

# Measurement of Mark Houwink's Constants, Reactivity Ratios and Kinetics in Radical Copolymerization of Linalool with Methyl Methacrylate Initiated by BPO

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**ABSTRACT:** Radical copolymerization methodology was explored by and making use of acyclic terpenoids namely linalool with methyl methacrylate (MMA) initiated by benzoyl peroxide (BPO) in xylene at  $80 \pm 1$  °C for 50 minutes under inert atmosphere of  $N_2$ . The reaction results in alternating copolymer as evidenced from reactivity ratios. The system follows ideal kinetics. The overall activation energy is 57.0 kJ / mol . The values of Mark-Houwink constants for present copolymer have been evaluated as  $\alpha = 0.3$  and  $K = 2.39 \times 10^{-4}$  dl/g with the help of gel permeation chromatography. Alfrey Price, Q - e parameters for linalool have been evaluated as 4.59 and -2.24. The copolymer has been characterized by  $^1H$ -NMR, FTIR and GPC.

**Key words :** Copolymerization, Linalool, Mark-Houwink's constant, Methyl methacrylate, Reactivity ratio.

## Introduction

Polymers with unsaturated functional groups are applicable as reactive polymers which can be functionalized by polymer reactions. Polymerization of monomers with higher degrees of unsaturation is an attractive method to produce polymers bearing unsaturated moieties. These polymerizations, however, often include problems such as instability of monomers, and side reactions giving unregulated polymer structures. To construct well-defined polymers bearing unsaturated moieties, many efforts have been made in the polymerizations of dienes<sup>1,2</sup> acetylenes<sup>3</sup>, cyclic olefins<sup>4</sup>, heterocumulenes<sup>5</sup> and so on. In this aspects , we have

developed the polymerization of monomers with high degree of unsaturation to give polymers containing unsaturated bonds.

A search of literature reveals that a voluminous literature is available on free radical copolymerization of vinyl monomers. Copolymerizations of acrylates, methacrylates, diacrylates and other vinyl monomers have been extensively studied<sup>6-8</sup>, but a very little attention has been devoted on polymerization of acyclic terpenoids<sup>9-12</sup>. It is because acyclic terpenoids do not undergo homopolymerization due to steric hindrance<sup>13,14</sup>, low stabilization energy between monomer and free radicals in transition state<sup>15</sup>, excessive chain transfer<sup>16</sup>, termination of cyclization as in case of 1,2 - disubstituted ethylenes<sup>17</sup>. The polymerization of few terpenoids like  $\alpha / \beta$  - pinenes<sup>18-21</sup>, have attracted polymer chemists, since it yields optical active and functional copolymers. Therefore, the field of polymers of terpenoids is very challenging area of research with unlimited future prospects.

In the present article, acyclic monoterpenoid, namely linalool is copolymerized with methyl methacrylate using BPO as an initiator in xylene at 80 °C for 50 minutes and the kinetics, mechanism and the values of Mark Houwink constants  $K$  and  $\alpha$  have been evaluated.

## Experimental

### Materials

Reagent grade methyl methacrylate (MMA) (Merck Schuchardt) and solvents were purified by usual methods<sup>22</sup>; stored over an anhydrous silica gel and distilled under vacuum before use. Benzoyl peroxide (M.P. = 105 °C), was recrystallized twice with methanol. Linalool<sup>23</sup> (B.P.=196 °C);  $d_{150} = 0.8621$ ; specific rotation  $[\alpha] = (-) 20.7^\circ$  was used after fractional distillation.

### Polymerization Procedure

Polymerization of a solution containing requisite concentration of linalool with MMA in presence of BPO was carried out in a dilatometric apparatus (capillary dia. = 2 mm; capillary length = 9.1 cm; lower bulb capacity = 2.5 ml). The copolymerization runs were performed for 50 min. at  $80 \pm 1^\circ\text{C}$  under an inert atmosphere of  $\text{N}_2$ . The copolymer, precipitated with acidified methanol, was dried to constant weight. It was refluxed with acetonitrile to remove poly (MMA) and then reprecipitated. The weight loss was negligible. Rate of polymerization ( $R_p$ ) was calculated from the slope of linear portion of % conversion vs time plots.

## Characterization

The copolymers were characterized by FTIR, <sup>1</sup>H-NMR, and GPC.

<sup>1</sup>H-NMR spectra were recorded with Varian 100HA Joel LA 400 spectrometer using CDCl<sub>3</sub> as solvent and tetramethyl silane as internal reference.

The GPC studies were made with E. Merck RI-L-7490. The elution solvent was tetrahydrofuran at temperature 25 °C.

## Results and Discussion

The kinetic studies have been studied by varying the concentrations of initiator (BPO), monomer(s) and temperature. The results have been illustrated in Tables 1 - 2 and Figures 1. The effect of [BPO] on rate of copolymerization (Rp) is shown in Table 1. It is clear that the Rp increases with increasing concentration of BPO as expected for free radical copolymerization. The order of reaction with respect to BPO, calculated from the slope of the plot of log Rp vs log [BPO] is 0.5±0.03.

**TABLE 1**

**Effect of [BPO] on the Rate of Copolymerization of Linalool and Methyl Methacrylate**

[BPO] x 10 <sup>-3</sup> (mol/L)	% Conversion	Rp X10 <sup>6</sup> (mol/L/s)
1.3	9.02	4.5
2.75	10.4	4.0
4.1	12.1	3.0
5.5	13.8	2.5
6.8	16.8	2.1

[LIN] = 1.3 mol/l; [MMA] = 2.1 mol/l; Copolymerization time = 50 minutes;  
Copolymerization temperature = 80±1 °C.

The effect of [MMA] on the  $R_p$  has been studied by varying [MMA] from 1.5 mol / l to 3.1 mol / l where [LIN] and [BPO] were kept constant (Tab. 2). A plot between log  $R_p$  and log [MMA] is linear, the slope of which gives relationship  $R_p \propto [\text{MMA}]^{1.0 \pm 0.04}$ .

The effect of [LIN] on  $R_p$  has been studied by varying [LIN] from 0.93 mol/l to 1.8 mol / l keeping [MMA] and [BPO] constant (Table. 2). A plot between log  $R_p$  vs log [LIN] is linear; the order of reaction gives the relationship of unity.

$$R_p \propto [\text{LIN}]^{1.0 \pm 0.02}$$

**TABLE 2**  
Effect of [Comonomer(s)] on the Rate of Copolymerization using BPO as an initiator

[LIN] (Mol/L)	[MMA] (Mol/L)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)
1.3	1.5	10.2	13.2
1.3	1.8	11.8	14.4
1.3	2.1	13.8	16.2
1.3	2.5	15.6	17.7
1.3	3.0	20.4	20.4
0.9	2.1	10.0	13.8
1.1	2.1	11.9	14.7
1.3	2.1	13.8	16.2
1.4	2.1	14.4	16.8
1.8	2.1	15.8	17.7

[BPO] =  $5.5 \times 10^{-3}$  mol/l; Copolymerization time = 50 minutes; Copolymerization temperature =  $80 \pm 1$  °C.

The copolymerization runs were also carried out at 75 °C and 85 °C to evaluate the energy of activation. The  $R_p$  is direct function of temperatures and the apparent activation energy, determined from the slope of Arrhenius plot (Fig. 1), is 57.0 kJ / mol.

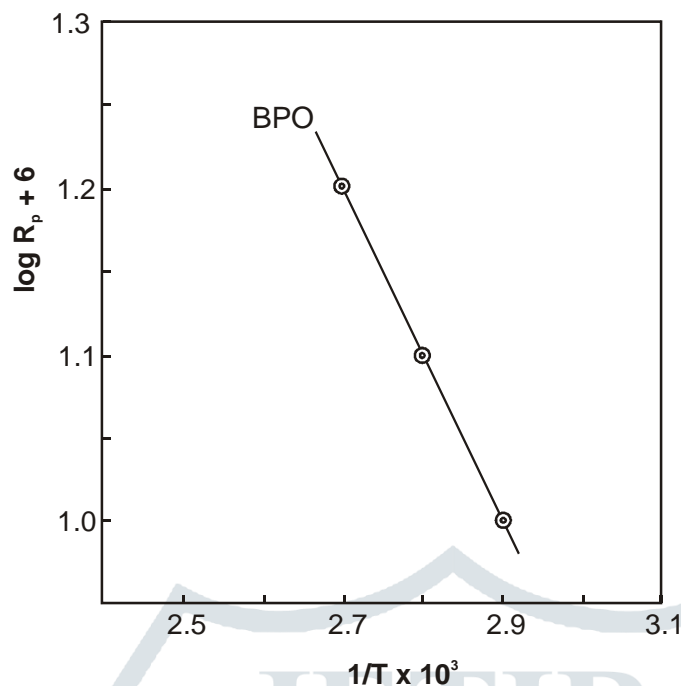


Fig 1. Arrhenius plot of rate of copolymerization vs copolymerization temperature  
 [LIN] = 1.3 mol l<sup>-1</sup>; [MMA] = 2.1 mol l<sup>-1</sup>; Copolymerization time = 50 minutes.

### Characterization of Copolymer(s)

#### <sup>1</sup>H-Nuclear Magnetic Resonance Spectroscopy

The chemical shifts of protons, attached to elements other than carbon like -OH, -NH and -SH to a greater or lesser extent, is influenced by related phenomenon of intermolecular exchange and hydrogen bonding. Appearance of signals in the NMR spectra, due to -OH proton with species of smaller molecular weight, where intermolecular association is not hindered, generally, resonate in the region of  $\delta = 3.0$  to 5.5 ppm (hydroxyl proton of CH<sub>3</sub>OH appears at 3.3  $\delta$  whereas that of CH<sub>3</sub>CH<sub>2</sub>OH at 5.4  $\delta$ ). However, with many large molecules, the hydroxyl proton often resonates near  $\delta = 8.0$  ppm even at relatively high concentration. This is partially because of molar concentration and partially due to steric effect<sup>24,25</sup>. Therefore, we have assigned the peak of -OH at 7.0 - 7.8  $\delta$  in the NMR spectra of linalool as well as in the copolymer of LIN-MMA.

The <sup>1</sup>H-NMR spectrum of copolymer shows peak at 7.0 - 7.8  $\delta$  of -OH group of linalool. The resonance signals at 3.6  $\delta$  were due to -OCH<sub>3</sub> protons of MMA, confirming the formation of poly (LIN-MMA) copolymer. The group peaks between 2.5 - 1.7  $\delta$  may originate from the back bone of -CH<sub>2</sub> and -CH protons.

## Fourier Transform Infrared Spectroscopy

In the FTIR spectrum of copolymer bands due to acrylate group of MMA is observed at  $1735\text{ cm}^{-1}$  and band due to -OH group of linalool is observed at  $3500\text{ cm}^{-1}$ . This confirms the incorporation of both the monomers in the copolymer.

## Gel Permeation Chromatography

The intrinsic viscosity measured in a specific solvent is related to the molecular weight [M], by the Mark-Houwink equation-

$$[\eta] = K [M]^\alpha$$

where K and  $\alpha$  are Mark-Houwink constants that depend upon the type of polymer, solvent and the temperature of the viscosity determinations. The exponent  $\alpha$  is a function of polymer geometry and varies from 0.5 to 1.0. These constants can be determined experimentally by measuring the intrinsic viscosities of several polymer samples for which the molecular weight has been determined by an independent method (GPC). Using the polymer standards, a plot of the  $\log [\eta]$  vs  $\log [M]$  usually gives a straight line. The slope of this line is the  $\alpha$  value and the intercept is equal to the log of the K value.

From the plot of  $\log [\eta]$  vs  $\log \bar{M}_v$  for samples (Fig. 2), the value of K and  $\alpha$  were determined from the intercept and slope of the plot as  $2.39 \times 10^{-4}\text{ dl/g}$  and 0.30 respectively.

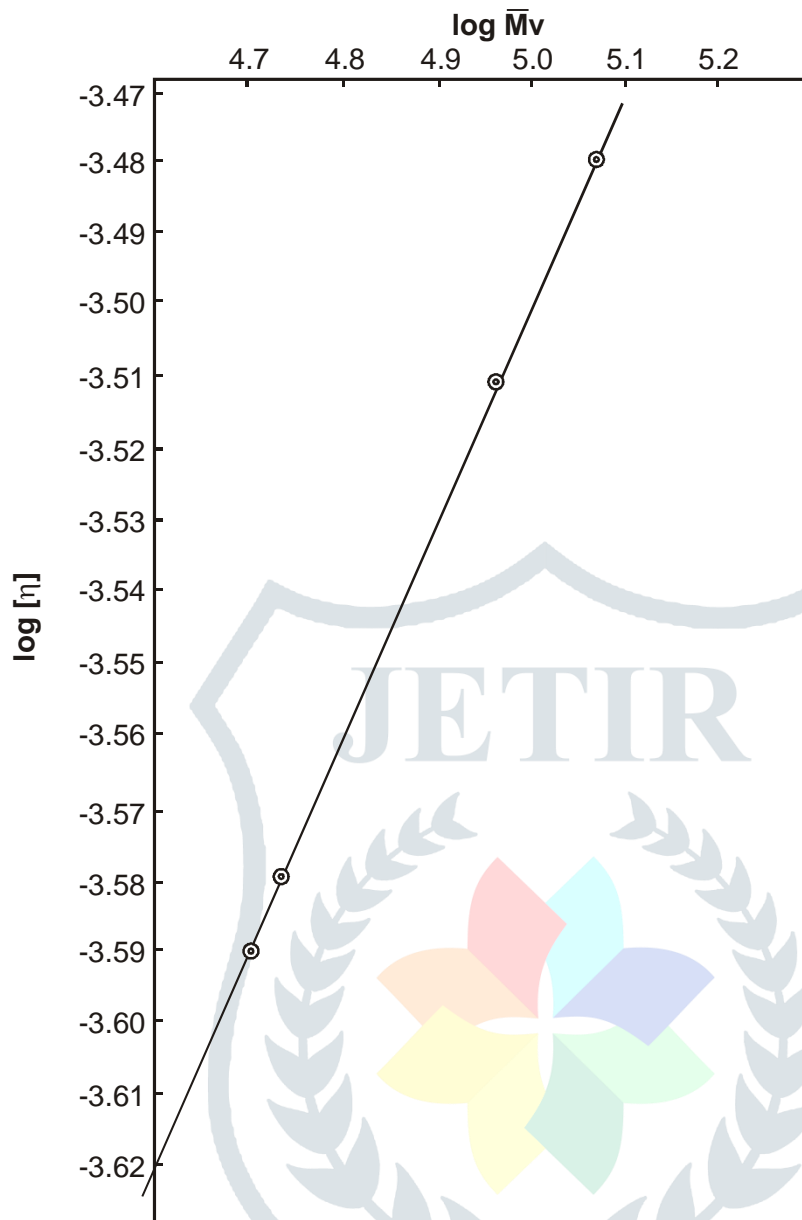


Fig 2. Plot of  $[\eta]$  vs  $\log M_v$  (Mark-Houwink curve)

The fact that the intrinsic viscosity of a given polymer sample is different in different solvents gives one insight into the general shape of polymer molecules in solution. A long-chain polymer molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly curled mass (coil) and a rigid linear configuration. All possible degrees of curling may be displayed by any one molecule, but there will be an average configuration which will depend on the solvent. In a “good” solvent, one that shows a zero or negative heat of mixing with the polymer, the molecule is fairly loosely extended, and the intrinsic viscosity is high. The Mark-Houwink  $\alpha$  constant is close to 0.75 or higher for these “good” solvents. In a “poor” solvent, one that shows a positive heat of mixing, segments of a polymer molecule attract each other in solution more strongly

than they attract surrounding solvent molecules. The polymer molecule assumes a tighter configuration and the solution has a lower intrinsic viscosity. The Mark-Houwink  $\alpha$  constant is close to 0.5 in “poor” solvents<sup>26</sup>, as in our system is 0.3.

When using GPC systems the average molecular weight of copolymers was eluted are monitored and automatically printed out by the data processor (Table 3). It is found that weight average molecular weights ( $\bar{M}_w$ ) are always greater than number average molecular weights ( $\bar{M}_n$ ) excepts, of course, when all molecules are of the same weight;  $\bar{M}_w = \bar{M}_n$ . The narrower the molecular weight range, the closer are the values of  $\bar{M}_w$  and  $\bar{M}_n$  and the ratio  $\bar{M}_w / \bar{M}_n$  may thus be used as an indication of the breadth of the molecular weight range in a polymer sample. This ratio is called polydispersity index, and any system having a range of molecular weights is said to be polydisperse. If all polymer molecules present have the same molecular weight, the system is monodisperse. A study of Table 3 shows that the present system is polydisperse but as the molar ratio of monomer [MMA]/ [LIN] decreases its molecular weight distribution becomes narrower. This is because<sup>27</sup> of the unequal interactions of monomer and co monomer units with the solvents and with each other.

**TABLE 3**

**GPC Parameters of Copolymerization of Linalool with MMA using BPO as an Initiator**

Sample no.	$[\eta] \times 10^4$	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$
20	3.08	91725	19245	49007	89432
21	2.63	53788	52382	52947	53514
04	2.56	49864	47367	48369	50391
19	3.31	117100	26582	64308	11207

[BPO] =  $5.5 \times 10^{-3}$  mol/l; Copolymerization time = 50 minutes;

Copolymerization temperature =  $80 \pm 1$  °C; Viscosity temperature = 25 °C.



## Copolymer Composition

<sup>1</sup>H-NMR analysis has been used to calculate the copolymer composition. The copolymer composition (Tab. 4) was determined by the peak area at 7.0 - 7.8  $\delta$  due to -OH protons and at 3.6  $\delta$  due to -OCH<sub>3</sub>. These were used to calculate the reactivity ratio value using Kelen-Tudos method<sup>28</sup> (Fig. 3), taking MMA (monomer 1) and linalool (monomer 2) as follows:

$$\eta = r_1\xi - r_2(1 - \xi)/\alpha$$

$$\text{Where } \eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H)$$

The transformed variables G and H are given by -

$$G = \frac{[M_1]/[M_2][(d[M_1]/d[M_2]) - 1]}{d[M_1]/d[M_2]}$$

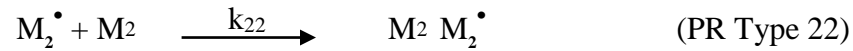
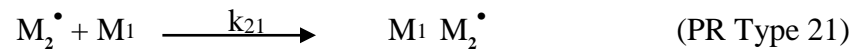
$$H = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

**Table 4:Composition of Copolymer**

Molar ratio in monomer feed [MMA]/[LIN]	% Conversion	Molar ratio in copolymer composition [MMA]/[LIN]
1.62	13.6	1.03
1.90	14.6	1.05
1.50	14.0	1.01
2.30	17.7	1.07

The parameter  $\alpha$  is calculated by taking the square root of the product of the lowest and the highest values of H for the copolymerization series. The graphical evaluation for MMA/LIN yields values of  $r_1 = 0.056$  and  $r_2 = 0.017$  (Tab. 5). The product of  $r_1r_2$  is nearly 0 which is the sign of nearly alternating copolymerization.

According to the Alfery-Price Q-e scheme, the alternating tendency of the copolymer is given by a product of monomer reactivity ratios  $r_1$  and  $r_2$  with respect to monomers  $M_1$  (MMA) and  $M_2$  (LIN) in the four growing propagating reactions (PR) as:



$$r_1 = K_{11}/K_{12} \quad \text{and} \quad r_2 = K_{22}/K_{21}$$

By the values of  $r_1$  and  $r_2$ , it is clear that  $r_1$  and  $r_2$  are less than 1 i.e. the propagation reaction type 12 and 21 are preferred to type 11 and 22. The value of  $r_2$  may be taken as zero, which shows that the probability of propagation reaction 22 is very less or somewhat impossible due to the fact that no homopolymerization of  $M_2$  takes place and hence a chain ending with  $M_2^\bullet$  will add only a  $M_1$ .

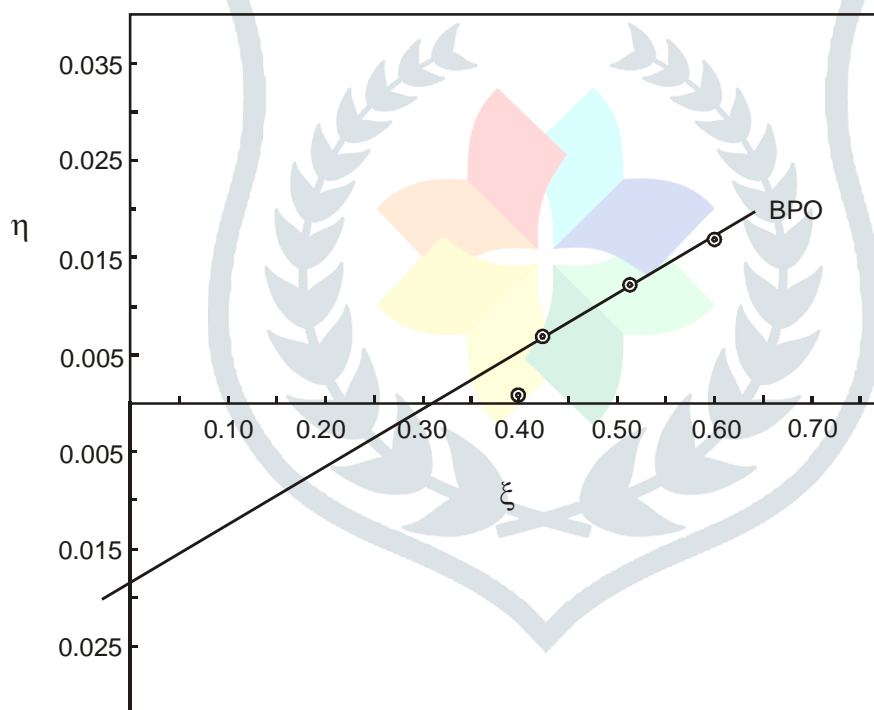


Fig 3. Kelen-Tudos plot of copolymer for determination of reactivity ratio.

The  $e_2$  and  $Q_2$  values for linalool were calculated (Table 5), using  $e_1 = 0.40$  and  $Q_1 = 0.74$  for MMA, by following Alfrey - Price equation<sup>29,30</sup> :

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{0.5}$$

$$Q_2 = Q_1 / r_1 \exp[-e_1(e_1 - e_2)]$$

These equations express  $r_1$  and  $r_2$  in terms of constants  $Q$  and  $e$ , are assumed to be characteristic of each monomer.  $Q$  is related to the extent of resonance stabilization in the monomer i.e. its reactivity and  $e$  is related to the polarity of double bond. It has been found that strong alternating copolymers are formed when co monomers with widely differing polarities are reacted together. Thus an alternating copolymerization is suggested from high difference of  $e$  values of MMA and LIN.

**TABLE 5**  
**Reactivity Parameters using Kelen-Tudos Method**

$r^1$	$r^2$	$r^1 r^2$	$Q_2$	$e_2$
0.056	0.017	0.0009	4.59	-2.24

### Conclusion

Poly (LIN-alt-MMA) has been synthesized via free radical solution polymerization using BPO as radical initiator. The Mark Houwink constants  $K = 2.39 \times 10^{-4} \text{ dl/g}$  &  $\alpha = 0.30$  are evaluated. The system follows ideal kinetics and the energy of activation is evaluated as 57.0 kJ/mole.

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## Figures Captions

1. Relationship between the rate of copolymerization and [BPO]  
[LIN] = 1.3 mol l<sup>-1</sup>; [MMA] = 2.1 mol l<sup>-1</sup>; Copolymerization time = 50 minutes;  
Copolymerization temperature = 80±1 °C.
2. Relationship between the rate of copolymerization and [MMA]  
[LIN] = 1.3 mol l<sup>-1</sup>; [BPO] = 5.5 x 10<sup>-3</sup> mol l<sup>-1</sup>; Copolymerization time =50 minutes;  
Copolymerization temperature = 80±1 °C.
3. Relationship between the rate of copolymerization and [LIN]  
[MMA] = 2.1 mol l<sup>-1</sup>; [BPO] = 5.5 x 10<sup>-3</sup> mol l<sup>-1</sup>;  
Copolymerization time =5 0 minutes; Copolymerization temperature = 80±1 °C.
4. Arrhenius plot of rate of copolymerization vs copolymerization temperature  
[LIN] = 1.3 mol l<sup>-1</sup>; [MMA] = 2.1 mol l<sup>-1</sup>; Copolymerization time = 50 minutes.
5. <sup>1</sup>H-NMR spectrum of copolymer using BPO as an initiator.
6. FTIR spectrum of copolymer using BPO as an initiator.
7. <sup>13</sup>C-NMR spectrum of copolymer using BPO as an initiator.
8. Plot of [η] vs log  $\overline{M}_v$  (Mark-Houwink curve)
9. Kelen-Tudos plot of copolymer for determination of reactivity ratio.

TABLE 1

Effect of [BPO] on the Rate of Copolymerization of Linalool and Methyl Methacrylate

<b>[BPO] x 10<sup>3</sup></b> <b>(mol/L)</b>	<b>% Conversion</b>	<b>R<sub>p</sub> X10<sup>6</sup></b> <b>(mol/L/s)</b>
<b>1.3</b>	<b>9.02</b>	<b>4.5</b>
<b>2.75</b>	<b>10.4</b>	<b>4.0</b>
<b>4.1</b>	<b>12.1</b>	<b>3.0</b>
<b>5.5</b>	<b>13.8</b>	<b>2.5</b>
<b>6.8</b>	<b>16.8</b>	<b>2.1</b>

[LIN] = 1.3 mol/l; [MMA] = 2.1 mol/l; Copolymerization time = 50 minutes;  
Copolymerization temperature = 80±1 °C.

**TABLE 2****Effect of [Comonomer(s)] on the Rate of Copolymerization using BPO as an initiator**

[LIN] (Mol/L)	[MMA] (Mol/L)	Conversion (%)	Rp X 10 <sup>6</sup> (mol/L/s)
1.3	1.5	10.2	13.2
1.3	1.8	11.8	14.4
1.3	2.1	13.8	16.2
1.3	2.5	15.6	17.7
1.3	3.0	20.4	20.4
0.9	2.1	10.0	13.8
1.1	2.1	11.9	14.7
1.3	2.1	13.8	16.2
1.4	2.1	14.4	16.8
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[BPO] =  $5.5 \times 10^{-3}$  mol/l; Copolymerization time = 50 minutes; Copolymerization temperature =  $80 \pm 1$  °C.

**TABLE 3****GPC Parameters of Copolymerization of Linalool with MMA using BPO as an Initiator**

Sample no.	$[\eta] \times 10^4$	$M_v^-$	$M_n^-$	$M_w^-$	Mz
20	3.08	91725	19245	49007	89432
21	2.63	53788	52382	52947	53514
04	2.56	49864	47367	48369	50391
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[BPO] =  $5.5 \times 10^{-3}$  mol/l; Copolymerization time = 50 minutes;

Copolymerization temperature =  $80 \pm 1$  °C; Viscosity temperature = 25 °C.

**Table 4:Composition of Copolymer**

<b>Molar ratio in monomer feed [MMA]/[LIN]</b>	<b>% Conversion</b>	<b>Molar ratio in copolymer composition [MMA]/[LIN]</b>
<b>1.62</b>	<b>13.6</b>	<b>1.03</b>
<b>1.90</b>	<b>14.6</b>	<b>1.05</b>
<b>1.50</b>	<b>14.0</b>	<b>1.01</b>
<b>2.30</b>	<b>17.7</b>	<b>1.07</b>

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**TABLE 5****Reactivity Parameters using Kelen-Tudos Method**

<b>r<sup>1</sup></b>	<b>r<sup>2</sup></b>	<b>r<sup>1</sup> r<sup>2</sup></b>	<b>Q<sub>2</sub></b>	<b>e<sub>2</sub></b>
<b>0.056</b>	<b>0.017</b>	<b>0.0009</b>	<b>4.59</b>	<b>-2.24</b>



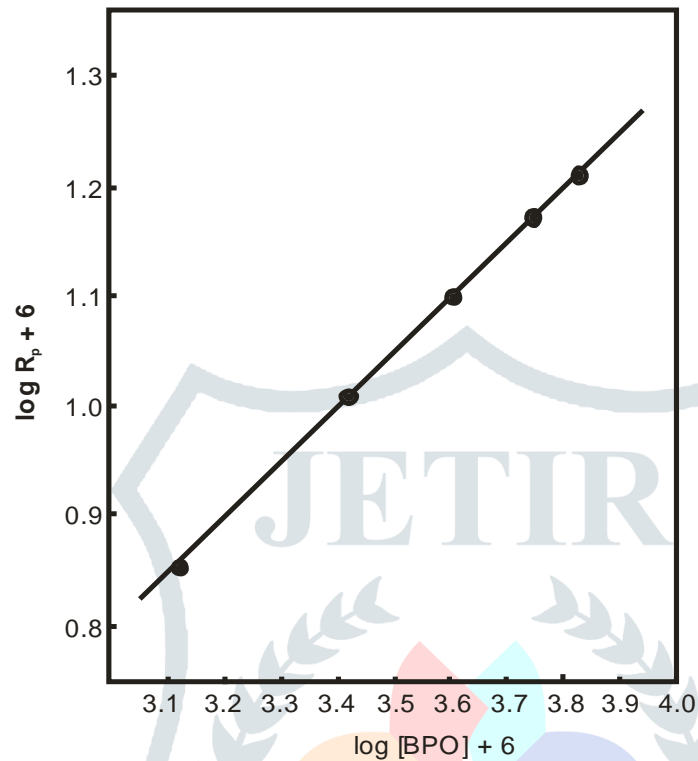


Fig.1. Relationship between the rate of copolymerization and [BPO]  
[LIN] = 1.3 mol l<sup>-1</sup>; [MMA] = 2.1 mol l<sup>-1</sup>; Copolymerization time = 50 minutes;  
Copolymerization temperature = 80±1 °C.

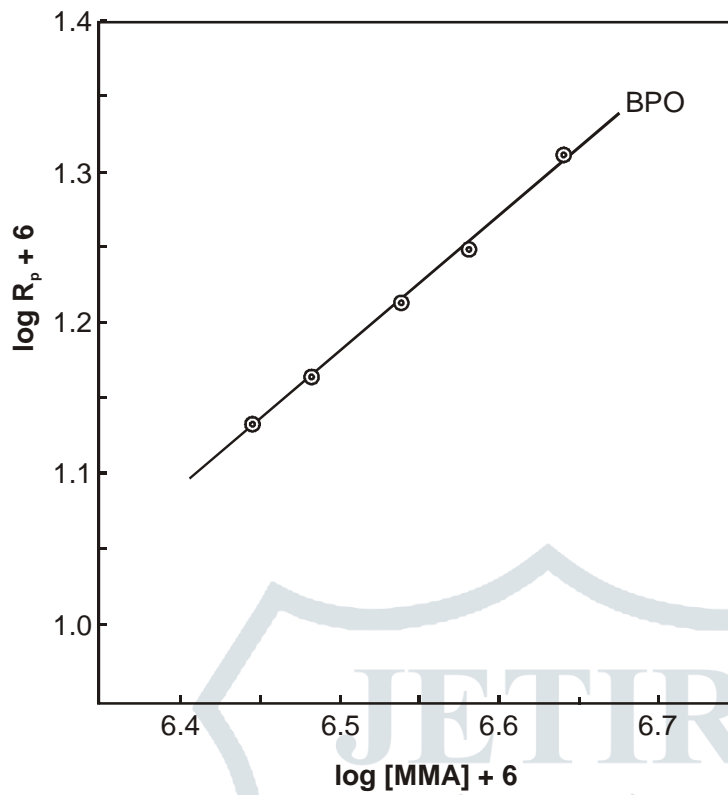


Fig: 2 Relationship between the rate of copolymerization and [MMA]  
[LIN] = 1.3 mol l<sup>-1</sup>; [BPO] = 5.5 x 10<sup>-3</sup> mol l<sup>-1</sup>; Copolymerization time =50 minutes;  
Copolymerization temperature = 80±1 °C.

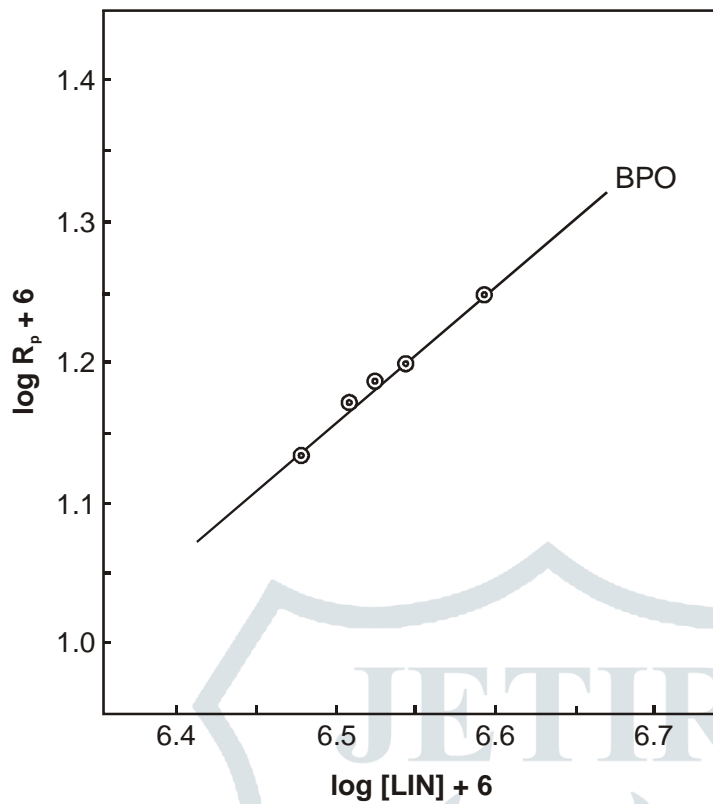


Fig 3. Relationship between the rate of copolymerization and [LIN]  
[MMA] = 2.1 mol l<sup>-1</sup>; [BPO] = 5.5 x 10<sup>-3</sup> mol l<sup>-1</sup>; Copolymerization time = 50 minutes;  
Copolymerization temperature = 80±1 °C.

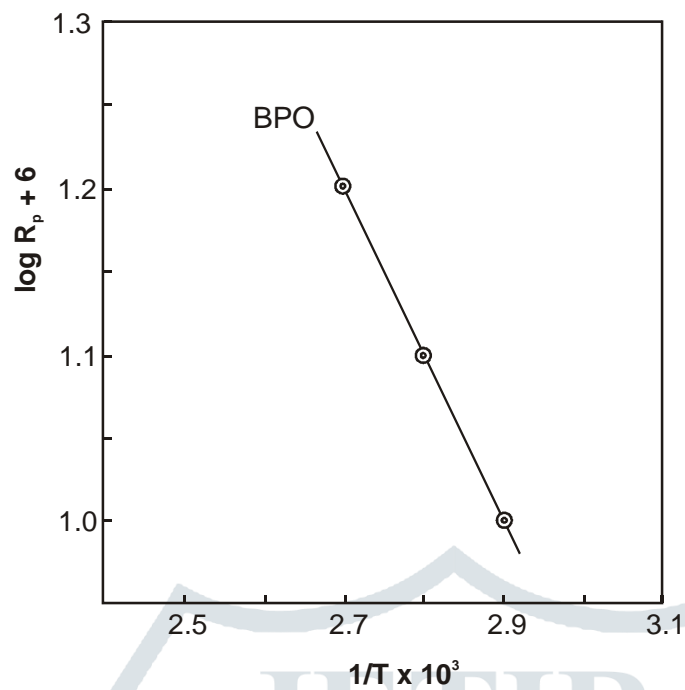


Fig 4. Arrhenius plot of rate of copolymerization vs copolymerization temperature  
[LIN] = 1.3 mol l<sup>-1</sup>; [MMA] = 2.1 mol l<sup>-1</sup>; Copolymerization time = 50 minutes.

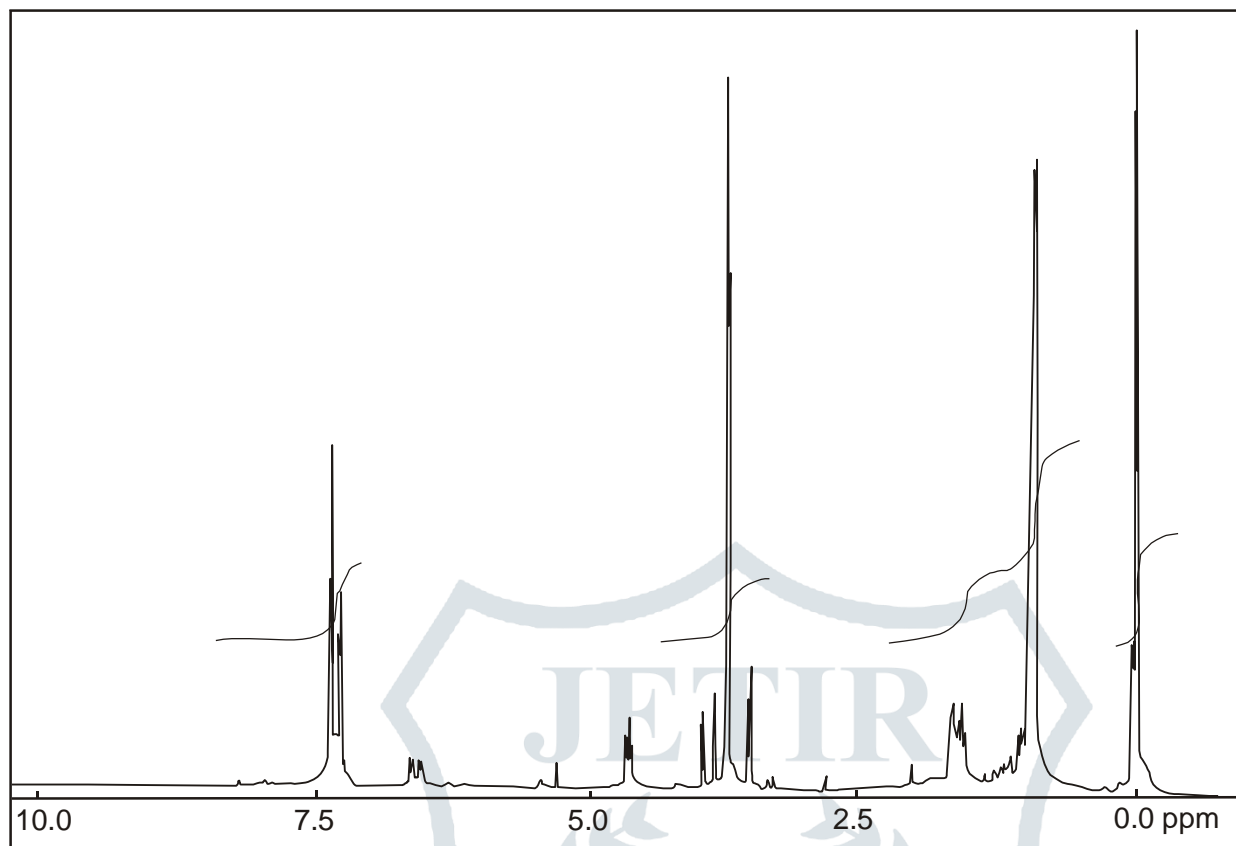


Fig 5. <sup>1</sup>H-NMR spectrum of copolymer using BPO as an initiator.

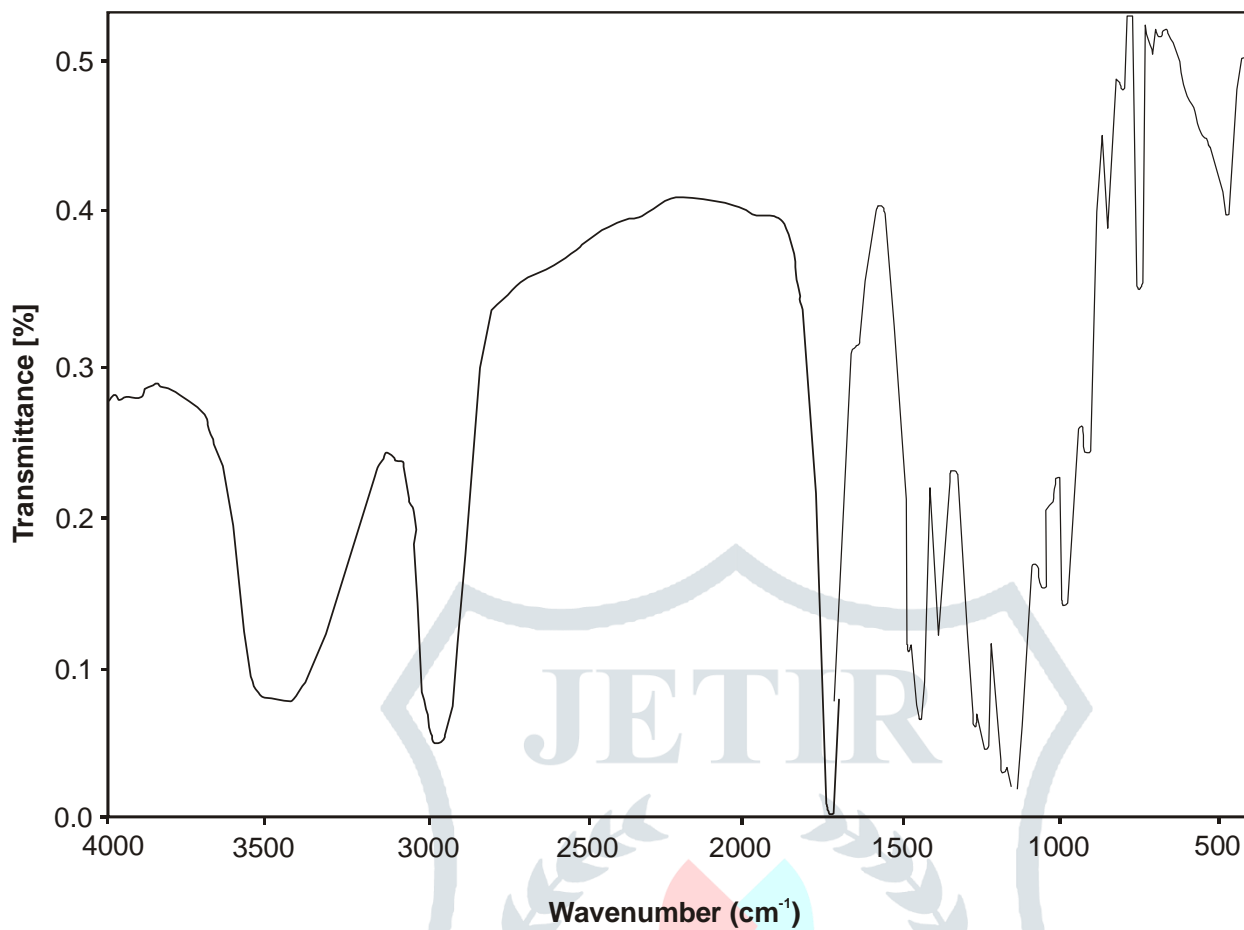


Fig 6. FTIR spectrum of copolymer using BPO as an initiator.

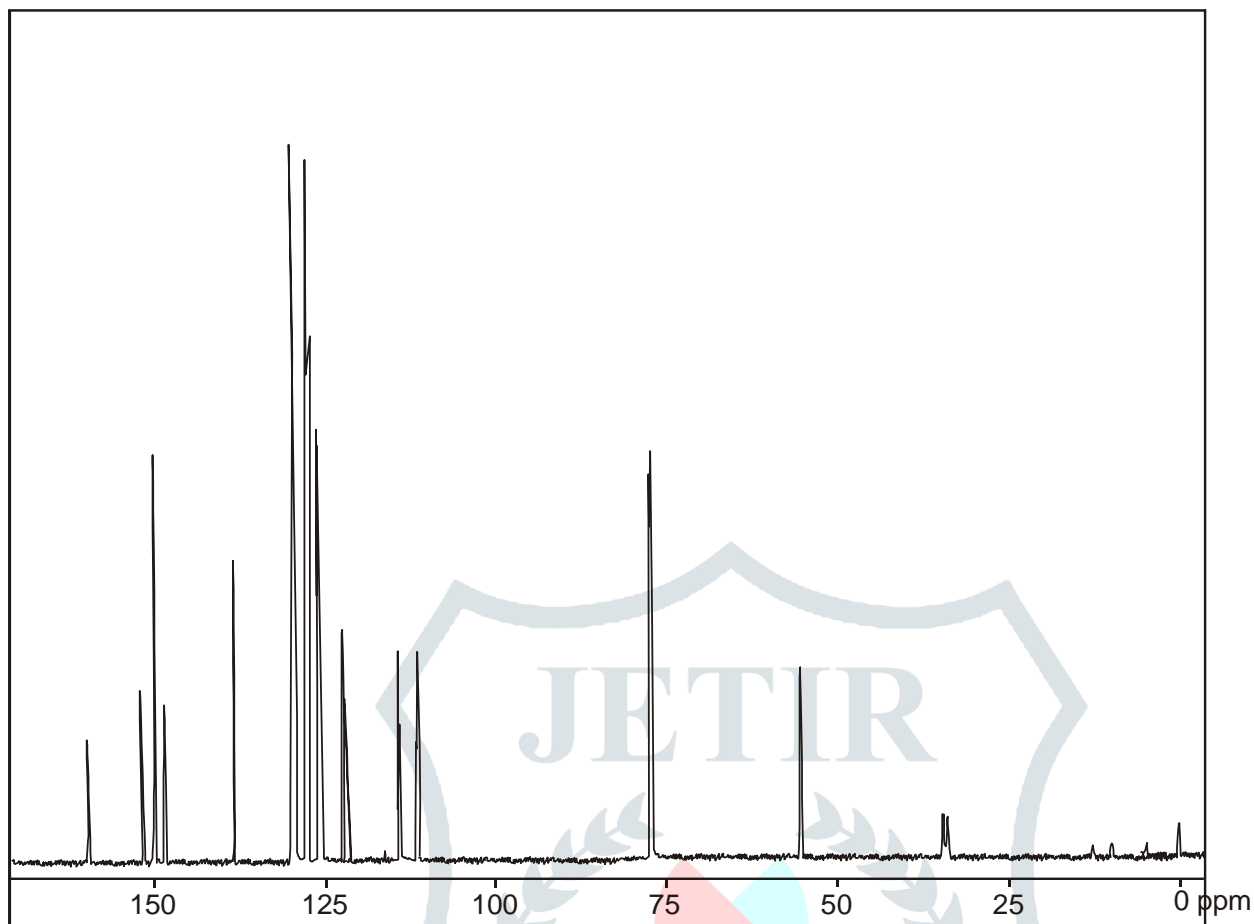


Fig 7. <sup>13</sup>C-NMR spectrum of copolymer using BPO as an initiator.

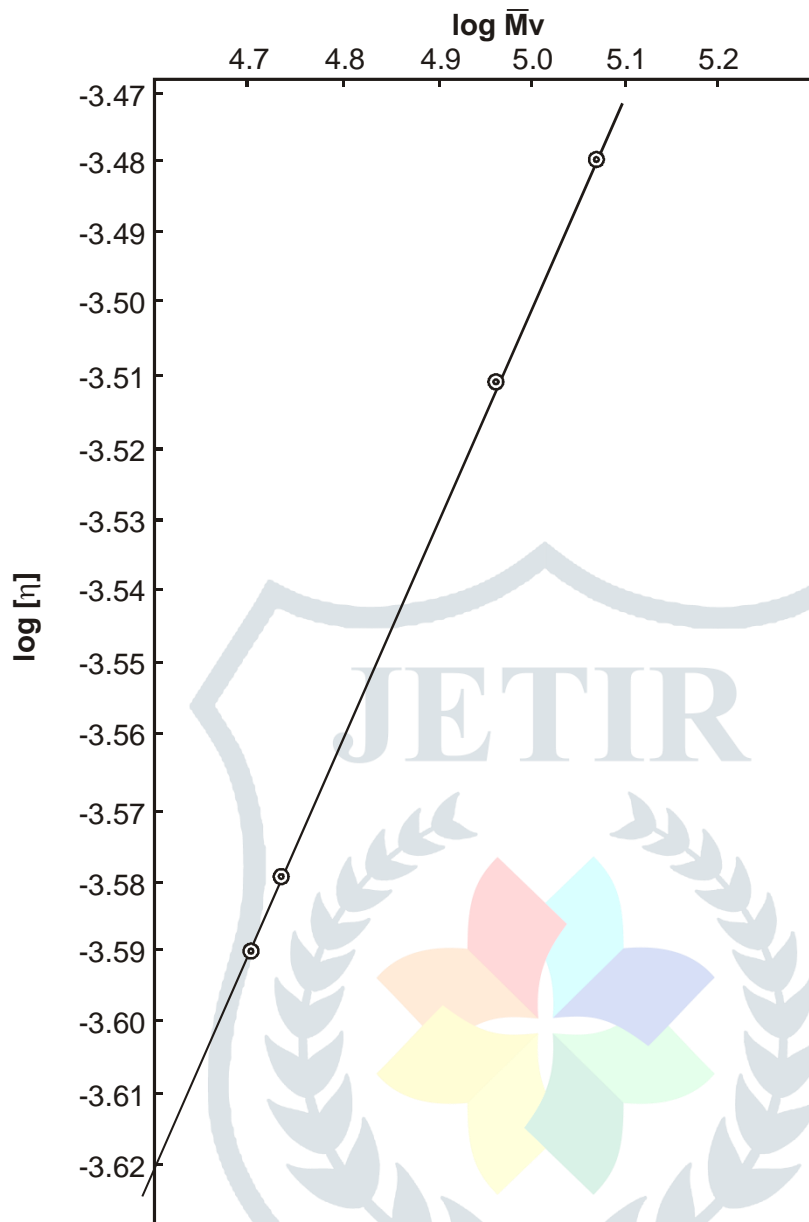


Fig 8. Plot of  $[\eta]$  vs  $\log M_v$  (Mark-Houwink curve)



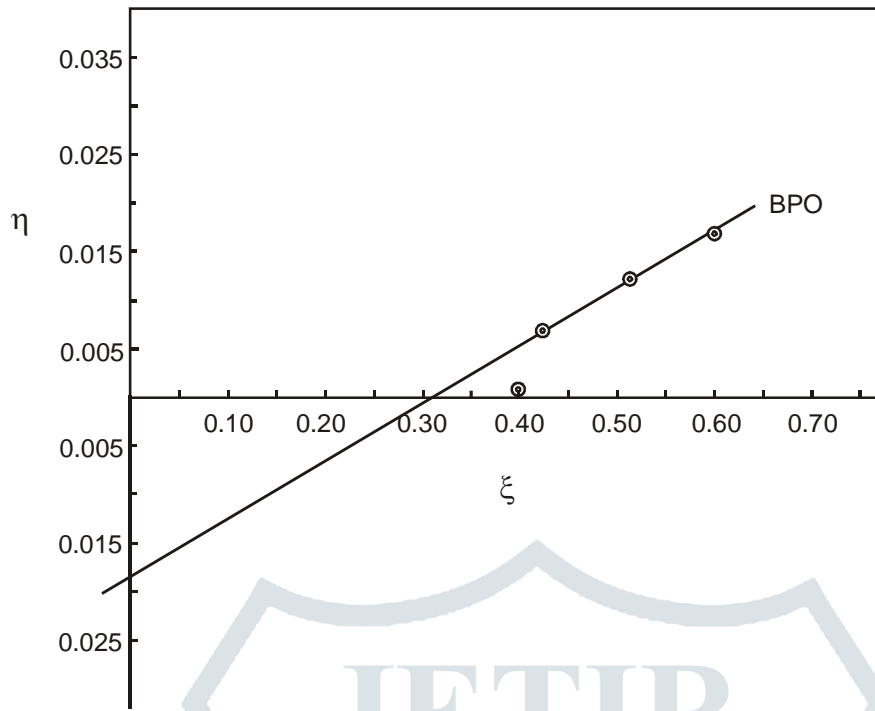


Fig 9. Kelen-Tudos plot of copolymer for determination of reactivity ratio.

