

## Reactivity Ratios of the Copolymerization Styrene/ Methyl Methacrylate Using FT-IR Spectroscopy with Comparing to Mathematically Method

*Tariq Abdul-Jaleel\**

*Wajeih Younis\**

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### Abstract:

Free Radical Copolymerization of Styrene/ Methyl Methacrylate were prepared chemically under Nitrogen ,which was investigated, in the present of Benzoyl Peroxide as Initiator at concentration of  $2 \times 10^{-3}$  molar at 70 °C, which was carried out in Benzene as solvent to a certain low conversion . FT-IR spectra were used for determining of the monomer reactivity ratios ,which was obtained by employing the conventional linearization method of Fineman-Ross (F-R) and Kelen-Tüdös (K- T). The experimental results showed the average value for the Styrene  $r_1$  / Methyl Methacrylate  $r_2$  system, Sty  $r_1 = 0.45$  , MMA  $r_2 = 0.38$  in the (F-R) Method and  $r_1 = 0.49$  ,  $r_2 = 0.35$  in the (K-T) Method, The Results of this indicated show the random distribution of monomers in the copolymer.Likewise The monomer reactivity ratios were evaluated Mathematically in comparison in the (F-R) Method with the data STY  $r_1 = 0.61$  , MMA  $r_2 = 0.47$  , and  $r_1 = 0.45$  ,  $r_2 = 0.38$  in the (K-T) Method. And were used the values  $r_1, r_2$  for STY / MMA Copolymers in computing integral curves for the instantaneous Copolymer composition throughout the whole range of conversion.

**Key Words:** Reactivity Ratios , Copolymerization, Styrene , Methyl Methacrylate

### Introduction:

Copolymerization is the most successful and powerful method for effecting systematic change in polymer and extensively used in industrial processes, because their physical properties, [1] ,such as elasticity, permeability, glass transition temperature ( $T_g$ ) ,and Copolymerization is one of the common ways to improve the homopolymers and increased the areas uses in industrial, agricultural and medical displines . Researchers have hence combined various homopolymer mixtures to form new types of polymers that exploit the desired properties of one type of monomer. Reactivity ratios ( $r_1$  ,  $r_2$ ) are among the most important parameters for the composition equation of copolymers, which can offer information such as the relative reactivity of monomer

pairs and help to estimate the copolymer composition. [2 ,3].

Reactivity ratios are to perform a low conversion copolymerization at various initial monomers feed compositions, It may be evaluated by various procedures: linear procedures, nonlinear procedures, [4] which can be Classified as approximation (Alfrey) , curve fitting (san Roman and Madruga) , intersection (Mayo & Lewis) Linearization (Fineman and Ross F-R , Kelen & Tudose K-T) this method is the widely used for Copolymers , and non- linear Least Squares . [5].Methyl methacrylate (MMA) and Styrene (STY) are considered as reactive monomers primarily because of the presence of aromatic ring in Styrene there is more reactive. Choudhary Veena and coworkers prepared copolymer of

\*Department of Chemistry - college of Science -University of Anbar

e-Mail : tarik \_jm@yahoo.com

methyl methacrylate (MMA) with a variety of vinyl monomers. [6]. A new prepared methacrylate monomer and copolymerized it with different feed ratio of styrene/ methyl acrylate/N-vinyl pyrrolidone. Reactivity ratio was calculated by applying conventional linearization method of F-R and K-T. [7]. The copolymers derived from STY / MMA have found wide spread of industrial and medical applications, Poly methyl methacrylate (PMMA) is widely used as a sheet glazing material, optical lens and fluorescent solar collectors, because of its optical clarity and UV resistance. Polystyrene has reasonably good mechanical and thermal prosperities with its high refractive index, but its stability to outside weathering is poor: it becomes yellow easily on exposure. The optical properties of a cyclic olefin copolymer are attractive on account of their high use temperature, excellent optical transmission, low birefringence and low moisture uptake. [8 –11] .

In this research, the Reactivity ratios of Copolymerization Reaction were determined, by using F-R and K-T methods and the copolymers composition was determined by FT- IR spectroscopy. An afford has made on predications of compositional heterogeneity for the system STY / MMA .

## Materials and Methods :

### Chemicals ;

Styrene ( Aldrich Chemical Co ), Methyl Methacrylate ( Fluka Chemical Co ), has been freed from the inhibitor By being washed and shaken three times first 10% With NaOH and then washed with water several times , after drying over anhydrous  $MgSO_4$  , it was distilled under Vacuum distillation at  $65^\circ C / 2.0 \text{ mmHg}$  and  $70^\circ C / 3.0 \text{ mmHg}$ , respectively .Benzoyl Peroxide the initiator from Sigma ,was purified by Recrystallization twice from

methanol. Acetonitrile , Benzene, Chloroform, Acetone and methanol used in the present work were of analytical grade and were used as received.

### Instrumentation;

FT-IR spectra were recorded on SHIMADZU Spectrum of infrared spectrophotometer, specimens from each copolymer were subjected to elemental analysis (C, H, N,O) Analyzer, Canon Viscometer tube were used to measurement the Number average Molecular Weight  $M_n$  and Weight average Molecular Weight  $M_w$  .

### Copolymerization;

Low-conversion(<10wt%)

copolymerization kinetics of the STY / MMA Systems were studied. copolymers with different compositions Table(1), were synthesized. Mixtures of monomer-solvent-initiator, dosed in test tubes tight with stopper having conical joints, were conditioned through nitrogen bubbling and then placed in thermostatic baths at  $70^\circ C$ . initiation concentration (Benzoyl Peroxide) at  $2 \times 10^{-3}$  molarity, The glass tubes were charged with the mixtures of monomers with total molar composition at  $(4 \text{ mol dm}^{-3})$  , and were then sealed under vacuum . After the requested time (<10wt% Conversion) , the Copolymer were precipitated in petroleum ether ( bp  $40 - 60^\circ C$  ) , The precipitates were filtered off, dissolved again in benzene and precipitated in petroleum ether prior to drying to constant weight in vacuum  $40^\circ C$ . The Copolymer compositions were determined by element analysis and FT – IR Spectrum .

### Conversion:

After Copolymerization the discs were swollen to equilibrium Solvent (benzene ) at  $30^\circ C$  over 2 days, to remove any possible unreacted monomers or linear polymer. These

samples were dried to constant weight in 40°C In an oven and 30°C in a vacuum oven. The quantity ( $m_1$ ), the mass of the copolymers, and the ratio of ( $m_1$ ) to known mass ( $m_0$ ) of ( STY +MMA+BPO ) in the feed mixture represents the fractional conversion to copolymer. The ratio ( $r$ ) represents the minimum value of the conversion of monomers .The ratio of  $r = m_1 / m_0$

**Isolation of Copolymers:**

Was done by using a selective solvent as ( Aceto nitrile) which dissolves the PMMA and doesn't dissolve PSTY and Copolymer. Then the mixture was filtrated and deposited with the quantity of methanol to obtain a homogeneous polymer PMMA which Isolated from the Copolymer. And in the same way the PSTY was isolated by using selective solvent (Cyclohexane) Which dissolves the

PSTY and doesn't dissolve others. The copolymers were characterized by FT – IR Spectral and determined the M.Wt by viscosity Method.

**Results and Discussion :**

**Reactivity Ratios:**

The Fineman Ross [6] and Kelen Tudos [7] graphical methods were used to determine the reactivity ratios  $r_1, r_2$  for STY / MMA Copolymerization system ,was been prepared a series of solutions for each reaction and total weights (9.1) g of two Monomers and the values are given in Table (2) .

**Table 1. The copolymers compositions**

STY (mol)	0.8	0.7	0.6	0.4	0.3	0.2	M <sub>1</sub>
MMA (mol)	0.2	0.3	0.4	0.6	0.7	0.8	M <sub>2</sub>

**Table 2. Reactivity ratios of STY / MMA Copolymer.**

Method	FT – IR Spectral		Mathematical		Literature		% Error STY / MMA
	r <sub>1</sub> STY	r <sub>2</sub> MMA	r <sub>1</sub> STY	r <sub>2</sub> MMA	r <sub>1</sub> STY	r <sub>2</sub> MMA	
F – R	0.45	0.38	0.61	0.47	0.54	0.47	± 0.07
K – T	0.49	0.35	0.45	0.38	0.52	0.43	± 0.05

The Mol Fraction  $f$  and  $F$  to feeding mixture in Copolymer Composite and

Obtained by F-R and K-T equations,show in Table ( 3 ,4 ).

**Table 3. Mol Fraction  $f$  and  $F$  to feeding mixture, Copolymer Composite&M.wt**

Exp.No	Monomer in Feed		Monomer in Copolymer		Conversion%	M <sub>v</sub>	M <sub>w</sub> /M <sub>n</sub>
	STY f <sub>1</sub>	MMA f <sub>2</sub>	STY F <sub>1</sub>	MMA F <sub>2</sub>			
1	0.7884	0.1953	0.4230	0.5776	8.11	56420	1.84
2	0.5951	0.4147	0.3782	0.7743	7.23	51210	1.65
3	0.3953	0.5977	0.2537	0.7534	8.4	38610	1.43
4	0.2967	0.7121	0.2228	0.8623	5.8	28920	1.20
5	0.1978	0.8055	0.14491	0.8567	7.0	43120	1.27

**Table 4. Mol Fraction  $f$  and  $F$ ,was Obtained by F-R and K-T equations,  $\alpha=0.362$**

No.	$f=f_1/f_2$	$F=F_1/F_2$	F-R Equation Parameters		K-T Equation Parameters	
			$f^2/F$	$f(F-1)/F$	$n$	$\zeta$
1	0.247	1.364	0.473	0.154	0.1652	0.113
2	0.678	2.05	0.498	0.275	0.600	0.3875
3	1.513	3.0	0.967	0.905	0.895	0.6831
4	2.359	3.6	1.88	1.93	0.90	0.814
5	4.0698	5.94	2.989	3.674	1.079	0.8872

FT - IR is a powerful tool to obtain the copolymerization reactivity Ratios because it allows simultaneous monitoring of individual monomer consumption rates .Based on the F - R ,and K - T reactivity ratios have been showed that ratios can be defined as the ratios of apparent rate constants of monomer consumption.[12]The presence of active groups (C = O) in the spectrum of PMMA and (C = C) in the STY ring. has been characterized, And after determination of the all each effective groups for two Monomers that will mainly be relied upon in to determination of the Copolymers Composition. The general Copolymerization equation where  $[m_1]$  , $[m_2]$  concentration of monomers,  $(r_1 ,r_2 )$  reactivity ratios  $(f)$  is feed of monomers Composition, $(F)$ is the Copolymer Composition, The equation can be written ; [13]

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

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

The effective absorption of the functional groups and molecular weights of the monomers have been used this equation in FT - IR Spectral method ;

$$\frac{\Delta A}{A_{ref}} = \dots \dots \dots 3$$

Were A = Adsorption of the functional groups ,  $A_{ref}$  = Adsorption of the reference band,  $F_1$  = mole Fraction of STY in Copolymer,  $F_2$  = mole Fraction of MMA in Copolymer Have been

calculated and the absorbed of the peak (top of the Band), is determined by using the following relationship

$$A = 2 - \log T \% \dots \dots 4$$

Were A = Absorbent , T% = Permeability ( Transient ) , and  $A = \log \frac{I_0}{I}$  ,

$I_0$  = The intensity of the inside beam ,  $I$  = the outside Beam then calculated the absorbency of the bottom band in the same way of the previous method. [14].

**Reactivity Ratios by FT-IR Spectral of Copolymers:**

The Copolymers spectra in fig ( 1 , 2 ) showed absorption band to C = C in  $1605\text{cm}^{-1}$  to Styrene  $m_1$ ,and the band absorption of carbonyl group C = O in  $1728\text{cm}^{-1}$  to MMA  $m_2$ , At the start of the copolymerization reaction the percentage of each monomers is equal in a copolymer composite. After the reaction continues, the percentage of Monomers will change depended on the reactivity of each monomers so the most reactive monomer was a higher proportion in the composition of copolymer. But in the low conversion ( < 10% ) the concentrated of the two monomers will not change much. And the Copolymer composition will reflect the real of reactivity ratios of two monomers. From drawing of the relationship graphs between  $f$  (F-1) versus  $f^2 / F$  to the F-R equation as described in fig (3) .and as well as when drawing the relationship graphs between  $\eta$  versus  $\zeta$  to the KT equation as shown in fig (4)

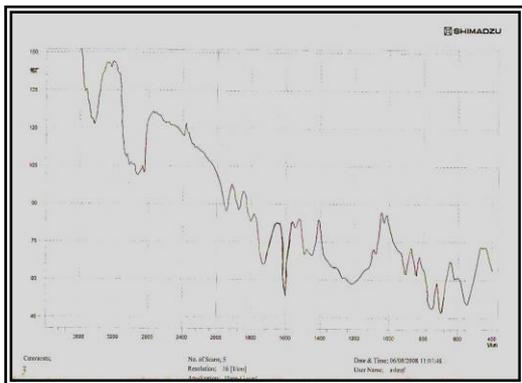


Fig 1. FT - -IR Spectral of Copolymer P(STY -MMA) system  $m_1 = 0.8$ ,  $m_2 = 0.2$

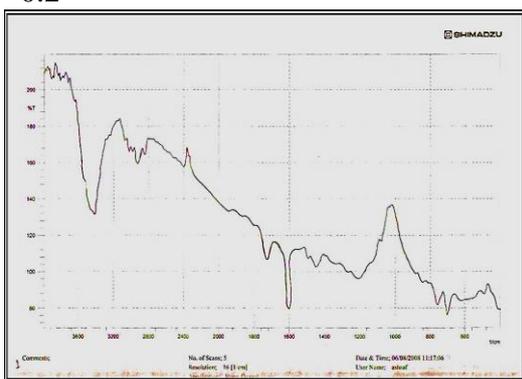


Fig 2. FT - -IR Spectral of Copolymer to P(STY -MMA) system  $m_1 = 0.2$ ,  $m_2 = 0.8$

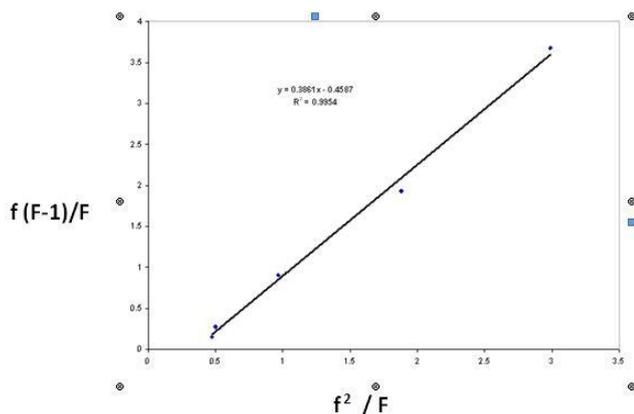


fig. 3. The relationship graphs between  $f(F-1) / F$  versus  $f^2 / F$  to the Copolymer by F-R equation

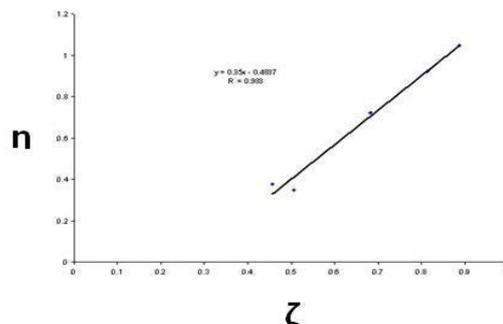


fig. 4. The relationship graphs between  $\eta$  versus  $\zeta$  to the Copolymer by K-T, Eq.

**Reactivity Ratios calculated Mathematically Methods of Copolymers:**

Fineman and Ross (F-R) method is the linearization method, in this method the Copolymer equation is Modified to

$$F = f \frac{r_1 f_1 + 1}{r_2 + f} \quad \dots\dots 5$$

$$\frac{F-1}{f} = -r_2 \frac{F}{f^2} + r_1 \quad \dots\dots 6$$

And draw graphs as relationship between the  $[(F-1) / f]$  on the y-axis and  $(F/f^2)$  on the x-axis, we get a straight line represents the slope  $(-r_2)$  and intercepted on the y-axis represents the  $(r_1)$  by application Least Square Method, the Reactivity ratios values also represent an improvement to F – R equation.. Table (5) and fig. (5). Kelen and Tudos (K-T) method, Account of this method availability is quickly and acceptable to Table (6) .and fig (6) . show the Calculated values in (K-T) method. The rearrangement of F – R equation become;

$$G = r_1 X - r_2 \quad \dots\dots 7$$

where :  $G = f(F-1) / F \quad \dots\dots 8$

$$X = f^2 / F \quad \dots\dots 10$$

$$N = (r_1 + \frac{r_2}{\alpha})A - \frac{r_2}{\alpha} \dots\dots 9$$

$$\text{or: } N = r_1 A - \frac{r_2}{\alpha} (1 - A)$$

draw graphs as the relationship between the (N) value as the Function to(A) value .gives a straight line in cross-section with the y-axis were (A=0) Represents (-r<sub>2</sub>/α) and the intercepted with x- axis were (A=1) Represents (r<sub>1</sub>) , The term (α) in the equation gives the best distribution is limited to the experimental values between zero to one, The equation of (Kelen and Tods) Availability of Possibility to verify that the system of Copolymerization obey the conditions and assumptions used in formulating the equation of copolymer composition .

Table 5.The value of F-1 / f and F / f<sup>2</sup>were mathematically calculated by F-R. Eq.

Exp. NO	F-1 / f	F / f <sup>2</sup>
1	0.072	0.046
2	0.241	0.167
3	0.607	0.291
4	1.807	0.701
5	2.99	1.509

Table 6. The mathematically calculated value of Copolymers by K-T Eq.

Exp. NO	G	X	O	A
1	-	20.012	-	0.901
	2.050		0.100	
2	-	8.122	-	0.677
	1.618		0.105	
3	-	6.124	-	0.612
	1.772		0.214	
4	-	1.781	-	0.302
	1.825		0.332	
5	-	1.273	-	0.200
	2.387		0.452	

From note the values of the Reactivity ratios of Monomers show that r<sub>1</sub>

greater than r<sub>2</sub> that mean the effectiveness of STY more than MMA because the Free Radical in styrene chains is more stable by high resonance with the electrons delocalized for aromatic ring. The radical of MMA was stable with α, β-unsaturated but there less stable than STY.The Copolymers form is determined within The Reactivity Ratios. If the product values of Reactivity ratios (r<sub>1</sub> , r<sub>2</sub>) for Monomers are less than the correct one

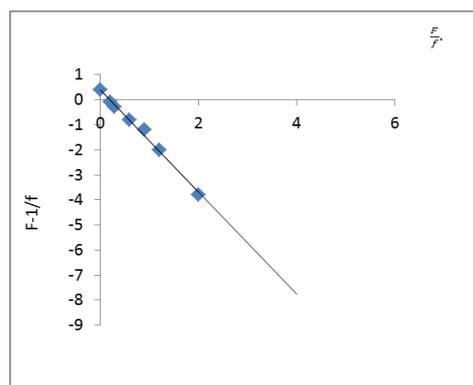


fig. 5. The relationship graphs between (F-1) / f versus F / f<sup>2</sup> for determined r<sub>1</sub> , r<sub>2</sub> mathematically by F-R Eq.

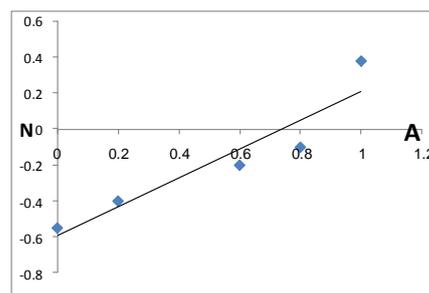


fig.6 The relationship graphs between (A) versus(N) to calculated r<sub>1</sub>, r<sub>2</sub> by K-T Eq .

The behavior of Copolymers in this system is random and is located between the ideal behavior and alternating 0 < r<sub>2</sub>, r<sub>1</sub> < 1 As if the multiply value product of the Reactivity ratios (r<sub>2</sub>\*r<sub>1</sub>) is closer to zero the random order of monomers in

copolymer becomes more near to the alternating composite of Semi-regular basis. [15]. The composition of Copolymers can be appointed to draw a relationship between the mole fraction of monomer in a feeding mixture  $f_1$  on the x-axis, and the mole Fraction of the monomer  $F_1$  on the y-axis. Fig. (7)

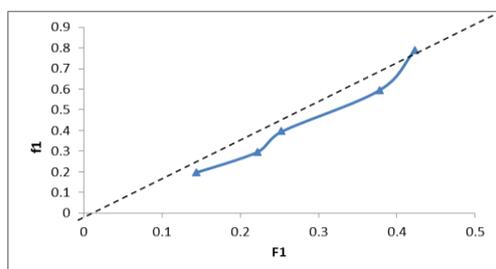


Fig .7 Copolymer Composition curves from experimental data .

### Conclusions:

The preparation of copolymer was randomly located between ideal behavior and alternating. The Calculated Values by spectral methods and mathematically are tight line with Literature, Reactivity of STY is more than MMA and these corresponds to the theoretical assumption, calculated of  $r_1$ ,  $r_2$  with Spectral method are a fast and easy than Mathematically Method, and M.Wt Distribution Shows The arrangement of monomer in the copolymer for between random and alternating.

### References :

1. Ankit k , Patel , Rajesh J, Patel and kirit H. 2009 .Free Radical Copolymerization N,N-Dimethyl amino Ethyl Methacrylate with Styrene and Methyl Methacrylate: . Patel .Chem. Soc. 54(3), 228-234.
2. Salem S . Al – Deyeb and Ali Mohsen Al – Hazim , 2010. Synthesis and Characterization of Organotin Containing Copolymers: Reactivity Ratio Studies J . Molecules , 15, 1784 – 1779 ; doi10.3390 molecules,
3. Liu, G.; Zhang, L.; Wang, Y.and Zhao Y. , 2009. Evaluation of the reactivity ratios for two copolymers of orthopaedic interst, J. Appl. Polym. Sci.,114, 3939–3944.
4. Hou, C.; Ji, C. and Ying, L. 2007. Synthesis and Characterization of Maleimide –Co - Polymers with Pendant Benzoxazine Groups by Photo induced Radical Polymerization J. Appl. Polym. Sci, 103, 3920–3923.
5. Liu, S.R.; Li, B.X.; Liu, J.Y.and Li, Y.S. 2010. Determination of Reactivity Ratios in the Copolymerization of Phosphaalkene and Styrene. Polymer, 51, 1921- 1925 .
6. Fineman, M. and Ross, S. D. 1975 .Reactivity Ratios of new vinyl monomers, J. Macromol, Sci. Chem. A9, 1.
7. Kelen, T. and Tudos, F. 1975 .copolymerization and determination  $r_1$ ,  $r_2$  for monomers, J. Macromol. Sci. Chem; A9, 1.
8. Mitesh G. Patel, Hetal J. Patel, Kirit H. Patel and Rajni M. Patel 2008 Synthesis and Characterization of Novel Acrylic Copolymers and Determination of Monomer Reactivity Ratios ,Malaysian Polymer Journal (MPJ), 3( 1) , 14-26.
9. Gillon Z . Li, X, M. Diallo, L. Houssiau, J. and Pireaux J., 2011 .butadiene, styrene, methyl methacrylate copolymer cross-linked with 1,3 butanediol dimethacrylate, European Conference on High Technology. Journal of physics Conference Series, 9(3) , 275.
- 10.Ivana,Soljic,AnteJukic and ZvonimirJanovic, 2009. Synthesis and Characterization of Homopolymer and Copolymer of Methyl Methacrylate with Maleimide , Society of Chemical Industry, Polym. Int ; 58: 1014n102 .
11. Hiran B. L., Rajesh Boriwal and S.N. Paliwal, 2011. Synthesis and Characterization of Homopolymer and Copolymer of Methyl Methacrylate

- with Maleimide J. Molecular Chem. Pharm. Res., 3 (1) ,793-799 .
12. Wang Zi, Qing-zhi Dong and Chunpu Hu, 2009. measurements monomer reactivity ratios for copolymerization of styrene and methyl methacrylate in carbon dioxide at vapor- liquid equilibrium state. Chinese J. of Poly. Sci., 27(3), 367-374 .
13. Bashir Ahmad and Shumaila Bashir, 2004. Chemically Crosslinked N-Vinyl-2-Pyrrolidone / 2-Hydroxyethyl Methacrylate .Turk .J .Chem .28 , 279 -285.
14. Patcharaporn Kaivalchatchawal , Piyasan Praserttham and Yuuichi Sogo, 2011. Styrene and methyl methacrylate copolymer synthesized by RF inductively coupled plasma, J. Molecules; 16, 4122-4130 doi: 10.3390 / molecules 16054122 .
15. Ankit. Patel, Rajesh j. Patel, Kirit H. Patel and Raajni M. Patel. 2009 . Synthesis, Characterization, Thermal Properties and Antimicrobial Activity of Acrylic Copolymers Derived From 2,4 -Dichlorophenyl Acrylate . J.Chil. Chemo. Soc. 54(3) , 229 -235.

## نسبة الفعالية للبلورة المشتركة ( ستايرين – مثيل ميثا أكريليت ) باستخدام مطيافية FT – IR ومقارنتها بالطرق الرياضية

وجيه يونس محمد\*

طارق عبدالجليل منديل\*

\*قسم الكيمياء – كلية العلوم – جامعة الأنبار

### الخلاصة :

أجريت بلورة مشتركة للمونومرين ستايرين – مثيل ميثاكريليت (STY-co- MMA) بطريقة الجذور الحرة في جو من النايتروجين النقي وبوجود بيروكسيد البنزويل كباديء ، بتركيز ثابت  $10^{-3} * 3$  مولاري. إستخدمت مطيافية الأشعة تحت الحمراء FT-IR في حساب نسبة الفعالية ( $r_1, r_2$ ) بطريقتين هما فينمان – روز ، وكليين – تودس. Fineman-Ross (F-R) and Kelen-Tüdös (K- T). وأظهرت القيم التجريبية أن نسبة الفعالية للمونومر الأول الستايرين ( $r_1$ STY) المحسوبة بطريقة F-R  $r_1 = 0.45$  وللمونومر الثاني المثيل ميثا أكريليت ( $r_2$  MMA)  $r_2 = 0.38$  في حين كانت القيم المحسوبة بطريقة K-T  $r_1 = 0.49$  ،  $r_2 = 0.35$  وأظهرت هذه القيم أن ترتيب وحدات الكوبوليمر بشكل عشوائي ، وبطريقة مقارنة تم حساب نسب الفعالية للكوبوليمر المشترك بالطرق الرياضية وبطريقتي (F – R , K – T) فكانت القيم المحسوبة حسب طريقة F-R :  $r_1 = 0.86$  ،  $r_2 = 0.47$  و بطريقة K-T كانت:  $r_1 = 0.45$  ،  $r_2 = 0.38$  ، كما تم حساب القيم التكاملية لشكل الكوبوليمر الناتج ، حيث أظهرت النتائج في هذه الدراسة تطابقها مع الأدبيات العلمية وصحة التوقعات النظرية .