



## Copolymerization of Ethyl Methacrylate and Vinyl Acetate with Methacrylamide: Synthesis, Characterization, and Reactivity Ratios

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### Abstract:

The properties of polymers can be most effectively modified with the help of the technique of copolymerisation. In this study, solution polymerization technique was used to obtain low conversion linear copolymer, in order to determine the reactivity ratios of the ethyl methacrylate EMA, vinyl acetate VAC, and methacrylamide MAM. These monomers were used in the synthesis of EMA-co-MAM and VAC-co-MAM with different compositions, initiated by benzoyl peroxide (BPO). The copolymers were characterized by Fourier Transform Infrared (FTIR) and their thermal stability was studied by thermogravimetric analysis (TGA). Their compositions and reactivity ratios ( $r_1$ ,  $r_2$ ) were determined by elemental analysis using linearization methods proposed by Fineman-Ross and Kelen-Tudos, and intersection method proposed by Mayo-Lewis procedure. The derived ( $r_1$ ,  $r_2$ ) for EMA-co-MAM and VAC-co-MAM are: (0.197, 0.230) and (0.294, 4.314), respectively. The microstructure of copolymers and sequence distribution of monomers in the copolymers were calculated by statistical method, the derived results are in agreement with ( $r_1$ ,  $r_2$ ) values. EMA with MAM form alternative copolymer whilst VAC-co-MAM tends to be block with MAM. No study has been reported on the copolymerization and reactivity relationships of hydrophobic monomers (EMA, VAC) with hydrophilic monomers (MAM).

**Key words:** Ethyl methacrylate, vinyl acetate, methacrylamide, reactivity ratios, thermal stability

### Introduction:

The incorporation of two different monomers, having different physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance [1, 2]. Copolymerization is a process of chain polymerization, whereby a combination of two monomers can be used to undertake copolymerization, which results in the formation of polymeric products with distinct compositions within the polymer chain that are called copolymers [3]. The relative concentrations and reactivity of the two monomers dictate the proportions in which they are introduced into the copolymer [4, 5]. In order to determine  $r_1$  and  $r_2$  it is, in principle, only necessary to take two monomer mixtures of known composition, polymerize them to a low conversion less than 15 % and isolate, purify and analysis the products. These results will give two relationships, in the form of equation (1) between the two unknowns  $r_1$  and  $r_2$ , and these can be solved to give  $r_1$  and  $r_2$  [6, 7]:

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

In practice, such a procedure is not reliable, because of experimental errors which arise in the analysis of copolymers, and it is necessary to prepare copolymers from monomer mixtures covering a wide, and preferably the whole, range of possible composition, such copolymerization yield a series of values of the mole fraction  $[M_1]$  and  $[M_2]$  of the two monomers in the monomer mixture together with the corresponding values of the mole fractions  $d[M_1]$  and  $d[M_2]$ , in the copolymer. Several methods have been proposed to arrive at a best fitting  $r_1$ ,  $r_2$  pair from a set of  $[M_1]$ ,  $[M_2]$  and  $d[M_1]$ ,  $d[M_2]$  pairs. In general, the determination of monomer reactivity ratios in copolymerization is entirely dependent on the accuracy of analysis of the products of low conversion experiments [8-10]. Methacrylate derivatives are attracting much attention and have been widely investigated for applications in different

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fields due to their low toxicity, biocompatibility and good film forming. In addition, they have been copolymerized with various other monomers including N-2-anisylmaleimide, naphthylacrylamide, butyl acrylate, maleic anhydride, and N-(4-carboxyphenyl) maleimide [11-15]. On the other hand, the amide group in acrylamide derivatives is highly polar, which confirms its hydrophilic; it has high affinity for many large and small molecules that are known to be good hydrogen-bond acceptors. Many studies have reported on the copolymerization and reactivity relationships of acrylamide derivatives with different other monomers such as acrylic acid, 2-acrylamido-2 methylpropane sulfonic acid, itaconic acid, acrylonitrile, methacryloxyethyltrimethyl ammonium chlorid, and methyl methacrylate [16-21]. In this study, hydrophobic monomers (EMA and VAC) and hydrophilic monomer (MAM) were selected to prepare copolymers at low conversion. This study also determines the reactivity ratios of EMA, VAC, and MAM. From these parameters, a specific comonomer distribution is estimated. So far there has been no investigation on the preparation and study the reactivity ratios of these copolymers

### Experimental:

#### Materials

Methacrylamide (Aldrich-oma chemical Co) was first recrystallized from chloroform. Ethyl methacrylate and vinyl acetate (Merck chemical Co) were shaken 2-3 times with 10% NaOH to eliminate hydroquinone inhibitor, then dried over anhydrous CaCl<sub>2</sub> for 10 h. Benzoyl peroxide (Aldrich-oma chemical Co) was recrystallized twice from methanol prior to use. All solvents were used as received.

#### Copolymerization [22]

The copolymerization were carried out in glass quick fit test tubes at 80 °C using BPO at an overall concentration of 0.001 mol dm<sup>-3</sup> as initiator and dimethylsulfoxide (DMSO) as solvent. As shown in table 1, five different feed compositions were used, the initial mole fraction of all the monomers (MAM, EMA and VAC) are lying within the range (0.1-0.9). In order to remove all oxygen which may inhibit polymerization, nitrogen gas was bubbled through the mixture for 15 minutes prior to the reaction. The reaction was initiated by placing the tubes in a thermostated water bath at 80 °C. The copolymers were isolated by precipitation in methanol. The precipitates were filtered off and purified by washing many times with the precipitant. Copolymers were dried in vacuum at 40 °C until constant weight. Calculations were then performed in order to determine the percent conversion of the copolymers. All the copolymers that were prepared in the study were produced during the first 15 monomer

conversion and the copolymers that were produced that had a higher value than 15 % conversion were set aside and not used in the current study on reactivity ratios. The structures of obtained copolymers are given in the following formulas (Formulas 1 and 2).

#### Characterization

Perken Elmer-1650 spectrophotometer completed with data processing facilities was used to determine the functional groups in the copolymers using a KBr disk method at wavenumber range of 400 to 4000 cm<sup>-1</sup>. Element analysis (N %) were performed by using Elemental Analyzer CHNS-932 instrument. Thermal stability of the copolymers was studied by TGA using Perkin Elmer. Ostwald viscometer was used to determine intrinsic viscosity [ $\eta$ ] according to the Solomon Gotesman relationship [23].

#### Results and Discussion:

The structures of (EMA-co-MAM) and (VA-co-MAM) are confirmed by FTIR as shown in Figures 1. The absorption bands which appear in the FTIR spectra of the copolymers belong to the stretching vibration in different functional groups of their corresponding monomers (EMA, VAC and MAM). The absorption bands of EMA/MAM copolymer as follows: 3400 cm<sup>-1</sup> (amide N-H), 2915 cm<sup>-1</sup> (alkane C-H), the carbonyl absorption of EMA observed at 1735 cm<sup>-1</sup> (ester C=O), 1665 cm<sup>-1</sup> (tertiary amide C=O), 1265 cm<sup>-1</sup> (amide C-N), 1450 cm<sup>-1</sup> (methyl C-H), and 1050 cm<sup>-1</sup> (ester C-O); VAC/MAM copolymer : 3410 cm<sup>-1</sup> (amide N-H), 2905 cm<sup>-1</sup> (alkane C-H), 1660 cm<sup>-1</sup> (tertiary amide carbonyl), 1410 cm<sup>-1</sup> (methyl C-H), 1260 cm<sup>-1</sup> (amide C-N), and 1035 cm<sup>-1</sup> (ester C-O).

#### Copolymer Composition

Characterization of copolymers samples requires determining the mole fractions (F<sub>1</sub>) of comonomer in the copolymer composition, which were obtained using elemental analysis to determine the (N %), in order to determine the MAM incorporated into the copolymer. Results of (N %) analysis, the copolymer composition, and the values of intrinsic viscosity are listed in Table 1. Figure 2 shows the plots of mole fraction of EMA and VAC in the feed (f<sub>1</sub>) versus that of mole fraction of EMA and VAC in the copolymer (F<sub>1</sub>). In EMA/MAM system, EMA forms alternate copolymer with MAM. On the other hand, VAC/MAM copolymer tends to be block with MAM units. Although VAC/MAM copolymer is rich with MAM units, the viscosity of all compositions is not affected because the molecular weight of VAC and MAM units are nearly equal (86 g/mol and 85 g/mol respectively).



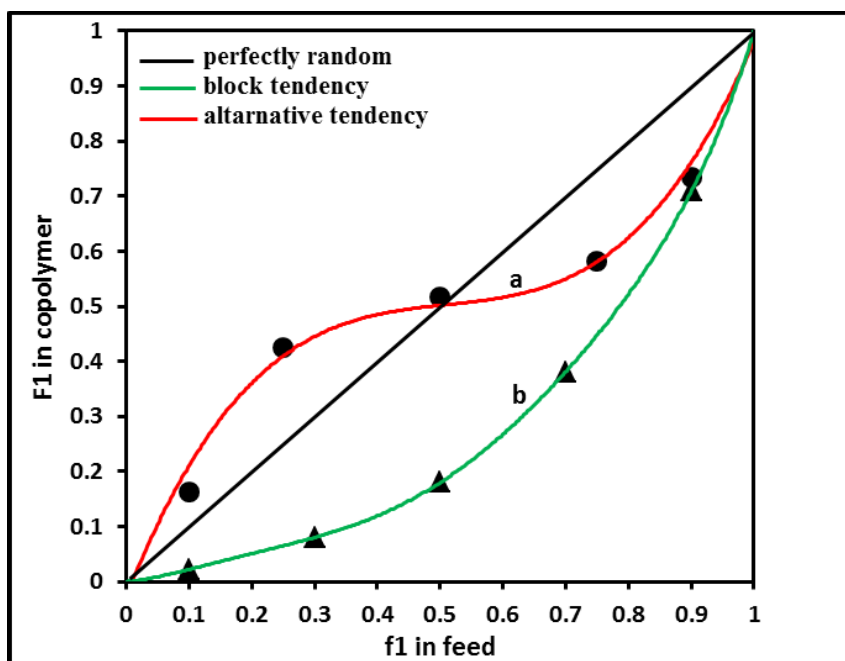


Figure 2: Variation of feed composition  $f_1$  (EMA) and  $f_1$  (VAC) with copolymer composition  $F_1$  (EMA) and  $F_1$  (VAC) of: a- EMA/MAM, b- VAC/MAM copolymers

Table 2: Fineman-Ross, Kelen-Tudos, and Mayo-Lewis parameters of: EMA/MAM, VAC/MAM copolymers

Sample Code	$G$ $f(F-1)/F$	$X$ $f^2/F$	$\eta$ $G/(\alpha+X)$	$\zeta$ $X/(\alpha+X)$	$f$	$1/F$
EMA/MAM-1	5.727	29.45	0.185	0.955	9	0.411
EMA/MAM-2	0.640	3.896	0.121	0.740	2.3	1.626
EMA/MAM-3	0.065	0.934	0.028	0.406	1	4.502
EMA/MAM-4	-0.148	0.246	-0.092	0.152	0.428	11.36
EMA/MAM-5	-0.464	0.063	-0.325	0.044	0.111	45.45
VAC/MAM-1	5.305	33.25	0.143	0.885	9	0.411
VAC/MAM-2	-1.439	8.780	-0.109	0.670	2.3	1.626
VAC/MAM-3	-3.504	4.504	-0.397	0.510	1	4.502
VAC/MAM-4	-4.435	2.071	-0.695	0.324	0.428	11.36
VAC/MAM-5	-4.934	0.559	-1.013	0.114	0.111	45.45

$\alpha = (X_{min} \times X_{max})^{0.5} = 1.362$  and  $4.311$  for EMA-co-MAM and VAC-co-MAM, respectively,  $f = f_1/f_2$ ,  $F = F_1/F_2$

The values of reactivity ratios calculated by various methods are listed in Table 3, the values are very close. In case of EMA/MAM copolymer, the reactivity of EMA (0.197) is of the same order as reactivity of MAM (0.230) due to the presence of the amide and carbonyl groups for each MAM and EMA units. These active groups gave rise to a significant attraction of free electron in the double bond and generate a positive charge in the growing polymer chain and stabilization of the corresponding macroradicals. Since both MAM and EMA are electron rich, it forms the bond easily with electron deficient species, thus they easily involved in polymerization. For this reason attendance to alternative copolymer forming can be postulated; that

is, both  $r_1$  and  $r_2$  are between 0 and 1 in addition to the value of  $r_1 r_2$  which is less than unity. This fact was discussed previously by many other researchers for other copolymer systems, for instant, N-(4-bromophenyl)-2-methacrylamide-co-glycidyl methacrylate ( $r_1 = 0.3453$ ;  $r_2 = 0.8606$ ) [27]. On the other hand, for VAC/MAM copolymer, the reactivity of MAM (4.314) is greater than reactivity of VAC (0.294) which leads to a greater incorporation of MAM units compared to VAC units and demonstrating the blockness behavior of the MAM monomers. In this case, the stabilization of VAC growing radical is weak due to absent the resonance in its structure.

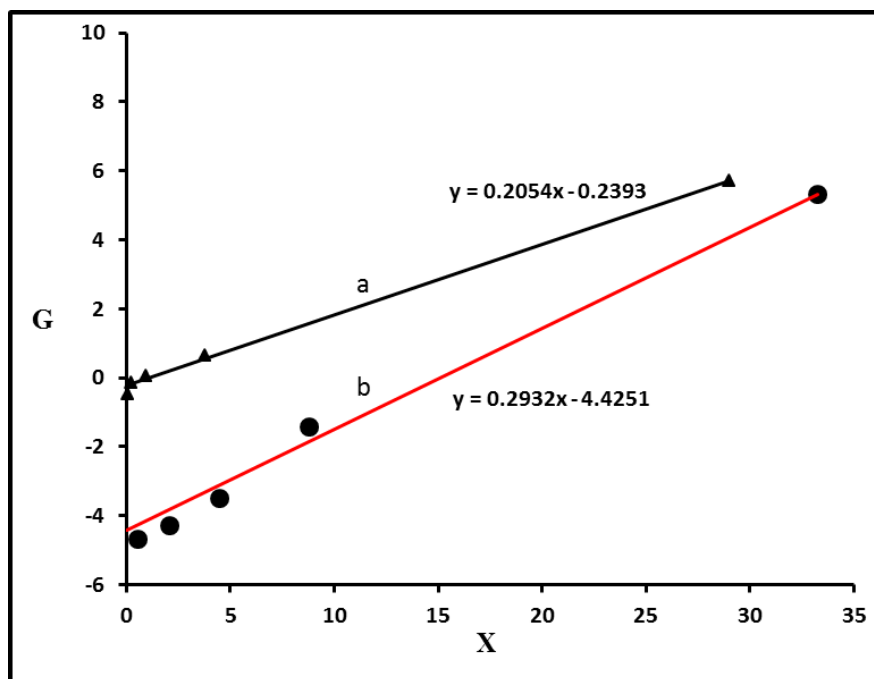


Figure 3: Fineman-Ross plot of: a- EMA/MAM, b- VAC/MAM copolymers

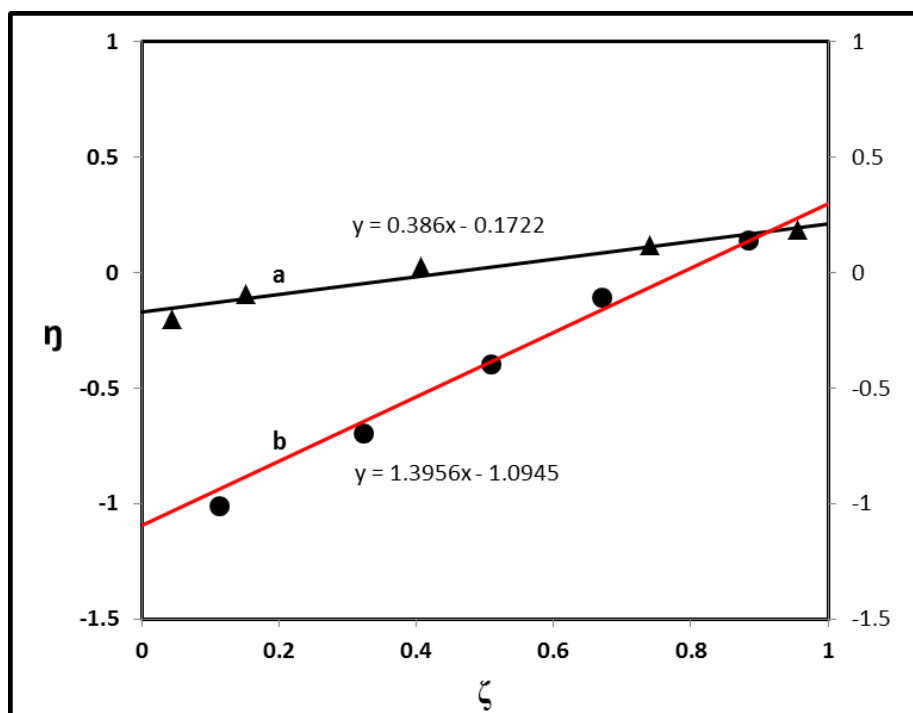


Figure 4: Kelen-Tudos plot of: a- EMA/MAM, b- VAC/MAM copolymers

Moreover, the spacing out of the carbonyl group of the main chain decreases the reactivity of this monomer. A similar behavior was described earlier by Garreti and Hegazy when vinyl acetate was copolymerized with methyl acrylate ( $r_1=0.029$ ,  $r_2=0.67$ ) [28] and N-(2-thiazolyl)methacrylamide ( $r_1=0.41$ ,  $r_2=0.81$ ) [29].

If feed and copolymer compositions are identical at the same point, azeotropic copolymerization ( $f_1$  (az.)) occurs, which can be expressed by the following equation:

$$f_1 \text{ (az)} = (1 - r_2) / (2 - r_1 - r_2) \quad (2)$$

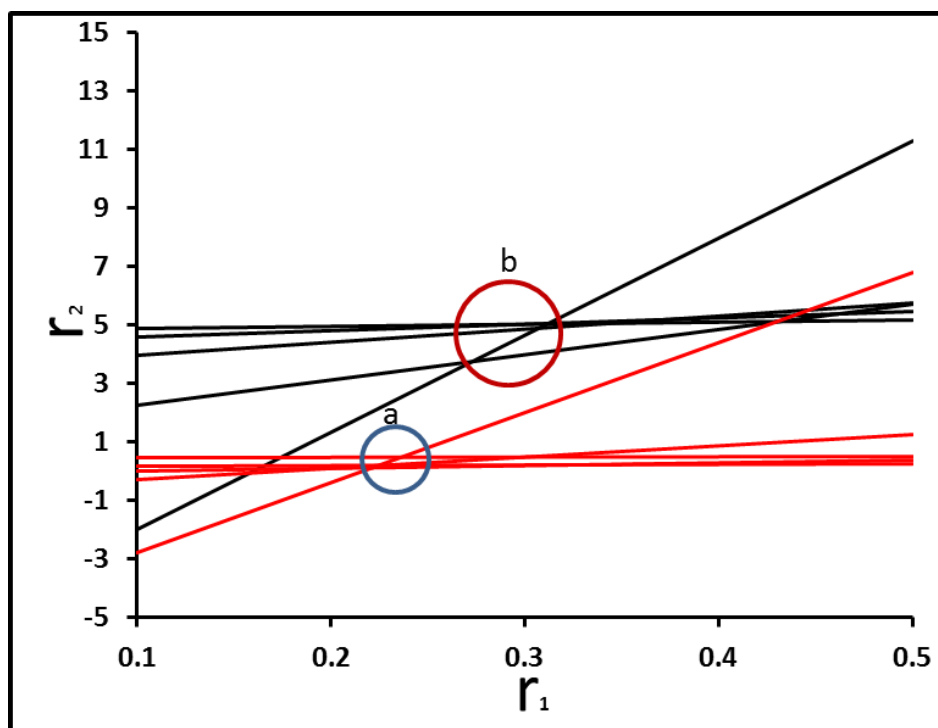


Figure 5: Mayo-Lewis plot of: a- EMA/MAM, b- VAC/MAM copolymers

Table 3: Monomer reactivity ratios values of: EMA/MAM, VAC/MAM copolymers

Copolymer	Procedure	$r_1$	$r_2$
EMA/MAM	Fineman-Ross	0.205	0.239
	Kelen-Tudos	0.194	0.225
	Mayo-Lewis	0.193	0.226
	<b>Average values</b>	<b>0.197</b>	<b>0.230</b>
VAC/MAM	Fineman-Ross	0.293	4.425
	Kelen-Tudos	0.298	4.411
	Mayo-Lewis	0.292	4.406
	<b>Average values</b>	<b>0.294</b>	<b>4.314</b>

If the values of  $r_1$ ,  $r_2$  are both more or less than 1, the possibility of an azeotropic composition increases. For EMA-co-MAM, this condition is fulfilled since  $r_1$  and  $r_2$  are less than 1. Figure 2 proves this fact, in which a value of 0.5 for  $f_1$  (az.) could be clearly observed. On the other hand, no azeotropic composition exists for VAC-co-MAM because  $r_1 < 1$  and  $r_2 > 1$ .

#### Copolymer Microstructure

The statistical distribution of the monomers (MAM, EMA and VAC) in the formation of the copolymers EMA/MAM and VAC/MAM are calculated using equation (3) [30], and listed in Table 4:

$$S_{1-1} = F_1 - \frac{2F_1F_2}{1+[(2F_1-1)^2+4r_1r_2F_1F_2]^{1/2}}$$

$$S_{2-2} = F_2 - \frac{2F_1F_2}{1+[(2F_1-1)^2+4r_1r_2F_1F_2]^{1/2}} \quad (3)$$

$$S_{1-2} = \frac{4F_1F_2}{1+[(2F_1-1)^2+4r_1r_2F_1F_2]^{1/2}}$$

Where  $S_{1-1}$ ,  $S_{2-2}$ , and  $S_{1-2}$  represent the mole fractions of 1-1, 2-2, and 1-2 sequences, respectively.

The probabilities of finding the sequence of monomer-1 (EMA or VAC) and monomer-2 (MAM) units are calculated by applying equation (4) [31, 32], and listed in Table 4:

$$P_{11} = r_1[f_1]/(r_1[f_1] + [f_2])$$

$$P_{22} = r_2[f_2]/(r_2[f_2] + [f_1]) \quad (4)$$

$$P_{12} = [f_2]/(r_1[f_1] + [f_2])$$

$$P_{21} = [f_1]/(r_2[f_2] + [f_1])$$

Where  $P_{11}$ ,  $P_{12}$ ,  $P_{21}$ , and  $P_{22}$  are the probabilities for forming the dyads,  $M_1M_1$ ,  $M_1M_2$ ,  $M_2M_1$ , and  $M_2M_2$ , respectively.

The average length sequences of monomer-1 (EMA or VAC) and monomer-2 (MAM) are calculated using equation (5) [33], and tabulated in Table 4:

$$\mu_1 = 1/P_{12} \quad (5)$$

$$\mu_2 = 1/P_{21}$$

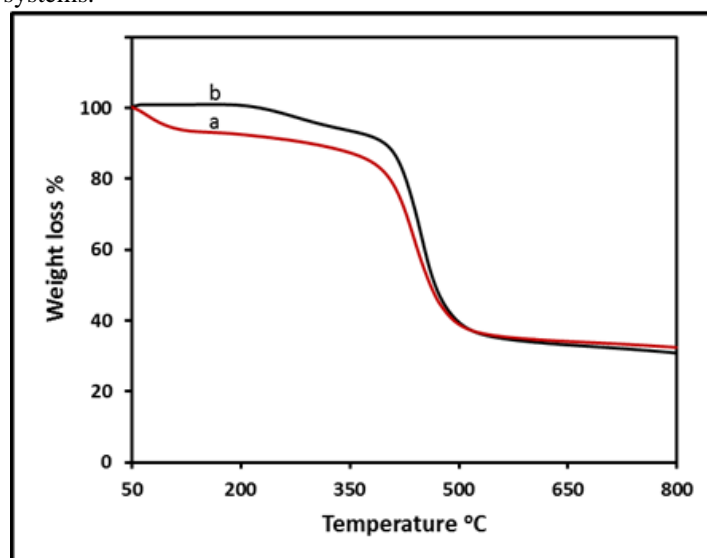
**Table 4: Statistical data of: EMA/MAM, VAC/MAM copolymers**

Sample Code	Blockness		Alternation	Sequence probability				Sequence length	
	$S_{1-1}$	$S_{2-2}$	$S_{1-2}$	$P_{11}$	$P_{22}$	$P_{12}$	$P_{21}$	$\mu_1$	$\mu_2$
EMA/MAM-1	0.475	0.006	0.519	0.639	0.024	0.360	0.975	2.773	1.025
EMA/MAM-2	0.241	0.025	0.734	0.314	0.089	0.685	0.910	1.459	1.098
EMA/MAM-3	0.106	0.073	0.821	0.164	0.186	0.835	0.813	1.197	1.230
EMA/MAM-4	0.032	0.209	0.759	0.077	0.349	0.922	0.650	1.084	1.536
EMA/MAM-5	0.002	0.669	0.329	0.021	0.672	0.978	0.325	1.021	3.070
VAC/MAM-1	0.512	0.094	0.394	0.725	0.324	0.274	0.675	3.649	1.481
VAC/MAM-2	0.150	0.385	0.465	0.406	0.648	0.593	0.351	1.686	2.849
VAC/MAM-3	0.038	0.677	0.285	0.227	0.811	0.772	0.188	1.295	5.319
VAC/MAM-4	0.021	0.857	0.122	0.111	0.909	0.888	0.090	1.126	11.11
VAC/MAM-5	0.001	0.956	0.043	0.031	0.974	0.968	0.025	1.033	40

In case of EMA/MAM copolymer,  $S_{1-1}$ ,  $P_{11}$ ,  $P_{21}$ , and  $\mu_1$  increase as EMA increases in the feed, whilst  $S_{2-2}$ ,  $P_{22}$ ,  $P_{12}$ , and  $\mu_2$  increase as MAM increases. From these results, both EMA and MAM have a tendency to react with the other monomer (MAM or EMA) in addition to itself in the growing chain to form alternative-block copolymer. On the other hand, for VAC/MAM copolymer, the values  $S_{2-2}$  (0.956),  $P_{22}$  (0.974),  $P_{12}$  (0.968) and  $\mu_2$  (40) for VAC/MAM-5 are much higher than  $S_{1-1}$  (0.512),  $P_{11}$  (0.725),  $P_{21}$  (0.675), and  $\mu_1$  (3.64) for the corresponding composition (VAC/MAM-1) indicating that MAM prefer to react with itself rather than VAC to form block (MMA) units distributed in the growing chain. These results are in agreement with the values of  $r_1$ ,  $r_2$  for both copolymers systems.

### Thermal properties

Figure 5 shows the results of TGA for both copolymers, VAC/MAM copolymer is more stable than the EMA/MAM copolymer with 10 % weight loss of VAC/MAM-1 at about 380 °C which is higher than 270 °C of EMA/MAM-1 copolymer. This result could be attributed to the presence of ethyl and methyl groups in the backbone of EMA side chain which significantly lowers the thermal stability of EMA/MAM copolymer. In addition, it is found that by increasing the amount of MAM content in both copolymers result in increased thermal stability, this may be due to the presence of rigid amide group in the backbone of MAM side chain.



**Figure 6: TGA thermogram of: (a) EMA/MAM-1, (b) VAC/MAM-1 copolymers**

### Conclusions:

The copolymers EMA/MAM and VAC/MAM were successfully prepared. FT-IR technique confirmed

formation of the synthesized copolymers. Nitrogen analysis test was employed to determine the copolymer compositions and the reactivity ratios by

various procedures: Fineman-Ross, Kelen-Tudos, and Mayo-Lewis, a good agreement was observed between the three methods. EMA-co-MAM tend to be alternative ( $r_1 = 0.197$ ,  $r_2 = 0.230$ ) whilst VAC-co-MAM form block copolymer with MAM units ( $r_1 = 0.294$ ,  $r_2 = 4.314$ ). Copolymer microstructure results were calculated by statistical method and showed a good agreement with the obtained reactivity ratios. VAC/MAM copolymer has more thermal stability than EMA/MAM copolymer.

#### References:

- Craciun G., Ighigeanu D., Manaila E., Stelescu M.D., Synthesis and characterization of poly (acrylamide-co- acrylic acid) flocculant obtained by electron beam irradiation. *Materials Research*, **18**(5), 984-93(2015).
- Mohammed, A., Dhedan, R. M., Mahmood, W. A., & Musa, A. (2021). Copolymers of Castor and Corn Oils with Lauryl Methacrylate as Green Lubricating Additives. *Egyptian Journal of Chemistry*, **64**(8), 1-2.
- Abed, N., & Mohammed, A. (2021). Synthesis and Characterization of (Methyl Methacrylate/Phenyl Acrylamide) Hydrogel for Biomedical Applications. *Egyptian Journal of Chemistry*, **64**(9), 5181-5187.
- Riahinezhad M., Kazemi N., McManus N., and Penlidis A., Effect of ionic strength on the reactivity ratios of acrylamide/acrylic acid (sodium acrylate) copolymerization. *Journal of Applied Polymer Science*, **131**, 20(2014).
- Gavrilov A.A. and Chertovich A.V., Copolymerization of Partly Incompatible Monomers: An Insight from Computer Simulations. *Macromolecules*, **50**(12), 4677-85(2017).
- Beckingham B.S., Sanoja G.E., and Lynd N.A., Simple and Accurate Determination of Reactivity Ratios Using a Nonterminal Model of Chain Copolymerization. *Macromolecules*, **48**(19), 6922-30(2015).
- El-Newehy M.H., Al-Deyab S.S., and Al-Hazmi A.M., Reactivity ratios for organotin copolymer systems. *Molecules*, **15**(4), 2749-58(2010).
- Acikses A., Taskan G., and Barim G., A Study on Copolymer Systems of Styrene with Diethanolamine Side Group and Methyl Methacrylate. *Journal of Chemistry*, **2018**(2018).
- Mohammed A.H., Ahmad, M.B., Ibrahim, N. A., and Zainuddin, N., Synthesis and monomer reactivity ratios of acrylamide with 3-(trimethoxysilyl) propyl methacrylate and tris (methoxyethoxy) vinylsilane copolymers. *Polimery*, **61**(11-12), 758-765(2016).
- Alazrak, S. M., Awad, S., Khalil, A. A., & El-DougDoug, W. (2021). Synthesis and evaluation of new cationic polymeric surfactant based on N-phthalimidomethyl methacrylate. *Egyptian Journal of Chemistry*, **64**(7), 3-4.
- Oswal S., Bhandari V.K., Bhamore P., and Malek N.I., Free radical copolymerization of methyl methacrylate and styrene with N-(4-carboxyphenyl) maleimide. *International Journal of Polymeric Materials*, **56**(4), 421-435(2007).
- Sengupta S., Das T., Ghorai U.K., and Bandyopadhyay A., Copolymers from methyl methacrylate and butyl acrylate with hyperbranched architecture. *Journal of Applied Polymer Science*, **134**(42), 45356(2017).
- Zhan P., Chen J., Zheng A., Huang T., Shi H., Wei D., and Guan Y., Preparation of methyl methacrylate-maleic anhydride copolymers via reactive extrusion by regulating the trommsdorff effect. *Materials Research Express*, **6**(2), 025315 (2018).
- Oswal S., Patel M.H., and Patel S.G., Copolymerization of methyl methacrylate, ethyl acrylate, and butyl acrylate with n-2-anisylmaleimide and characterization of the copolymers. *International Journal of Polymeric Materials*, **56**(3), 307-326(2007).
- Mohammed A.H., Studying Reactivity Relationships of Copolymers N-naphthylacrylamide with (Acrylic acid and Methylacrylate). *Baghdad Science Journal*, **16**(2)(2019).
- Riahinezhad M., Kazemi N., McManus N., and Penlidis A., Optimal estimation of reactivity ratios for acrylamide/acrylic acid copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, **51**(22), 4819-4827(2013).
- Scott A.J., Riahinezhad M., and Penlidis A., Optimal design for reactivity ratio estimation: A comparison of techniques for AMPS/acrylamide and AMPS/acrylic acid Copolymerizations. *Processes*, **3**(4), 749-768(2015).
- Wang Y., Zhang X., Li W., Cheng J., Liu C., and Zheng J., Determination of reactivity ratios of copolymerization of acrylamide (AM) and methacryloxyethyltrimethyl ammonium chloride (DMC) with ultraviolet initiation, and their sequence length distribution. *Polymers & Polymer Composites*, **24**(5), 307(2016).
- Erbil C., Özdemir S., and Uyanık N., Determination of the monomer reactivity ratios for copolymerization of itaconic acid and acrylamide by conductometric titration method. *Polymer*, **41**(4), 1391-1394(2000).



- 20-Hou C., Ying L., and Wang C. Determination of monomer apparent reactivity ratios for acrylonitrile-acrylamide copolymerization system. *Journal of Materials Science*, **40**(3), 609-612(2005).
- 21-Mohammed A.H., Mahmood T.A., Yousif S. A., Musa A., and Dally N.N., Synthesis, Characterization and Reactivity Ratios of Poly Phenyl Acrylamide-Co-Methyl Methacrylate. *Materials Science Forum*. **1002**, 66-74(2020).
- 22-Ashenagar, S., Ziaee, F., & Jalilian, S. M. (2013). Calculation of reactivity ratios of methacrylic acid-ethyl acrylate copolymer by on-line quantitative  $^1\text{H}$  NMR spectroscopy. *Iranian Polymer Journal*, **22**(9), 635-639.
- 23-Mohammed K.M., Abdalla I.K., Mohammed A.H., Khairuddin F.H., Ibrahim A.N.H., Rosyidi S.A.P., and Yusoff N.I.M., Determining the effects of Rh-Wma on the engineering properties of bitumen. *Jurnal Teknologi*, **81**(2) (2019).
- 24-Fineman M. and Ross S.D., Linear method for determining monomer reactivity ratios in copolymerization. *Journal of Polymer Science*, **5**(2) 259-62(1950).
- 25-Kelen T., Tüdös F., Turcsányi B., and Kennedy J.P., Analysis of the linear methods for determining copolymerization reactivity ratios. IV. A comprehensive and critical reexamination of carbocationic copolymerization data. *Journal of Polymer Science*, **15**(12), 3047-74(1977).
- 26-Mayo F.R. and Lewis F.M., Copolymerization. I. A basis for comparing the behavior of monomers in copolymerization; the copolymerization of styrene and methyl methacrylate. *Journal of the American Chemical Society*, **66**(9), 1594-1601(1944).
- 27-Igarashi S., Representation of composition and blockiness of the copolymer by a triangular coordinate system. *Journal of Polymer Science*, **1**(7), 359-63(1963).
- 28-Soykan, C., Delibaş, A., & Coşkun, R. (2008). Novel copolymers of N-(4-bromophenyl)-2-methacrylamide with glycidyl methacrylate: Synthesis, characterization, monomer reactivity ratios and thermal properties. *Reactive and Functional Polymers*, **68**(1), 114-124.
- 29-Garrett, T. A., & Park, G. S. (1966). Reactivity ratios for the copolymerization of vinyl acetate with methyl acrylate. *Journal of Polymer Science Part A-1: Polymer Chemistry*, **4**(10), 2714-2717.
- 30-Hegazy, M. A., El-Hamouly, S. H., Azab, M. M., Beshir, S. I., & Zayed, M. A. (2014). Homo-and copolymerization of N-(2-thiazolyl) methacrylamide with different vinyl monomers: Synthesis, characterization, determination of monomer reactivity ratios and biological activity. *Polymer Science Series B*, **56**(2), 182-190.
- 31-Vijaykumar S., Prasannkumar S., Sherigara B.S., Shelke N.B., Aminabhavi T.M., and Reddy B.S., Copolymerization of N-vinyl pyrrolidone with functionalized vinyl monomers: Synthesis, characterization and reactivity relationships. *Macromolecules Research*, **17**(12), 1003-9(2009).
- 32-Parambil A.M., Puttaiahgowda Y.M., and Shankarappa P., Copolymerization of N-Vinyl pyrrolidone with methyl methacrylate by Ti (III)-DMG redox initiator. *Turkish Journal of Chemistry*, **36**(3), 397-409(2012).
- 33-Mohammed A.H., Bin Ahmad M., and Shamel K., Copolymerization of tris (methoxyethoxy) vinyl silane with N-vinyl pyrrolidone: synthesis, characterization, and reactivity relationships. *International Journal of Polymer Science*, **2015**, 2015.

## البلمرة المشتركة للايثيل ميثاكريلات و خلات الفينيل مع الميثاكريلاميد: تحضير و تشخيص و حساب نسب الفعالية

### الخلاصة

ان البوليمرات تكون اكثر فعالية عند استخدام تقنية البلمرة المشتركة. يتضمن البحث استخدام تقنية بلمرة المحاليل لتحضير بوليمرات خطية بنسب تحويل واطنة وذلك لحساب نسب الفعالية لكل من الايثيل ميثاكريلات و خلات الفينيل و الميثاكريلاميد حيث استخدمت هذه المونومرات لتحضير بوليمرات الايثيل ميثاكريلات-مشتراك-ميثاكريلاميد و خلات الفينيل-مشتراك-ميثاكريلاميد بنسب مختلفة باستخدام بيروكسيد البنزويل كبادئ. تم تشخيص البوليمرات المحضرة بواسطة طيف الاشعة تحت الحمراء و تم دراسة استقراريتها الحرارية بواسطة التحليل الحراري الوزني. تم حساب نسب الفعالية بالاعتماد على نسبة النيتروجين المحددة بواسطة تحليل العناصر حيث استخدمت طرق مختلفة لحساب نسب الفعالية مثل فايتمان -روس وكابلن -تودوس و مايو- لوبس وكانت النتائج (0,197 و 0,230) و (0,294 و 4,314) على التوالي ومن ثم استخدمت هذه القيم لدراسة التراكيب المايكروية الدقيقة للبوليمرات المشتركة المحضرة حيث وجد بان نتائجها تتطابق مع قيم نسب الفعالية المحسوبة حيث كون الايثيل ميثاكريلات بوليمر مشترك متناوب مع الميثاكريلاميد اما خلات الفينيل فقد كونت بوليمرا مشتركا متكتل مع الميثاكريلاميد على كل حال فانه لا توجد دراسة مسبقه تتضمنت بلمرة مونومرات كاره للماء (الايثيل ميثاكريلات و خلات الفينيل) مع مونومرات محبة للماء (الميثاكريلاميد).

الكلمات المفتاحية: ايثيل ميثاكريلات ، خلات الفينيل ، الميثاكريلاميد، نسب الفعالية، الاستقرار الحراري