CHAPTER 6

A KINETIC STUDY ON COPOLYMERISATION OF MMA AND MA BY EMULSION TECHNIQUE
6.1. Introduction

Acrylics are generally chosen for outdoor purposes because of their unusual degree of resistance to the effects of longer exposure to sunlight, heat and weathering and they are much superior to styrene, polyvinyl chloride polyvinyl acetate and cellulose polymers. Depending upon the selection of monomer and method of polymerization they can be prepared from very low viscous materials to high viscous materials and solids. These are arbitrary terms that are used to describe polymer products and in general it can be said that lower the molecular weight softer the material and the higher the molecular weight tougher the material. The acrylic ester polymers can range from oily liquids to liquids and solids. The difference lies only in the degree of polymerization, and whether they belong to high, low or average molecular weight. The physical nature of the polymer is dependent on the monomer or combination of monomers used. In general, the lower acrylic esters are softer materials, ranging from the very soft and tacky 2-ethylhexyl acrylate and n-butyl acrylate to the tough but quite flexible methyl acrylate. The methacrylic esters are somewhat harder whereas esters of higher homologues range from amorphous to waxy polymers. The methods of polymerization and the variation of these methods can be classified into three main groups.

They are

1. Polymerization in bulk
2. Polymerization in solution
3. Polymerization in heterogeneous systems.

In bulk polymerization, the polymerization is carried out without any diluents, and this is the method used to make cast rods, sheets and tubes. Where as in solution
polymerization the monomer is added to an organic solvent and polymerization is in homogeneous solution in which both the monomer and the polymer are soluble. Solvents like ethyl acetate, toluene and acetone are used with acrylic esters. Catalysts generally used are benzoyl peroxide, lauryl peroxide and t-butyl peroxide which are soluble in the system. Some control over the molecular weight is possible by varying the amount of catalyst, ratio of solvent to monomer and reaction temperature, although the polymers obtained by solution polymerization have low molecular weight. Whereas heterogeneous polymerization is mainly divided into emulsion polymerization, suspension polymerization and granular polymerization. The emulsion polymerization is carried by dissolving a water soluble emulsifier and water soluble initiator. The monomer is polymerized in dispersed phase by agitation at 70-90°C. The growing interest in multicomponent polymerizations from both industry and academia has uncovered the need for a more systematic approach to the study of such systems. The aim of such a study is to understand the fundamental physico-chemical phenomena and thus, the production of improved paints, adhesives, waxes, coatings and plastisols. The approach consists of using mathematical modeling and experimental kinetics to examine all levels of the multicomponent polymerization-firstly to study the homopolymerization systems, followed by each of the copolymerization systems and continue with multicomponent polymerization system(s). In published studies on emulsion copolymerization, the main interest has been on explaining the copolymer composition and the differences in composition formed in emulsion vs. bulk copolymerization systems.

Recent interest in synthetic emulsion polymerization products has shifted from mass produced solid materials to specialty products such as paints, adhesives and binders.
These lattices have strict product specifications and hence, the commercial process must be carried out under controlled conditions. The problem of meeting product specifications is particularly acute when monomers with widely different reactivity ratios are polymerized. Traditionally, the control of the composition has been achieved by carrying out the polymerization under starved conditions. The kinetic behavior of emulsion polymerization is greatly affected by radical desorption from polymer particles [1-10].

The deviation of the kinetic behavior of the emulsion polymerization of water soluble monomers such as vinyl acetate and vinyl chloride from the Smith-Ewart case II kinetic theory [11] is partially due to dominant desorption of radicals from the polymer particles. Although Smith and Ewart pointed out the importance of this physical phenomenon in the 1940s, the quantitative understanding was insufficient to explain the kinetic deviation of the emulsion polymerization of vinyl acetate or vinyl chloride from the Smith-Ewart case II kinetic theory.

It is well known that the nature of the polymerization process can affect the kinetic behavior, microstructure, molecular weight, and homogeneity of the resulting polymers [12-16]. The purpose of present work is to study the effect of change in initiator concentration on MMA-MA copolymer in batch emulsion polymerization technique.

6.2 Experimental

6.2.1 Materials

Methyl methacrylate (MMA), methyl acrylate (MA) (Aldrich) were purified by treating with 5% solution of sodium hydroxide to remove the inhibitor and then washed with water and distilled under reduced pressure. Benzoyl peroxide was dissolved in
chloroform and then double the amount of methanol was added for recrystallization to remove water [17].

6.2.2 Emulsion copolymerization

Distilled water (100 mL) and surfactant sodium lauryl sulphate (1g) were taken in a four-neck round bottom flask fitted with overhead stirrer, condenser and a dropping funnel and a septum. The flask was flushed with Iolar grade nitrogen and this inert atmosphere was maintained throughout the experiment. The contents of the flask were heated to 70 ± 5° C. The monomer mixture, as shown in table 1, was added through the dropping funnel at a time. The initiator potassium persulphate (0.05 g) dissolved in distilled water (10 mL) separately was added through the top of the condenser before the addition of the monomer mixture. After the addition of the monomer mixture, a sample of 2 mL was drawn from the flask through the septum then, polymerization was continued and for every 15 min, the sample of each 2mL was drawn from the reaction flask through the septum and was taken in to vials containing 0.1g of hydroquinone for quenching. About 10-12 samples were drawn from the reaction kettle, and then the reaction was continued further for 30 min for complete polymerization. The emulsion was then cooled to 30° C and stored in glass bottles. In all the experiments the solid content was maintained at 40 (by weight). The viscosities of polymer emulsions were determined by using Brookfield viscometer (spindle No. 1, 50 rpm). The viscosities (m.Pa s) of the emulsions are given in table 1.
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Table 1:

Compositions of MMA- co-MA

<table>
<thead>
<tr>
<th>Serial No</th>
<th>MMA:MA (moles)</th>
<th>Viscosity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:3</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>1:1</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>3:1</td>
<td>98</td>
</tr>
</tbody>
</table>

6.2.3 Characterization

The gravimetric analysis was based on total polymer. Approximately a 2-3mL aliquot of the reaction mixture was taken out from the reaction flask in to the vials having 0.1g of hydroquinone using a syringe at regular intervals, and kept in ice-cold bath for 2-3h for quenching. The overall conversion of monomer to polymer is estimated by transferring the samples in the vials quantitatively into the pre-weighed petridishes. It is kept in oven at 50°C for 24h and then weighed. The percentage solids and percentage conversion of total monomer mixture to polymer is given by the relation [18].

\[
\text{% Solids} = \frac{(\text{Weight of dried sample and dish}) - (\text{weight of the empty dish})}{(\text{Weight of sample taken and dish}) - (\text{weight of the empty dish})} \times 100
\]

The sample also included solid residues other than polymer, so these residues (emulsifier, initiator, etc.) were taken into account to calculate conversion. The samples were corrected for the non-polymeric solid content from knowledge of the initial charge. The conversion was calculated by
(% Solids /100) - (Weight fraction of) - (Weight fraction of) 
Initiator  emulsifier
% Conversion = ______________________________________________________
Weight fraction of monomer

6.2.4 Isolation of polymer from emulsion

The isolation of pure polymer is effected by precipitating the emulsion with methanol and repeated by washing with methanol. The precipitated polymer is dried at 50°C in the oven for 24 h. It is then soaked in large amount of water to remove the absorbed emulsifier in the polymer. It is dried again in the oven at 50°C for 24h.

6.2.5 Spectral characterization of acrylic copolymers

The acrylic copolymers were characterized by using IR & NMR technique to find out the presence of free monomers if any. \textsuperscript{1}H NMR technique was used essentially to identify the acrylic copolymers. The spectra were recorded using Gemini 200 MHz coupled with a computer. The final emulsions were precipitated using acetic acid and separated polymer powder was filtered. The powder was washed several times with water to remove acetic acid till the washing is neutral to pH. The samples were then dried and were used in the form of solutions in CDCl\textsubscript{3} at ambient temperatures. Tetramethylsilane (TMS) was used as an internal standard. The absence of peaks between 4 –5 ppm (-CH=CH\textsubscript{2}) indicates the absence of free monomer in the copolymer. All the combinations of acrylic monomers contain ester group, which is indicated by the presence of peak at 3.5 –3.7 ppm. The weight average (\( \overline{M_w} \)) and number average (\( \overline{M_n} \)) molecular weights and molecular weight distribution (\( \overline{M_w}/\overline{M_n} \)) of the each copolymer were determined by using GPC.
6.3 Results and discussion

6.3.1 Synthesis of methyl methacrylate and methyl acrylate copolymers

The copolymer is prepared using methyl methacrylate and methyl acrylate with various concentrations of potassium persulphate as initiator (0.05% to 0.125%). The block copolymer is formed due to the difference in reactivities of methyl methacrylate and methyl acrylate [19].

\[
\text{CH}_3\text{CH} = \text{C} + \text{n CH}_2 = \text{CH} \rightarrow \text{m CH}_2\text{-C} = \text{m COOCH}_3 \quad \text{CH}_3\text{CH} = \text{CH} \rightarrow \text{m CH}_2\text{-C} = \text{m COOCH}_3
\]

Three compositions in the ratio of 1:3, 1:1 and 3:1 MMA: MA were prepared and effect of initiator concentration on its rate of copolymerization was studied. The conversion versus time was plotted; from the slope of straight-line portion of the curves the rate of copolymerization is calculated.

\[
\text{Slope} \quad \text{Rate of copolymerization} = \frac{\text{Slope}}{60} \quad \text{L/mol/s}
\]

6.3.2 Effect of initiator concentration on the rate of copolymerization of MMA and MA in 1:3 ratio

The rate of copolymerization increases with increase in initiator concentration from $1.3 \times 10^{-4}$ to $3.3 \times 10^{-4}$ L/mol/s. In initial stage, the rate of polymerization depends

\[
\text{CH}_3\text{CH} = \text{C} + \text{n CH}_2 = \text{CH} \rightarrow \text{m CH}_2\text{-C} = \text{m COOCH}_3 \quad \text{CH}_3\text{CH} = \text{CH} \rightarrow \text{m CH}_2\text{-C} = \text{m COOCH}_3
\]
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only on initiator concentration, which follows first order kinetics even though the reactivity of MMA, is very high; most of MMA droplets will be in aqueous phase and do not influence the rate of copolymerization. With increase in time, diffusion of MMA droplets to the polymer particle takes place and it influences the rate of copolymerization showing a steep increase in rate up to certain inflection point in which the order is II. After the inflection point, the monomer concentration reduces and it does not influence the rate of polymerization following first order kinetics.

Table 2

Effect of initiator concentration on the rate of copolymerization of monomers MMA and MA in 1:3 ratios

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Initiator concentration (%)</th>
<th>Rate of copolymerization ($R_p$) $1 \times 10^{-4}$ L/mol/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>0.075</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>3.3</td>
</tr>
</tbody>
</table>
6.3.3. Effect of initiator concentration on the rate of copolymerization of MMA and MA in 1:1 ratio

It has been found that the rate of copolymerization increases from $0.7 \times 10^{-4}$ L/mol/s to $2.5 \times 10^{-4}$ L/mol/s with increase in initiator concentration. The rate of copolymerization depends on initiator concentration initially, which is first order kinetics and then depends on monomer concentration also showing a steep rise in rate (second order kinetics). After the inflection point, the monomer concentration gradually reduces and it depends only on initiator concentration. Even though, two monomers MMA & MA were taken in equal parts, the polymer formed is generally block type copolymer due to the difference in reactivity ratios of monomers.
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Table 3: Effect of initiator concentration on rate of copolymerization of monomers MMA: MA in 1:1 ratio

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Initiator concentration (%)</th>
<th>Rate of copolymerization ($R_p$) $1 \times 10^4$ L/mol/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>0.77</td>
</tr>
<tr>
<td>2</td>
<td>0.075</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>2.50</td>
</tr>
</tbody>
</table>

![Graph](image)

Fig 2: Effect of initiator concentration on rate of copolymerization in 1:1 ratio of monomers MMA and MA

6.3.4. Effect of initiator concentration on the rate of copolymerization of MMA and MA in 3:1 ratio

Rate of copolymerization increases from $0.19 \times 10^{-4}$ to $0.5 \times 10^{-4}$ L/mol/s with increase initiator concentration from 0.05 to 0.125%. Initially, the rate of
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Copolymerization is dependent on initiator concentration only following first order kinetics. The time taken for the conversion of first order to second order is high due to the following reasons.

1. Low reactivity of methyl acrylate
2. Higher concentration of methyl methacrylate
3. High solubility of methyl acrylate

Table 4

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Initiator concentration (%)</th>
<th>Rate of copolymerization (R_P) 1 x 10^-4 L/mol/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>0.075</td>
<td>0.23</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Due to less reactivity and high solubility of methyl acrylate, the rate of copolymerization depends only on initiator concentration for a certain period of time. The above copolymers do not follow the Smith-Ewart case II kinetics that states the rate of polymerization containing constant number of radicals is independent of initiator concentration.
6.3.5 IR spectroscopy

The IR spectra of the copolymer showed peak due to C-C stretching of alkyl group at 2980-2990 cm\(^{-1}\) and C=O (stretching) of ester group at 1740 cm\(^{-1}\). The absence of peak around 1680 cm\(^{-1}\) confirms the absence of unreacted monomer (fig 4).
6.3.6. $^1$H NMR spectroscopy

$^1$H NMR spectrum of the copolymer sample shows the peaks due to CH$_3$ (0.9 ppm) (saturated 1.1 ppm), CH$_2$ (saturated (1.4ppm) and OCH$_3$ (3.3 ppm). The absence of peaks between 4-5ppm indicates the absence of any free monomer in the polymer.

![Fig 5: $^1$H NMR spectrum of copolymer of MA and MMA](image)

Table 5: Protons associated in different environment in MMA and MA copolymer

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Chemical shift values ($\delta$ ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>0.9</td>
</tr>
<tr>
<td>-CH$_2$ (saturated)</td>
<td>1.1</td>
</tr>
<tr>
<td>-CH (saturated)</td>
<td>1.4</td>
</tr>
<tr>
<td>-OCH$_3$</td>
<td>3.3</td>
</tr>
</tbody>
</table>

6.3.7 Effect of rate of copolymerization on molecular weight

It is very clear from the table 6 that with the increase in initiator concentration the number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weights are decreasing in 1:3
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and 1:1 of MMA: MA monomers and increase in the case of 3:1 up to the concentration of 0.075% of potassium persulphate and there afterwards decreases. It is due to the low reactivity of MA or in other wards high reactivity of MMA (high concentration of MMA), which confirms the block copolymer formation. In all the cases the polydispersity ranges between 1.1 and 1.15; it is due to the variation in the degree of polymerization attained by MMA and MA during polymerization process. In 1:3 MMA: MA copolymerization, it is following the first order kinetics for all initiator concentrations from 0.05% to 0.125%, which may be due to high reactivity of MMA monomer, whereas in case of 1:1 MMA: MA generally, block type of copolymer was formed due to difference in reactivity ratios of MMA and MA and it is following the first order reaction. In 1:1 ratios of MMA: MA the reaction kinetics was changed from first order to second order. This may be due to the low reactivity of MA, high concentration of MMA or high solubility of MA.

6.4 Conclusions

In all the cases of 1:3, 1:1 and 3:1 ratios of MMA: MA in emulsion copolymerization at different concentrations of potassium persulphate initiator (from 0.05% to 0.125 %), the block copolymer was formed due to the difference in reactivity ratios of MMA and MA. In case of 1:1 composition of MMA: MA the order of reaction was changed from first to second due to the low reactivity of MA or may be higher concentration of MMA.
Table 6

Molecular weights of MMA-co-MA prepared by emulsion technique

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Monomer ratio MMA: MA (mole ratio)</th>
<th>Initiator concentration</th>
<th>Number average mol. wt ($\overline{M_n}$)</th>
<th>Weight average mol. wt. ($\overline{M_w}$)</th>
<th>Molecular weight distribution ($\overline{M_w}/\overline{M_n}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:3</td>
<td>0.050</td>
<td>42,900</td>
<td>47,000</td>
<td>1.100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.075</td>
<td>40,000</td>
<td>45,500</td>
<td>1.138</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.100</td>
<td>39,000</td>
<td>42,200</td>
<td>1.080</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.125</td>
<td>29,000</td>
<td>34,800</td>
<td>1.190</td>
</tr>
<tr>
<td>2</td>
<td>1:1</td>
<td>0.050</td>
<td>40,190</td>
<td>44,000</td>
<td>1.103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.075</td>
<td>35,600</td>
<td>41,000</td>
<td>1.165</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.100</td>
<td>33,180</td>
<td>38,000</td>
<td>1.136</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.125</td>
<td>32,160</td>
<td>36,600</td>
<td>1.140</td>
</tr>
<tr>
<td>3</td>
<td>3:1</td>
<td>0.050</td>
<td>33,700</td>
<td>41,200</td>
<td>1.220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.075</td>
<td>36,800</td>
<td>40,960</td>
<td>1.110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.100</td>
<td>35,600</td>
<td>40,100</td>
<td>1.135</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.125</td>
<td>32,200</td>
<td>36,500</td>
<td>1.135</td>
</tr>
</tbody>
</table>
References

12. Makgawinata T, Ph.D. Dissertation (Chapter II), K. Lehigh University, Bethlehem, PA, [1981].
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