CHAPTER 1

INTRODUCTION
1.1 HISTORY

Among the monomers utilized in the production of polymeric materials, an important place is occupied by acrylic and methacrylic acids and especially their esters (i.e. acrylates). Acrylates are type of vinyl polymer which contain vinyl groups, that is, two carbon atoms double-bonded to each other and directly attached to the carbonyl carbon. Acrylate and methacrylate esters are unsymmetrical substituted ethylene and can be represented by the general formula:

\[
\begin{align*}
\text{H} & \quad \beta\text{-carbon atom} \\
\text{C} & \quad \alpha\text{-carbon atom} \\
\text{H} & \quad \text{carbonyl carbon atom} \\
\text{O} & \quad \text{R'} \\
\text{C} & \quad \text{R}
\end{align*}
\]

where R=H and R’=CH$_3$ for acrylates and R=R’=CH$_3$ for methacrylate. The identity and nature of the R and R’ groups determine the properties of both the monomers and polymers prepared from the respective monomers.

Acrylic materials with a broad property of spectrum are available today. Sparkling crystal clarity, remarkable surface hardness together with excellent weather ability and good chemical resistance are characteristic properties of acrylic polymers. These characteristics have made them the 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 automobiles parts and tail lamps, sanitary ware and bath tubs, optical lenses and other auxiliary items, as an emulsion and solution for paints, varnishes, coatings and adhesive applications. Acrylics also find applications in electronics, plastics, leather, inks, paper, minerals, cosmetics, pharmaceuticals, detergents etc.

The first acrylic acid derivatives were methyl acrylate and ethyl acrylate. Although these two monomers were synthesized in 1873, their utility in the polymer area was not discovered until 1880. In 1880, Fitting and Engelhorn [1] and Kahlbaum [2] polymerized the methyl acrylates and methacrylates. The commercial discovery of acrylic ester polymers took place while Otto Rohm [3] was conducting his doctoral research in 1901. Rohm obtained a U.S. patent in 1912 covering the vulcanization of acrylates with sulfur [4]. Barker and Skinner [5] published the details of the polymerization of methyl and ethyl methacrylates in 1924. Commercial production of
acrylic ester polymers by Rohm and Hass Co. of Germany, commended in 1927 [6]. Solution polymers have been produced from methyl methacrylate since 1927 by Rohm and Haas (Germany). Emulsion polymers were first developed on an industrial scale in 1929/1930 by Fikentscher [7,8] and were introduced into the market by BASF as a polymer dispersion named “Corial grund” for the surface finishing of leather. The use of polyacrylates in many fields of application increased rapidly with the development of new methods for producing acrylic acid and acrylate esters.

1.2 PRODUCTION OF ACRYLIC MONOMERS

Commercial productions of acrylic and methacrylic monomers were started first by improved elimination procedure based on cyanohydrins, acrylates from ethylene cyano hydrine and methacrylates from acetone cyano hydrine. Rohm and Hass Co. was the first manufacturer of acrylic in both Germany (1928) and the United States (1931).

The major production processes for the preparation of the acrylic and methacrylic monomers are discussed below.

1.2.1 Acrylic acid and esters

Reppe, the father of modern acetylene chemistry, discovered two methods for the carbonylation of acetylene with carbon monoxide and active hydrogen compounds to give acrylic acid or its derivatives [9]. A potential commercial process for acrylic acid is based on the condensation of formaldehyde. A number of catalysts have been patented for this reaction [10]. The conversion of acrylonitrile to acrylic acid or acrylate was proposed long ago. However, the commercial production by this route was achieved after the development of a suitable process by Standard Oil Co. of Ohio [11]. The most economical process for the manufacture of acrylic acid is based on the two-stage oxidation of propylene. It proceeds in two stages, first acrolein is obtained then acrylic acid is produced [12]. Bauer synthesized acrylic ester by the hydrolysis of ethylene cyano hydrine [13].

1.2.2 Methacrylic acid and esters

The first methacrylic esters were prepared by dehydration of hydroxy isobutyric esters, a prohibitively expensive starting material for the commercial synthesis [14]. Crawford [15] discovered a new route in 1932 to synthesize methacrylate using cheap and readily available raw materials i.e., acetone, hydrogen cyanide and sulfuric acid. This process gave product with 99.8 % purity and an overall yield of about 85 %. The technology is based on two stage oxidation of
isobutylene or t-butyl alcohol to methacrylic acid by a process very similar to the standard catalytic oxidation of propylene to acrylic acid. Methacrylic acid is separated from its products and then esterified [16].

1.2.3 Synthesis of higher esters

Hydroxyalkyl methacrylates were conveniently prepared by the addition of oxirane compounds to the acid in the presence of amines or quaternary ammonium salts as a catalyst [17]. Glycidyl methacrylate is prepared by the reaction of alkali salt of methacrylic acid with epichlorohydrin in the presence of a quaternary ammonium salt catalyst [18]. The ester interchange reaction between the lower (meth)acrylate and higher alcohol is the most widely used method for the synthesis of higher esters [19]. Direct esterification is the principle industrial route to the higher alkyl esters. The inhibited acid and alcohol were refluxed in presence of a strong acid catalyst such as sulfuric acid.

1.2.4 Synthesis of haloacrylic esters

Since 1938, a numbers of 2-haloacrylic esters have been polymerized. Marvel and co-workers [20] reported the preparation of some higher alkyl 2-chloro and 2-bromo acrylates by refluxing higher alkyl 2,3-dihalopropinotes in the presence of amines such as quinoline or dimethylaniline in 1990. The higher alkyl dihalopropinates were prepared by reacting methyl 2,4-dihalopropinates with thionyl chlorides and than reacting the resulting 2,3-dihalo propionic acid chlorides with higher alcohols.

1.3 POLYMERIZATION OF ACRYLIC ESTERS

Acrylates and methacrylates are highly reactive monomers and can be polymerized by free radical or ionic process 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 be used for the special applications such as in photography and in the preparation of graft copolymers. Anionically initiated processes provide 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 types and techniques employed for the commercial manufacture of the acrylic polymers are briefly discussed below.
1.4 POLYMERIZATION TECHNIQUES

1.4.1 Bulk Polymerization

The simplest technique that gives the highest purity polymer is bulk polymerization. The bulk polymerization of methacrylic esters is very important in manufacturing sheets, rods, tubes and molding material by cast molding techniques [21-23]. In this technique monomer, initiator and chain transfer agent are used. Advantages of this technique include polymer of highest purity, high yield per reactor volume, easy polymer recovery and option of casting the polymerization mixture into final product form. Main disadvantage of this technique is removal of the heat of polymerization. Heat removal becomes particularly difficult near the end of the polymerization when viscosity is high. In bulk polymerization auto-acceleration is observed at beginning causing increases in viscosity of the systems known as gel or Trommsdroff effect [24,25]. Thus it is necessary to regulate very carefully heat removal during the polymerization in bulk.

Yamawaki and Mashahiro [26] reported the bulk polymerization of MMA on the surface of glycerol under the nitrogen atmosphere in the presence of catalyst to give PMMA sheets with good surface luster. The use of dual initiator system for the bulk polymerization of MMA syrup has been reported by Novak [27]. Mayer [28] using long chain carboxylate esters as an opacifying agent prepared cast acrylic sheets by bulk polymerization of MMA syrup. Kim and co-workers [29] prepared methacrylate syrup by bulk polymerization. The method for producing an (meth)acrylate syrup of this invention has such advantages that reaction runaway does not occur, the control of molecular weight and conversion rate is possible even at low exothermic temperature without stirring failure, and a partially polymerized (meth)acrylate syrup can also be prepared therefrom. Brar and co-workers [30] synthesized copolymers of 2-hydroxy ethyl methacrylate and methyl acrylate of different compositions were synthesized by free radical bulk polymerization using azobisisobutyronitrile (AIBN) as an initiator under nitrogen atmosphere.

Kato and Demande [31] patented a continuous process for high quality PMMA sheets. Sinha and co-workers [32] observed that the combination of azo and peroxy initiator for the casting of PMMA reduces the polymerization cycle time, without affecting the properties of the cast sheets, which results in high productivity at low energy consumption. 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 substantial number of publications [33-41]. Anzlovar and co-workers [42] prepared ZnO nanocomposites with poly(methyl methacrylate) matrix have been prepared by the in-situ bulk polymerization of methyl methacrylate showed enhanced effect on the thermal stability of PMMA, ultraviolet,UV, absorption and transparency for visible light.

1.4.2 Suspension polymerization

In suspension polymerization batch reactor fitted with mechanical agitator is charged with a water insoluble monomer and initiator. Sometimes, a chain transfer agent may be added to control molecular weight in free radical polymerization. Droplets of monomer containing the initiator and chain transfer agent are formed. Coalescence of these sticky droplets is prevented by the addition of protective colloid and by constant agitation of polymerization mixture. At the end of polymerization the particles are harden and can be removed by filtration, which is followed by final washing step. Although solvent cost and recovery operations are minimum, but polymer purity is low due to presence of suspending and other stabilizing additives that are difficult to remove. 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 transfer agent and ease of processing.

Crawford [43] in 1933 first developed bead polymerization of MMA stabilized initially by gelatin or methylcellulose. Kajtna and co-workers [44] prepared microsphere acrylic pressure-sensitive adhesives from ethylacrylate/2-ethyl hexylacrylate by suspension polymerization. Luo and co-workers [45] synthesized poly(2,2,3,3-tetrafluoropropyl methacrylate) in presence of gelatin and sodium dodecyl benzene sulfonate by suspension polymerization. Hiroki and co-workers [46] prepared copolymer beads by suspension polymerization of neopentyl glycol dimethacrylate and 3-chloro-1,2-dimethylpropyl methacrylate using 2.1 : 1.9 monomer feed ratio. The resulting polymer beads after treatment with dimethylamine were useful as an ion-exchange resin in liquid chromatography. Narsimhaswamy and co-workers [47] reported copolymerization between various substituted phenyl acrylates with 4 mole % DVB in aqueous suspension at 80°C. Physical characterization like surface area, % swelling, apparent density, compressive strength and surface morphology of the
copolymers were investigated by Tank and co-workers [48]. Koehler prepared solid polyvinyl ester and poly(meth)acrylate resin with high polydispersity gives excellent adhesion properties [49]. H Feng reported study on synthesis of MMA/Styrene copolymer by Suspension polymerization [50].

1.4.3 Emulsion Polymerization

Another technique that utilizes water as a heat-transfer agent is emulsion polymerization. In addition to water and monomer, a typical reactor charge for an emulsion polymerization consists of a water-soluble initiator, chain transfer agent and a surfactant such as sodium salt of long chain fatty acid. Emulsion polymerization is the most important industrial process for producing polyacrylates and their copolymers [51-54]. Copolymers having a wide range of complicated structure 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. Products with fairly high molecular weight ($10^5-10^6$) and low latex viscosity can be prepared.

Patrick and co-workers [55] prepared polymers from styrene and its derivatives with vinyl halides by emulsion polymerization which is used as impact modifiers. The prepared polymer has good thermal stability and optical properties. Sakdapipanich and co-workers [56] synthesized acrylate polymers by a novel emulsion polymerization for adhesive applications. A novel emulsion polymerization was established to improve the low physical properties of PSA on the basis of conventional poly(n-butyl acrylate) by emulsion polymerization. Kang and co-workers [57] synthesized monodisperse soap-free P(MMA-EA-MAA) latex particles by seeded emulsion polymerization of methyl methacrylate (MMA), ethyl acrylate (EA) and methacrylic acid (MAA), and the particles with void morphology were obtained after undergoing alkali post-treatment. Kato and co-workers [58] prepared copolymer of methyl methacrylate and methacrylic acid to be used as a polymeric surfactant by emulsifier free semi batch emulsion copolymerization. There are several process reported for the emulsion polymerization of acrylates [59-61]. Emulsion polymerization of polymerizable coumarin derivatives reported by Oh and co-workers [62].
1.4.4 Solution Polymerization

In industrial processes it is sometimes advantageous to have a strong solvent–polymer interaction. Thus solution polymerization is often performed for applications in which the solvent remains present e.g., in protective coatings, adhesives, and viscosity modifiers. In this technique, both the monomer and initiator are soluble in solvent and the solvent have acceptable chain transfer characteristics and suitable boiling point for the conditions of polymerization and subsequent solvent removal step. Solvent choice may be influenced by the factor such as flash point, cost and toxicity. The obvious disadvantages of solution polymerization are low production rate and high cost.

Erol and co-workers [63] prepared copolymers of [2-oxo-2-(4-methyl) phenyl amino] ethylene methacrylate with styrene in presence of benzoyl peroxide in 1,4- dioxane solvent at 65ºC. Vijayanand and co-workers [64] synthesized copolymers of 4-cynophenyl methacrylate with methyl methacrylate at different feed composition by free radical solution polymerization at 70±1ºC using benzoylperoxide as an initiator and methyl ethyl ketone as solvent. Soyakan and co-workers [65] prepared copolymers of N-(4-bromophenyl)-2-methacrylamide with glycidyl methacrylate in 1,4-dioxane solution at 70±1ºC using 2,2’-azobisisobutyronitrile as an initiator with different monomer ratios.

1.5 GENERAL PROPERTIES OF ACRYLIC POLYMERS

Poly(methyl methacrylate) (PMMA) is a hard, rigid transparent substance. PMMA is somewhat tougher than polystyrene but less tough than ABS (acrylobutystyrene) polymer. An outstanding property of PMMA is its clarity. The material absorbs very little visible light but there is about 4% reflection at each polymer-air interface for normal incident light. Thus the transmission of normal incident light through a sheet of the polymer is about 92%. PMMA is a polar material and has a rather high dielectric constant and power factor; it is a good electrical insulator at low frequencies but is less satisfactory at high frequencies.

PMMA prepared by free radical polymerization is amorphous and is therefore soluble in solvents of similar solubility parameter. Effective solvents include aromatic hydrocarbons such as benzene and toluene; chlorinated hydrocarbons such as chloroform and ethylene dichloride; and esters such as ethyl acetate and amyl acetate. Some organic materials, although not solvents for the polymer, cause crazing and cracking. PMMA has very good resistance to attack by water, alkalies, aqueous
inorganic salts and most dilute acids. PMMA has much better resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α-methyl group.

A further outstanding property of PMMA is its good outdoor weathering, than most other thermoplastics. After several years under tropical conditions the color change is extremely small. When PMMA is heated above the glass transition temperature (105°C) it becomes rubbery and sheet material is easily manipulated at 150-160°C. Above about 200°C decomposition becomes appreciable and at 350-450°C a nearly quantitative yield of monomer is readily obtained. Thus the recovery of monomer from scrap polymer is a feasible proposition.

1.6 APPLICATIONS OF ACRYLIC POLYMERS

A wide variety of properties range, transparency, weather ability, chemical resistance, toughness, hardness, clarity and resistance to degradation by environmental forces, acrylic polymers are used in an outstanding variety of applications that span the range from very soft adhesive materials to rigid non film forming products. The most important areas of application are concerned with coatings, adhesives, paper, textiles, oil additives, biomedical application and in polymeric drug delivery. Various applications of acrylic polymers and copolymers are briefly discussed below.

1.6.1 Coatings

Acrylic ester polymers are used widely as high quality paint binders because of their excellent durability, toughness, optical clarity, UV stability and color retention. These properties allow acrylic to find use as binder vehicles in all types of coatings [66,67]: interior and exterior, flats, semi-gloss and gloss as well as primers to topcoats. The development of solvent free products is one of most significant advancements in the coating industry. Water based coatings are now used worldwide in many diverse applications. Pure acrylic emulsions are the premium binders for high-performance water based coatings because of their unique balance of properties: high quality, easy to formulate and versatile and environmentally friendly. Liu [68] prepared water based coating from silicon modified acrylic resin which can be used as interior/exterior water based coat material, high temperature and fire resistant coating material and corrosion resistant metal or boat coating material with ease at low cost. Water reducible polyester resins, used for improving the humidity and chip resistant of water borne coatings is reported [69]. Gould and co-workers [70] synthesized
coatings formulations based on multifunctional acrylate resins with $\beta$-keto esters, $\beta$-diketones and/or $\beta$-keto amides. Coatings based on these novel multifunctional acrylate resins exhibit excellent adhesion and shrinkage control, flexibility, solvent resistant, scratch and mar resistance, impact resistance and durability across wide range of plastic materials. Douglas [71] prepared in-mold thermosetting acrylic coating materials with high adhesion strength.

1.6.2 Adhesives

Adhesives based on (meth)acrylic monomers or oligomers are known. Such (meth)acrylic adhesives are usually two component adhesives; one of which comprises a radical initiator, typically a peroxide. The advantage of such adhesives is that they exhibit a fast development of mechanical strength. Laminating adhesives, pressure sensitive adhesive, building construction adhesives and sealing compounds are produced from polyacrylates. Nishina and Tokuyama [72] prepared pressure sensitive adhesive based on (meth)acrylic polymers which have excellent durability and light leakage prevention and are capable of avoiding any bleeding and suppressing any staining at removing time and any detachment under harsh conditions. Shingo and Cooman [73] prepared (meth)acrylic adhesives with high impact resistance and no or low odor. Koji and co-workers [74] synthesized thermally expandable acrylic polymer adhesive films with good balanced adhesion and peelability. There are various types of acrylate adhesive which are reported in literature [75-80].

1.6.3 Textiles

Acrylic is lightweight, soft, and warm, with a wool-like feel. It dyes very well and has excellent colorfastness. It is resilient, retains its shape, and resists shrinkage and wrinkles. In the textile industry polyacrylates are used almost exclusively as emulsion polymers [81,82]. Vitkovskaya and co-workers [83] prepared acrylic fiber containing textiles with catalytic properties. The uses of acrylics in textile finishing are numerous and diverse. Water-soluble polymers are used as thickeners in the formulation of textile finishes. Acrylic emulsion polymers are also used to reduce the shrinkage of wool, to improve abrasion resistance of textiles, to bond non woven fabrics, to bind pigments and for antimicrobial coating [84-86]. The fluorinated acrylic monomers were used in polymerization with non fluorinated acrylic monomers to obtain copolymers suitable for use in textile finishing [87].
1.6.4 Paper

Speciality acrylic monomers are used in water based acrylic dispersions applied to paper sheets. They provide a nice appearance to the paper; allow inks and colors not to be absorbed by the paper. Speciality acrylic monomers can be used to glue cellulosic fiber when manufacturing paper. Yoko and co-workers [88] prepared oil resistant paper with good flexibility and heat resistance. The paper is useful for food packaging material and masking sheets. Kurt and Guenther [89] prepared emulsion copolymers made of acrylates as sole binder for paper coating compositions. Duan and co-workers [90] prepared styrene/acrylate copolymer latex which is suitable for paper coating with satisfactory properties in glossiness, smoothness as well as ink absorbability. High quality papers are coated with pigments to improve their printability, appearance, gloss and other properties [91].

1.6.5 Oil Additives

Long-chain acrylic esters are used as additives to improve the performance of internal combustion engine lubricating oils and hydraulic fluids for smooth starting of engine. It is desirable that the viscosity of lubricating oil is low when cold and as the temperature of the oil increases the viscosity must be maintained at some acceptable level [92]. Polyalkyl(meth)acrylates are used in lubricating oil composition to reduce overheating [93]. Phosphoric acid ester containing additives are used for corrosion protection during combustion sulfur poor fuel oils [94].

1.6.6 Biomedical Applications

Over the past decade the use of polymeric materials for the administration of pharmaceuticals and as biomedical devices has increased dramatically. For years, dentures, dental fillings and denture bases have been made using methacrylic ester polymers [95,96]. These polymers can also be used to prevent tooth decay in natural teeth by serving as a barrier which can be coated over the surface of teeth. The dimensional behaviour of these bone-cement composites has been reported [97,98]. Lutz [99] prepared polymers from meth(acrylate) moiety and poly(ethylene)glycol (PEG) which can be used for building a wide variety of modern materials such as biosensors, artificial tissues, smart gels for chromatography and drug carriers. Both hard and soft contact lenses have been made using polymethacrylates [100-102]. Hydrogels comprising poly(2-hydroxy ethylmethacrylate) are used in soft contact lenses [103,104]. Polymer networks that can serve as model systems for dental applications were prepared by photopolymerizations of 1,1,1-trimethylolpropane.

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triacylate, 1,1,1-trimethylolpropane trimethacrylate, 1,1,1-trimethylethane trimethacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, photomer 2028 and photomer 3015 [105].

1.6.7 Polymeric Drug Delivery

Acrylates are biocompatible and have been widely used in synthesis of polymeric drugs [106,107]. Florence and co-workers [108] prepared pH sensitive polymer blends which can be used as coating materials to control drug release from beads. Farhadieh [109] studied the simultaneous release of mixtures of noninteracting chemicals incorporated in a methyl acrylate-methyl methacrylate copolymer. Arun and Reddy [110] studied in vitro drug release studies from the polymeric hydrogels based on 2-hydroxyethyl acrylate and 2-hydroxypropyl methacrylate using 4-\{(E)-[(3Z)-3-(4-(acryloyloxy)benzylidene)-2-hexylidene]methyl\}phenyl acrylate as a crosslinker. Babazadeh M [111] studied in vitro drug release studies from 2-hydroxyethyl methacrylate copolymers.

1.6.8 Other Applications

Acrylic esters are used for exterior paints because of their resistance to photodegradation and hydrolytic stability. Acrylic and styrene-acrylic latexes are being used increasingly for industrial maintenance coatings.

Synthetic marble fixtures and bathtubs are made using methacrylic ester polymers [112,113]. Opaque and clear methacrylate sheets have been used for structural components in the manufacturing of recreational vehicles [114]. These materials are additionally used for electrical insulation. Thermoplastic methacrylate resins are used in lacquer coatings for plastics, in printing inks, as heat seal lacquers for packaging, as screen printing media for decorative porcelain, in traffic paints and for protection of buildings from acid rain and weathering [115]. Jing Hu and co-workers reported alkali soluble copolymers of acrylic acid and butyl acrylate used as leather finishing agent [116].

Polymethacrylates are naturally good choices for fiber optics market because of their optical clarity and low thermal resistance [117].

1.7 HETEROCYCLES

Pyrrole, furan, thiophene, quinoline, isoquinoline, coumarin are the hetrocyclic compounds. A hetrocyclic compound is one that contains a ring made up of more than one kind of atom. Heterocyclic intermediates are being used more and more in synthesis as protecting groups and in the biological world. Coumarins (2H-1-
benzopyran-2-ones) form an important class of oxygen containing heterocycles and are widely distributed in nature [118,119]. They occur either in the free state or as glycosides. As the present work deals with coumarin derivative, some aspects of the chemistry of coumarin are presented over here.

1.7.1 Medicinal and industrial application of coumarin and its polymers

Coumarin and its derivatives have attracted considerable interest because of their various physiological and biochemical properties. Coumarin itself inhibits the germination and subsequent root growth of plants. Novel fully aromatic coumarin-containing polyesters were reported by Fomine and co-workers [120]. Rebound and co-workers [121] prepared coumarin derivatives which can be used as active substances of medicines as inhibitors of protease. Photocurable, liquid polymers incorporating coumarin ester endgroups into their molecular structure, which polymers are crosslinked upon irradiation with ultraviolet light by photochemically allowed [2+2] cycloaddition reactions among the chain ends, and which crosslinked polymers are useful in the preparation of medical devices, tissue engineering scaffolds, drug delivery systems and, in particular, in vivo preparation of implants, in an open surgical procedure or laparoscopically [122,123].

Although simple coumarin has a very low fluorescence quantum yield, many natural coumarins and synthetic derivatives are highly fluorescent and have high quantum yields. The synthetic coumarins have been used extensively as fluorescent brightening agents in detergents, paper and textiles to mask yellowing in white materials [124]. 7-(2’-benzoxazolyl)-3-phenyl coumarin [125] and 2-(3’-coumarinyl)benzoxazoles [126] have been reported to be optical brighteners for polyesters, polyamides and polyvinylchlorides. 2-(3’-coumarinyl)-naphthoxazoles with a dialkyamine substituent in 7 position of coumarin ring exhibit brilliant fluorescence with absorption in visible range and are useful for dyeing of organic fibres [127]. A recent application of coumarin fluorescence is in the field of tunable laser dyes [128]. Reddy [129] and other have reported synthesis of 3-heteroaryl coumarins as optical brighteners. Erol and co-workers [130] prepared novel methacrylate copolymers based on sulfonamide and coumarine gives good optical and biological activity.

1.8 AIM OF THE PRESENT WORK

Coumarin and its derivatives represent one of the most affective classes of compounds possessing a wide spectrum of biological activity. 4-hydroxy-coumarin
moiety, a well known biocide has been anchored to polymers by copolymerizing coumaryl methacrylate with various other vinyl monomers. With this view, the aim of present work follows:

1. Synthesis of methacrylic ester of 4-hydroxy-coumarin i.e. coumaryl methacrylate (CMA) under the optimized conditions has been done. These are characterized by FT-IR spectroscopy, $^1$H-NMR and $^{13}$C-NMR spectroscopy and High performance liquid chromatography (HPLC). Further poly(CMA) has been synthesized and characterized.

2. The copolymers of CMA with methyl methacrylate (MMA), perachlorophenyl methacrylate (PCPMA), 2,4-dichlorophenyl methacrylate (2,4DCPMA), 8-quinolynyl methacrylate (8-QMA), glycedyl methacrylate (GMA) and p-acetamidophenyl methacrylate (PAPM) by free radical solution polymerization technique using different feed ratio for each pair are obtained.

3. Solution copolymerization of CMA with MMA, PCPMA, 2,4-DCPMA, 8-QMA, GMA and PAPM at low conversion to calculate the reactivity ratio for each monomeric pairs by different methods has been studied.

4. Characterization of homo- and copolymers by FT-IR spectra, $^1$H-NMR spectroscopy, gel permeation chromatography (GPC), solution viscosity, thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and melt flow index (MFI) has been carried out.

5. The ion-exchange properties of CMA/8-QMA homo and copolymers by batch equilibrium method using Cu$^{+2}$, Ni$^{+2}$, Zn$^{+2}$, Co$^{+2}$ and Fe$^{+3}$ metal ions under various experimental variables such as electrolyte, electrolyte concentration and pH of the medium and time are evaluated.

6. Evaluation of the antimicrobial properties of poly(CMA) and its copolymers against bacteria, fungi and yeast has been done.
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