

# Synthesis, characterization, reactivity ratio of the copolymer of linoleic acid with methyl methacrylate using ferric chloride-potassium metabisulphite redox pair as initiator

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**Abstract**— Aqueous co-polymerization of linoleic acid (a renewable monomer source) and methyl methacrylate initiated by the redox system Ferric (III)- $K_2S_2O_5$  has been studied under nitrogen atmosphere. The formation of the polymer has been confirmed using techniques of IR, UV, XRD,  $^1H$ NMR and  $^{13}C$ NMR spectroscopy. The co-polymer has been characterized by DSC; the glass transition temperature of copolymer shows a single  $T_g$  indicating the formation of random copolymer for all the monomer feed composition. On the basis of experimental results a suitable mechanism has been proposed. Monomer reactivity ratio was determined to know the composition of copolymer and its properties.

**Index Terms**— Redox pair; Linoleic acid (LA); Methylmethacrylate (MMA); Redox polymerization; Copolymer composition; Monomer reactivity ratio.

## 1 Introduction

Use of renewable raw materials is of growing interest in material preparations because of depletion in petroleum sources and environmental reasons. Vegetable oils derived fatty acids find application as raw materials for many industries such as food, pharmaceutical, cosmetics, surface coatings and detergents [1, 2]. Recently, fatty acid methyl esters derived from vegetable oils have assumed importance as a potential diesel fuel extender known as bio diesel with worldwide consumption approaching a billion gallons per year [3]. Plant oil derived alkyd resins are extensively used as base in coating industries and share about 15 % of the total surface coating market. Attempts are being made to extend the applicability of plant oils for synthesis of polymer for house hold and industrial applications. Synthesis of Rigid thermosetting liquid moulding resin from different vegetable oils [4- 6] and their applications for fabrication of motor vehicles components is an encouraging invention. Various polymerizations methods, including condensation, radical, cationic and metathesis procedures have been applied [7].

Copolymers based on methacrylate monomers are important base for oil additives with several functions, such as viscosity index improver, pour-point depressant and anti-foam agent [8]. Moreover, renewable resource based compounds have important applications in several areas and hence they are made industrially on a large scale. Polymer having low  $T_g$  are used for pressure-sensitive

adhesives [9]. Polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. Various redox pairs such as poly (vinyl alcohol)/Cu (II) [10],  $FeCl_3/K_2S_2O_5$  [11], ferric salt/ acyl hydrazide [12], Fe (III)/thiourea [13], Ce (IV)/ ethylene glycol [14] can be used. Some redox reactions give rise to radicals which can be used as initiators for polymerization reaction [15]. This type of polymerization initiation is referred to as redox polymerization, redox catalysis, or redox activation [16, 17].

Monomer reactivity ratios help predicts the copolymer composition and copolymerization behaviors for any initial feed of monomers in the reactor. These data are also helpful in understanding the kinetics and mechanism of the reaction. A list of methods to calculate reactivity ratios is reported by Rintoul and Wandrey [18]. Various methods such as Infrared, Nuclear magnetic resonance and UV-VIS spectroscopy have been used to estimate the monomer and copolymer concentrations. A Variety of redox pairs can be used to initiate free radical homopolymerization, copolymerization and graft polymerization. The method seems to be cheaper and ecofriendly as it is carried out in aqueous solution.  $FeCl_3/K_2S_2O_5$  redox pair has been used for free radical graft polymerization of methylmethacrylate by Choudhary et al [11].

There are reports on the free radical polymerization of cinnamate esters of epoxidized plant oil triglycerides [19], dimer fatty acids, transformation of fatty

acids into moldable resins [20] and use of use of fatty acid-based monomers as styrene replacement for liquid moulding resins. There is beautiful review on plant oil renewable resources as green alternatives in polymer science by Meier et al [21]. To the best of our knowledge there is no report on the co-polymerization of linoleic acid (LA) with methylmethacrylate (MMA) using  $\text{FeCl}_3/\text{K}_2\text{S}_2\text{O}_5$  redox pair. The present work was therefore undertaken to examine the suitability of  $\text{FeCl}_3/\text{K}_2\text{S}_2\text{O}_5$  redox pair for copolymerization of LA with MMA; to characterize the copolymer and to find its composition by determination of monomer reactivity ratio. Although linoleic acid does not polymerize easily, it copolymerized considerably with MMA. We decided to determine the monomer reactivity ratio to understand the composition of the copolymer and its property.

## 2. Experimental

### Materials

Iron(III) chloride ( $\text{FeCl}_3$ ), Potassium metabisulphite ( $\text{K}_2\text{S}_2\text{O}_5$ ), Methylmethacrylate (MMA), Methanol, Chloroform were purchased from s d fine chemical Ltd. (Mumbai). Fatty acid (Linoleic acid) was donated from Cherry Paints and polymers Private Ltd. (Indore). All materials were used as received without further purification.

### Synthesis of Co-polymer

The preparation of co-polymer was performed from fatty acid and methylmethacrylate by free radical polymerization using ferric chloride/ potassium metabisulphite as redox couple. In a typical run 7gm of fatty acid was placed in a three necked flask equipped with a thermometer, an inert gas inlet tube and a mechanical stirrer. 13 gm of methylmethacrylate was added and the contents has heated to 20 °C. 50 mL of distilled water was added slowly over 15 minute. To this 0.6 mL of 5 % aq. Solution of  $\text{FeCl}_3$  and 4 mL of 0.5 % (w/v) aq. Solution of  $\text{K}_2\text{S}_2\text{O}_5$  was added to the flask. The temperature was set to below 20 °C and reaction was continued for another three hours till completion. The reaction was stopped by addition of hydroquinone. At the end of reaction, the flask contents were poured over 25ml methanol. A precipitate was formed which consisted of linoleic acid-MMA copolymer and homopolymer of MMA. The latter was removed by washing with 400 ml water-methanol mixture (30:70) several times at room temperature. Finally the co-polymer was filtered and finally dried for 48h in an air at 50 °C. The

powder sample thus obtained was subjected do different characterizations.

## 3. Characterization

The reactivity ratios of LA and MMA were determined by estimating the concentrations of monomers and the copolymers employing a UV spectrometer and using Mayo-Lewis equation [22]. Viscosity of the polymer was measured using an Ostwald viscometer. Fourier transfer infrared (FTIR) spectra were recorded at room temperature in the range 4000- 400  $\text{cm}^{-1}$  as KBr pellets using a Bruker VERTEX 70 spectrometer with a wave number resolution of 10  $\text{cm}^{-1}$  at sophisticated analytical instrumentation facilities (SAIF), Chandigarh, India.  $^1\text{H}$ NMR and  $^{13}\text{C}$  NMR spectra were recorded at room temperature using a Bruker AVANCE II 400 NMR instrument at SAIF, Chandigarh. Thermal analyses were performed with a 2910 MDSC under a nitrogen atmosphere at rate of 44 cc /sec and 10 °C /min with a modulation of  $\pm 0.47$  °C. The XRD measurements were performed using a Rigaku X-ray powder diffractometer equipped with a graphite-crystal monochromator (for the diffracted beam) and a scintillation counter:  $\text{CuK}\alpha$  radiation with wavelength 1.5406 Å was used as source in the  $2\theta$  range 10 – 95 A°. The mean crystallite size was determined by measuring the broadening of the peak and applying the Debye equation.

## 4. Result and Discussions

Co-polymer was obtained from record of  $^1\text{H}$  NMR spectrum of the polymer reproduced in Table 1 and Fig. 1.

Table 1

Characteristic  $^1\text{H}$ NMR shifts of the Linoleic acid-MMA copolymer.

No.	Chemical shift $\delta$ (ppm)	Assignment
1	0.8386	$\text{CH}_3$
2	1.2351	- $(\text{CH}_2)_n\text{CH}_3$
3	1.7802	- $\text{CH}_2=\text{CH}-$
4	2.0051	- $\text{CH}_2\text{COOCH}_3$
5	3.5603	- $\text{CH}_2\text{O}$
6	7.2685	Solvent

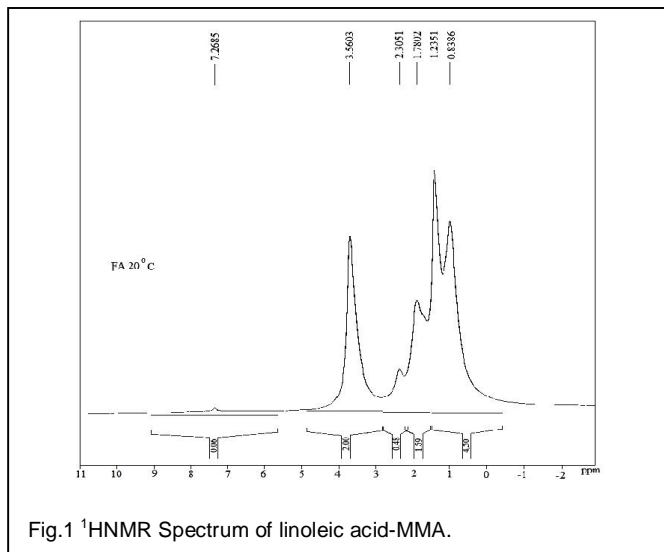


Fig.1 <sup>1</sup>H NMR Spectrum of linoleic acid-MMA.

Absence of any shift in the range 5-6 ppm for unsaturated vinyl proton confirms the absence of C=C and formation of the polymer.

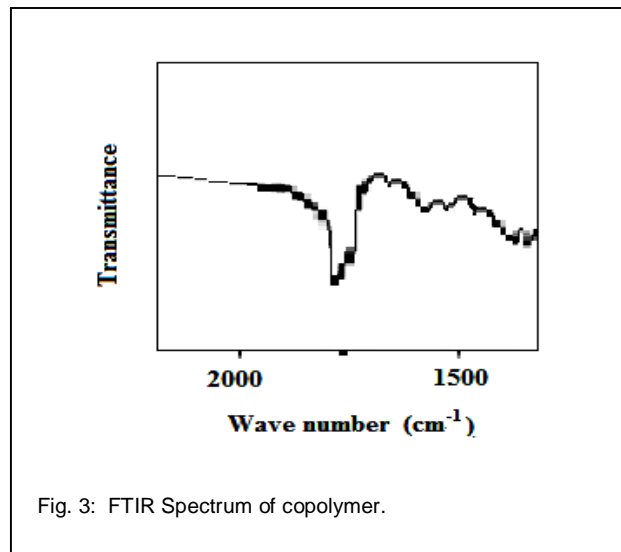


Fig. 3: FTIR Spectrum of copolymer.

The XRD pattern of the powder sampled is reproduced in Fig. 4. It shows that sample to be semi crystalline.

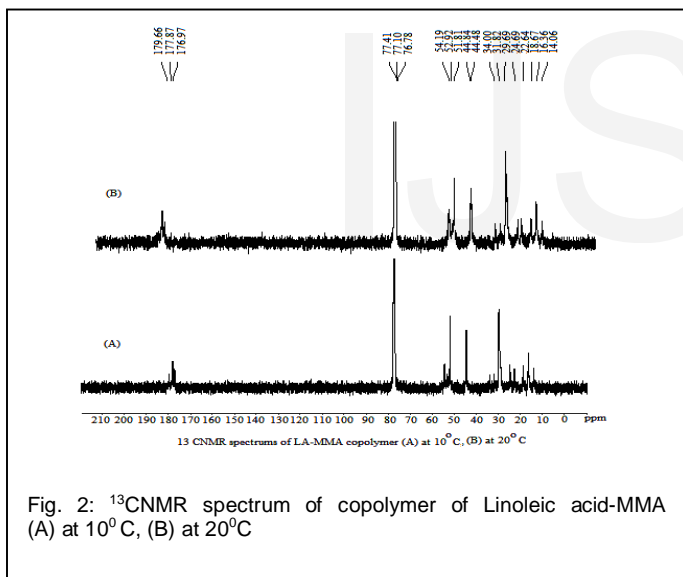


Fig. 2: <sup>13</sup>C NMR spectrum of copolymer of Linoleic acid-MMA (A) at 10<sup>o</sup> C, (B) at 20<sup>o</sup> C

The <sup>13</sup>C NMR spectrums are reproduced in Fig. 2. Absence of shift around at 130 ppm for unsaturated vinyl proton further confirmed the formation of the co-polymer. The FT-IR spectrum of the polymer in the range 2000-1500 cm<sup>-1</sup> is reproduced in Fig. 3. Absence of the band around 1600 cm<sup>-1</sup>, for C=C suggest the formation of the co-polymer.

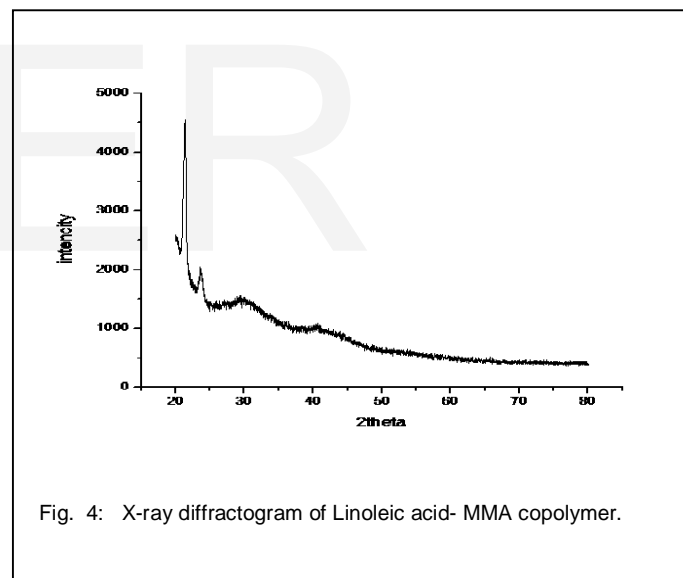
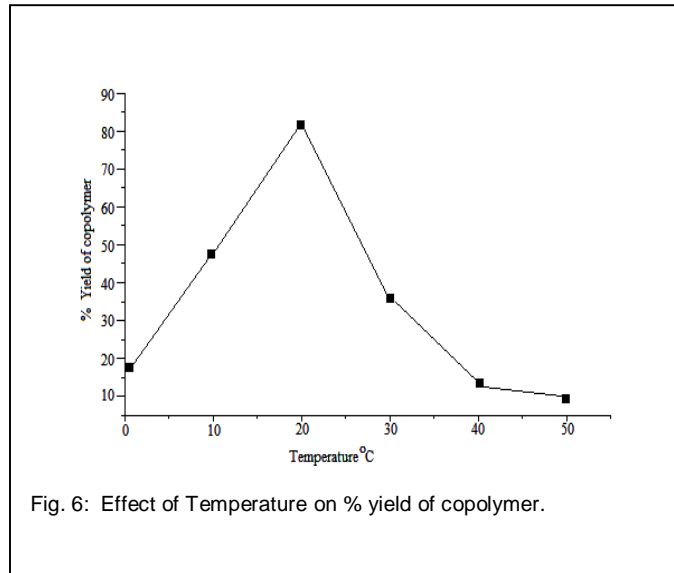
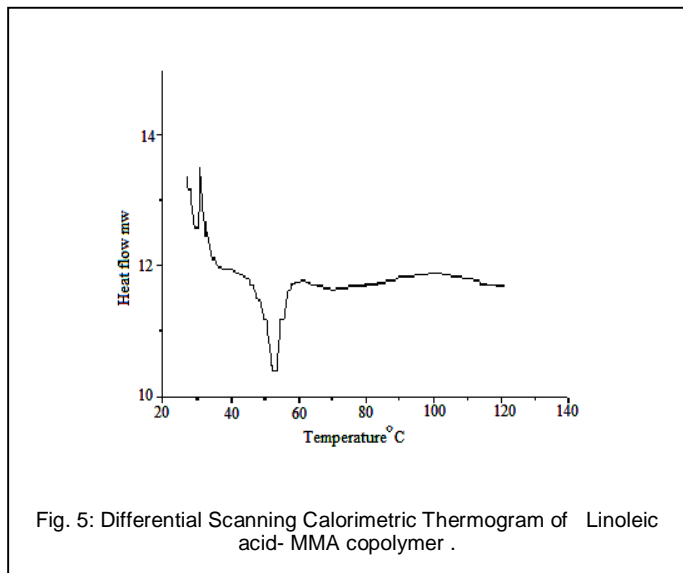


Fig. 4: X-ray diffractogram of Linoleic acid- MMA copolymer.

The DSC thermogram of the co-polymer is reproduced in Fig. 5. The endothermic peak appeared at 52 °C can be assigned softening point of the co-polymer which is different from that of poly methylmethacrylate (140 °C). The cream colored linoleic acid-MMA copolymer is stable at room temperature.



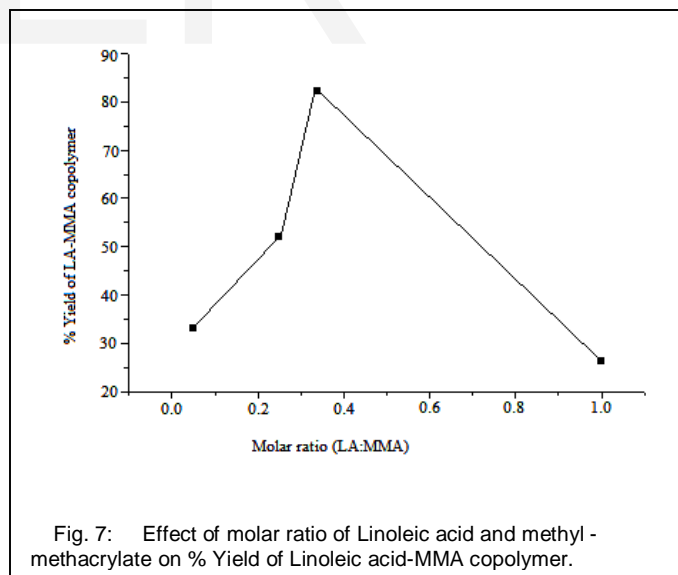
An important criterion that should be satisfied by most of the co-polymers is solubility. The solubility of the copolymer was tested in various organic solvents. The copolymer was easily dissolved in chlorinated solvent such as chloroform. They are insoluble in hydrocarbons such as benzene, toluene and xylene.

### Effect of temperature

Effect of temperature is presented in Fig. 6. The yield of the polymer is low at 0 °C which increases up to 20 °C. A maximum yield of 83 % was obtained at 20 °C. Further increase in temperature leads to decrease in the yield perhaps due to no formation of the iron complex. This was indicated by sudden disappearance of the red colour of the reaction mixture [11].

### Effect of linoleic acid /MMA molar ratio

The effect of linoleic acid /MMA molar ratio is graphically represented in Fig. 7. The yield of the copolymer increases up to LA/MMA mole ratio of 0.37 with a maximum yield of 82 % of co-polymer. Further increase in the mole ratio decreases the yield of co-polymer due increased homopolymerization.



### Effect of concentration of redox pair

The effect of redox pair concentration on the yield of copolymer was studied at constant temperature and constant molar ratio of LA/MMA and the results are shown in Fig. 8. Increase in concentration decreased the yield of copolymer and increased the yield of homopolymers. On the whole polymerization increased with increase in the concentration of redox pair.

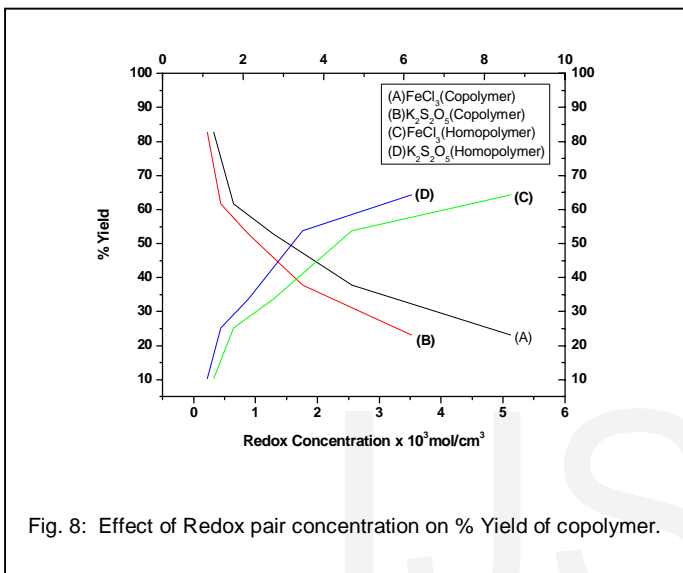


Fig. 8: Effect of Redox pair concentration on % Yield of copolymer.

### Reactivity ratio estimation experiments

Copolymer composition, its sequence distribution, molecular weight and viscosity are few important parameters to characterize a polymer. Monomer reactivity ratios can help understand the copolymer composition. The monomer reactivity ratio is determined by using the following relation between *f* and *F*, two parameters defined in terms of concentration of the monomers *M*<sub>1</sub> and *M*<sub>2</sub>.

$$f(1-F) = r_2 - r_1 \left( \frac{f}{F} \right) \quad (1)$$

$f = \frac{[M_1]}{[M_2]}$  in the feed and  $F = \frac{d[M_1]}{d[M_2]}$  in the copolymer at low conversion level

$$r = \frac{k_{11}}{k_{12}} \quad \& \quad r_2 = \frac{k_{22}}{k_{21}}$$

*r*<sub>1</sub> & *r*<sub>2</sub> are the reactivity ratios for monomer *M*<sub>1</sub> & *M*<sub>2</sub> described by above equation. *k*<sub>11</sub> & *k*<sub>22</sub> are rate constants for homopolymerization of *M*<sub>1</sub> & *M*<sub>2</sub> respectively. *k*<sub>12</sub> and *k*<sub>21</sub> are rate constants for copolymerization of *M*<sub>1</sub> with *M*<sub>2</sub> and

*M*<sub>2</sub> with *M*<sub>1</sub> respectively. Different feed ratio of monomers presented in table 2 and a plot of equation (1) in shown in Fig. 9. From the slop and intercept value of *r*<sub>1</sub> & *r*<sub>2</sub> were found to be 1.06 and 1.3±.2 respectively. This suggests formation of random polymer [23].

Table 2

Co-polymers were prepared by using different feed ratio of monomers. The monomer reactivity ratios determined by the Mayo Lewis method.

No.	Mole ratio FA: MMA	Absorbance Ratio of Copolymer (F= A1/A2)	Feed composition f
1	0.37	0.307	0.37
2	0.21	0.160	0.21
3	0.58	0.470	0.58
4	0.5	0.398	0.5

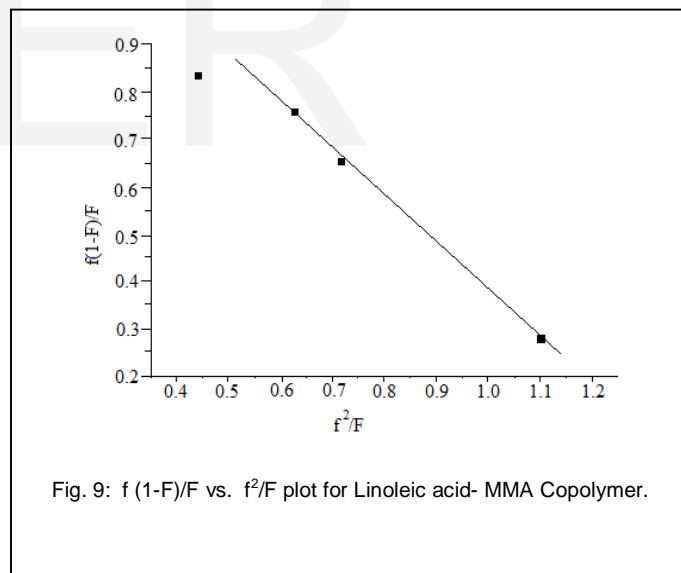
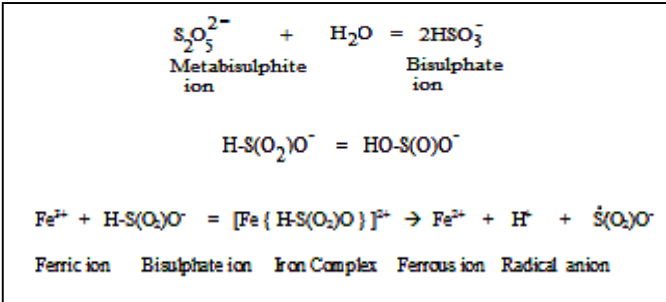


Fig. 9: *f* (1-*F*)/*F* vs. *f*<sup>2</sup>/*F* plot for Linoleic acid- MMA Copolymer.

A reaction scheme for the free radical polymerization process of methylmethacrylate and linoleic acid using FeCl<sub>3</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> redox pair is proposed. It is known that when K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> is added to H<sub>2</sub>O produces bisulphate HSO<sub>3</sub><sup>-</sup> ion. The HSO<sub>3</sub><sup>-</sup> ion react with Fe<sup>+3</sup> ions react to produce an orange red colored complex [24].

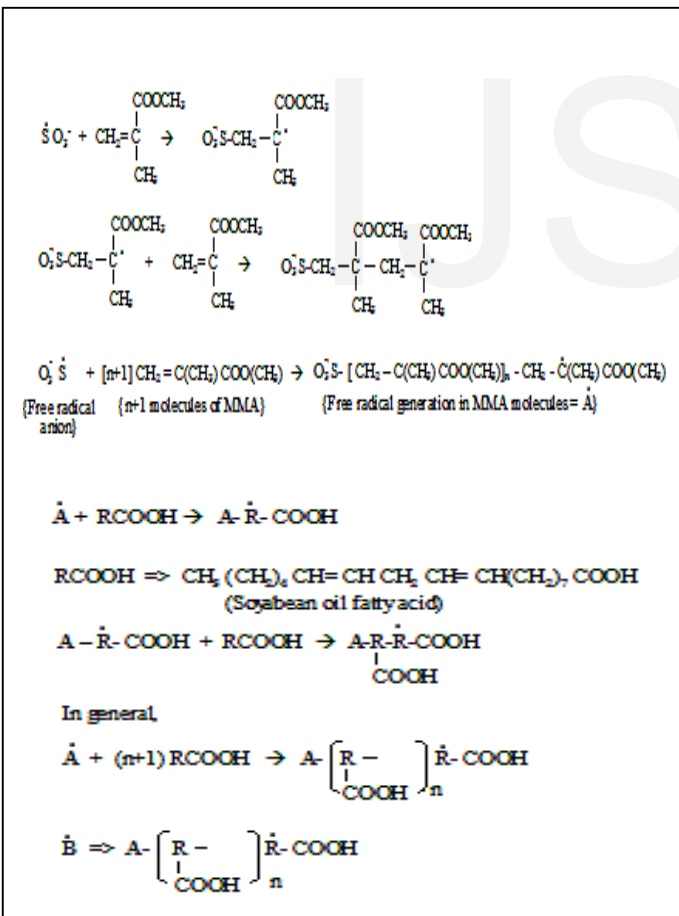
(1) Initiation:

S<sup>•</sup> (O<sub>2</sub>)<sup>•-</sup> radical anion responsible for Initiation of the polymerization as follows:

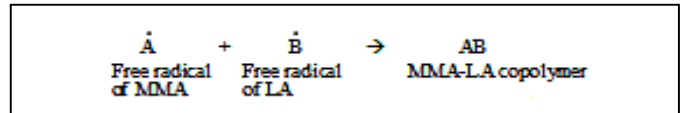


(2) Propagation:

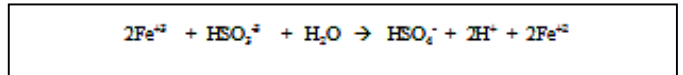
Free radical propagation step methylmethacrylate radical anion.



(3) Termination:



The chemical test revealed the formation of bisulphate and ferrous ion at 30 °C. Since no free radical is formed at higher temperature no polymer is obtained [25]. The tautomeric Forms of bisulphate ion are responsible for its reducing property and complex formation ability respectively.



Co-polymers of linoleic acid (LA) and methylmethacrylate (MMA) were prepared in an aqueous solution with FeCl<sub>3</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as a redox initiator in the temperature range 10 - 20 °C. Polymers were characterized employing the techniques of XRD, UV, FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and DSC. Copolymers were prepared by using different feed ratio of monomers. The monomer reactivity ratios determined by method of mayo-lewis were found to be: r<sub>1</sub> =1.06, r<sub>2</sub> =1.3±.2 both values approaching 1. This suggests formation of random polymer.

5. Conclusion

Co-polymers of linoleic acid (LA) and methylmethacrylate (MMA) were prepared in an aqueous solution with FeCl<sub>3</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as a redox initiator in the temperature range 10 - 20 °C. Polymers were characterized employing the techniques of XRD, UV, FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and DSC. Copolymers were prepared by using different feed ratio of monomers. The monomer reactivity ratios determined by method of mayo-lewis were found to be: r<sub>1</sub> =1.06, r<sub>2</sub> =1.3±.2 both values approaching 1. This suggests formation of random polymer.

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