Copolymerization of Acrylamide with Acrylic acid

*Mahmoud A. Al-Issa** *Ameen H. Mohammed**

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Abstract:

Low conversion copolymerization of acrylamide AM (monomer-1) have been conducted with acrylic acid AA in dry benzene 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: (0.620, 0.996) for (AM / AA) systems , and found that the reactivity of the monomer AA is more than the monomer AM in the copolymerization of (AA/AM) system. The reactivity ratios values were used for microstructures calculation.

Key words : Acrylamide , acrylic acid , copolymerization , reactivity ratio.

Introduction:

Poly (acrylamide - Co- acrylic acid) PAM/AA is generally made by free radical polymerization [1]. It prepared successfully in aqueous salt solution using anionic polyelectrolytes as stabilizers [2]. PAM/AA resin prepared from AA and AM by inverse suspension polymerization; it used to separate transitional metal ions Cu^{+2}, Ni^{+2}, Co^{+2}[3]. Goa and Wu prepare (PAM/AA) / poly(vinyl pyrrolidone) blends by dispersion polymerization [4]. PAM/AA is important classes of water-soluble polymers due to their numerous applications in fields such as super absorbents additives in cosmetics, membrane technology , waste-water treatment and oil field operations[5]. The photolytic and photocatalytic degradation of this copolymer has been conducted in the presence of combustion-synthesized nanoanatase titania [6].

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 segments and consequently properties such as glass transition temperature, melting point, solubility, permeability, adhesion, dye-ability 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 [7] and on the 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 cross-propagating is required for estimation of the absolute reactivities of the polymer radical and of the monomer [8].

Materials and Methods:

All , monomer, initiator, and solvent have been obtained from Aldrich-Oma Chemical Co.Acrylamide was recrystillized from chloroform several time and dried under vacuum

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*Department of Chemistry, college of science for Women, Baghdad Universit.

until all chloroform are removed. Initiator (Benzoyl peroxide) was purified by twice recrystallizations from chloroform and refrigerated prior to use.

Copolymerization of AM with AA was carried out using (1×10^{-3} mol dm^{-3}) BPO as initiator and (8 ml) dry benzene as solvent at 70° C in glass tubes. The glass tubes were charged with the prescribed amount of monomers. The total molar composition of the monomer mixture was maintained at (3.5 mol dm^{-3}) 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 in benzene and precipitated in petroleum ether prior to constant weight in vacuum at 35°C. The copolymer compositions were determined by elemental analysis.

Results and Discussion:

The reactivity ratios r_1 and r_2 of copolymerization of AM (monomer-1) with AA has been determined using Fineman-Ross [9] and Kelen-Tudos [10] procedures . For mathematical details of these procedures, the original papers [9-10] should be consulted. The plots are show in fig.(1,2) for Fineman-Ross and Kelen-tudos respectively. The results of the reactivity ratios are given in table (1).

Table (1): Monomer reactivity ratios for the copolymerization of AM with AA

Procedure	AM(M) r_1	AA(M) r_2
Fineman-Ross	0.613	0.971
Kelen-Tudos	0.628	1.022
Avrage-values	0.620	0.996
	±0.008	±0.026

With these values of r_1 and r_2, the variation of the instantaneous mole fraction f_1 of AM in the initial feed may be calculated using the following copolymer composition eqn. [11]

$$F= r_1f_1^2 + f_1f_2 / r_1f_1^2 + 2f_1f_2 + r_2 f_2^2$$

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

Figure (3), shows the copolymer composition curves of AM/AA 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 AM at the conditions employed here, comparisons 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 expected to be very important in determining the solution properties which the copolymer exhibit [12]. Igarashi 's [13] methods used to calculate the fraction of M_1-M_1 , M_2-M_2 and M_1-M_2 units (the mole % of blockness , the mole % of altervation and the mean sequence length of the comonomers respectively) in the copolymers as a function of reactivity ratios.

The copolymer composition, tables (1 and 2), lists the structural data for the copolymer AM/AA . For the system of AM/AA copolymers, table

(2) the mean sequence length of AM, μ_1, Varied from 1.182 to 3.021. For these copolymer compositions, values of μ_2 were 5.056 and 1.253 respectively.

Table (2): Structural data for the copolymers AA/ AM

Test No.	Blockiness (mol%)	Alternation (mol%)	Mean Seqeunce length
	M_1-M_1 M_2-M_2	M_1-M_2	μ_1 μ_2
1	36.67 26.01	37.32	1.182 5.056
2	34.65 22.64	42.71	1.435 2.549
3	33.22 20.95	45.83	1.679 2.037
4	31.45 19.53	49.02	1.914 1.681
5	29.07 17.09	53.84	3.021 1.253

Figure (4): shows the rate of copolymerization of M_1 , M_2 for different composition, the rate of copolymerization increases with increase the percentage (%) of AA , ($r_2 > r_1$) , because the monomer AA is more reactive than the monomer AM in the copolymerization of (AA/AM) system.

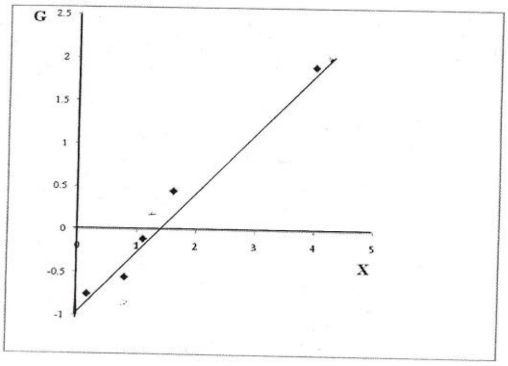

Fig. (1): Determination of the reactivity ratios for AM / AA system at 70°C Finemon – Ross plot . where $G=(F-1)f/F$, $X = f^2/F$

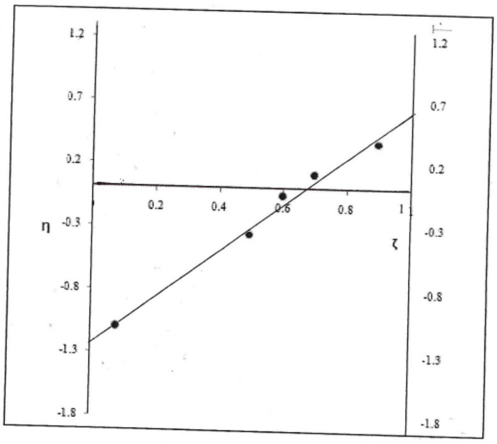

Fig.(2): Determination of the reactivity ratios for AM/AA system at via Kelen – Tudos plot. Where $\eta = G/(\alpha + X)$, $\zeta = X/ (\alpha + X)$, $\alpha =(X_{min.}\times X_{max.})^{1/2}$.

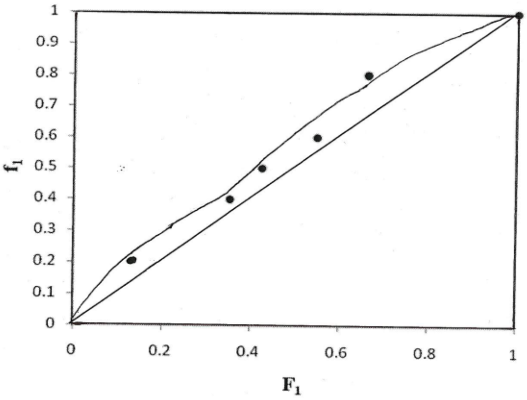

Fig. (3): Coploymer composition curves. Experimental data are represented by (●) – AM/AA System.

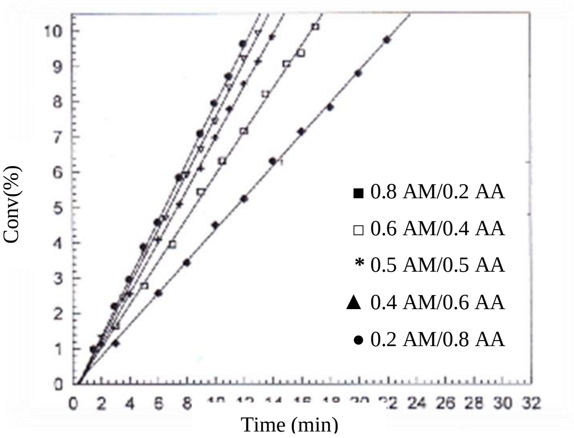

Fig. (4): Time – conversion curves for radical copolymerization of AM/AA system

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البلمرة المشتركة للأكريل امايد مع حامض الأكريليك

محمود عبد الجبار العيسى* ***أمين هادي محمد****

*قسم الكيمياء ـ كلية العلوم للبنات ـ جامعة بغداد

الخلاصة :

تمت البلمرة المشتركة لمونومير الاكريل امايد مع حامض الاكريليك في مذيب البنزين الجاف بوجود البادئ مولاري عند درجة حرارة ثابتة 70 م°. تم حساب نسب الفعالية للمونوميرات الداخلة (1×10^{-3})بيروكسيد البنزويل Fineman and Ross Method باستخدام طريقتين: فاينمان وروس AM-CO-AA في تركيب البوليمرالمشترك على التوالي .ثم r_1 , r_2 (0.620 , 0.996) وكانت قيم Kelen and Tudos Method وطريقة كالين وتودس استخدمت قيم نسب الفعالية لحساب التراكيب المايكروية (الدقيقة) .ووجد ان فعالية حامض الاكريليك اكبر من فعالية الاكريل امايد في نظام البلمرة المشتركة .