Chapter - 1

General Introduction
1.1 HISTORY

Acrylic polymers are well known for sparkling crystal clarity and outstanding surface hardness together with superior weatherability and good chemical resistance. These characteristics have made them the material of choice for a wide range of applications such as cast and extruded sheets for exterior and interior building applications, furniture, aircraft canopies and windows; molding powder and pellets for automobile parts and tail lamps, sanitaryware and bath tubs, optical lenses and other auxiliary items; as a emulsion and solution for paints, varnishes, coatings and adhesive applications.

The term 'acrylic' covers a wide range of compounds having general formula \( CH_2=\text{CRR'} \) that includes acids, esters, amides, nitriles and alcohols. These compounds are reactive monomers and find their principle use in the manufacture of polymeric products. Since the present work is related to the esters, the term 'acrylic' will be use in a restrictive sense to indicate the subject compounds. Acrylic and methacrylic compounds are derived from acrylic acid, the simplest unsaturated acid or methacrylic acid, its \( \alpha \)-methyl derivative. The availability of large group of monomeric compounds offers the possibility of tailor made products with a wide range of physico-chemical and physico-mechanical properties required for the various applications. The huge number of publications in the form of patents, articles, trade literature and reviews have described the chemistry, preparation and polymerization of acrylic compounds and the properties and applications of the acrylic polymers [1-18].

The monograph by Riddle [19] was the first full length summary of the vast literature and has signaled the commercial maturity of the acrylic esters. In 1873, Caspry and Tollens [20] first prepared methyl, ethyl and allyl acrylate and of these three, allyl acrylate was observed to polymerize. In 1880, Khalbaum [21] reported the polymerization of methyl acrylate and at the same time Fitting [22,23] found that methacrylic acid and some of its derivatives were readily polymerized. Commercial interest in the acrylic polymers began in the early 1930. The publication of Otto Röhm’s doctoral thesis in 1901 marked the beginning of the eventual commercialization of acrylies. Röhm [24], in his doctoral dissertation studied polymethyl acrylate and was impressed by the clarity, rubber elasticity and lack of color of the acrylic films. He was the first to be granted patent coverage on applications for the acrylic polymers [25]. His interest, however, in these materials did not
cease at this stage and eventually in 1927 the Röhm and Haas concern at Darmstadt, Germany, commenced the limited production of polymethyl acrylate. These polymers were thermal or photochemical products. The discovery of initiation by organic peroxides was found useful in acrylic polymerization. The first commercial offerings were soft and gummy polyacrylate solution, intended for various coating and adhesive applications rather than moldable plastics material, under the trade names of Plexigum and Acryloid (Röhm & Hass Company) and Acronal (Badische Anilin-& Soda-Fabrik A.-G.).

In 1930, Bauer [26] and co-workers in Germany and Hill [27] and co-workers in England independently prepared polymethyl methacrylate (PMMA) and found it to be a rigid, transparent and non-adhesive polymer. PMMA sheets and molding powder very soon followed and won the rapid acceptance in glazing and moulding applications, architecture, lighting, signs, displays, automotive parts and decoration etc. under the various trade names such as Plexiglas and Oroglas (Röhm and Hass Company), Perspex (Imperial Chem. Ind. Ltd.) and Lucite (E.I. du Pont de Nemours and Co.). These applications have made MMA polymers the large individual group of products in the acrylic field. Acrylic emulsions, such as Rhoplex (Röhm and Haas Co.), were not adopted on a large scale until about 1952. But after that they have achieved a unique position in exterior and interior paints, floor polishes and finishes for flexible substrates such as textiles, paper and lather. Thermoplastic automotive coatings based on PMMA solutions and thermosetting acrylic copolymer compositions for appliances and automotive finishes were among the major applications.

1.2 POLYMERIZATION OF ACRYLIC ESTERS :-

Acrylic monomers, both acrylates and methacrylates are highly reactive towards polymerization and can be polymerized by free radical or ionic processes using various techniques. In industries, free radical initiator such as peroxides, hydroperoxides, persulphates and azo compounds are commonly used for the commercial productions. Photo-initiated or high energy radiation initiated processes may used for the special applications such as in the manufacture of printing inks or in photography and in the preparation of graft
copolymers. Anionically initiated processes provides a means of steric control of the tactic structure of the polymer and serve as a route to synthesize crystalline products for speciality applications. The various techniques employed for the commercial manufacture of the acrylic polymers are briefly discussed below.

1.2.1 **BULK OR MASS POLYMERIZATION**

This technique is very widely used for the casting of acrylic sheets, blocks, rods and tubes as well as in the embedding process, acrylic dental plastics and contact lenses. In cast polymerization, clear liquid monomers or partially polymerized syrups are transformed directly into shapes such as sheet, tube, rod, block from which useful article can be made by further heating or machining. Since no solvents or dispersing agents are used, cast polymers or copolymers are better in clarity, homogeneity and color than those prepared by other techniques. Main disadvantage of this technique is removal of the heat of polymerization. Precautions must be taken for the controlled removal of the heat of polymerization. The discovery by Trommsdorff and co-workers [28] regarding the acceleration of polymerization rate by increased viscosity was of great significance especially in the bulk polymerization of MMA. The increase in viscosity reduces the termination rate by reaction of radicals ends of growing chains which leads to autoacceleration even when the temperature is controlled. In the early German process, purified MMA containing 0.02-0.1 % benzoyl peroxide (BPO) was heated in a glass flask at 80° - 100°C until a syrup formed. The reaction mass was quench cooled with agitation to prevent "run away" and was degassed by applying the vacuum before pouring into the mould. The prepolymer syrup of molasseslike consistency was poured into a casting cell consisting of two clean glass plates separated by spacing strips and held in place by coated gummed paper. The hand loaded cells were heated at 60°C or above for ten or more hours. In order to complete the polymerization and to make the finished PMMA sheets resistant to "crazing " (formation of fine cracks with the loss of residual monomer) the sheets after removal of the glass cells were given a heat treatment at 80-120°C. Earlier only BPO was available as an initiator for adding into syrup before casting. From 0.02-0.05% BPO was used to accelerate syrup formation and then larger amount was added for the casting. Later initiators liberating free radicals at lower temperatures such as
diacetyl peroxide (0.5%) and isopropylpercarbonate made possible the use of heated rooms (40-55°C) to replace ovens for the casting of thin sheets.

Degussa corporation [29] patented a process in which MMA syrup (10-20% polymer content) containing 0.05% diisopropylpercarbonate and 0.05% lauryl peroxide was heated at 40°C for 4.5 hrs. and then for 2 hr. at 100°C to give cast polymer containing only 0.58% residual monomer. Yamawaki and co-workers [30] reported the bulk polymerization of a MMA on the surface of glycerol under the nitrogen atmosphere in the presence of catalyst to give PMMA sheets with good surface luster.

Novak [31] reported the use of dual initiator system for the bulk polymerization of MMA syrup. The prepolymer syrup (containing 24% polymer) was mixed with 3.19 mole azobisisovaleronitril (ABVN) and 0.62 mole azobisisobutyronitrile (AIBN) at room temperature to give 80% conversion to PMMA in 17-18 min. The polymer had intrinsic viscosity 1.667 (0.5 g polymer/100 ml CH₂Cl₂ @ 25°C) and residual monomer of 1.54%. Sterling [32] evaluated nine different peroxides as an initiator in equal amount of 0.2% by weight to reduce the cycle time in the casting of PMMA sheets. Out of nine, three per oxyneodecanoate esters viz., cumyl per oxyneodecanoate, t-amylper oxyneodecanoate and t-butylper oxyneodecanoate as a polymerization initiator, decreases the cycle time without deleterious effect on the optical properties of the PMMA cast sheets which is essential for its use in spectroscopic cells. Sinha and co-workers [33] studied the combination of azo and peroxy initiator for the casting of PMMA sheets and observed that the proper combination of AIBN and ABVN reduces the polymerization cycle time, without affecting the properties of the cast sheets, which results in high productivity at low energy consumption. Toritani and co-workers [34] reported a process to manufacture transparent and impact resistance casting panels by bulk polymerization of partially polymerized MMA, butyl acrylate based grafted rubber and (meth)acrylic ester-acrylosilane macromer using ABVN initiator. The resulting 3 mm casting panel head notched impact strength 4.8 kg./cm², light transmittance 92.5%, and haze 1.4%. Mayer [35] prepared cast acrylic sheets by bulk polymerization of MMA syrup using long chain carboxylate esters as an opacifying agent which was opaque and had light transmittance 5% at 550 nm and light reflection 94% compared to 44% and 24% respectively for a common opaque PMMA sheets. Resulting sheets were useful as a lighting fixtures.
Continuous casting of PMMA sheets has been one of the most challenging and difficult objectives of the acrylic technology. Williams [36] at ICI polymerized MMA syrup between moving steel bands provided by two endless belts, each moving about two rotating cylinders of 18 inch diameter and about 8 feet apart. Latham [37] at Swedlow Plastics Co. used supported cellophane films passing through a long photopolymerization tunnel for the continuous casting of thin PMMA sheets. Kato [38] of Mistubishi Rayon Co. patented a continuous process for high quality PMMA sheets in which a prepolymer syrup of 1 P viscosity and 25% PMMA in MMA, 0.05% AIBN and 0.05% silicon based release agent was introduced to the one end of the gap between two polished steel belts, 1200 mm wide, moving in the same direction at 1 meter/min. The prepolymer progressed through 40 meter long heating zone at 85 °C and 2 meter long zone at 135 °C followed by slow cooling to 80 °C through 12 meter cooling zone. The resulting PMMA sheet had degree of polymerization 5000, thickness 3 ± 0.3 mm, heat distortion temperature (HDT) 96 °C and contained 1.4% residual monomer. The intensive search in bulk polymerization technique for acrylic esters and its wide adaptability for the casting of tubes, rods and blocks, in the embedding process, acrylic dental plastic, contact lenses and coatings has resulted in a large extent in literature [39-47].

1.2.2 SUSPENSION POLYMERIZATION

Suspension polymerization of acrylic esters offers many advantages over bulk polymerization such as better heat dissipation during the polymerization, better control over physico-mechanical properties by controlling molecular weight distribution through the use of chain regulators and ease of processing. In a typical suspension system, one or more water immiscible monomers containing initiator are mixed in aqueous phase and dispersed into tiny droplets by strong stirring. The suitable conditions of mechanical agitation are maintained with heating the system to the polymerization temperature while polymerization is completed to solid beads or pearls. Suspension polymerization of acrylates in water requires small amount of substances that hinder the coalescence of monomer droplets and sticking together of beads during the course of polymerization. They are known as suspension stabilizers or suspending agents.
Bauer and Lauth [48] dispersed acrylic esters in water or electrolyte solution and removed the heat of polymerization through the agitated aqueous phase. Substantial progress in the art and applications of the suspension polymerization followed the introduction of suspending agents. Crawford [49] in 1933 first developed bead polymerization of MMA stabilized initially by gelatin or methyl cellulose. Natural water soluble polymers soon were succeeded by synthetic dispersing agents. Two of the most useful dispersing agents in commercial production were partially saponified polyvinyl acetates (more often called PVA) and alkali salt of methacrylic acid copolymers. Weinning [50] studied the relation of the structure of these polymers to their effectiveness as a suspending agents. Mendizabal and co-workers [51] during their studies on effectiveness of polyvinyl alcohol as a suspension stabilizer reported that the polyvinyl alcohol of moderate degree of hydrolysis (88%) and relatively high molecular weight (>70,000) was performing best as a suspension stabilizer for acrylic polymers. Röhm and Trommsdorff [52] discovered that certain water-insoluble finely dived powders were useful as suspending agents. Talmud [53] reported that the addition of soluble phosphate buffer may be critical in the MMA suspension polymerization. These process were much further develop during the last five decades and today they formed a strong basis for the commercial production of acrylic polymers by the suspension techniques.

The use of suspension technique did not restricted for the manufacture of ordinary homo- and copolymers. An outstanding application was the preparation of high impact plastics and other multiphase copolymers. A three step suspension polymerization for preparing high impact methacrylate polymer was suggested by successive polymerization of MMA, butyl acrylate and again MMA. MAA based polymers of different molecular weight ranges and softening behavior made by suspension method are used for the injection molding and extrusion. Polymers of average molecular weight 100,000 to 200,000 are usually prepared in the presence of long alkyl mercaptans or ester of thioglycolic acid. The softening range and melt viscosity may also be controlled by copolymerization with small proportion of alkyl (meth)acrylates or other comonomers. Griffin [54] at ICI patented a process to synthesized a plastic copolymer which is resistance to stress crazing. The synthesis of crosslinked macroporous suspension beads has been reported in a patent [55]. These crosslinked porous beads have achieved industrial importance for chromatography and
adsorption and their derivatives are used as an ion exchange resins. Hiroki and co-workers [56] prepared copolymer beads by suspension polymerization of neopentyl glycol dimethacrylate and 3-chloro-1,2-dimethylpropyl methacrylate using 10.5:9.5 monomer feed ratio. The resulting polymer beads after treatment with dimethyl amine were useful as an ion-exchange resins in liquid chromatography. Walenius and co-workers [57] studied the effect of monomer feed composition and monomer:porogen ratio on the pore size of the suspension copolymers of GMA (I) and trimethyloyl propane trimethacrylate using toluene as a porogen and ethyl hydroxyethyl cellulose as suspension stabilizer. It was found that the pore size distribution (PDS) in the dry state shifted towards larger pores as the (I) : (II) ratio increase were as pore volume distribution in the swollen state did not change appreciably and the PDS in the dry state shifted towards smaller pores as the monomers to toluene ratio increased. Pinrathnam and co-workers [58] prepared the crosslinked macroporous GMA-EGDMA copolymers beads with uniform bead size and distribution by suspension technique. The resulting bead has absorption capacity of 20-20 mg of penicillin G amylose per gram of the matrix and useful as a matrix in the preparation of immobilized penicillin G amylose.

1.2.3 EMULSION POLYMERIZATION

Industrial polymerization of acrylic monomers in emulsion provides strong base for making many synthetic rubbers and structural plastics from coagulated or spray dried latexes, paints and coatings, adhesives, sealents and finishes for textiles, leather and paper. Copolymer having a wide range of complicated structures may be prepared by this technique and the final properties of the emulsion polymers are considerably influenced by the method of monomer addition, temperature, choice of initiator, stabilizers and chain transfer agents. Emulsion polymerization offers some unique advantages over other techniques. The products with fairly high molecular weight and low latex viscosity can be prepared. Water provides an ideal heat transfer medium during the polymerization thereby minimizing the run away reaction. The essential components of a typical industrial emulsion polymerization receipt are as listed below.

[a] Monomers having limited solubility in water and whose polymers are completely water insoluble such as alkyl (meth) acrylates.
[b] **Functional monomers** that may or may not be water soluble and added usually as a small fraction of the total monomer volume (0.1 - 10 %) to impart greater emulsion stability, viscosity, adhesive bonding character, susceptibility to crosslinking after application or in situ crosslinking. Examples of such a reactive monomers are (meth)acrylic acid, hydroxyalkyl (meth)acrylates, glycol di (meth)acrylates and glyciclyl (meth)acrylates.

[C] **Initiators** such as peroxo compounds viz., persulfates of sodium, potassium or ammonium, hydrogen peroxide, t-butyl hydroperoxide, cumene hydroperoxide, lauryl peroxide, benzoyl peroxide, methyl ethyl ketone peroxide and azobisisobutyronitrile are generally used. The single initiator or combination of more than one may be used.

[d] **Surfactants and Stabilizers** viz., anionic or non-ionic surfactants such as long chain fatty acids or alcohols, sulfonates or alkyl and aryl compounds, alkyl sulphosuccinates, fatty acids or esters of sugars, “protective colloids” such as polyvinyl alcohol, partially hydrolyzed polyvinyl acetate, water soluble cellulose derivatives and alkali metal salts of MAA copolymers can be used.

[E] **Chain transfer agents** such as mercaptans or halogenated compounds can be used.

[F] **Buffers** such as phosphate or citrate salts, sodium carbonate or bicarbonate can be used.

Much industrial technology of emulsion polymerization has been summarized by Warson [59]. The technical literature from various manufacturers provides an important source of information for the technology and applications of emulsion polymerization [60,61]. Naumova and co-workers [62] prepared acrylic copolymer composition by aqueous emulsion copolymerization of butyl acrylate, methyl acrylate, methacrylic acid and acrylic monomers having long alkyl chain(C₁₀₋₁₂) as a surface active agent. The resulting composition gave coatings with improved mechanical properties. Wu and co-workers[63] studied the effect of tempererture,emulsifier concentration,initiator concentration and cross-linking agent concentration on the rate of emulsion polymerization of butyl acrylate and properties of the polymer. The rate of emulsion polymerization increased with increasing polymerization temperutures,initiator concentration and cross-linking agent concentration while the average particle size of the emulsion decreased. The increase in EGDMA concentration increased the degree of cross-linking and the effective molecular weight was decreased. Klavins and co-workers [64] reported the two stage emulsion copolymerization of
butyl methacrylate in aqueous surfactant solution with GMA or allyl glycidyl ether in the presence of diethyleneglycol dimethacrylate cross-linker and organic solvent as pore forming agent. The resulting cross-linked porous copolymer was useful as polymeric carrier for covalent immobilization of biologically active compounds. Zou and co-workers [65] synthesized monodispersed cross-linked PS and PMMA beads of 1 mm diameter by particle nucleation onto pre-existing polymeric seeds in a multistage emulsion polymerization without using emulsifier. During preparation of monodispersed multicomposition beads by polymerizing styrene onto PMMA seeds, it was found that an adequate seed concentration, which decreased with increasing seed size, was necessary to achieve monodispersed beads. The resulting beads were useful as a heat resistant molding compounds.

1.2.4 SOLUTION POLYMERIZATION

In industries, solution polymerization is favored especially when the polymer is to be further reacted or processed directly from solution as in the fiber spinning process using solution, in the manufactures of coating and adhesive to be applied directly after addition of other solvents, curing agents and auxiliary agents. Some addition polymerizations tends to occur too rapidly in a large scale to control without the use of some solvents as a rate regulator and to facilitate the removal of polymerization heat by lowering the viscosity. The selection of the solvents also has the specific interest in the preparation of the solution product. The solubility parameter ($\delta$) of acrylic ester polymers and copolymers ranges from about 8.0 - 9.7. Acrylate and methacrylate polymers are soluble in the corresponding monomers and in organic solvents having similar $\delta$ value such as aromatic hydrocarbons, esters, halogenated solvents and aliphatic ketones. These solvents are the acceptable media for polymerization of acrylates in solution and for preparation of lacquers.

Burnett and co-workers [66] studied the accelerating effect of some halogenated solvents on the AIBN initiated polymerization of MMA and found that the MMA polymerization was accelerated by various solvents in the order: $\text{C}_6\text{H}_5\text{F} < \text{C}_6\text{H}_5\text{Cl} < \text{C}_6\text{H}_5\text{Br} < \text{C}_6\text{H}_5\text{I}$. Bamford and co-workers [67] measured the rate constants of individual steps in the photopolymerizatoin of MMA sensitized by AIBN at 25 °C in a number of aromatic solvents.
and found that the rate of polymerization increased in the order: Benzene < fluorobenzene < chlorobenzene < anisole < bromobenzene < bezonitrile. Addition of solvent such as benzene, toluene and xylene enhance the rate of polymerization of MMA but not of other vinyl monomers such as acrylonitrile, styrene, vinyl acetate and methyl acrylate. The rate enhancement of MAA polymerization was observed in the order: xylene > toluene > benzene. Watanabe and co-workers [68] carried out MMA polymerization in several solvents at 30-160 °C and estimated the activation energy between syndiotactic and isotactic addition. Lazer and co-workers [69] studied the variation in molecular weights of the MMA polymer obtained by the radical polymerization in different mixtures of chloroform and acetone. Jiang [70] studied the effect of solvents, temperature and catalyst on solution polymerization of hydroxymethyl methacrylate, butyl acrylate, MMA, styrene and/or acrylic acid while preparing the coating composition and found that molecular weight and its distribution was decreased with increase in the polymerization temperature. Spinner [71] and Blauer [72] reported a profound effect of the pH of the reaction medium on the polymerization rate of MAA as well as on the stereochemistry of the resulting polymers. Smets and co-workers [73] found a significant effect of the water content of the reaction medium on polymerization of MAA and acrylamide initiated by AIBN.

Formerly it was believed that monomer reactivity ratios for the radical copolymerization were not affected by the nature of the medium except in the case of heterogeneous copolymerization or ionizable monomers. Many studies reported that the solvent effects upon copolymer compositions were observed only for copolymerization of the acidic or basic monomers in aqueous solution at different pH values [74,75]. The ionization of the monomers can vary the reactivity of double bonds to a great extent. Extensive studies on the copolymerizations of acrylic acid and methacrylic acid with styrene and MMA were made in various organic solvents. It was concluded that the variation of the reactivity ratio may be attributed not to the strength of hydrogen bonding between (meth) acrylic acid and solvent, but rather to the amount of dimerization of (meth)acrylic acid. Ito and Ostu [76] reported that there are small solvent effects on the copolymerization parameters for styrene and MMA. Maanim and co-workers [77] reported the process for continuous solution polymerization of MMA and other co-monomers for preparing the acrylic polymers with
narrow molecular weight distribution and improved heat resistance in which monomers were first polymerized in the presence of a chain transfer agent (CTA) upto 20-95% conversion and then excess initiator and modifiers were removed. The partial addition of CTA in a later stage was found useful for improving the final product quality. Copolymers of MMA with other acrylic esters or related monomers, prepared in solution, used widely in coatings such as backing enamels and high gloss lacquers, pressure sensitive adhesives and lubricating oil modifiers.

1.3 GENERAL PROPERTIES OF ACRYLIC POLYMERS

Weatherability and optical properties of acrylics are superior to most other plastics. They also have good electrical and chemical properties.

Weatherability:- Acrylics withstand prolonged periods of exposure to weather and sunlight without yellowing or stress cracking. For extreme cases like exposure to mercury vapour lamp, as in the case of their use as a light defusers, addition of ultraviolet absorber (UVA) is recommended. UVA grades have a higher edge color than normal grades, but the color is not noticeable in most applications.

Optical:- The transmission of visible light is 92% which is equal to glass. Haze is measured less than 2%. The refractive index of PMMA measures 1.49.

Electrical:- Acrylics have good dielectric strength, low electrical conductivity and excellent arc resistance.

Chemical:- Acrylics are resistant to most detergents like solutions of inorganic alkalies, acids and aliphatic hydrocarbons, but are not recommended for aromatic hydrocarbons, esters or ketones.

Toughness:- Tensile strength of 8000 to 9000 p.s.i. and flexural strength of 14,000 to 17,000 p.s.i. indicate the rigidity of the material, but it is notch sensitive. The average of 0.35 ft.-lb./in. for notched Izod can be improved with modifiers, but will result in less rigidity. If unmodified acrylic is exposed to stresses in excess of 1200 p.s.i. for a long periods of time, stress crazing will occur. It can be exposed to higher loads for short periods of times.

Thermal:- ASTM Grade 8 materials can be used upto 160oF continuously and certain grades can be used upto 200oF under no load conditions. The deflection temperature load varies
from 165 to 212°F. The thermal expansion of acrylics is greater than most thermoplastics, and must be taken into consideration when acrylics are used in conjunction with other materials. For example, an acrylic glazing should not be mounted rigidly to steel or wood. It must be allowed to expand or contract to prevent cracking.

**Flammability:** Most acrylics have UL-94-HB rating. Most building codes indicate the amount of non-combustible material that can be used in construction.

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<th>METHOD (ASTM)</th>
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<td>Light transmittance (total)</td>
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### 1.4 APPLICATIONS OF ACRYLIC POLYMERS

The major commercial markets of acrylic polymers make use of combination of different properties such as transparency, weatherability, chemical resistancy, toughness and hardness for various applications. Some important commercial applications of acrylic polymers and copolymers are briefly discussed below.
1.4.1 CAST SHEETS AND MOLDING COMPOUNDS

Signs produced from acrylic sheets have proven their excellent weatherability long back. Cast and extruded sheets are fabricated into decorative signs. Impact modified acrylic sheets are replacing standard sheets especially in automotive applications were breakage. Cast acrylic sheets are used for safety glazing and as a replacement material on strom doors, patio doors or in any hazardous location. Insulated skylights have increased the use of acrylic sheets in recent years. The use of cast sheets in sanitary wares is also growing steadily. Cast acrylic sheets are steel being used in one of their first applications, aircraft canopies and windows. Sheets and molding compounds share the lighting market for both outdoor and indoor applications. Resistance to yellowing in both clear and translucent material make acrylic the choice for extended life in these application. Acrylic molding compound are used mostly in the automotive industries. Molded tail light covers is the single largest application of the acrylic molding pallets. Acrylic materials offers excellent weatherability and ability to reproduces reflex optics. Other automotive applications are side markers, piller posts, instrument covers and name plates. Acrylic lighting lenses are increasing in popularity due to their low smoke density rating. Burning acrylic emits a white smoke which does not obscure exit signs during a fire. Other areas of application were acrylic sheets and molding compound widely used are roof glazing partitions, show-cases, door handles, house furniture like sofa-sets, chairs, dining tables, telephone stands, bath tubes, wash-basins, service cores for bathrooms, reflecting mirrors and gift articles, construction of green houses, transparent automotive roofing and windows, helmets with visors, dishware and cutlary, television filter screens, geometrical instruments, watch glasses, industrial models, jewellary boxes and decorative photoframes. The availability of cast acrylic sheets and molding pellets in various attractive colors both transparent and opaque alongwith their easy machining by cutting, drilling, routing and processing by vacuum forming, blow forming and cementing make the fabrication of end-use articles very easy. Moreover acrylic sheets and molding compounds can easily be produced with required properties to meet the demand of each end application.

Jung and co-workers[78] prepared fire resistance acrylate glass by cast polymerization of MMA and comonomers in the presence of Phosguard-C22R (Chloroethyl triphosphonate) using monomer feed ratio MMA:MAA:Tribromoneopentyl...
methacrylate(67:3:20). The resulting polymer had vicat softening temperature 117°C and was self-extinguishing in ASTM-D-635-56 T test.

Sinha and co-workers[79] reported the preparation of thermally stable PMMA cast sheets by polymerizing MMA syrup(10-15% polymer content) and EGDMA cross-linking agent(5-10%). The resulting cast sheets had good thermal stability and resistance to stress crazing and was used in the manufacturing air-craft.

Tone and co-workers [80] reported the process for the manufacturing of transparent and heat resistant methacrylate resin useful as optical material and sign boards. Hugo [81] patented the process for producing transparent windows with high absorption capacity for radiant heat(>80%) by laminating 50mm thick polyethylene film(whose refractive index was increased to 2 by adding 20% colloidal Ag particals) with cast acrylic sheet. The resulting composite had controlled heat transmission properties and was suitable for use on hot houses. Takeru and co-workers [82] prepared metal deposited laminated acrylic sheets useful as self adhesive plastic mirrors.

1.4.2 COATINGS AND RELATED APPLICATIONS

Most acrylic resins for coatings and related applications are copolymers composed entirely of acrylic monomers or mixtures with other common comonomers and are available as aqueous latexes or dispersions and organic solutions. Latexes have the advantages of high molecular weight, low viscosity, freedom from the hazards and expenses of solvents, speedy film formation and drying. Because of their lower molecular weights and non-particulate nature, solution coatings show better flow, gloss and transparency. Many acrylic products are thermoplastic copolymers of esters, into which minor amounts of (meth)acrylic acids are incorporated to improve adhesion. Acrylic emulsion coatings finds use in exterior and interior applications, textile and paper finishes and impregnants and floor polishes. The principal application of the solutions products is in automotive coatings where their weatherability, sunlight resistancy, tint retention and high gloss have made them the material of choice. Thermosetting or self curing compositions constitute a major new extension of the utility of acrylic resins in coatings for automobiles and industrial applications[83-86]. The acrylic polyol cured with alkoxy melamine resins have been used as a mechanically, artistically and
economically sufficient coatings for a long time. However, at present they are faced with acid-etching problems due to easy hydrolysis of their crosslinked ether bonds caused by \( \text{NO}_x, \text{SO}_2, \text{sulfuric acid and nitric acid arising from the exhaust gas of automobiles or wasted industrial gases. The measure of acid rain etching will become important increasingly for the coatings of buildings, bridges and culture properties depending on the environmental conditions around the objects. Recently, crosslinkable fluorinated and siloxane containing acrylic coatings have been developed very widely. Iwai and co-workers [87] reported tentatively on comparison of durability of coatings for architectures since 1991 for fluorinated acrylics cured with isocyanate, moisture cured acrylosilane, siloxane modified acrylics or common acrylics cured with isocyanate. The higher durability was approved in the order of fluorinated acrylics, acrylosilane, siloxane modified acrylics and common acrylics. Predominately good adhesion of acrylosilane and siloxane modified acrylics was shown for the cements, concretes or stones although urethane or epoxide resins were easily peeled off. Nagai and co-workers [88] reported an outdoor weather test in Okinawa, Japan of top coat degradation of fluorinated acrylics, isocyanate cured acrylic, chlorinated rubber and alkyd by evaluating surface appearance, gloss retention, SEM, three dimensional surface roughness and color change. It was found that fluoroacrylics were predominately excellent in these tests and top coat durability. Nakaya [89] modified the fluorinated acrylics with siloxane in the way to make higher surface energy that enables rain to adhere on the coats surface and washaway the oil and dust and renew the coat surface, keeping substantial excellent durability. Furukawa and co-workers [90] reported on the detailed crosslinking reaction mechanism of acrylosilane with molecular weight 10,000-15,000 for architecture coatings and that with molecular weight 4,000 for the automotives. Weathering and outdoor test indicated the comparable durability of the acrylosilane with that of fluorinated vinyl acrylics, both showed superior gloss retention. A sulfuric acid spot test with 10\% aqueous sulfuric acid at 85\(^\circ\)C for 30 min. in a sealed tray showed no spots for the acrylosilane where as the other showed remarkably greater etching in the order of the acrylic melamine and urethane.

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1.4.3 ADHESIVES AND SEALENTS

Acrylic adhesives and sealants are formulated from functional acrylic monomers which achieve excellent bonding upon polymerization. Among the most important and widely used are cyanoacrylates and anaerobic adhesives both are the one component system and marketed as a contact adhesives. Polycyanometacrylates is capable of providing strong bonds between metals, glass, ceramics and certain plastics. Alkyl-α-cyanoacrylate polymerize rapidly through an ionic mechanism and solidify at room temperature. Bonds formed by cyanoacrylates are serviceable at temperatures as low as -17°C and upto 80 °C and more. Bonds formed with glass, rubber and wood are generally stronger than the material being bonded [91]. Guthrie [92] has described the detailed commercial and technical aspects of poly(alkyl-2-cyanoacrylate)s such as chemistry, preparation, mechanism of polymerization, properties modification and applications.

Anaerobic adhesives are obtained with aliphatic diols such as tetramethylene glycol dimethacrylate. These monomers have the property, when in contact with air, of remaining freely fluid in the presence of free radical initiator, but of polymerizing at room temperature when penetrating between closely fitted surfaces of metal, glass, ceramics and certain polymers. These particular feature of the reaction enable it to be used for locking thread grooves, the resulting bond being stronger than achieved by locknuts [93].

Modern sealants may be define as a class of macromolecular compounds generally marketed in three main forms viz. putty like mastics, non-cured tapes and cured gaskets and whose function is to prevent the passage of moisture, air, dust, gases and heat through various joints. Solvent based acrylic sealent are used effectively in a wide variety of joints. They are recommended for perimeter caulking (windows, door and panels), control joints, precast concrete joints, panel to panel joints, bedding of mullions, panels and frames. In glazing they are used for filling the complete channels, cap beads over tape, heel beads under glass and back bedding [94]. Blaga and co-workers [95] prepared sealent composition by blending acrylic terpolymer with PVC, with improve mechanical properties and enhanced outdoor resistance.
1.4.4 POLYMER CONCRETE AND BUILDING APPLICATIONS

Acrylic polymer containing large amount of filler such as polymer mortars without cement and polymer concretes are increasingly being used in building and other structures. Polymer mortars are mainly used as protective coatings on concrete, reinforced concrete and rarely on steel while polymer concretes represent a new type of structural material capable of withstanding highly corrosive environment. A wide range of polymer concrete compositions have been investigated, the most important and used in many applications are: polymer impregnated concrete (PIC), polymer cement concrete (PCC), polymer concrete (PC) and fiber reinforced polymer concrete. Most widely used acrylic monomers for polymer concrete system are MMA, butyl acrylate, methyl acrylate, ethylene glycol dimethacrylate and trimethyl propane trimethacrylate. Fukuchi and co-workers [96] have used a mixture of styrene and trimethacrylate as a comonomer, AIBN catalyst and silane type coupling agent for the concrete impregnation in their study for finding an appropriate process for manufacturing high strength concrete. Webster and co-worker [97] applied formulation, based on MMA and trimethacrylate comonomer, for partial-depth polymer impregnation of concrete bridge decks. Fowler and co-workers [98] have found that the strength and durability of polymer concrete, particularly produced by the full impregnation process, are generally much greater than for the plain concrete. The addition of a comonomer with MMA which may lead to a copolymer with lower Tg results in much more ductile behavior. Limsuwan [99] made PIC with varying combination of MMA and butyl acrylate and studied the stress-strain behavior. The found that ultimate compressive stress decreases and ultimate strain increases with increasing amount of butyl acrylate. The important applications of polymer impregnated concretes are bridge decking, tunnel support-lining system, pipes, desalting plants, beams, underwater habitats, dam outlets, off-shore structures, underwater oil storage vessels and in chemicals and fertilizer plant buildings.

1.4.5 CONTACT LENSES AND DENTAL APPLICATIONS

Acrylic polymers, as a biomedical materials, finds important use in contact lenses and dental plastics. Contact lens development was very rapid following world war II with the availability of PMMA. Two types of the polymers are being used as a materials for contact
lenses: thermoplastics and hydrogels. The rigid types of contact lenses which became widely used in the 1960's were generally copolymers of MMA or ethyl methacrylate with small proportions of other monomers such as dimethylacrylates or allyl methacrylates. Most hard lenses are crosslinked with ethylene glycol dimethacrylate to improve their strength hardness and scratch resistance. Bulk polymerization is the preferred method for lenses preparation. MMA with minor proportions of CR-39 and methacrylic acid were polymerized in glass molds for lenses [100]. The most serious drawbacks of the hard contact lenses are their hydrophobic properties and resultant low oxygen permeability. Wichterle and Lim [101] pioneered in the development of soft, hydrophilic copolymers for use as contact lenses and other medical applications. According to a patent application, hydrogel useful as contact lenses and other having selective permeability in the presence of physiological saline water solution were compatible with body tissues. In a typical process patented by Wichterle and Lim [102] for the preparation of the hydrogel, in which a mixture of hydroxyethyl methacrylate, diethylene glycol monomethacrylate, diethylene glycol dimethacrylate, ammonium persulphate and aminoethyl acetate was polymerized to a transparent gel after 4 hr. at 0 °C followed by warming to 40 °C. After drying a week at 25 °C and 40% RH portion were ground and polished to lens shape. Bulk polymerization of these monomers in presence of tertiary amines gave hydrophilic gel useful in fractionating gamma globulin in presence of 0.5 % NaCl aqueous solution. In another patent application, a mixture of 2-hydroxyethyl methacrylate, methacrylamide containing 0.4% ethylene glycol dimethacrylate and 0.5% BPO was copolymerized in a rotating mold at 80°C for 6 hr. The purified, lightly crosslinked gel obtained after absorption of isotonic salts solution was suggested as a contact lens [103]. Flexible content lenses may be prepared from the copolymers of glycidyl methacrylate [104]. Some other applications of hydrophilic acrylic copolymers are as a dental prostheses, semipermeable membranes and column packings have also been reported [105,106].

The early development of acrylic dental plastics reviewed the use of MMA as a common monomer for dental filling material. Composite resins containing a large amount of filler and methacrylate monomers have been widely used as a restorative materials for hard tooth tissue. Benzoyl peroxide-N-N-dimethyl-p-toluidine initiator system was used earlier but it was found that the amine cause color change in the resulting polymers. More recently p-
toluene sulfonic acid, trimethyl barbituric acid ester or tri-n-butyl borane derivatives have been found to be suitable initiator system. Photoinitiator systems are now becoming more practical [107]. Although, PMMA has a wide application as a dental polymer, it has a serious defect in that it has very poor adhesive power with tooth surfaces. An effective way to come out this defect was the application of functional monomers that could chelate with calcium ions or couple with dentine collagen. It was found that the monomers having both hydrophilic and hydrophobic groups have good adhesion properties for tooth tissue. Yamauchi and co-workers [108] reported the synthesis of 2-methacyrloyloxyethyl-2'-bromoethyl phosphoric acid, useful as a dental filling material with good adhesion properties. Yamauchi and co-workers [109,110] synthesized dental adhesive composition using PMMA containing BPO, MMA with 2'-methacyrloyloxyethyl phenyl phosphoric acid and p-toluene sulphonic acid. The harden mixture gave bond strength of 160 Kg/cm². MMA monomer-polymer slurries in acrylic dental filling have been largely replaced by superior formulations of inorganic fillers with a bifunctional viscous liquid “Epoxy acrylic monomer” (made by reaction of GMA with bisphenol-A) and diluted by MMA monomer [111].

1.4.6 ACRYLICS IN SOLAR ENERGY CONSERVATION

Solar energy is a ideal source of energy not only for the space heating but also for the power generation. Acrylic polymers have a share in the development of the solar energy conservation systems. They offer potentially lower cost, easy processing, light weight and greater design flexibility. Acrylic polymers and copolymers are used in many of the solar systems as covers, thin film honeycombs and housing for flat-plate collectors, reflecting surfaces and optical lenses for concentrating collectors, reflector shells, structural and support members, insulation, piping, moisture barriers, adhesives and silence. It is of great interest that a cover of PIMA can have its original transmittance restored after a decade of exposure by polishing away the weathered layer. Manedelsohn and co-workers [112] studied the durability characteristic of various polymers, including acrylcs, inside a solar collector and have found good results. Brauman and co-workers [113] studied the reactivity of eight different polymers, used as a protective coatings for solar mirrors, with mirror materials. Using loss in reflectance as a indication of mirror failure and change in tensile properties as an
indication of polymer failure, the authors ranked the polymer-mirror assemblies and found that PMMA-Al-adhesive is the most durable of the polymer-mirror systems studied.

1.4.7 NON-LINEAR OPTICAL APPLICATIONS

Non-linear optics is the study of the response of a dielectric medium to an intense electromagnetic field, such as that produced by the propagation of laser radiation through the materials. This finds applications in fast response modulators, waveguides and optical fibers for telecommunication and transmission technology. Currently the inorganic materials, such as lithium niobate are used in manufacture of non-linear optical devices. However, some speciality polymer have been tested recently for this applications due to several advantages over the inorganic material such as scope of designing a polymeric molecules with required properties, relatively low cost, low dielectric constant and ease of processing. Hill and co-workers [114] reported the use of PMMA coating on conducting indium tin oxide to protect it from alkaline etching and electrochemical degradation. Early work on electro-optic polymers used active monomeric guests in a polymeric host. Singer and co-workers [115] reported the use of azo dye Disperse Red 1 in a PMMA matrix for preparing electro modulators. Haga and co-workers [116] made 10 mm long channel waveguide using MNA in PMMA and observed 16% modulation depth for an applied voltage of 100 V at a wavelength of 633 nm. There have been reports on side chain polymers based on acrylates. Hoechst Celanese Corporation have been the most prolific producer of side-chain electro-optic polymers, mainly acrylate copolymers [117]. These copolymers have been used by Lockheed to make electro-optic devices [118]. Hill and co-workers [119] reported on a demonstrator modulator based on acrylated homopolymer which showed 17% modulation depth without any observable degradation in its performance over a period of two years.

1.4.8 MICROLITHOGRAPHY

Microlithography has played an important role in the last thirty years and is likely to retain its key role in determining the pace of development in modern semiconductor technology for the next fifteen years. The use of acrylic polymers and copolymers in microlithography has been reported. Hatzakis [120] reported the use of PMMA as a
“classical” positive resist in electron beam lithography. PMMA is capable of producing the highest possible resolution, nanometer features have been achieved in special conditions, however it is very insensitive. A wide variety of copolymers have been studied in an attempt to improve the sensitivity of the resist. Tada [121,122] reported that poly(2,2,2-trifluoroethyl-α-chloroacrylate) shows good adhesive properties and sensitivity. Their are several reports regarding the applications of acrylic copolymer as a resists in microlithography [123].

1.5 AIM OF THE PRESENT WORK

It is known that 8-hydroxyquinoline (8-HQ) and its derivatives possess antibacterial, antimycotic and ameobicidal properties. Several authors have suggested that their antimicrobial properties are due to their complex forming ability. The chelating ion-exchange properties of 8-HQ and its derivatives have been widely exploited for many applications such as in metallurgical operations, separation and estimation of metals, effluent treatment, purification of water and as a catalyst in many organic syntheses. The polymeric 8-HQ derivatives have been synthesized by its condensation with aldehydes and by modification of poly(ethylene glycol)s and poly(ξ-caprolactone)s. There are few examples of synthesis and polymerization of vinyl monomers containing quinolinyl groups. Data are lacking for the synthesis of copolymers of acrylic ester of 8-HQ with commonly used vinyl monomers. With this view, the present work was aimed as follows:

(1) Synthesis of monomeric acrylic ester with pendent quinolinyl group, i.e. 8-quinolinyl acrylate (8-QA), under the optimized reaction conditions and its characterization by FT-IR spectroscopy, ¹H-NMR spectroscopy, high performance liquid chromatography (HPLC), elemental analysis and differential scanning calorimetry (DSC).

(2) Study of the kinetics of solution polymerization of 8-QA in different experimental conditions.

(3) Study of the polymerization kinetics of 8-QA using various initiator concentration at different heating rates by DSC and evaluation of various kinetic parameters useful in optimization of polymerization conditions.
(4) Study of the kinetics of solution copolymerization of 8-QA with MMA, styrene, and n-butyl methacrylate (BMA) in dimethyl formamide (DMF) at low conversion and calculation of the reactivity ratios for this monomer pairs.

(5) Synthesis of copolymer of 8-QA with MMA, styrene, BMA, MA and VAc by free radical solution copolymerization technique using different monomer feed ratio for each pair using DMF and AIBN as a solvent and an initiator, respectively.

(6) Characterization of homo- and copolymers by FT-IR spectra, UV spectrophotometry, gel permeation chromatography (GPC), solution viscosity and thermal analysis (TG and DSC). Corelation and comparison of the effect of poly-8-quinolinyl acrylate [P(8-QA)] composition on the molecular weight distribution and thermal behavior of the individual homopolymer.

(7) Evaluation of the chelating ion-exchange properties of P(8-QA) and its copolymer by batch equilibration method using Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Co$^{2+}$, and Fe$^{3+}$ metal ions under various experimental variables such as electrolyte, electrolyte concentration, pH of the medium and time.
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