Synthesis: The monomer, 8-quinolinyl acrylate (8-QA), its homo-and copolymers
2.1 INTRODUCTION

The chemistry of the functional monomers and polymers containing 8-hydroxy quinoline (8-HQ) or its derivatives has received considerable attention in recent years. These materials find numerous applications in many fields of modern science and technology due to their antimicrobial and ion-exchange properties [1-3].

The survey of literature reveals that there are some reports on the synthesis of monomeric and polymeric derivatives of 8-HQ. Kirienko and co-workers [4-6] synthesized several acrylic esters by esterification of alkali metal salts of halogen and alkyl substituted 8-HQs with (meth) acryloyl chloride using benzene or ethyl alcohol as a reaction medium. The resulting esters were mostly studied for their biological activity. Huber and co-workers [7] reported the synthesis of acrylic esters, useful as agricultural fungicides, by reacting 5-chloro-7-alkyl substituted 8-HQs with acryloyl chloride. Strem [8] reported about thirty eight esters useful as commercial bactericides and fungicides. These esters were prepared by halogenation or nitration of 5-acetyl-8-HQ followed by esterification with acryloyl chloride or acetyl chloride. Polymeric 8-HQ derivatives were synthesized by modification of poly(ethylene glycol)s and poly (ξ-caprolactone)s with 5-nitro- or 5-chloro-substituted 8-HQs [9, 10]. Warshawsky and co-workers [11] prepared the polymers with 5-chloromethyl-8-HQ as a substituent in the side polymer chain by alkylation of styrene polymers and copolymers with 5-chloromethyl-8-HQ. Kim and co-workers [12] studied the ion-exchange properties of the chelate resins prepared by the condensation reaction of 8-HQ or 8-HQ-salicylic acid(S), in the presence of resorcinol (R), with formaldehyde. The ion-exchange capacity of 8-HQR and 8-HQRS resins were 4.1 and 5.9 m.equiv./g respectively and maximum adsorption and distribution of various metal ions such as Cu(II), Pb(II), Co(II), Ni(II) and Fe(III) in these resins was observed at pH 7. Aristov [13] reported the copolymers of 5-(Hydroxymethyl)-8-HQ alkyl ether with styrene and MMA and studied the thermal stability and softening points of pure copolymers and soluble thermoplastic polychelates based on them. Slovak and co-workers [14] reported that 8-HQ, bound to an azo group and a flexible side chain of a hydrophilic macroporous copolymer of glycol mono-and dimethacrylate, possesses high selectivity for heavy metal ions with the exchange capacity of ~ 0.2 m.mol.g⁻¹. The use of these copolymers in the chromatographic metal separations,
trace analysis and selective purification of concentrated salt solutions was also discussed.

Balakin and co-workers [15] prepared complex forming modified anion exchangers with high ion-exchange capacity, predominantly for Cu-ions, by chemical modification of polyethylene-polyamine type anion exchanger with equimolar ratio of anion exchanger with 8-HQ in excess HCHO in ethanolic solution. They found that an increase in the number of 8-HQ groups in the modified resins increases the static ion-exchange capacity for 0.06 N CuSO₄ solution at pH 1.5. Pittman and co-workers [16] studied the fungicidal properties of the vinyl acetate and ethyl acrylate copolymer coating films prepared by incorporating 0-5 mol % comonomers such as 8-quinolinyl acrylate and pentachlorophenylacrylate and found that the resulting coating film shows good fungal resistance against many deteriorating fungi. Rashkov and co-workers [17] synthesized polyethers with 5-nitro-8-quinolinolxy terminated end groups and studied the microbial activity against some gram +ve and gram-ve microorganisms. Bankova and co-workers [18-19] synthesized homopolymers of 5-chloro-8-quinolinyl (meth)acrylate and their copolymers with hydrophilic monomers such as (meth)acrylic acid N-vinyl pyrrolidone and studied the interpolymer complex formation between polyacids and polybases segments, i.e. PAA and PMAA with P(8-QA), P(8-QMA) and PVP. They also evaluated the antibacterial activity of the homo- and co-polymers against some selected microorganisms. Durand and co-workers [20] copolymerized various R-Silyl methacrylates (where R=C₁) t-butyldimethyl, (2) t-butyldiphenyl and (3) diphenylmethyl with MMA at 60°C in bulk and determined the reactivity ratios. The influence of R-substituents was also studied and it was found that the phenyl substituent deactivated the macroradicals during the polymerization and accordingly the monomer reactivities were found to be in order of 1 > 2 > 3.

The present chapter deals with the synthesis and characterization of the monomer as well as the synthesis of the homo- and copolymers using different monomer feed ratios and determination of the copolymer composition by UV spectroscopy. Accordingly, the present chapter is divided into two parts as follows: [A] Monomer Synthesis and characterization. [B] Homo-and copolymers synthesis and copolymer composition.
PART - A
SYNTHESIS AND CHARACTERIZATION OF MONOMER (8-QA)

2[A].1 EXPERIMENTAL

(a) Materials :-

All the chemicals used during the study were of analytical grade reagents. The solvents and monomers were purified by the conventional methods[21].

(b) Synthesis of acryloyl chloride :-

Acryloyl chloride was prepared according to the process reported in the literature [22]. A mixture of acrylic acid (1mol), benzoyl chloride (2 mols) and hydroquinone (0.0025 mol) was distilled at a fairly high rate through an efficient column. The distillate was collected in a receiver containing hydroquinone(0.0025 mol). The product was obtained at a temperature between 70-80°C. The crude product was redistilled through the same column. The pure acryloyl chloride was distilled out at 72-76°C. The product yield was 68%.

\[
\text{CH}_2=\text{CH} + \text{C}_8\text{H}_5\text{COCl} \rightarrow \text{CH}_2=\text{CH} + \text{C}_8\text{H}_5\text{COOH} \\
\text{COOH} \quad \text{COCI}
\]

(c) Synthesis of 8-quinolinyl acrylate(8-QA) :-

The esterification was performed with acryloyl chloride and 8-HQ. To a one liter three necked flask, equipped with stirrer, condensor and thermometer and placed in a water-bath, absolute alcohol(400 ml) and NaOH(0.2 mol, 8.0 g) were added and the contents were stirred until all the NaOH dissolved. To this, finely powdered 8-HQ (0.2 mol, 29.0 g) was added. The reaction mixture was heated to 60°C for 30 min with stirring, cooled to room temperature and then to 0-5°C by ice. To the cooled reaction mixture freshly prepared acryloyl chloride (0.21 mol, 17.1 ml) was added dropwise within 60 min. The reaction temperature was maintained to 0-5°C during the addition. After completion of the addition reaction mixture was stirred for 90 min and it was poured into crushed ice-water mixture where a light yellow colored product was separated out. It was filtered out, washed thoroughly with cold water, dried at 40°C in vacuum and recrystallized from petroleum ether. The recrystallized product yield was 62%.
2[A].1.1 CHARACTERIZATION OF 8-QA

(a) FT-IR Spectrophotometry :-
NICOLET-400D FT-IR spectrophotometer was used to record the infra-red spectrum of 8-QA in the KBr dispersed pellet form.

(b) ¹H-NMR Spectroscopy :-
HITACHI-R-1500 permanent magnet FT-NMR spectrometer (60MHz) was used for recording the NMR spectrum. CDCl₃ and tetramethyl silane (TMS) were used as a solvent and internal standard respectively.

(c) Elemental analysis :-
FOSS-HAREAUS CHN-O rapid elemental analyzer was used for the elemental analysis. The system was calibrated with the acetanilide standard.

(d) High performance liquid chromatography (HPLC) :-
WATERS HPLC system equipped with 600E multisolvent delivery pump, U6K injector, µ-bondapak C₁₈ column, 991-photodiode array detector (PDA) and NEC powermat 386/25 data acquisition and processing unit loaded with 991-PDA data processing software was used. Methanol at 1 ml/min flow rate was used as a mobile phase and 10 µl 0.05 % methanolic sample solution was injected for the analysis.

(e) Differential scanning calorimetry (DSC) :-
Du Pont-910 differential scanning calorimeter attached with 9900 thermal analyzer data acquisition and processing unit was used. About 5 mg sample was sealed in an aluminium pan and DSC scan was recorded in a nitrogen atmosphere at 10°C/min heating rate. The data processing was done using du-Pont V1.1A purity determination software.
2[A].2 RESULTS AND DISCUSSION

The monomer, 8-QA, obtained in a light yellow colored powder form soluble in the common organic solvents like acetone, methanol, chloroform, THF, aromatic solvents etc. but it is insoluble in water. Fig. 2.1 shows the IR spectrum of 8-QA. All the important absorption bands required for confirming the structure of the ester are observed and are tentatively assigned as follows: 1730 cm\(^{-1}\) (\(\nu_{C=O}\)), 1635 cm\(^{-1}\) (\(\nu_{C-C}\)), 1310 cm\(^{-1}\) (\(\nu_{C-O}\)), 1230 and 1160 cm\(^{-1}\) (\(\nu_{C-O-C}\)), 970 and 950 cm\(^{-1}\) (\(\nu_{\text{out of plane banding mode of vinyl group}}\)), 880 and 860 cm\(^{-1}\) (\(\nu_{\text{rocking mode of vinyl group}}\)). The three absorption bands at 1590, 1500 and 1470 cm\(^{-1}\) may be assigned as the characteristic absorption of 8-0-substituted quinolinyl ring [23,24].

Fig.2.2 shows the \(^1\)H-NMR spectrum of 8-QA. All the expected signals are observed, but due to low sensitivity of the instrument (60 MHz), spin-spin coupling is not properly resolved. The signal at \(\delta\) 5.977 - 6.279 ppm is attributed to the \(\text{He}\) proton of the vinyl group. The signal at \(\delta\) 6.553 - 6.689 ppm is attributed to the two non-equivalent protons (\(\text{H}_a\) and \(\text{H}_b\)) of the methylene group. For six aromatic protons of the quinolinyl moiety there are three different signals observed in the aromatic region. The multiplet between \(\delta\) 7.266-7.803 ppm may be attributed to four equal protons i.e. \(\text{H}_3\), \(\text{H}_4\), \(\text{H}_5\) and \(\text{H}_6\) whereas two doublets of nearly equal intensities at \(\delta\) 8.076-8.203 and 8.877-8.926 ppm are due to \(\text{H}_7\) and \(\text{H}_2\) protons respectively. The resonance signals of the aromatic protons were shifted towards the lower field compared to those of 8-HQ due to ester bonding of quinolinyl group with the vinyl group [25].

The practically found values of the elemental analysis of 8-QA are very close to that of theoretical values. Both, practically found and theoretical values are as follows.

<table>
<thead>
<tr>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical :</td>
<td>72.36</td>
<td>4.52</td>
<td>7.04</td>
</tr>
<tr>
<td>Found :</td>
<td>72.37</td>
<td>4.53</td>
<td>7.00</td>
</tr>
</tbody>
</table>

The HPLC Chromatogram of the 8-QA is shown in the fig. 2.3. It is apparent from the liquid chromatogram that the ester prepared has the chromatographic purity of 100%. Fig. 2.4 shows the DSC thermogram of 8-QA. The endothermic peak shown in the
Fig : 2.1 FT-IR Spectrum of 8-QA monomer
Fig. 2.2 FT-NMR Spectrum of 8-QA monomer
Fig. 2.3 HPLC chromatogram and analysis report of 8-QA monomer
Fig: 2.4 DSC thermogram and analysis report of 8-QA monomer

- Purity: 94.97 mol %
- Melting Point: 49.2 °C
- Depression: 2.28 °C
- ΔH: 19.0 kJ mol⁻¹
- Correction: 20.00%
- Mol. Weight: 199.2 g mol⁻¹
- Cell Const.: 1.245
- Onset slope: -9.77 mW/°C
thermogram shown is the melting transition of 8-QA. The values of calorific purity, melting point and ΔH are 94.97%, 49.2 °C and 19.0 kJ mol⁻¹ respectively. The difference in the values of chromatographic and calorific purity of 8-QA may be justified as the limitation of the DSC method [26].

PART -B
SYNTHESIS OF HOMO- / COPOLYMERS OF 8-QA AND COMPOSITION

2[B].1 EXPERIMENTAL
(a) General Procedure for synthesis of homo- and copolymers:–
Homo-and co-polymerization of 8-QA and other vinyl monomers was carried out in solution using free radical technique. 8-QA and/or other vinyl monomer in a different proportions (as listed in Table 2.1 to 2.5) were placed in a round bottom flask equipped with mechanical stirrer and reflux condenser. To this, dimethyl formamide (50% w/v) and AIBN (1% w/w of total monomer(s) weight) were added. The reaction mixture was heated at 70°C with constant stirring and maintained for 5 hr. After that, it was cooled to a room temp. and slowly poured in a large volume of methanol as a precipitant, with constant stirring, where solid polymer was precipitated out, which was then filtered, washed thoroughly with methanol and hot water and dried in vacuum at 60°C till constant weight (see reaction schemes).

(b) Determination of the copolymer composition:–
The composition of 8-QA in the copolymers was determined by UV-spectrophotometry. Shimadzu-l60A-recording UV-visible spectrophotometer was used for this study. The whole experiment was conducted in a three part using chloroform as a solvent and reference standard as follows.
(1) Determination of $\lambda_{\text{max}}$ for 8-QA:–
The maximum absorption ($\lambda_{\text{max}}$) of the dilute solution of 8-QA in chloroform was determined by scanning the ultraviolet spectrum in the wavelength range of 200-400nm using chloroform as a reference standard. The $\lambda_{\text{max}}$ of 8-QA in chloroform was found 281 nm.
Table 2.1

Reaction Parameters for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and methyl methacrylate (MMA)

Solvent: Dimethyl formamide (DMF) (50% w/v)
Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight)
Reaction Size: 10 gm.
Reaction Temperature: 70 ± 2°C
Reaction Time: 5 hr.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code No.</th>
<th>Designation of Polymer/Copolymer</th>
<th>Monomer feed Composition</th>
<th>Composition of 8-QA in copolymer</th>
<th>Yield (%)</th>
<th>Softening range (°C)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8-QA</td>
<td>MMA</td>
<td>mol.</td>
<td>gms.</td>
</tr>
<tr>
<td>1</td>
<td>P-1</td>
<td>P(8-QA)</td>
<td>0.0503</td>
<td>10</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>P-2</td>
<td>P(8-QA-co-MMA) 50:50</td>
<td>0.0252</td>
<td>05</td>
<td>50</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>P-3</td>
<td>P(8-QA-co-MMA) 40:60</td>
<td>0.0201</td>
<td>04</td>
<td>40</td>
<td>0.06</td>
</tr>
<tr>
<td>4</td>
<td>P-4</td>
<td>P(8-QA-co-MMA) 30:70</td>
<td>0.0151</td>
<td>03</td>
<td>30</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>P-5</td>
<td>P(8-QA-co-MMA) 20:80</td>
<td>0.0101</td>
<td>02</td>
<td>20</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>P-6</td>
<td>P(8-QA-co-MMA) 10:90</td>
<td>0.0050</td>
<td>01</td>
<td>10</td>
<td>0.09</td>
</tr>
<tr>
<td>7</td>
<td>P-7</td>
<td>PMMA</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.10</td>
</tr>
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</table>
Table 2.2
Reaction Parameters for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and styrene (S)

| Solvent: Dimethyl formamide (DMF) (50% w/v) |
| Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight) |
| Reaction Size: 10 gm. |
| Reaction Temperature: 70 ± 2°C |
| Reaction Time: 5 hr. |

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code No.</th>
<th>Designation of Polymer/Copolymer</th>
<th>Monomer feed Composition</th>
<th>Composition of 8-QA in copolymer</th>
<th>Yield (%)</th>
<th>Softening range (°C)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8-QA</td>
<td>Styrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mol.</td>
<td>gms.</td>
<td>%Wt.</td>
<td>mol.</td>
</tr>
<tr>
<td>8</td>
<td>P-8</td>
<td>P(8-QA-co-S) 50:50</td>
<td>0.0252</td>
<td>05</td>
<td>50</td>
<td>0.0481</td>
</tr>
<tr>
<td>9</td>
<td>P-9</td>
<td>P(8-QA-co-S) 40:60</td>
<td>0.0201</td>
<td>04</td>
<td>40</td>
<td>0.0577</td>
</tr>
<tr>
<td>10</td>
<td>P-10</td>
<td>P(8-QA-co-S) 30:70</td>
<td>0.0151</td>
<td>03</td>
<td>30</td>
<td>0.0673</td>
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<tr>
<td>11</td>
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<td>P(8-QA-co-S) 20:80</td>
<td>0.0101</td>
<td>02</td>
<td>20</td>
<td>0.0769</td>
</tr>
<tr>
<td>12</td>
<td>P-12</td>
<td>P(8-QA-co-S) 10:90</td>
<td>0.0050</td>
<td>01</td>
<td>10</td>
<td>0.0865</td>
</tr>
<tr>
<td>13</td>
<td>P-13</td>
<td>PS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0962</td>
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</table>
Table 2.3

Reaction Parameters for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and n-butyl methacrylate (BMA)

Solvent: Dimethyl formamide (DMF) (50% w/v)
Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight)
Reaction Size: 10 gm.
Reaction Temperature: 70 ± 2°C
Reaction Time: 5 hr.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code No.</th>
<th>Designation of Polymer/Copolymer</th>
<th>Monomer feed Composition</th>
<th>Composition of 8-QA in copolymer</th>
<th>Yield (%)</th>
<th>Softening range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>P-14</td>
<td>P(8-QA-co-BMA) 50:50</td>
<td>0.0252 mol. 0.0352 mol.</td>
<td>49.09</td>
<td>90</td>
<td>112 - 130</td>
</tr>
<tr>
<td>15</td>
<td>P-15</td>
<td>P(8-QA-co-BMA) 40:60</td>
<td>0.0201 mol. 0.0423 mol.</td>
<td>38.13</td>
<td>92</td>
<td>110 - 122</td>
</tr>
<tr>
<td>16</td>
<td>P-16</td>
<td>P(8-QA-co-BMA) 30:70</td>
<td>0.0151 mol. 0.0493 mol.</td>
<td>28.88</td>
<td>91</td>
<td>100 - 118</td>
</tr>
<tr>
<td>17</td>
<td>P-17</td>
<td>P(8-QA-co-BMA) 20:80</td>
<td>0.0101 mol. 0.0563 mol.</td>
<td>20.06</td>
<td>89</td>
<td>89 - 109</td>
</tr>
<tr>
<td>18</td>
<td>P-18</td>
<td>P(8-QA-co-BMA) 10:90</td>
<td>0.0050 mol. 0.0634 mol.</td>
<td>09.08</td>
<td>96</td>
<td>-</td>
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<tr>
<td>19</td>
<td>P-19</td>
<td>PBMA</td>
<td>-</td>
<td>09.08</td>
<td>98</td>
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</table>
Table 2.4

Reaction Parameters for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and methyl acrylate (MA)

Solvent: Dimethyl formamide (DMF) (50% w/v)
Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight)
Reaction Size: 10 gm.
Reaction Temperature: 70 ± 2°C
Reaction Time: 5 hr.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code No.</th>
<th>Designation of Polymer/Copolymer</th>
<th>Monomer feed Composition</th>
<th>Composition of 8-QA in copolymer</th>
<th>Yield (%)</th>
<th>Softening range (°C)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>8-QA</td>
<td>MA</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mol.</td>
<td>gms.</td>
<td>%Wt.</td>
<td>mol.</td>
</tr>
<tr>
<td>20</td>
<td>P-20</td>
<td>P(8-QA-co-MA) 50 : 50</td>
<td>0.0252</td>
<td>05</td>
<td>50</td>
<td>0.0581</td>
</tr>
<tr>
<td>21</td>
<td>P-21</td>
<td>P(8-QA-co-MA) 40 : 60</td>
<td>0.0201</td>
<td>04</td>
<td>40</td>
<td>0.0698</td>
</tr>
<tr>
<td>22</td>
<td>P-22</td>
<td>P(8-QA-co-MA) 30 : 70</td>
<td>0.0151</td>
<td>03</td>
<td>30</td>
<td>0.0814</td>
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<tr>
<td>23</td>
<td>P-23</td>
<td>P(8-QA-co-MA) 20 : 80</td>
<td>0.0101</td>
<td>02</td>
<td>20</td>
<td>0.0930</td>
</tr>
<tr>
<td>24</td>
<td>P-24</td>
<td>P(8-QA-co-MA) 10 : 90</td>
<td>0.0050</td>
<td>01</td>
<td>10</td>
<td>0.1047</td>
</tr>
<tr>
<td>25</td>
<td>P-25</td>
<td>PMA</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.1163</td>
</tr>
</tbody>
</table>
Table 2.5

Reaction Parameters for the solution (co)polymerization of 8-quinolinyl acrylate (8-QA) and vinyl acetate (VAc)

Solvent: Dimethyl formamide (DMF) (50% w/v)
Initiator: Azobisisobutyronitrile (AIBN) (1% w/w of total monomer(s) weight)
Reaction Size: 10 gm.
Reaction Temperature: 70 ± 2°C
Reaction Time: 5 hr.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code No.</th>
<th>Designation of Polymer/Copolymer</th>
<th>Monomer feed Composition</th>
<th>Composition of 8-QA in copolymer (%)</th>
<th>Yield (%)</th>
<th>Softening range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>P-26</td>
<td>P(8-QA-co-VAc) 50:50</td>
<td>0.0252 05 50 0.0581 05 50</td>
<td>78.70</td>
<td>51</td>
<td>108 - 122</td>
</tr>
<tr>
<td>27</td>
<td>P-27</td>
<td>P(8-QA-co-VAc) 40:60</td>
<td>0.0201 04 40 0.0698 06 60</td>
<td>70.81</td>
<td>42</td>
<td>98 - 121</td>
</tr>
<tr>
<td>28</td>
<td>P-28</td>
<td>P(8-QA-co-VAc) 30:70</td>
<td>0.0151 03 30 0.0814 07 70</td>
<td>58.02</td>
<td>47</td>
<td>96 - 108</td>
</tr>
<tr>
<td>29</td>
<td>P-29</td>
<td>P(8-QA-co-VAc) 20:80</td>
<td>0.0101 02 20 0.0930 08 80</td>
<td>31.04</td>
<td>40</td>
<td>–</td>
</tr>
<tr>
<td>30</td>
<td>P-30</td>
<td>P(8-QA-co-VAc) 10:90</td>
<td>0.0050 01 10 0.1047 09 90</td>
<td>18.98</td>
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<td>–</td>
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<tr>
<td>31</td>
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<td>PVAc</td>
<td>– – – 0.1163 10 100</td>
<td>–</td>
<td>92</td>
<td>–</td>
</tr>
</tbody>
</table>
Reaction schemes:

(1) For P-1:

\[ \text{CH}_2=\text{CH} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_2=\text{CH} \]

\[ \text{C}_6\text{H}_5\text{N}_\text{N} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{C}_6\text{H}_5\text{N}_\text{N} \]

8-QA \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{P}(8-\text{QA})

(2) For P-2 to P-6:

\[ \text{CH}_2=\text{CH} \quad + \quad \text{CH}_3 \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_2=\text{CH} \]

\[ \text{C}_6\text{H}_5\text{N}_\text{N} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{C}_6\text{H}_5\text{N}_\text{N} \]

8-QA \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{MMA} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_3 \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_3 \]

\[ \text{OCH}_3 \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{OCH}_3 \]

P(8-QA) \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{P}(\text{MMA})

(3) For P-7:

\[ \text{CH}_3 \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_3 \]

\[ \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_3 \]

\[ \text{C}_6\text{H}_5\text{N}_\text{N} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{C}_6\text{H}_5\text{N}_\text{N} \]

MMA \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{P}(\text{MMA})

(4) For P-8 to P-12:

\[ \text{CH}_2=\text{CH} \quad + \quad \text{CH}_3=\text{CH} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_2=\text{CH} \]

\[ \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{CH}_2=\text{CH} \]

\[ \text{8-QA} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{Styrene} \quad \xrightarrow{\text{AIBN/70 °C, DMF/5 hr.}} \quad \text{P}(8-\text{QA}) \]
(5) For P-13:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \xrightarrow{\text{AIBN/70°C}} \quad \text{CH}_2-\text{CH} \quad \xrightarrow{\text{DMF/5 hr.}} \quad \text{P (ST)} \\
\text{Styrene} & \quad \quad \\
\end{align*}
\]

(6) For P-14 to P-18:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{CH}_2\text{=C} & \quad \text{CH}_2=\text{CH} & \quad \xrightarrow{\text{AIBN/70°C}} & \quad \text{CH}_2-\text{CH} \quad \xrightarrow{\text{DMF/5 hr.}} & \quad \text{P (n-BMA)} \\
\quad & \quad \quad & \quad & \quad & \quad & \quad \\
\text{8-QA} & \quad & \quad & \quad & \quad & \quad \\
\end{align*}
\]

(7) For P-19:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{CH}_2\text{=C} & \quad \xrightarrow{\text{AIBN/70°C}} & \quad \text{CH}_2-\text{CH} \quad \xrightarrow{\text{DMF/5 hr.}} & \quad \text{P (n-BMA)} \\
\quad & \quad & \quad & \quad & \quad \\
\text{8-QA} & \quad & \quad & \quad & \quad \\
\end{align*}
\]

(8) For P-20 to P-24:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{CH}_2\text{=C} & \quad \xrightarrow{\text{AIBN/70°C}} & \quad \text{CH}_2-\text{CH} \quad \xrightarrow{\text{DMF/5 hr.}} & \quad \text{P (n-BMA)} \\
\quad & \quad & \quad & \quad & \quad \\
\text{8-QA} & \quad & \quad & \quad & \quad \\
\end{align*}
\]
(9) For P-25:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \overset{\text{AIBN/70 °C}}{\longrightarrow} \quad \text{CH}_2-\text{CH} \quad \text{P}(\text{MA}) \\
\text{C}=\text{O} \quad \overset{\text{DMF/5 hr.}}{\longrightarrow} \\
\text{OCOCH}_3
\end{align*}
\]

(10) For P-26 to P-30:

\[
\begin{align*}
\text{CH}_2=\text{CH} \quad + & \quad \overset{\text{AIBN/70 °C}}{\longrightarrow} \quad \text{CH}_2-\text{CH} \quad \text{P}(\text{VAc}) \\
\text{C}=\text{O} \quad \overset{\text{DMF/5 hr.}}{\longrightarrow} \\
\text{OCOCH}_3 \\
\text{VAC}
\end{align*}
\]

(11) For P-31:

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \overset{\text{AIBN/70 °C}}{\longrightarrow} \quad \text{CH}_2-\text{CH} \quad \text{P}(\text{VAc}) \\
\text{OCOCH}_3 \\
\text{VAC}
\end{align*}
\]
Constructing a working curve of 8-QA concentration v/s absorption:-

Ten dilute solutions of 8-QA with known and exact concentration were prepared in chloroform and absorption of each solution, at $\lambda_{\text{max}}$ of 8-QA, was recorded using chloroform as a reference standard. The values of absorption were plotted against corresponding concentration values.

Determination of the 8-QA content in the copolymers :-

A dilute solution of each copolymer, containing different amounts of 8-QA, was prepared by dissolving known and exact amount of the polymer in to the chloroform. The weight of the polymer sample taken should be such that the concentration of the resulting solution be remain within the concentration range of the working curve. The absorption of each solution was recorded, at $\lambda_{\text{max}}$ of 8-QA , using chloroform as a reference standard. By using these absorption values, the corresponding concentration values for 8-QA composition in the copolymers were findout from the working curve. The values of 8-QA content in the copolymers were converted into the appropriate units.

2[B].2 RESULTS AND DISCUSSION

The detailed experimental conditions, monomer feed ratios, copolymer composition, % yield of each experiment and softening range of the polymers are shown in the Table 2.1 to 2.5. All the homo- and copolymers, except PBMA, PMA and their copolymers with 10% 8-QA, are obtained in a light yellow colored amorphous powder form. The homopolymers of BMA and MA and their copolymers with low 8-QA content are obtained in a semisolid rubbery forms. This may be due to the low Tg of PBMA and PMA. The % yield ranges between 90-98 % for 8-QA-MMA, 32-91 % for 8-QA-Styrene, 89-98 % for 8-QA-BMA, 73-98 % for 8-QA-MA and 38-92 % for 8-QA-VAC homo-and copolymers. The lower yield in some cases may be due to the difference in the relative reactivity of each monomer during the copolymerization under specified experimental conditions. The P(8-QA) homopolymer soften in the range of 232-258°C whereas copolymers with MMA, Styrene, BMA, MA and VAc, prepared using different monomer feed ratios, soften respectively in the range of 190-226, 132-202, 89-130, 92-123 and 96-122°C depending upon the copolymer composition. Fig. 2.5 shows the values of UV-absorption of standard solutions of 8-QA in
CALIBRATION

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<th>ABS.</th>
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<tr>
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Fig: 2.6 Calibration curve of concentration v/s UV absorption for 8-QA at 281 nm

Fig: 2.5 UV absorption values for std. solution of 8-QA in CHCl₃ at 281 nm

WORKING CURVE

+2.50A
0.500 (A/DIV.)
+0.00A
0.0  CONC. 0.2000/DIV.  1.000

14:18 12/18 '96

281.0M - 0.095M

Fig: 2.6 Calibration curve of concentration v/s UV absorption for 8-QA at 281 nm
Fig : 2.7 UV spectra of 9-QA-AIMA copolymers in CHCl₃

Fig : 2.8 UV spectra of 9-QA-BMA copolymers in CHCl₃
Fig: 2.9 UV spectra of 8-QA-MA copolymers in CHCl₃.

Fig: 2.10 UV spectra of 8-QA-VAc copolymers in CHCl₃.
chloroform, measured at 281 nm ($\lambda_{\text{max}}$ for 8-QA in chloroform). These absorption values are plotted against known concentration of 8-QA which gives straight line working curve as shown in the fig. 2.6. The UV spectra of the copolymers of 8-QA with MMA, BMA, MA and VAc are respectively shown in fig. 2.7 to 2.10. From the absorption values of each copolymer solution in chloroform at 281 nm ($\lambda_{\text{max}}$), the corresponding concentration of 8-QA was determined from the working curve. Each value was converted into the % of 8-QA in the copolymer. Five different monomer feed ratios i.e. 50:50, 60:40, 70:30, 80:20 and 90:10 were taken for each monomer pair for the copolymerization. The copolymer composition data in Table 2.1 to 2.5 reveals that in case of the copolymers of 8-QA with MMA, n-BMA and MA, the values of % 8-QA in the copolymers are very close to the % values of 8-QA in the monomer feed composition, which indicates that 8-QA copolymers nearly at an equal rate with MMA, n-BMA and MA. Whereas, in case of the copolymers of 8-QA with styrene and VAc at a random and uneven rate under the specified reaction conditions. In case of styrene this may be due to the steric effect of the phenyl substituent which in turn may deactivate the growing macroradicals during copolymerization. Durand and co-workers [20] observed similar effect during the copolymerization of MMA with various phenyl substituted silyl methacrylates.
REFERENCES


