Estimation of Reactivity Ratios of Linoleic Acid and Methyl Methacrylate Copolymer using Ultraviolet Spectroscopy

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Abstract—*A new method for estimation of reactivity ratios of copolymerization of linoleic acid and methylmethacrylate copolymer, by sequentially sampling the reaction medium under nitrogen atmosphere and analyzing the samples by ultraviolet spectroscopy was developed. The data were analyzed by a new mayo-lewis kinetic model. This model relates the comonomer feed, the copolymer composition, and the copolymer sequence distribution and the single copolymer reactivity ratio technique can be used to predict reactivity ratios. The reactivity ratios values of linoleic acid-methyl methacrylate obtained from f(1-F)/F vs. f²/F plot are r_1 =1.06, r_2 =1.3±.2 both values approaching 1. This suggests formation of random polymer.*

Keywords*: Reactivity ratio, mayo-lewis equation, Copolymer composition.*

1. INTRODUCTION

Copolymerization of vegetable based monomers such as linoleic acid has attracted attention in recent years because of several applications of copolymer. The polymer derived from the renewable materials such as vegetable oils are ecofriendly and degradable compare to polymeric materials derived from petroleum origin. These polymers are used as coatings, adhesives, insulators, varnish, paints, binders, medicinal sutures, and matrixes for the preparation of composites [1-6].

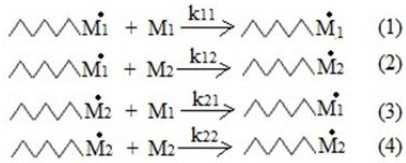
The rate of copolymerization strongly depends upon the structure of monomers. Contrary to homopolymers, copolymers can posses a large number of different sequences of monomers. Relative amounts and structures of the monomers can produce polymers possessing different chemical and physical properties.

On the basis of distribution of monomers, the copolymer can be divided into different categories. If the two monomers are randomly distributed, the polymer is termed random copolymer:

—— M1M1M2M2M2M1M2M1M2M2M1M1M2M1 ——

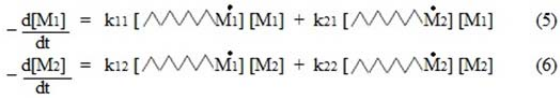
The monomers in such polymers are supposed to follow Markov, or Bernoullian process [7-9].

It is possible to determine copolymerization composition by chemical reactivity of free radical propagating chain terminal unit during copolymerization, applying first order Markov statistics [10-12] Suppose M_1 and M_2 are two monomers used in a copolymerization reaction and /\/\/\/\/\$M_1^*$ /\/\/\/\/\$M_2^*$ are the two propagating chains possessing M_1^* and M_2^* as the radicals at the growing end of the chain and /\/\/\/\/\ as the chain. With these following four propagation reactions are possible for the monomer system under consideration:

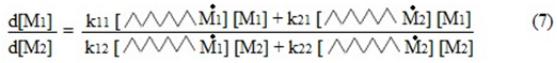


It has been assume that reactivity of the propagating chains depend upon the monomer unit at the end of the propagating chain. The model is also known as terminal unit model [13]. The subscripts associated with rate constants represent terminal monomer associated with the growing chain and the reacting monomer.

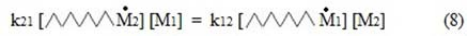
The rate of consumption of monomer M_1 and M_2 can be written as:



The copolymer composition equation can be obtained simply by dividing (5) by (6):



Applying steady state approximation for /\/\/\/\/\$M_1^*$ and /\/\/\/\/\$M_2^*$ we get



Substituting for /\/\/\/\/\M_1^* in eq (7) from eq (8)

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{21}k_{11}[\wedge\wedge\wedge\wedge\dot{M}_2][M_1]^2 + k_{21}[\wedge\wedge\wedge\wedge\dot{M}_2][M_1]}{k_{12}[M_2]} \quad (9)$$
$$k_{22}[\wedge\wedge\wedge\wedge\dot{M}_2][M_2] + k_{21}[\wedge\wedge\wedge\wedge\dot{M}_2][M_1]$$

Eq (9) can be written as:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\{r_1[M_1] + [M_2]\}}{[M_2]\{[M_1] + r_2[M_2]\}} \quad (10)$$

Where

$$r_1 = \frac{k_{11}}{k_{12}} \text{ and } r_2 = \frac{k_{22}}{k_{21}} \quad (11)$$

r_1 and r_2 are called reactivity ratios.

The ratio of the rates of addition of each monomer can also be expressed in terms of the ratio of the molar concentrations of the two monomers present in the copolymer, which is denoted by (m_1/m_2). The copolymer composition equation can then be written as:

$$\frac{m_1}{m_2} = \frac{[M_1]\{r_1[M_1] + [M_2]\}}{[M_2]\{[M_1] + r_2[M_2]\}} \quad (12)$$

Reactivity ratio can also be expressed in terms of mole fraction of each monomer in the copolymer (F) and mole fraction of each monomer in the feed (f). It is easy to understand that:

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (13)$$

And

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (14)$$

Then, combining equations 13, 14 and 11 gives:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (15)$$

This form of the copolymer equation gives the mole fraction of monomer M_1 introduced into the copolymer [11].

In copolymerization studies, the estimation of reactivity ratios is of a great significance. For this reason, many different approaches have been used to estimate these parameters. Different techniques (both linear and nonlinear) are utilized to obtain are extensively used for the determination of monomer reactivity ratios at low conversions including Fineman-Ross [12], Yezrielev-Brokhina-Roskin (YBR) [13], Mayo-Lewis (ML) [11], Kelen-Tüdös (KT), Extended Kelen-Tüdös (EKT), Error-in-Variables-Model (EVM) method [15-17], Tidwell-Mortimer (TM) [18], and Mao-Huglin (MH) [19]. The literature available outlines various techniques to determine copolymer composition via elemental analysis [14]. Additional techniques include ^{13}C and ^{1}H-NMR, IR spectroscopy, and UV spectrophotometry. In this work, the analysis is done by UV spectrophotometry.

In the present research work, we concentrate on estimation of reactivity ratios by using a linear graphical method, which is based upon the terminal model developed by mayo and lewis. The average composition of each polymer sample was determined from the corresponding UV spectrum. The reaction time was selected in such a way that conversion was less than 10% in weight. The assignment of the absorption in the UV spectrum allows accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chain [12]. In UV spectrophotometry, the monomer concentrations are obtained, by UV detection that give linearly independent combinations of concentrations.

The application of UV-vis spectroscopy was performed on the isolated copolymers at low conversion to determine the copolymer composition [14, 20]. Furthermore, the investigation of linear methodologies, originally reported by mayo–lewis [11], to calculate reactivity ratios was performed [22].

The reactivity ratios are not just parameters suited for the estimation of relative reactivities of monomers, but can also provide valuable and precise information for the determination of microstructural parameters such as the distribution of units and sequence lengths along the macromolecular chains [21-24]. The present work was therefore undertaken to examine copolymer absorbance using online UV spectrophotometer and to find its composition by determination of monomer reactivity ratio. We decided to determine the monomer concentration to find reactivity ratio to understand the composition of the copolymer and its property.

2. CHARACTERIZATION

The reactivity ratios of linoleic and methylmethacrylate were determined by estimating the concentrations of monomers and the copolymers employing a UV spectrometer and using mayo-lewis equation. Copolymer composition, its sequence distribution, molecular weight and viscosity are few important parameters to characterize a polymer [23-25]. 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_1 and M_2

The concentration data are then compared with a numerical solution of the mayo equation.

The equation (16) involved in the mayo-lewis method is:

$$\frac{f(1-F)}{F} = r_2 - r_1\left(\frac{f^2}{F}\right) \quad (16)$$

with

$f = \frac{[M_1]}{[M_2]}$ in the feed

and

$F = \frac{d[M_1]}{d[M_2]}$ in the copolymer

Plots of f (1- F)/F versus f^2/F gives a straight line with slope r_1 and intercept r_2.

r_1 & r_2 are the reactivity ratios for monomer M_1 & M_2 described by

$$r_1 = \frac{k_{11}}{k_{12}} \quad \& \quad r_2 = \frac{k_{22}}{k_{21}}$$

k_{11} & k_{22} are rate constants for homopolymerization of M_1 & M_2 respectively. k_{12} and k_{21} are rate constants for copolymerization of M_1 with M_2 and M_2 with M_1 respectively [16].

UV-Vis spectrophotometer is used to observe the concentration of substances in solution. The spectra were recorded under ambient conditions in reflectance mode on a Perkin Elmer Lamba 950 UV/Vis/NIR spectrometer.

The concentration data are then compared with a numerical solution of the Mayo-Lewis equation. This is undoubtedly the most accurate method for determining the concentration of substances in solution.. The absorbance of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner. The instrument employed for this purpose is spectro-photometer and the process is known as spectrophotometry.

For presenting the absorption characteristics of a spectrum, the positions of peaks are reported as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis. ε is constant for particular solvent and l is 1cm then

A α c

Absorbance is directly proportional to concentration of sample.

$$A_1 / A_2 = c_1 / c_2 \qquad (20)$$

Beer-Lambert law offers a valuable and simple method for quantitative analysis. The concentration data are then compared with a numerical solution of the Mayo-Lewis equation [15-16]. Copolymer composition measurement can be achieved by ultraviolet spectroscopy.

3. RESULT AND DISCUSSION

A plot of mayo-lewis equation is in shown in (figure 1). From the slop and intercept value of r_1 & r_2 were found to be 1.06 and 1.3±.2 respectively. This suggests formation of random polymer.

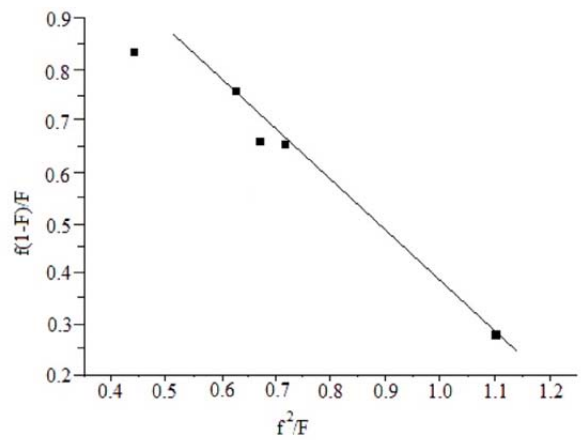


Figure 1: f(1-F)/F vs. f^2/F plot for Linoleic acid- MMA Copolymer.

Different feed ratios of monomers were determined by the *Mayo-Lewis* method shown in table 1.

Table 1: Different feed ratios of monomers determined by mayo-lewis equation

No.	mole ratio of monomers	absorbance ratio of copolymer	feed composition
	m_1/m_2	$F = A_1 / A_2$	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
5	0.66	0.591	0.66

4. CONCLUSION

Co-polymers of linoleic acid and methylmethacrylate were synthesized by free radical polymerization method. The monomer reactivity ratios were determined by mayo-lewis linearization method, employing the technique of UV-vis spectroscopy and are found to be good agreement. The absorbance ratios are compared to different concentration ratios of monomers and use as different feed ratio of monomers. The r_1 and r_2 values are approaching 1; this indicates that the system follows random polymerization. The reactivity ratios values of product were found to be: r_1 =1.06, r_2 =1.3±.2 both values approaching 1. This suggests formation of random polymer.

5. ACKNOWLEDGEMENT

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