

## Copolymerization of N-vinyl-2-pyrrolidone with Acrylic Acid and Methymethacrylate

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### Abstract:

Low conversion copolymerization of N-vinyl-2-pyrrolidone M.W = (111.14) VP (monomer-1) has been conducted with acrylic acid AA and methymethacrylate MMA in ethanol at 70°C, using Benzoyl peroxide BPO as initiator. The copolymer composition has been determined by elemental analysis. The monomer reactivity ratios have been calculated by the Kelen-Tudos and Finman-Ross graphical procedures. The derived reactivity ratios ( $r_1$ ,  $r_2$ ) are: (0.51, 4.85) for (VP / AA) systems and (0.34, 7.58) for (VP, MMA) systems, and found the reactivity ratios of the monomer AA, MMA is more than the monomer VP in the copolymerization of (VP / AA) and (VP / MMA) systems respectively. The reactivity ratios values were used for microstructures calculation.

**Key words:** n-vinyl-2-pyrrolidone, acrylic acid, methymethacrylate, copolymerization, reactivity ratio.

### Introduction:

Poly (N-vinyl-2-pyrrolidone-co- acrylic acid) PVP/AA and poly (N-vinyl-2-pyrrolidone- co- methymethacrylate ) PVP/MMA is generally made by free radical polymerization. It prepared successfully in aqueous salt solution using cationic polyelectrolytes as stabilizers[1].

Moreover knowledge of copolymer's composition is an important factor in the evaluation of its utility [2-4]. The estimation of copolymer composition and determination of reactivity ratios are significant for tailor-making properties.

Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segment and consequently properties such as glass transition temperature, melting point, solubility, permeability, adhesion, dyeability and chemical reactivity may be varied within a wide limits. The utility of copolymerization is exemplified on the one hand by the

fundamental investigation of structure property relation [5] and on other hand by the wide range of commercial application. The relative reactivity of a monomer toward a certain polymer radical is readily calculated from the monomer reactivity ratios of copolymerization. However, evaluation of the rate constants of crosspropagating is required for estimation of the absolute reactivities of the polymer radical and of the monomer [6].

### Materials and Methods:

All monomers, initiator, and solvent have been obtained from Aldrich- Oma Chemical Co. N-vinyl-2-pyrrolidone was dried over anhydrous  $MgSO_4$  and vacuum distilled (B.P. 345°K at 2.5 mmHg), and should not be left more than 24 hours prior to use. Initiator (Benzoyl peroxide) was purified by twice recrystallizations from

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chloroform and refrigerated prior to use.

Copolymerization of VP M.W = (111.14) with AA and MMA was carried out using ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>) BPO as initiator and (8 ml) ethanol as solvent at 70°C in glass tubes. The glass tubes were charged with the prescribed amount of monomer. The total molar composition of the monomer mixture was maintained at (3.5 mol dm<sup>-3</sup>) while the feed ratio was varied. Placed in water bath at 70°C. After the required time (< 10% conversion). The copolymers were precipitated in petroleum ether (b.p 40-60 °C). The precipitates were filtered off, dissolved again ethanol and precipitated in petroleum ether prior to constant weight in vacuum at 35°C. The copolymer composition determined by elemental analysis.

**Results and Discussion :**

The reactivity ratio  $r_1$  and  $r_2$  of copolymerization of VP (monomer-1) with AA and MMA have been determined using Fineman-Ross [7] and Kelen-Tudos [8] procedures. For mathematical details of these procedures, the original papers [8- 9] should be consulted. The plots are shown in fig. (1, 2, 3, 4) for Fineman-Ross and Kelen-tudos respectively. The results of the reactivity ratios are given in table (1).

**Table (1) : Monomer reactivity ratios for copolymerization of VP with AA and MMA**

procedure	VP (M) $r_1$	AA (M) $r_2$	VP(M) $r_1$	MMA(M) $r_2$
Fineman-Ross	0.5	4.40	0.4	8.30
Kelen-Tudos	0.1	4.52	0.2	6.24
Average-values	0.3	4.46	0.3	7.27
	±0.2	±0.06	±0.1	±1.03

With these values of  $r_1$  and  $r_2$ , the variation of the instantaneous mole fraction  $f_1$  of VP in the initial feed may be calculated using the following copolymer composition eqn.[9]

$$F = r_1 f_1^2 + f_1 f_2 / r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2$$

Where  $F = F_1/F_2$ ,  $r_1$  = reactivity ratio of (AA ,MMA),  $r_2$ = reactivity ratio of VP,  $f_1$ = mole fraction of (AA, MMA) in the feed,  $f_2$ = mole fraction of VP in the feed.

Figure (5,6), show the copolymer composition curves of VP/AA system and VP/MMA system, which shows no azeotropic composition.

The azeotropic feed composition  $f_1(az.)$  is given by :

$$f_1(az) = (1 - r_1) / (2 - r_1 - r_2).$$

$f_1(az)$  = azeotropic feed composition.

The cross – propagation step in copolymerization reaction in values. Addition of certain polymer radical to a monomer molecule. The corresponding rate constant  $k_{ij}$  of cross-propagation reflecting the relative reactivity of monomer-j toward a given polymer radical-I may be readily calculated from reactivity ratios ( $K_{12} = K_{11}/r_1$ ,  $K_{21} = K_{22}/r_2$ ).

In absence of reliable data on the absolute rate constants of propagation of VP at the conditions employed here, compositions may be made on the basis of reactivity ratios alone.

The reactivity ratios were then used for microstructural calculation. The microstructure of the copolymers was to be very important in determining the solution properties which the copolymer exhibit [10]. Igarashi ‘s [11] methods used to calculate the fraction of  $M_1-M_1$ ,  $M_2-M_2$  and  $M_1-M_2$  units (the mole % of blackness, the mole % of alternation and the mean sequence length of the copolymers respectively) in the copolymers as a function of reactivity ratios.

The copolymer composition, tables (1,2 and 3), lists the structural data for the copolymer VP/AA and VP /MMA. For

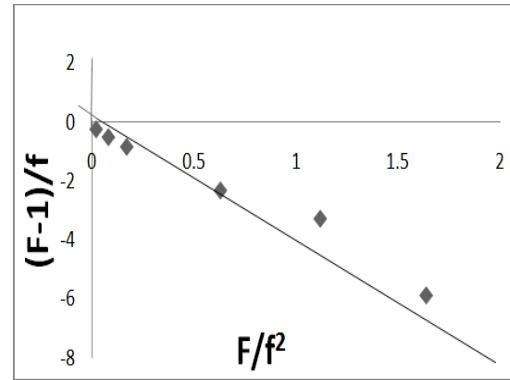
the system of VP/AA, VP/MMA copolymers, table (2) the mean sequence length of VP,  $\mu_1$ , Varied from 1.002 to 1.009 for the copolymer composition, values of  $\mu_2$  were 1208.52 and 250.05 respectively. Table (3) the mean sequence length of VP,  $\mu_1$ , varied from 1.0008 to 1.0092 for the copolymer composition, values of  $\mu_2$  were 3151.43 and 278.35 respectively.

**Table (2) : Structural data for the copolymer VP/AA**

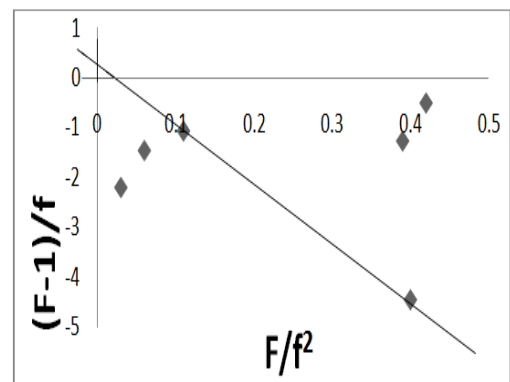
EXP. NO.	Blockiness (mol%)	Alternation (mol%)	Mean Sequence length
	M1-M1 M2-M2	M1-M2	$\mu_1$ $\mu_2$
1.	50.09 49.12	0.79	1.0020 1208.52
2.	50.17 48.34	1.49	1.0039 634.24
3.	50.23 47.82	1.95	1.0051 481.10
4.	50.31 47.06	2.63	1.0070 352.73
5.	50.35 46.61	3.04	1.0081 303.08
6.	50.42 45.94	3.64	1.0099 250.05

**Table (3) : Structural data for the copolymer VP/MMA**

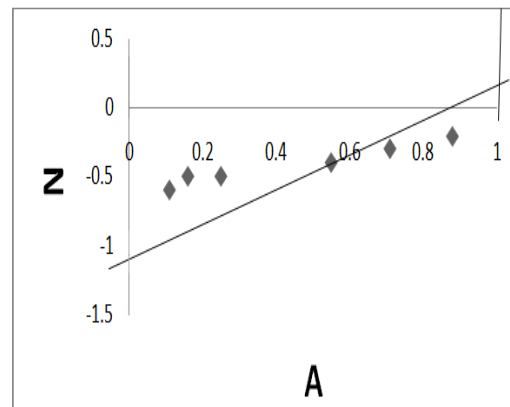
EXP. NO.	Blockiness (mol%)	Alternation (mol%)	Mean Sequence length
	M <sub>1</sub> -M <sub>1</sub> M <sub>2</sub> -M <sub>2</sub>	M <sub>1</sub> -M <sub>2</sub>	$\mu_1$ $\mu_2$
1.	50.08 49.45	0.47	1.0008 3151.43
2.	50.15 48.89	0.96	1.0016 1540.20
3.	50.34 47.24	2.42	1.0043 599.75
4.	51.32 45.52	3.16	1.0058 444.56
5.	50.57 45.38	4.05	1.0074 347.59
6.	50.68 44.34	4.98	1.0092 278.35



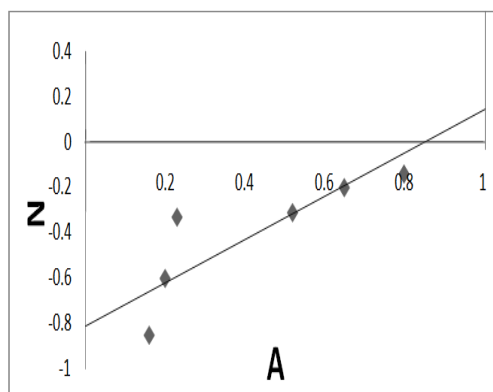
**Fig. (1): Determination of the reactivity ratios for VP/ AA system at 70°C Finemon-Ross plot .**



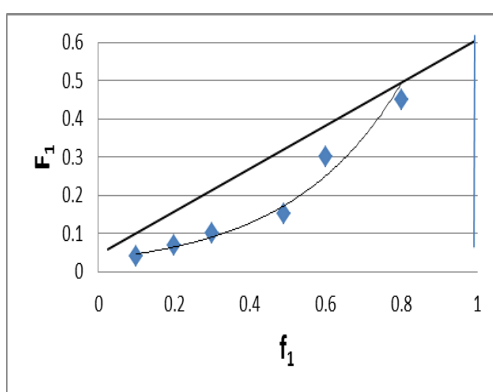
**Fig. (2): Determination of the reactivity ratios for VP / MMA system at 70°C Finemon-Ross plot .**



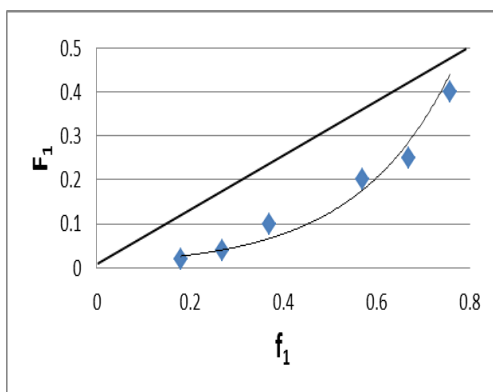
**Fig. (3): Determination of the reactivity ratios for VP / AA system at via Kelen-Tudos plot .Where  $N=G/(\alpha+X)$  ,  $A= X/(\alpha+X)$  ,  $\alpha=(X_{min.} \times X_{max.})^{1/2}$  .**



**Fig. (4) : Determination of the reactivity ratios for VP / MMA system at via Kelen-Tudos plot .Where  $N=G/(\alpha+X)$  ,  $A= X/(\alpha+X)$  ,  $\alpha=(X_{\min.} \times X_{\max.})^{1/2}$  .**



**Fig. (5) : Copolymer composition curves . Experimental data are represented by (◆) – VP/AA system.**



**Fig. (6) : Copolymer composition curves . Experimental data are represented by (◆) – VP/MMA system .**

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## البلمرة المشتركة لمونومير N- فينايل-2- بايروليدون مع حامض الاكريلك والميثايل ميثاكريليت

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### الخلاصة:

تمت البلمرة المشتركة لمونومير N – فينايل-2- بايروليدون مع حامض الاكريلك و الميثايل ميثاكريليت على التوالي في مذيب الايثانول بوجود البادئ بيروكسيد البنزويل ( $10 \times 10^{-3}$ ) مولاري عند درجة حرارة ثابتة 70 °م. تم حساب نسب الفعالية للمونوميرات الداخلة في تركيب البوليمر المشترك باستخدام طريقتين: فاينمان وروس Fineman and Ross Method و طريقة كالين وتودس Kelen-Tudos وكانت قيم نسب الفعالية  $r_1$  و  $r_2$  (0.51 , 4.85) على التوالي لنظام البلمرة (VP / AA ) systems و (0.34 , 7.58) لنظام البلمرة (VP , MMA) systems . استخدمت قيم نسب الفعالية لحساب التراكيب المايكروية (الدقيقة).