SUMMARY

The present work is divided into six chapters, each covers the different aspect of the study. The main objective of the study was to synthesize and characterize acrylic copolymers with ion-exchangable groups and to evaluate their properties.

In the first chapter, brief introduction about the development of acrylic polymers with historical background, various polymerization techniques, general properties and some commercial important application of the acrylic polymers are described. The aim of the present work is also briefly described in this chapter.

The second chapter is divided into two parts. The first part describes the synthesis and characterization of the monomer, 8-quinolinyle acrylate (8-QA). The 8-QA monomer was prepared by esterification of acryloyl chloride with 8-hydroxy quinoline and characterized by IR and NMR spectroscopy, HPLC, elemental analysis and DSC to confirm the structure and determine the purity. IR and NMR spectra shows all the expected signal for 8-QA, the practical values of elemental analysis are very close to theoretically calculated values, the HPLC shows that the synthesized monomer is of greater than 99 % whereas DSC shows that 8-QA sharply melts at 49.2 °C.

The second part of the chapter described general method of homo- and copolymers synthesis. The 8-QA homopolymer and its copolymer with MMA, styrene BMA, MA and VAc were prepared by solution polymerization technique using AIBN and DMF as an initiator and solvent respectively. The copolymers were prepared using different monomer feed ratio and their composition was determined by UV spectroscopy. The % yield of the polymer ranges between 32 - 98 % whereas their softening starts between 89 - 258°C which is depending upon the structure and copolymer composition.

The third chapter is divided into two parts. The first part describes the polymerization kinetics of 8-QA studied by DSC technique under different experimental condition and copolymerization kinetics by solution polymerization technique. From the DSC study various kinetic parameters such as activation energy for polymerization, heat of fusion, heat of reaction and reaction order were calculated by Borchardt-Daniels Kinetic method and correlated with experimental variables. The effect of temperature, heating rate and initiator concentration on the rate of polymerization was also observed and it was found that the rate
of polymerization is directly proportional to the polymerization temperature, rate of heating and initiator concentration. The solution copolymerization of 8-QA was carried out with MMA styrene and BMA using different feed ratio and copolymers were isolated at low conversion (~10%). The copolymer composition was determine by UV spectroscopy and reactivity ratio for each monomer pair was calculated. The relative reactivity of the comonomers with respect to that of 8-QA follows the order: MMA > BMA > Styrene and is governed by the steric factor and resonance. From the results of reactivity ratios, it was observed that the copolymers are weakly ordered with a random distribution of two monomers in the polymer chain.

The second part of the chapter deals with the kinetics of radical homopolymerization of 8-QA initiated by azobisisobutyronitrile was studied. Various experimental conditions were employed with the variation in the monomer concentration, initiator concentration and temperature. The kinetic parameters were calculated from the percent conversion and consequently rate of polymerization is calculated from gravimetric data. From this data, the order of polymerization reaction was established with respect to monomer concentration, initiator concentration etc. using kinetic parameters of different temperature.

The fourth chapter is divided into two parts. The first part describes molecular weight determination of the polymers by GPC and viscosity determination. The GPC results shows that the copolymers are relatively of high molecular weight and medium polydispersity. The viscosity of the polymers is directly related with the molecular weight i.e. with increase in molecular weight, viscosity also increases and vice-versa. The examination of GPC results also shows that the varied content of 8-QA in the copolymers does not have any regular effect on the molecular weight and polydispersity of the resulting copolymers.

The second part described IR spectral analysis of the copolymers. The IR spectra of copolymers shows all the expected bands of 8-QA and comonomers. The shift in IR frequencies of 8-QA after polymerization is explained on the basis of extended conjugation present in the 8-QA monomer. The characteristic bands due to 8-O-substituted quinolinyl group were assingned. The IR spectra provides the qualitative information about the copolymer structure. The relative changes in the intensity of the bands due to individual component in the copolymers may be due to the changes in the copolymer composition.
The fifth chapter described thermal analysis of polymer by TGA and DSC. The examination of TG thermograms reveals that the thermal degradation of all the polymers started between 175-300°C and almost completed around 450-550°C. Moreover it is also observed that the copolymers degrade with a maximum rate near their half volatilization temperature. The values of IPDT, calculated by Doyle’s method indicates that all the polymer possesses the moderate thermal stability and overall thermal stability of the copolymers of 8-QA with other vinyl monomers follows the order of BMA < VAc < MMA < Styrene < MA. The values of heat of fusion (ΔH_f) derived from DSC ranges from 0.08 to 2.30 kJ.g⁻¹ and represent overall melting behaviour of the copolymers.

The examination of TG thermograms also indicates that the incorporation of 8-QA in the polymer chain slightly increases the thermal stability of some polymers and it also affects the thermal degradation profile of the individual homopolymers.

The sixth chapter describes the chelating ion-exchange properties of the 8-QA homo- and copolymers. The presence of quinolinyl pendant group in the polymer chain imparts ion-exchange properties to the polymers. The ion exchange properties were determined by batch equilibration method using Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺ and Fe³⁺ metal ions as a function of pH, nature and concentration of the electrolyte and shaking time. The results shows that:

(i) The amount of metal adsorbed by each sample depends upon its 8-QA content.
(ii) As the pH of the aqueous medium increases, the amount of metal adsorbed by the polymers also increases and follows the treand of : Ni²⁺ > Cu²⁺ > Co²⁺ > Zn²⁺. The Fe³⁺ adsorption was studied in the pH range of 1.5 to 3.5 and it is also increases with increasing pH.
(iii) The adsorption of Cu²⁺, Ni²⁺ and Co²⁺ at pH 5.5 increases with increasing NO₃⁻ and Cl⁻ ion concentration in the aqueous phase were as that of Zn²⁺ and Fe³⁺ decreases with increasing ions NO₃⁻ and Cl⁻.
(iv) The adsorption of all the metal ions decreases with increasing SO₄²⁻ ion concentration in the aqueous phase which may be attributed to the very low stability constants of SO₄²⁻.
(v) From the results of distribution ratios it can be observed that among five metal ions studied for the ion exchange properties, all the polymers show highest affinity for Ni\textsuperscript{2+} whereas least affinity for the Zn\textsuperscript{2+}.

(vi) The results of the rate of metal uptake shows that Zn\textsuperscript{2+} and Fe\textsuperscript{3+} metal ions are adsorbed at higher speed compare to Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, and Co\textsuperscript{2+} metal ions.

(vii) Due to the considerable difference between the adsorption capacity at different pH, rate of metal uptake and distribution ratio at equilibrium, it may be possible to use the polymers for separation of particular metal ions from their admixtures.