Copolymerazaion of N-vinyl-2-pyrrolidon with Acrylic Acid and Methylmethacrylate

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Abstract:

Low conversion copolymerization of N-vinyl-2-pyrrolidon M.W = (111.14) VP (monomer-1) has been conducted with acrylic acid AA and methymethacrylate MMA in ethanol at 70ºC , 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 mor than the monomer VP in the copolymerization of (VP / AA) and (VP /MMA) systems respectly . The reactivity ratios values were used for microstructures calculation.

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

Introduction:

Poly (N-vinyl-2-pyrrolidon–co- acrylic acid) PVP/AA and poly (N-vinyl-2-pyrrolidon- 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 determindation of reactivity ratios are significant for tailor-making properties. Copolymerization modulates both the intramolecular and intermolecylar 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 withen 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, evalution 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 , monome , initiator , and solvent have been obtained from Aldrich- Oma Chemical Co. N-vinyl-2-pyrrolidon was dried over anhydrous $MgSO_4$ and vacuum distilled (B.P. 345ºK at 2.5 mmHg) , and should not be left more than 24 hour 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 (1×10^{-3} mol dm^{-3}) BPO as initiator and (8 ml) ethanol as solvent at 70ºC 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^{-3}) while the feed ratio was varid . Placed in water bath at 70ºC. After the required time (< 10%conversion). The copolymers were precipitated in petroleum ether (b.p 40-60 ºC) . The precipitates were filtered off, dissolved again ethanol and precipitated in petroleum ether prior to constant weight in vacuum at 35ºC. The copolymer composition determind 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 datermind using Fineman-Ross [7] and Kelen-Tudos [8] procedures. For mathemathcal 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 copolymerizaton 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
Avrage-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]

$F= r_1f_1^2 + f_1f_2 / r_1f_1^2 + 2f_1f_2 + r_2f_2^2$

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 azotropic composition .

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

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

f_1 (az) = azotropic feed composition.

The cross – propagation step in copolymerization reaction in values. Addition of certain polymer radical to a monomer molecule. The corresponding rate constant kij 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 microstructural 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 altervation 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, μ_{1}, Varied from 1.002 to 1.009 for the copolymer composition, values of μ_2 were 1208.52 and 250.05 respectively. Table (3) the mean sequence length of VP, μ_{1}, varied from 1.0008 to 1.0092 for the copolymer composition, values of μ_2 were 3151.43 and 278.35 respectively.

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

EXP. NO.	Blockiness (mol%)	Alternation (mol%)	Mean Seqeunce lengh
	M1-M1 M2-M2	M1-M2	µ1 µ2
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 Seqeunce lengh
	M_1-M_1 M_2-M_2	M_1-M_2	μ_1 μ_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

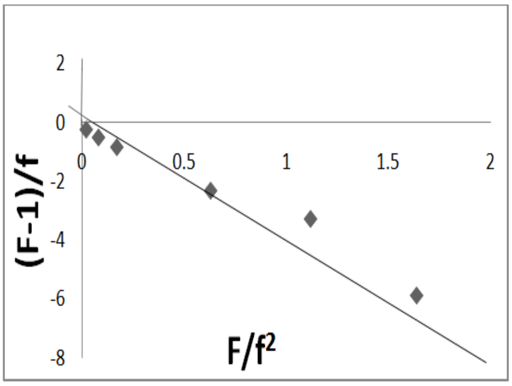

Fig. (1): Determination of the reactivity ratios for VP/ AA system at 70°C Finemon-Ross plot .

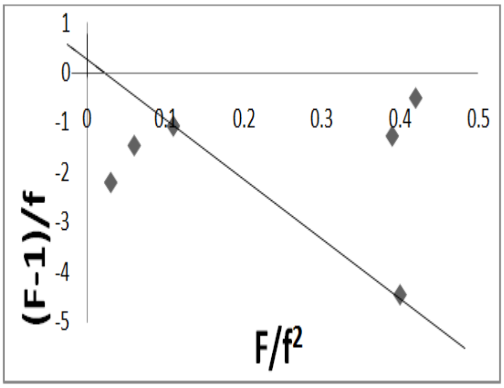

Fig. (2): Determination of the reactivity ratios for VP / MMA system at 70°C Finemon-Ross plot .

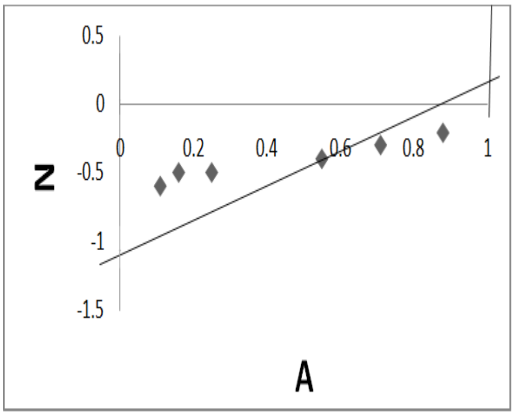

Fig. (3): Determination of the reactivity ratios for VP / AA system at via Kelen-Tudos plot .Where $N=G/(\alpha+X)$, $A= X/(\alpha+X)$, $\alpha=(X_{min.}\times X_{max.})^{1/2}$.

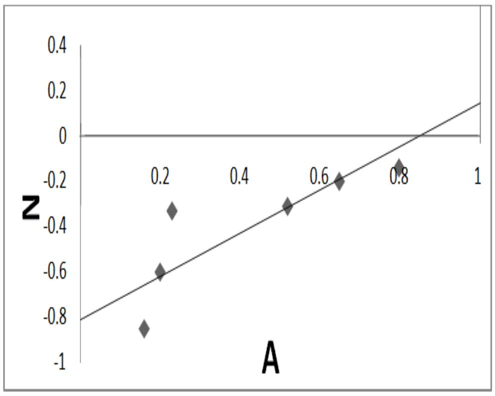

Fig. (4) : Determination of the reactivity ratios for VP / MMA system at via Kelen-Tudos plot .Where N=G/(α+X) , A= X/(α+X) , $\alpha=(X_{min.}\times X_{max.})^{1/2}$.

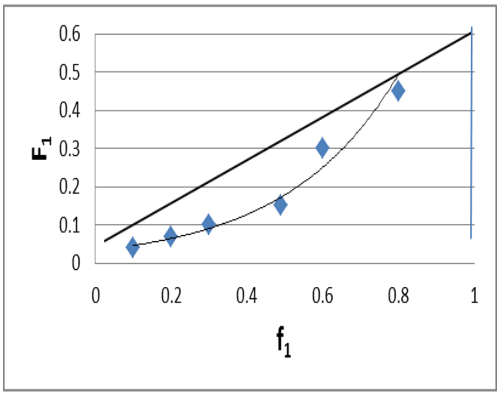

Fig. (5) : Copolymer composition curves . Experimental data are represented by (◆) – VP/AA system.

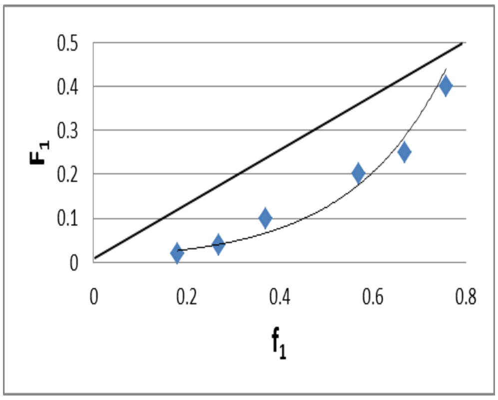

Fig. (6) : Copolymer composition curves . Experimental data are represented by (◆) – VP/MMA system .

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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 ميثاكريلت على التوالي في مذيب الايثانول بوجود البادئ بيروكسيد البنزويل (1×10^{-3}) مولاري عند درجة حرارة ثابتة 70 ^{o}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 r1 و r2 (4.85 , 0.51) على التوالي لنظام البلمرة systems (VP / AA) و (7.58 , 0.34) لنظام البلمرة (VP , MMA) systems . استخدمت قيم نسب الفعالية لحساب التراكيب المايكروية (الدقيقة).