>Good</td>
<td>Variable</td>
</tr>
<tr>
<td>6.</td>
<td>Chemical resistance</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>
New photocrosslinkable polysiloxane containing gem-dioxaalkylene-styrenyl groups and gem diurethane-\(\alpha\)-methylstyrenyl groups have been synthesized by copolycondensation of \(\alpha,\omega\)-dihydroxypolydimethylsiloxanes and dichlorosiloxanes bearing either cyclic acetal groups or Si-H groups and dichlorosilanes bearing alkyl groups. The introduction of styrenyl groups have achieved by hydrolysis of the acetal groups into the corresponding alcohol followed by reaction with chloromethyl styrene with benzyl isocyanates (Abdulah et al 2003). They have found that the \(\alpha\)-methyl styrene compounds are more reactive in cationic polymerization than styrene compounds. These compounds have used in the insulator.

1.5.3 **Epoxy Acrylates**

An epoxy acrylates have obtained by reacting 1 mol of diglycidyl ether of bisphenol-a with 2 mol of acrylic acid. An epoxy acrylate is well known and established raw material. Undiluted form of an epoxy acrylate is highly viscous. It is soluble in most diluents and the rate of viscosity decreases rapidly. The high reactivity, compared to urethane and polyester acrylates, coatings used for wood or paper substrates is formulated from epoxy acrylates.

A series of UV-curable acrylated hyperbranched polyisophthalesters prepolymer with various numbers of acrylate end groups possess high refractive index have been synthesized by modifying the hyperbranched polyisophthalesters with hydroxy ethyl acrylate and \(\beta\)-naphthol. They have reported that the refractive index increases with increase in naphthyl group concentration.

The photosensitive oligomer containing a chalcone moiety in the main chain has been synthesized by the reaction of a diepoxide compound with methacrylic acid (Choi & Oh 2002). The chalcone-epoxy oligomer compound
has been synthesized by the reaction of 4,4’-dihydroxy chalcone with epichlorohydrin. They have observed that the photodimerization behaviour under UV-irradiation, a trace amount of dimethoxy acetophenone present in the photocured compound.

A new photochemical bifunctional chalcone-epoxy compound has been synthesized by the reaction of 4,4'-dihydroxychalcone and epichlorohydrin (Choi et al 2001). They have found that the chalcone-epoxy compound undergo photodimerization by UV-irradiation. New chalcone-epoxy compound has found a special application in adhesives for microelectronics and display panel assembly of the liquid crystal device.

The epoxy acrylates prepolymer suitable for use in UV and thermal curing systems, command the largest use in the market place and have been used in applications ranging paper and card overprint varnishes, wood coatings, screen lithographic inks and solder resist inks for printed circuit board (Holman & Oldring 1988, Hourston & Zia 1984, Cassidy et al 1984). The other areas, vacuum metalizing base coatings, printing inks, adhesives, microelectronics, laminates, optical, release coatings, and videodisc, coatings are also very important. Epoxy acrylates have been found that an excellent characteristic of moisture, solvent, and chemical resistance, low shrinkage on cure, superior electrical, and chemical properties and good adhesion to many substrates (Wang & Shieh 2000). The epoxy acrylates have been noted that for adhesive properties, flexibility, non-yellowing, hardness and chemical resistance (Roffey 1982). The epoxy backbone promotes toughness and flexibility to cured films while the carbon-carbon and other bonds of the same improve the chemical resistance. The reaction with an acid produces hydroxyl groups introducing polarity, which can improve adhesive and pigment wetting characteristics.
The effect of the storage time on the thermal properties of tri(ethylene glycol) dimethacrylate, 2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)-phenyl]propane, and bisphenyl-α-glycidyl ether dimethacrylate copolymers has been used to formulate dental composite resins and then photopolymerization by UV-light (Rigoli et al 2009). DMA studies have shown that, a plot of the log of tangent versus the temperature initially has shown the presence of two well-defined peaks. The presences of both peaks have confirmed the presence of residual monomers is not converted during the photopolymerization process.

A novel hyperbranched polyphosphonate acrylate (HBPPA) has been used as a flame retardant in UV-curable systems. Wang et al (2009) have synthesized the HBPPA by the reaction of di (acryloxyethyl) benzene phosphonate (DABP) with N-(2-aminoethyl)-piperazine. The UV-cured films have expanded when burning and the degree of expansion is increased which depends on concentration BBPPA. The crosslink density and the Tg of the cured films decrease depends on the content of HBPPA.

Wang et al (2012) have synthesized 1-adamantyl acrylate by the reaction 1-adamantanol with acryloyl chloride in the presence of the tertiary amine and characterized by FTIR and $^1\text{H}$-NMR spectroscopy. They have found that the introduction of 1-adamantyl acrylate group reduces the photopolymerization shrinkage. Thermogravimetric analysis (TGA) of 1-adamantyl acrylate has shown that thermally stable than the general commercial product. This indicated that the synthesized monomers are used in the coating industry.

Bretterbauer et al (2013) have synthesized UV-curable $N^1,N^2,N^3$-trimethyl melamine based (meth) acrylates, characterized and used as components of UV-curable lacquers. The UV-cured monomeric trimethyl
melamine tri acrylate coatings have shown an excellent physicochemical property concerns hardness, abrasion resistance, scratch resistance, chemical resistance, and high heat-resistance.

Canak et al (2014) boron acrylate monomer has been synthesized by esterification reaction. UV-curable boron contains epoxy acrylate coatings have prepared and applied to plexiglass substrates to obtain thermally and mechanically stable coatings. They have observed that the tensile properties and thermal stabilities of boron modified epoxy coatings primarily depend on the boron content.

A series of UV-curable hydrophilic acrylate polymers contain sulphonic acid group has been prepared by free radical copolymerization using 2-acrylamido-2-methyl propane sulphonic acid (AMPS) as a hydrophilic monomer have used as prepolymers for anti-fog coatings. The structures have confirmed by FTIR, $^1$H-NMR, and GPC. They have found that the AMPS content in prepolymer has affected the anti-fog properties of UV-cured coating. The UV-cured acrylate polymer coatings have shown to good mechanical properties, great optical transparency, and excellent anti-fog performance (Yuan et al 2014).

1.5.4 Urethane Acrylates

A urethane acrylate has been synthesized by end-capping polyester or polyether polyols with proper diisocyanate followed by reaction with a hydroxyl alkyl acrylate and the structure, performance relationship of urethane acrylate has been reviewed by McConnell & Willard (1990). The urethane acrylate has used in many industrial applications because they have imparted toughness, abrasion resistance, and elastomeric properties. These oligomers cover a wide range of industrial applications, including binders, vehicles for inks, and
coatings for vinyl floor tiles, optical fibers, and papers. Noren & Murphy (1990), Noren et al (1990) have shown that the molecular weight of the diol influences the mechanical properties of the UV-cured films.

Urethane acrylates have developed to give flexible coatings which have normally high viscosity. The diluents have been added to reach the application viscosity would strongly influence the final properties. The coatings become less flexible, which make it seems unacceptable for coatings on flexible substrates.

Kim et al (1996) have synthesized UV-curable polyurethane acrylates from polypropylene glycol, isophorone diisocyanate and three types of reactive diluents, i.e 2-hydroxyethyl acrylates, tri (propylene glycol) diacrylates and tri (methylolpropane) triacrylate. They have studied the soft segment length, type and concentration of a reactive diluent on the mechanical and dynamic properties.

A new ultraviolet curable waterborne polyurethane acrylate ionomer has been prepared from toluene diisocyanate, polyurethane glycol, dimethylolpropionic acid, and triethylamine and 2-hydroxyethyl methacrylate. They have modified by mixing the prepolymer and water has served as a chain extender and dispersion (Wang et al 1999). Polyurethane cured films have exhibited an excellent adhesion, gloss, hardness, flexibility and, impact strength, pendulum hardness depending upon hard segment content.

Ultraviolet curable polyurethane acrylate ionomers prepolymerms have been synthesized from isophorone diisocyanate, poly (methylene ether) glycol, 2,2-bis(hydroxymethyl) propionic acid (PMPA), triethylamine, 2-hydroxy ethylacrylate, and dibutyltindilaurate used as a catalyst (Kim & Kim 1998). The UV-curable polyurethane acrylate ionomers aqueous dispersion has been
formulated from the prepolymer, water (30%) and 1-hydroxycyclohexylphenylketone as photoinitiator. The storage modulus and glass transition temperature has increased with increasing PMPA increase.

Water-soluble urethane acrylate cationomers have been synthesized by incorporating N-methyldiethanol amine in the molecular backbone of the urethane acrylate (Ryu et al 1999). The UV-cured films of the urethane acrylate cationomers have shown that the coating properties have been improved than conventional urethane acrylate derivative is the formulation of the ionic hard domains in the urethane acrylate networks.

1.5.5 Polyester Acrylates

Polyester acrylates have been obtained by acrylation of hydroxy functional polyesters. The esterification reaction at high temperatures, however, causes problems, and therefore, a low-temperature reaction is preferred in order to avoid polymerization of acrylic monomer. Polyether acrylates have low molecular weights with low viscosities and are used as reactive diluents.

Synthesis, properties and photopolymerization of dendritic methacrylate polyesters have been studied by Shi & Ranby (1996). The synthesis of a series of polydisperse dendritic polyesters based on a pentaerythritol and ortho, meta, para benzenetricarboxylic anhydride, modified by glycidylmethacrylate and methacrylic anhydride. These starburst dendritic polyesters differ from classical polymers by their structural symmetry, a high degree of branching, and high density of terminal functionality. They have concluded that the thermal, mechanical properties and glass transition temperature of the UV-cured films increases with the degree of terminal functionality.

The UV-curable waterborne unsaturated polyesters for wood coatings have been prepared from three different polyols, ethylene glycol, di(ethylene-
glycol) and propylene glycol and three different anhydride, mono hydrophthalic-
anhydride, trihydrophthalic anhydride (TMAn), and tetra hydrophthalic-
anhydride (THPAn) (Jung et al 1998) and their properties have been studied. The unsaturated polyester have been prepared by the reaction of an equal molar mixture of TMAn and THPAn exhibits good tensile properties, weatherability, and proper viscosity when using distilled water as a diluent.

1.5.6 Epoxy Resins

Epoxy resins have been used together with cationic photoinitiators. The most suitable epoxy resins for cationic photopolymerization are bisphenol glycidyl ether, cyclo aliphatic epoxide based on cyclohexene oxide derivative and hexahydrophthalic diglycidyl ether or multifunctional novolacs.

Novel multifunctional photopolymers with both pendant epoxy groups and phenacyl ester groups have been synthesized by the reaction of poly-(methacrylic acid) with epibromohydrin and then followed by a reaction with phenacylbromide with 1,8-diazabiscyclo[5.4.0]undecane-7 as condensation reagent (Inomata et al 2001). They have concluded that the photochemical reactivity of the resulting polymers was affected by the structure of the phenacyl ester group.

1.5.7 Other Oligomers

Several other types of prepolymer/oligomer have been used in UV-curable coating in the literature. These systems are especially interesting due to their performance advantages. Wu et al (1990) has reported that the synthesis and photocuring of oligomers based on propargyl ethers of bisphenol group.

These oligomers have been found to photocured quickly in the presence of benzophenone and the coating based on such oligomers have shown
excellent adhesion to metals, hardness, flexibility, impact strength, solvent resistance, low water absorption, and corrosion resistance.

1.6 DILUENTS

Diluents have been used in UV-curing formulations to control the rheology or the flow properties of the systems and to control the degree of crosslinking in cured films. The main criteria for the selection of a diluent are viscosity reduction power, cured speed, mechanical properties, glass transition temperature (\(T_g\)), volatility, toxicity, odour and cost (Paul 1996).

UV-curable formulation is depending on the molar concentration of the monomer/diluent and oligomer/prepolymer. The concentration of diluent, functionality of the diluent and the structure of the diluent has influenced final properties of the UV-cured film such as film hardness, chemical resistance and flexibility. Diluent/monomer has performed the following functions in a system as a solvent for the prepolymer, as a theological such as viscosity, tack control agent, and a crosslinking agent. They have determined that the photoresponse speed in conjunction with the photoinitiator/sensitizer and determine the nature of a surface of a coating. The diluents have been classified into two types (Roffey 1982).

i) Reactive diluents/ monomers, and

ii) Non-photopolymerizable compounds that effectively plasticize the final cured films

1.6.1 Reactive Diluents/ Monomers

Monomers fall into three main chemical categories such as acrylics and derivatives, vinyls and acrylics. The functionality of a monomer can be
defined as the number of reactive double bonds per units, and it has an effect on
cure speed.

1.6.2 Plasticizing Diluents

Plasticizers are compounds introduced to a system to modify its flow
properties and often to reduce the final film brittleness. They are two categories
of plasticizers, primary and secondary.

1.6.2.1 Primary Plasticizers

These contain polar groups, which neutralize the force fields of
polymer polar groups and consequently reduce the Vander Walls forces between
adjacent polymer chains.

1.6.2.2 Secondary Plasticizers

These are inert materials without polar groups that exist are dispersed
throughout the polymer providing mechanical separators between the polymer
chains and thus reducing the Vander Walls forces of attraction between them.
Plasticizers can also classify as internal or external. Internal plasticization occurs
when the polymer chains are modified by incorporating small quantities of
another monomer during photopolymerization. This second monomer needs
bulky side groups.

External plasticization occurs when the plasticizer is dispersed in
molecular form throughout a polymer to form a viscous solution.
A polymerizable coating must have good photocured and application properties
depending on the end use.
The use of diluents is important since it is capable of reacting and crosslinking hence, contributing to the physical properties of the films (Blair 1995). The general effects of functionality of diluent are summarized in Table 1.2.

The chemical structure of acrylic monomers influences on properties such as tensile strength, elongation at break, viscosity reduction power, hardness, flexibility, cured speed and glass transition temperature (Tg) for a system based on epoxy acrylate oligomer.

The four analogues dimethacrylate diluents, 2,2'-thiobisethanol-dimethacrylate, 2,2'-oxybisethanol dimethacrylate and 1, 5-pentanediol dimethacrylate, 1,4-butanediol dimethacrylate and 1,5-pentanedioldimethacrylate have been synthesized by the transesterification of methymethacrylate with appropriate glycols in a solvent-free process or in cyclohexane in the presence of sodium methoxide or anhydrous K$_2$ CO$_3$ (Andrzejewska & Andrzejewski 1993). They have found that the presence of a heteroatom in the monomer molecule may facilitate hydrogen abstraction from the adjacent carbon atom and accelerate initiation by act as type II initiators, but should not influence the rate of formation of initiating radicals when thermal initiators are used.

A photoreactive diluent, 1,4-butanediylidimethacrylate has been synthesized by an unusual transesterification reaction with 1,4-butanediol in the presence of triethyl amine (Derouet et al 2002). They have concluded that the transesterification occurs in two stages, 4-hydroxybutyl methacrylate intermediate formed is the first stage, which is transformed into 1,4-butanediylidimethacrylate is the second stage.
Table 1.2  Effect of functionality of diluents on mechanical properties of photocrosslinked polymer film

<table>
<thead>
<tr>
<th>S. No</th>
<th>Properties</th>
<th>Increasing Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Elongation</td>
<td>+</td>
</tr>
<tr>
<td>2.</td>
<td>Hardness</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Flexibility</td>
<td>+</td>
</tr>
<tr>
<td>4.</td>
<td>Impact resistance</td>
<td>+</td>
</tr>
<tr>
<td>5.</td>
<td>Chemical resistance</td>
<td>+</td>
</tr>
<tr>
<td>6.</td>
<td>Tensile strength</td>
<td>+</td>
</tr>
<tr>
<td>7.</td>
<td>Weatherability</td>
<td>+</td>
</tr>
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</table>
A photoreactive diluent, 1,4-butanediyl(dimethacrylate) has been synthesized by an unusual transesterification reaction with 1,4-butanediol in the presence of triethyl amine (Derouet et al 2002). They have concluded that the transesterification occurs in two stages. 4-hydroxybutyl methacrylate intermediate formed is the first stage, which is transformed into 1,4-butanediyl(dimethacrylate) is the second stage.

The effects of some aliphatic sulphides on the UV-initiated polymerization of butanediol dimethacrylate in the presence of benzophenone have been investigated by Andrzejewska (1992). They have found that the addition of aliphatic sulphides to a photocurable formulation based on methacrylates improves the polymerization yield both in the presence or absence of oxygen.

The choice of the reactive diluent used in UV-curable resins are indeed crucial, because it affects both polymerization rate and final degree of conversion, while it also remarkably influences the properties of the polymer formed. Acrylic monomers contain an oxetane, dioxolane group. Oxazolidone or carbonate group in their structural unit has been copolymerized rapidly and extensively with polyurethane diacrylate upon UV-radiation (Moussa & Decker 1993). They have found that soft and highly flexible, low-modulus was produced with the oxetane, dioxolane and chlorinated monomers, while the carbonate-acrylate compounds lead to hard and glossy material.

*p*-substituted-2-allylphenyl acrylates, and diallyl, dipropenyl and dipropyl bisphenol-A diacrylates have been synthesized in high yield and characterized by spectroscopic methods (Rupa vani et al 1993). Their film properties and UV-cured coatings have been studied.
UV-curable, low functionality acrylic diluent, ditrimethylolpropane-acrylate (DTMPA) has been synthesized by esterification of ditrimethylol-propane and acrylic acid. The chemical structures of the DTMPA have characterized by FTIR, $^1$H-NMR, and $^{13}$C-NMR spectra (Jiang et al 2012). They have found that the yield of DTMPA has 86.5% and a pale colour. UV-curing test indicate that the DTMPA has a higher curing speed than that of trimethylolpropane triacrylate

1.7 THE KINETICS OF PHOTOPOLYMERIZATION

The photoinduced polymerizations of multifunctional monomers have been produced a highly crosslinked networks, which depends upon the kinetics of a reaction. Several parameters influence the kinetics of photopolymerization such as temperature, photoinitiator concentration, light intensity, viscosity, and material thickness. Liquid-solid transition has been found to increase the viscosity, limited conversion of polymerizable functions, propagation and termination reactions controlled by diffusion (Cook 1993) and volume shrinkage (Andrzejewka et al 2001).

The effect of monomer chain length and the kinetics of reaction of diacrylate photopolymerizations have been investigated by Kurdikar & Peppas (1994). They have concluded that an increase monomer chain length has caused an increase in conversion due to the increase in diffusivity of the pendent double bonds.

The kinetics of reaction and chemical changes during polymerization of multifunctional (meth) acrylates have been studied by Dietz & Peppas (1997). They have concluded that the double bond conversion depending on rank, pendent group size and functionality. The overall mechanical and thermal behaviour is a function of the size and structure of the monomer used.
Isothermal photocalorimetry has been used to study the kinetics of the photoinitiated polymerization of dimethacrylate oligomer with 2,2’-dimethyl-2-hydroxy acetophenone as a radical photoinitiator (Lecamp et al. 1997). They have reported that a maximum conversion obtained for a photoinitiator concentration of 1% (w/w) and for the highest light intensity (2.7 MW/cm²).

The polymerization kinetics of photocurable compositions based an epoxy acrylate oligomer and three analogous diacrylate monomers: 2,2'-thiobisethanol diacrylate, 2,2’-oxybisethanol diacrylate and pentane-1,5–diol diacrylate have been studied by Andrzejewska & Andrzejewski (1998). Synergism is observed for the maximum polymerization rate both in the air and argon and for final conversion in an air. The presence of heteroatom (sulphur or oxygen) in the ester group of the reactive diluent is beneficial for the polymerization in the air. The best result has been obtained for the sulphur-containing monomer.

The effect of –S– and –O– linkages present in the monomer molecule on the polymerization of dimethacrylates in various reaction conditions has been investigated by Andrzejewska & Andrzejewski (1993). They have found that the introduction of –S– and –O– linkages into the dimethacrylate monomer results in higher rates and extent of polymerization.

The photocrosslinking kinetics of silicone acrylate and methacrylates have been investigated by calorimetric and ESR measurements (Muller et al. 1992). The length of the spacer group plays an important role for an efficient crosslinking. They have found that the length the spacer group, the longer the inhibition time and higher the maximum rate of polymerization value. These effects combine with better flexibility of the longer spacer group, which favours both the propagation and termination rates.
Camphorquinone (CQ) belonged to the α-diketones, and in connection with amines, gives an effective photoinitiated system. It is widely used in the curing of (meth) acrylate-based dental restorative resins (Linden 1993, Watts 1992, Linden 1996, Song et al 2014). Effects of peroxides and hydroperoxides on the camphorquinone initiated photopolymerization of tri (ethylene glycol) dimethacrylate have been studied by Nie et al 1999. They have concluded that an addition of tertiary peroxides to the polymerizing system accelerated the CQ-initiated process, whereas addition of tertiary hydroperoxides generally has slowed down the polymerization.

The effect of comonomer concentration and functionality on polymerization rates, glass transition temperature, storage modulus, molecular weight between crosslinks and heterogeneity of the final polymer products have been studied by Yong et al (1998). They have found that the trimethacrylate system has a higher glass transition temperature, large storage modulus and smaller molecular weight between crosslinks than comparable to dimethacrylate system. The maximum rate of polymerization has found to increase with an increasing crosslinking agent when octyl methacrylate is used as the monomethacrylate; but passed through a maximum when 2-hydroxyethyl methacrylate is used.

The kinetics of photopolymerization of butyl acrylate in direct micelles has been studied by Capek & Fouassier (1997). The photolysis of the monomer swollen emulsifier micelles is generated with the initiating radicals. They have found that the rate of polymerization, particle size, and number of particles, molecular weights, and limiting conversion increased with increasing monomer concentration. The rate of polymerization has found to be proportional to the 0.7 the power of the incident light intensity.
Differential scanning calorimetry has been used to study the temperature dependence of the laser-initiated polymerization of a thiol-ene system (Hoyle et al 1994). They have found that the rate of polymerization and the extent of reaction (area) increase initially as the temperature increases above a certain temperature (above 40 °C), then slightly decreased and then increase.

The photopolymerization kinetics of a homologous series of four dimethacrylate resins with bisphenol-a-backbone has been studied by Cook (1992). The limiting extent of conversion has low at temperatures near the Tg of the monomer, but increased readily at the curing temperature is raised as expected from diffusion-controlled of the final stages of the reaction.

The influence of temperature on the photopolymerization kinetics, such as maximum rate and conversion of oligo (methylene) oxide and oligo (ethylene oxide) dimethacrylate series has been investigated by isothermal DSC (Cook 1993). It is found that final degree of conversion increases with increasing curing temperature.

The temperature effect of the photopolymerization kinetics of three analogous monomers, 2,2'-thiobisethanol diacrylate, 2,2'-oxybisethanol-diacrylate and pentane 1,5–diol diacrylate, have been studied by isothermal differential scanning calorimetry in the temperature range of 30–100°C on air and in Ar atmosphere (Andrzejewska 1995). The presence of the heteroatom markedly enhanced the final conversion and maximum polymerization rate in an air over the whole temperature range. The final conversions of the monomer increase in temperature up to 100°C on air, but in Ar they pass through a maximum at about 70°C in the case of monomers that does not contain sulphur.
Fourier transform infrared spectroscopy has been used to study the quantum yield of polymerization, the rate of polymerization and kinetic chain length of a polyurethane-diacrylate photoresists exposed to UV-radiation or to a Kr⁺ laser beam (Decker 1990). In O₂-free systems, the quantum yield of polymerization reaches a maximum value after 130 ms of exposure and a conversion of 6%. A sharp drop of the quantum yield of polymerization value have been observed after 25% conversion; it is attributed to a decrease of the initiation quantum yield due to segmental mobility restrictions brought on areaction.

UV-curable prepolymer films have been prepared by the addition of 2,2'-dimethyl-2-hydroxyacetophenone (Darocure 1173) as a radical initiator to aliphatic urethane tetraacrylate (Craynor 925). The Kinetic of polymerization of the UV-cured films have been studied by FTIR spectra. They found have that the photoinitiator concentration, the light intensity, sample coating thickness, and UV-light intensity are the most significant factors affecting the kinetics of photopolymerization (Jancovicova et al 2013).

1.8 SCOPE AND OBJECTIVE OF THE PRESENT WORK

Photoinduced polymerization is a process of converting liquid multifunctional monomer and oligomers into a solid polymer using radiation energy (Yang 1993).

The advantages of photocuring over other conventional curing methods include, high cure speed, spatial sensitivity (Moussa & Decker 1993), eliminates solvent which reduces environmental pollution and saves raw material, energy and induces low thermal stressing of substrate material (Yang 1993)
Radiation curing technology has been used in a large number of industrial applications, mainly in the coating, printing, microelectronics (Scherzer & Decker 2000), adhesives, sealants, resin/glass fiber composite materials, lacquer surface coatings, photoresists, lithographic applications for electronic industries (Roffey 1982, Rabek 1987, Allen 1989), dental composite (Sankarapandian et al 1997) and manufacture of laser videodiscs or compact discs (Kurdikar & Peppas 1994).

In many applications, the important parameters of the crosslinked polymers are the maximum extent of reaction, rate of polymerization, dimensional and thermal stability, scratch resistance, low shrinkage, and low moisture absorption (Andrzejewska & Andrzejewski 1993). All of these parameters depend on the irradiation time, reaction temperature, the viscosity of the system, diluent structure, oligomer structure, photoinitiator concentration and the photoinitiator used (Young et al 1998). The significance of the research work is summarized as follows:

i) The production cost of the synthesized acrylate and methacrylate prepolymers are one third of the actual cost of production of the other commercial prepolymers (Kumar & Jaikumar 2015).

ii) The synthetic procedure is very easy (Kumar & Jaikumar 2015).

iii) The reactivity of the synthesized acrylate and methacrylate prepolymers are high when compared to the commercial prepolymer, BISGA (Kumar & Jaikumar 2015, Kumar & Jaikumar 2014b).

iv) The unique properties of the synthesized acrylate and methacrylate prepolymers are the PDC, Rp and hardness are higher and also curing is also very fast when compared to the commercial prepolymer, BISGA. In many of the research work, commercial prepolymer, bisphenol–a–glycerolate(1-glycerol/phenol)diacrylate (BISGA) is used to study the kinetics of photopolymerization. In this compound
ethyl group present in between the bisphenol epoxy acrylate. The curing speed is one of the very important parameters in the kinetics of photopolymerization (Kumar & Jaikumar 2015).

v) The statement of research problem is to study the synthesis of a new acrylate/methacrylate prepolymer, $2$–hydroxy–$3$–{$p$–{$1$–{$p$–[hydroxy-$3$–(vinylcarbonyloxy)propoxy]phenol}$–R$–$$(or) Ar$–$(or) $p$–substituted–Ar$}$phenoxy]propylacrylate and $2$–hydroxy–$3$–{$p$–{$1$–{$p$–[2–hydroxy–3(vinylcarbonyloxy)propoxy]phenol}$–R$–$$(or) Ar$–$(or) $p$–substituted Ar$}$phenoxy]propyl methacrylate. The synthesized compounds were characterized by FTIR, $^1$H–NMR and $^{13}$C–NMR spectroscopy (Kumar & Jaikumar 2014b, Kumar & Jaikumar 2015).

vi) In this compound, R are methane, ethane, cyclopentane and cyclohexane. Ar are phenylethane, $p$-methylphenylethane, $p$-methoxyphenylethane, $p$-chlorophenylethane, $p$-aminophenylethane and diphenyl methane are introduced in between the bisphenol epoxy acrylate and methacrylate to improve the reactivity, curing speed, hardness and gel content (%) in synthesized acrylates and methacrylates, when compared to the commercially available prepolymer, BISGA (Kumar & Jaikumar 2015, Kumar & Jaikumar 2014b).

vii) Many researchers have studied the kinetics of photopolymerization of commercial prepolymers, BISGA and BISGMA (Sankarapandian et al 1997, Lecamp et al 1997) but in the present work, new acrylate and methacrylate prepolymers are synthesized. The influence of photoinitiator concentration, various photoinitiators, diluent concentration, functionality of diluents, the viscosity of the system, various prepolymers and the temperature of the system on the kinetics of photopolymerization such as PDC and Rp are studied with the synthesized prepolymer (Kumar & Jaikumar 2014a, Kumar & Jaikumar 2014b). The PDC and Rp of the photocrosslinked polymers
were compared to the commercial prepolymer, BISGA by FTIR (Kumar & Jaikumar 2015).

To synthesize UV-curable acrylate prepolymer containing free hydroxyl groups (Kumar & Jaikumar 2015, Kumar & Jaikumar 2014b).


II. 2-hydroxy-3-[p-(1-({p-[2-hydroxyvinylcarbonyloxy]propoxy} phenyl} ethyl)phenoxy] propyl acrylate (HEPA).

III. 2-hydroxy-3-[p-(1-({p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy] phenyl}cyclopentyl)phenoxy]propyl acrylate (HCPPA).

IV. 2-hydroxy-3-[p-(1-({p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy] phenyl}cyclohexyl)phenoxy] propyl acrylate (HCHPA).

V. 2-hydroxy-3-[p-(1-({p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy] phenyl}-1-phenylethyl)phenoxy]propyl acrylate (HPEPA).

VI. 2-hydroxy-3-[p-(1-({p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy] phenyl}-1-(p-tolyl) ethyl)phenoxy] propyl acrylate (HTEPA).

VII. 2-hydroxy-3-[p-(1-({p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy] phenyl}-1-(p-methoxyphenyl)ethyl)phenoxy]propyl acrylate (HMEPA).

VIII. 2-hydroxy-3-{p-(1-{p-chlorophenyl}-1-{p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy]phenyl}ethyl)phenoxy]-2-hydroxypropyl acrylate (HCHHA).

IX. 2-hydroxy-3-{p-(1-{p-aminophenyl}-1-{p-[2-hydroxy-3-(vinylcarbonyloxy)propoxy]phenyl}ethyl)phenoxy]-2-propyl acrylate (HAPPA).

To synthesize UV-curable methacrylate prepolymer containing free hydroxyl groups (Kumar & Jaikumar 2015, Kumar & Jaikumar 2014b).

I. 2-hydroxy-3-\{p-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)methyl\}phenoxy\{propylmethacrylate (HMPMA).

II. 2-hydroxy-3-\{p-(1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]ethyl)phenoxy\}propylmethacrylate (HEPMA).

III. 2-hydroxy-3-\{p-(1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)cyclopentylphenoxy\}propyl methacrylate (HCPPMA).

IV. 2-hydroxy-3-\{p-(1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)cyclohexylphenoxy\}propyl methacrylate (HCPPMA).

V. 2-hydroxy-3-\{p-(1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)-1-phenylethylphenoxy\}propyl methacrylate (HPEPMA).

VI. 2-hydroxy-3-\{p-1-((p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)-1-(p-tolyl)ethylphenoxy\}propyl methacrylate (HTEPMA).

VII. 2-hydroxy-3-\{p-(1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)-1-(p-methoxyphenyl)ethylphenoxy\}propylmethacrylate (HMEPMA).

VIII. 2-hydroxy-3-\{p-(1-[p-chlorophenyl]-1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy)propoxy]phenyl)ethylphenoxy\}propyl methacrylate (HCHHMA).

IX. 2-hydroxy-3-\{p-(1-[p-aminophenyl]-1-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy)propoxy]phenyl)ethylphenoxy\}propyl methacrylate (HAPPMA).

X. 2-hydroxy-3-\{p-(p-[2-hydroxy-3-(isoprophenylcarbonyloxy) propoxy]phenyl)diphenylmethylphenoxy\}propyl methacrylate (HHDPMA).
To study the influence of photoinitiator concentration, various photoinitiators, diluent concentration, functionality of diluents, viscosity of the system, various prepolymer and temperature of the system on the kinetics of photopolymerization such PDC and Rp are studied with the synthesized prepolymer. Several formulations have been prepared from synthesized prepolymer, diluents and photoinitiators separately (Kumar & Jaikumar 2015, Kumar & Jaikumar 2014b). These are given as follows:

- To study the influence of photoinitiator concentration on the kinetics of photopolymerization and swelling, several formulations have been prepared separately from the prepolymer, 2-hydroxy-3-[p-(1-{p-[2-hydroxy-3(vinylcarbonyloxy)propoxy]phenyl}phenyl-ethyl)phenoxy]propyl acrylate (HPEPA) (75%) and the diluent, tri(ethylene glycol) diacrylate (TEGDA) (25%) are mixed with various concentration of the photoinitiator, DMPA (0.25, 0.50, 0.75, 1.00 and 1.25%) respectively (Kumar & Jaikumar 2015).

- To study the influence of photoinitiators on the kinetics, the following efficient photoinitiators are selected based on relatively large absorption at 313 nm and a high quantum yield. 2-hydroxy-2-methyl-1-phenylpropane (Darocure1173/HMPP), 1-hydroxycyclohexylphenylketone (Irgacure184/HCPK), 2,2-dimethoxy-2-phenylacetophenone (Irgacure651/DMPA) 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one (Irgacure 907/TPMK) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (Irgacure369/BDMB) (Decker 1983, Scherzer & Decker 2000). Several formulations have been prepared separately from the prepolymer, HPEPA (75%) and TEGDA (25%) are mixed with various photoinitiator (1.00%), HMPP, HCPK, DMPA, TPMK and BDMB respectively.
To study the influence of diluent concentration on the kinetics of photopolymerization, several UV-curable formulated solution have been prepared from the prepolymer, HPEPA (90, 70 and 50%) is mixed separately with the diluent, TEGDA (10, 30 and 50%) in the presence of the photoinitiator, DMPA (1.00%) (Kumar & Jaikumar 2014a).

To study the influence of the functionality of diluents on the kinetics of photopolymerization, several formulations have been prepared from the prepolymer, HPEPA (75%) mixed separately with the three functional diluents (25%), namely, DEGEEA, TEGDA and TMPEOTA in the presence of DMPA (1.00%) respectively (Kumar & Jaikumar 2014a).

To study the influence of viscosity on the kinetics of photopolymerization, several formulations such as 1000, 2000, 3000, 4000 and 5000 cP have been prepared from the prepolymer, HPEPA is mixed with the difunctional diluent, TEGDA in the presence of DMPA (1.00%). The viscosity of UV-curable samples of different viscosities has been measured by Brookfield RVDV-II+ Viscometer (Kumar & Jaikumar 2015).

To study the influence of temperature on the kinetics of photopolymerization, several formulations have been prepared from the prepolymer, HPEPA (75%) is mixed with the diluent, TEGDA (25%) in the presence of DMPA (1.00%).

To study the influence of acrylate prepolymers, HMPA, HEPA, HCPPA, HCHPA, and HPEPA on the kinetics of photopolymerization, several UV-curable formulated solution have been prepared from the prepolymer (75%) is mixed separately with the diluent, TEGDA (25%) is presence of DMPA (1.00%).
To study the influence of methacrylate prepolymers, HMPMA, HEPMA, HCPPMA, HCHPMA and HPEPMA on the kinetics of photopolymerization, several UV-curable formulated solution have been prepared from the prepolymer (75%) is mixed separately with the diluent, TEGDA (25%) in the presence of DMPA (1.00%).

To study the photocrosslinking of above UV-curable solutions at varying time intervals with the help of medium pressure mercury vapour lamp.

To study the influence of various photoinitiator, photoinitiator concentration, diluent concentration, diluent functionality, viscosity of UV-curable formulated solution and temperature on the kinetics of photopolymerization such as PDC and Rp of the photocrosslinked polymers by FTIR (Kumar & Jaikumar 2015).

To study the influence of photoinitiator concentration, diluent concentration and diluent functionality on the density, hardness and gel content (%) of the photocrosslinked polymers (Kumar & Jaikumar 2014a).

To study the influence of photoinitiator concentration, diluent concentration and functionality of diluents on swelling coefficient, crosslink density and molecular weight between crosslinks of the UV-cured polymers by swelling experiment using N,N'-dimethyl-formamide (DMF) as a solvent (Kumar & Jaikumar 2014a).

To study the thermal behaviour of the photocrosslinked polymers by TGA and DSC techniques.