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Studying Reactivity Relationships of Copolymers N-naphthylacrylamide with (Acrylicacid and Methylacrylate)

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Abstract:

The organation⁄monomer N-naphthylacrylamide (NAA) was prepared; subsequently the synthesized monomer was successfully copolymerized with acrylicacid (AA) and methylacrylate (MA) by free radical technique using dry benzene as solvent and benzoyl peroxide (BPO) as initiator. The overall conversion was kept low (≤ 10% wt/wt) for all studies copolymers samples. The synthesized monomer and copolymers were characterized using Fourier transform infrared spectroscopy (FT-IR), and their thermal properties were studied by DSC and TGA. The copolymers compositions were determined by elemental analysis. Kelen-Tudes and Finmman-Ross graphical procedures were employed to determine the monomers reactivity ratios. The derived reactivity ratios (r_1, r_2) are: (0.048, 0.687) for (NAA-co-AA) and (0.066, 0.346) for (NAA-co-MA). Based on the average reactivity ratios, sequence distribution of monomers in the copolymers and the microstructure of copolymers were calculated by statistical method and found that these values are in agreement with the derived reactivity ratios.

Key words: Acrylic acid, Methyl acrylate, N-naphthylacrylamide, Reactivity relationships.

Introduction:

Monomers of N-substituted acryl amide were prepared by a reaction of acryloyl chloride with different amines (1, 2). Many of these monomers were copolymerized and terpolymerized with other monomers (3, 4), several of these copolymers were used as drugs and pigments (5, 6). 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 (7). The relative concentrations and reactivities of the two monomers dictate the proportions in which they are introduced into the copolymer. A combination of at least three monomers can enable the chain polymerization of different monomers to be conducted at the same time (8). These kinds of polymerizations are usually known as multicomponent copolymerizations, with a system of three monomers being termed terpolymerization. Valuable data have been derived from the implementation of chain copolymerization (9). Indeed, research on chain copolymerization has been the primary source of information about monomer reactivities underpinned by carbocations, free radicals and carbanions in chain polymerization. In particular, the response of reactivity to the chemical structure can be effectively investigated based on how monomers behave in reactions of copolymerization. Furthermore, copolymerization possesses technological significance as well. For example, it facilitates the development of a polymer product in accordance with a specific set of optimal attributes (10).

The properties of polymers can be most effectively modified with the help of the technique of copolymerisation (11). This technique is designed to manipulate the intra- and inter-molecular forces that are exerted amongst similar and dissimilar polymer segments, engendering broad variation in properties like temperature of glass transition, melting point, solubility, permeability, dyeability, adhesion, elasticity and chemical reactivity. The basic explorations of structure property correlations and the variety of commercial and biological applications all attest to the fact that copolymerisation is highly useful (12). A copolymer composition equation relies greatly on reactivity ratios, which not only indicate the relative reactivity of pairs of monomers, but also outline the elements making up the copolymers. To understand how its utility has developed, it is first necessary to understand the copolymer composition itself. As

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emphasised above, the reactivity ratios are essential for copolymer composition and the manner in which it is distributed. The empirical data regarding copolymer composition and monomer feed mixtures must be mathematically processed before the monomer reactivity ratios can be determined. The reactivity of various comonomers can be calculated via a range of techniques. Furthermore, different analytical methods have been proposed to find out how much of a comonomer has been included in the copolymer (13).

New scientifically and commercially relevant materials can be obtained when two distinct monomers with various physical and or chemical attributes are incorporated in the same polymer molecule at different ratios. The monomer reactivity ratios of copolymerisation enable the determination of the relative reactivity of a monomer toward a specific polymer radical.

A copolymers composition is a critical factor in the assessment of its uses. Controlling the polymer property parameters, for example, molecular weight averages, sequence distribution, and copolymer composition, which is a specific significance in the copolymerization forms (14). To figure the rate of polymerization or polymer profitability and copolymer synthesis, monomer reactivity proportions must be known (15). Reactivity ratios are among the most essential parameters for the structure condition of the copolymer, as they can offer data, for example, the copolymer piece. Assurance of the monomer reactivity ratios with little interims requires delicate systematic methods (16).

The technique which is utilized frequently recently for evaluating monomer reactivity ratios is to perform low conversion copolymerization at different starting monomer feed compositions. In this way, the copolymer composition is resolved for every reaction. Conventional techniques for evaluating monomer reactivity ratios depend on, first, changing the momentary copolymer composition equation into a frame that is straight in the parameters r_1 and r_2 and after that assessing the monomer reactivity ratios by graphical plotting or by the direct minimum squares technique. Linearization of the copolymer composition condition will contort the blunder dispersions related with the information (17, 18, 19).

The aims of this work are to synthesize a new monomer (NAA) then copolymerized with different monomers (AA and MA). This work also studied the reactivity relationships of the prepared copolymers further than their thermal properties.

Material and Methods:

Materials

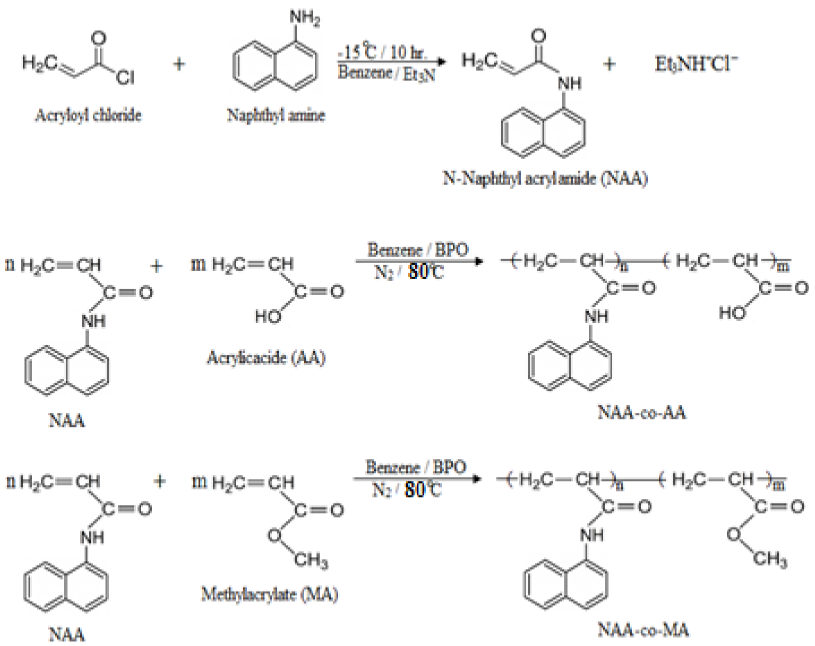
The monomers, initiator, and solvents were obtained from Aldrich-oma chemical Co, (AA) and (MA) were freed from the inhibitor by shaking with 10% W/V aqueous NaOH. After washing with water, they were vacuum distilled immediately prior to the copolymerization experiment. Initiator (benzoyl peroxide) was purified by twice recrystallizations from chloroform and refrigerated prior to use.

Preparation of NAA Monomer

N-Naphthyl acryl amide (NAA) was prepared as a reported procedure (20) by the reaction of Naphthyl amine (14.3 g, 0.1 mole) and acryloyl chloride (9.5 g, 0.1 mole) in 200 ml dry benzene containing (0.2 g) of hydroquinone and (2 ml) of triethylamine. With continuous stirring for 10 hours, the reaction mixture was maintained at -15 °C. Then, the precipitated, N-Naphthylacryloyl amide was filtered off. The crude product was fractionated under reduced pressure, after evaporation of benzene and acryloyl chloride. Red N-Naphthyl acrylamide was obtained then purified by washing many times with ethanol; the reaction of preparation (NAA) monomer is shown in Scheme 1.

Copolymerization

Copolymerization of (NAA) with (AA) and (MA) were carried out using (10 ml) dry benzene as solvent and (1×10^{-3}mol dm^{-3}) (BPO) as initiator. In quick fit test glass tubes, the prescribed amount of monomers, initiator and solvent were charged, and then put in water bath at (80 °C). As shown in Table 1, the feed ratio was varied in a series of copolymerization of (NAA) with (AA) and (MA) (NAA-co-AA) and (NAA-co-MA) whilst the total molar composition of the monomer mixture was maintained at (1 mol dm^{-3}). Before starting the reaction, Nitrogen gas was bubbled through the mixture for 5 minutes in order to remove all oxygen. Low conversion (<10%) of copolymers was obtained by controlling the time of copolymerization. Petroleum ether (b.p. 40-60°C) was used to precipitate the obtained copolymers. All the copolymers were filtered off, dissolved again in benzene, and precipitated in petroleum ether prior to constant weight in vacuum at 40°C. In order to determine the copolymer compositions, samples of the copolymer (0.2 mg) were checked by elemental analysis. Scheme 1 shows the reaction of copolymerization (NAA) with (AA) and (MA) monomers.



Scheme 1.Schematic illustration of the preparation (NAA), subsequently copolymerization with (AA) and (MA).

Characterization

Perken Elmer-1650 spectrometer was used to record FTIR spectra of the copolymers on KBr Pellets in the range 200-4000 cm^{-1}. Intrinsic viscosity [ŋ] was determined according to the Solomon Gotessman relationship (21) by using an Ostwald Viscometer with negligible kinetic energy correction. By following the variation of estimated nitrogen content arising from (NAA) comonomers units, copolymer compositions were determined by elemental analysis. DSC-Mettler calorimetric system was employed to determine the glass transition temperature (Tg) whilst Perkin Elmer in a nitrogen atmosphere at a heating rate of 10 °C /min from 0 to 800 °C was used to study the thermal degradability of the copolymers.

Results and Discussion:

The structure of the prepared monomer and copolymers is confirmed by FT-IR as shown in Fig. 1. NAA structure was confirmed from the appearance of 3300 cm^{1} (amide N-H), 1590 cm^{-1} (alkene C=C) which merged with 1650 cm^{-1} (amide C=0), 3150 cm^{-1} (alkene C-H), 1230 cm^{-1} (amide C-N); NAA-co-AA: 3320 cm^{1} (amide N-H), 3000 cm^{1} (hydroxyl O-H), 1660 cm^{-1} (amide C=0), 1720 cm^{-1} (carboxyl C=0), 1240 cm^{-1} (amide C-N), 2910 cm^{-1} (alkane C-H); NAA-co-MA: 3300 cm^{1} (amide N-H), 1650 cm^{-1} (amide C=0), 1750 cm^{-1} (ester C=0), 1350 cm^{-1} (methyl C-H), 1220 cm^{-1} (amide C-N), 1010 cm^{-1} (ester C-O), 2900 cm^{-1} (alkane C-H).

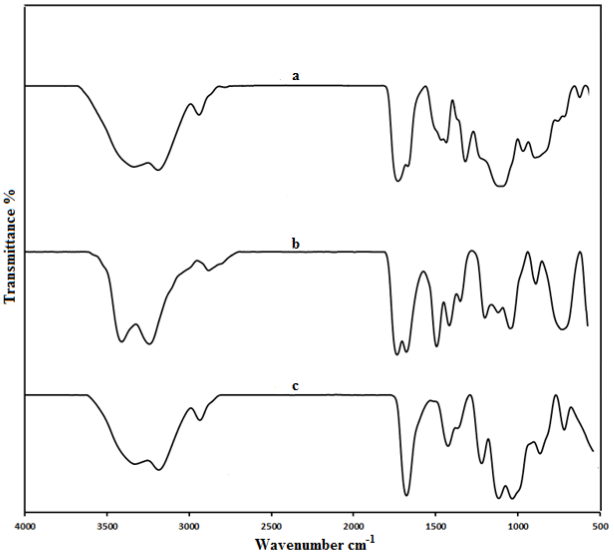


Figure 1. FT-IR of: a – NAA/AA copolymer, b – NAA/MA copolymer, c – NAA monomer.

Copolymer Composition

It is very useful to study the monomer reactivity in the copolymer system because the composition of the copolymer depends mainly on the monomer feed composition. In NAA/AA and NAA/MA copolymers, composition of the monomer in the copolymer was assessed by assurance N % in the copolymers and this proportion indirectly gave the mole fraction of NAA in the copolymer. The monomer composition and the results of elemental analysis in addition to intrinsic viscosity values [Ƞ] for samples of five different compositions are listed in Table 1. The values of [Ƞ] should be used in estimating qualitatively degree of polymerization (22). Figure 2 shows the plots of mole fraction of NAA in the copolymer (F_1) *vs*. that of mole fraction of NAA in the feed (f_1).

In the two systems, NAA forms alternates copolymer with AA and MA (Fig. 2a and b). Here, the presence of carbonyl and amide groups for each NAA monomer unit 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 macroradical. Since NAA is electron rich, it forms the bond easily with electron deficient species, thus it is easily involved in polymerization.

When NAA is copolymerized with MA (Fig. 2a), a greater incorporation of NAA unit compared to NAA-AA copolymer has been observed. In this case, the double bond of MA appears to have slightly more positive charge due to the presence of carbonyl ester bond. The charge density generated on carbonyl carbon atom would favor a significant electron attraction in MA radicals, which creates a slightly more positive charge on the double bond. Due to electron deficiency in the double bond of MA, the electron-rich NAA is easily involved in copolymerization and hence, higher content of NAA is observed as compared to NAA-AA copolymer. A similar behavior was observed in our earlier case (23) wherein acrylamide was copolymerized with 3-(Trimethoxysilyl) Propyl Methacrylate, which contained similar carbonyl ester bond attached to the double bond.

Table 1.Feed and copolymer compositions, conversion, nitrogen analysis and intrinsic viscosity values $[\eta]$ of NAA/AA and NAA/MA copolymers.

Sample Code	f_1 (feed)	Conversion%	N%	F_1 (copolymer)	$[\eta]$(dL/g)
NAA/AA-1	0.10	7.7	1.97	0.117	0.75
NAA/AA-2	0.25	8.1	3.38	0.226	0.83
NAA/AA-3	0.50	8.5	4.06	0.284	0.95
NAA/AA-4	0.75	9.1	5.11	0.406	1.51
NAA/AA-5	0.90	9.6	6.48	0.608	2.12
NAA/MA-1	0.10	9.8	2.87	0.212	0.88
NAA/MA-2	0.25	9.5	3.98	0.316	0.94
NAA/MA-3	0.50	8.9	4.91	0.426	1.73
NAA/MA-4	0.75	8.2	6.02	0.575	2.25
NAA/MA-5	0.90	7.8	7.26	0.772	2.91

(a) f_1 is the mole fraction of monomer-1 (NAA) in the initial feed; $f_2 = 1 - f_1$

(b) F_1 is the mole fraction of monomer-1 (NAA) in the copolymer; $F_2 = 1 - F_1$

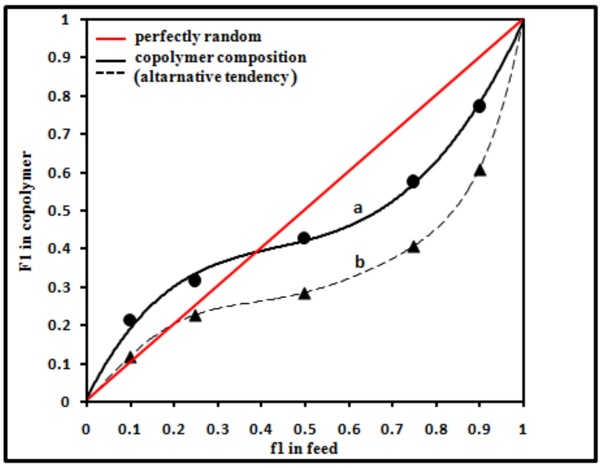


Figure 2. Variation of copolymer composition F_1 (AA) and F_1 (MA) with feed composition f_1 (AA) and f_1 (MA) for: a– NAA/AA, b–NAA/MA copolymers

Reactivity Ratio

The sort of copolymer framed can be best comprehended from the information of reactivity ratios of the copolymers. The most widely recognized scientific model of copolymerization depends on finding the connection between the composition of the monomer feed and the composition of copolymers in which the monomer reactivity ratios are the parameters to be resolved (24).In our work, two procedures have been used for the best fitting of (r_1& r_2) pair from a set of [M_1], [M_2], d [M_1] and d [M_2] pair, using linearization methods representing by Kelen-Tudos and Fineman-Ross. The references (25, 26) of these methods should be consulted for more details about the mathematical processes. The values are showed in Fig.3, 4, 5, 6, and represented in Table 2.

Table 2.Kelen-Tudos and Fineman-Ross parameters of NAA/AA and NAA/MA copolymers.

Sample Code	f_1 (feed)	G	X	η	ζ
NAA/AA-1	0.10	-7.81	10.73	-0.699	0.959
NAA/AA-2	0.25	-2.12	2.62	-0.693	0.853
NAA/AA-3	0.50	-0.60	0.39	-0.713	0.467
NAA/AA-4	0.75	-0.10	0.07	-0.199	0.142
NAA/AA-5	0.90	0.06	0.01	0.130	0.042
NAA/MA-1	0.10	-6.58	21.86	-0.288	0.958
NAA/MA-2	0.25	-1.61	4.15	-0.316	0.813
NAA/MA-3	0.50	-0.25	0.74	-0.152	0.437
NAA/MA-4	0.75	0.11	0.15	0.105	0.135
NAA/MA-5	0.90	0.26	0.04	0.266	0.041

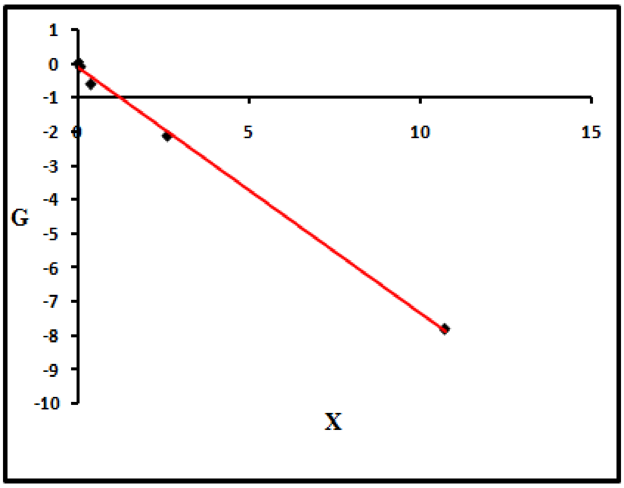


Figure 3.Fineman-Ross plot of NAA/AA copolymer.

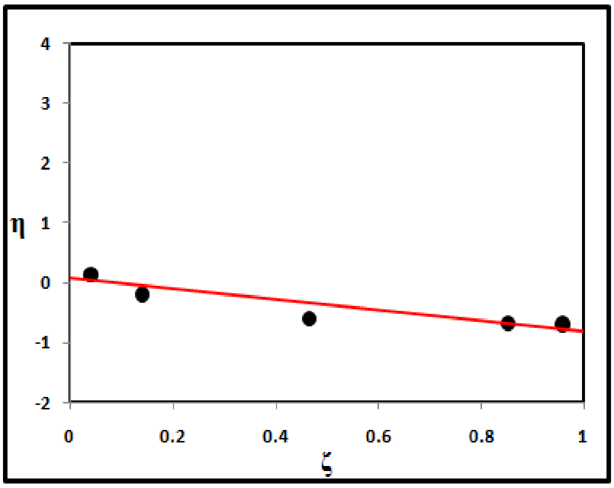


Figure 5.Kelen-Tudos plot of NAA/AA copolymer.

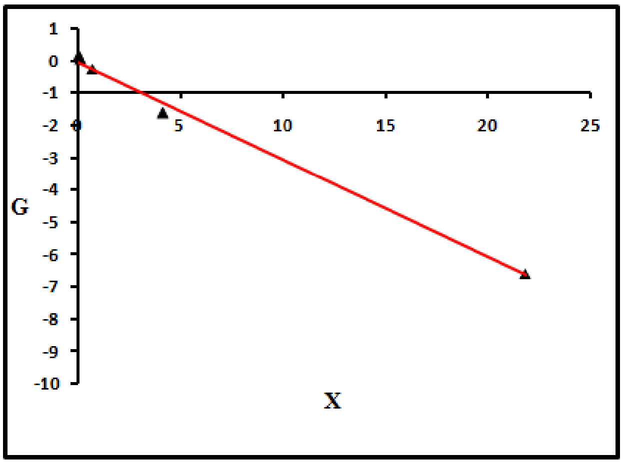


Figure 4.Fineman-Ross plot of NAA/MA copolymer.

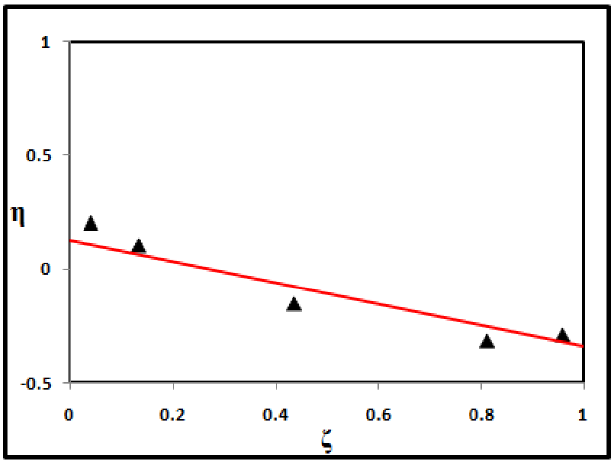


Figure 6.Kelen-Tudos plot of NAA/MA copolymer.

Table 3. Monomer reactivity ratios values for NAA-co-AA and NAA-co-MA

Copolymer	Procedure	r_1	r_2
NAA/AA	Kelen-Tudos	0.051	0.679
	Fineman-Ross	0.046	0.695
	Average values	0.048	0.687
NAA/MA	Kelen-Tudos	0.071	0.342
	Fineman-Ross	0.062	0.351
	Average values	0.066	0.346

Table 3 shows the values of reactivity ratios by different methods,the values (r_1, r_2)from the different methods are very close. It is easy to observed that both (NAA/AA) and (NAA/MA) copolymers have the r_1r_2 values less than unity, demonstrating the alternation behavior of the monomers. The alternative behavior for the three monomers (NAA, AA and MA) could be explained in terms of increasing the stabilization of their radicals by the carbonyl groups resonance.

When the reactivity ratios of the two monomers are less than unity, the synthesized copolymer shows an alternating behavior. Each monomer prefers to react with other monomer more than itself (27).

The possibility of an azeotropic composition increases in case of r_1, r_2 are both > 1 and < 1. For both copolymers systems (NAA/AA and NAA/MA), this condition is fulfilled since r_1 and $r_2 < 1$. Fig. 2 (copolymer composition curve) proves this fact, in which a value of 0.41 for f_1 (az.)in (NAA/MA) system and 0.23 in (NAA/AA) system. The azeotropic feed composition f_1(az.) can be expressed by the following equation:

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

Copolymer Microstructure

The results of reactivity ratios were then utilized for microstructural figuring. The microstructure of the copolymers is required to be critical in deciding the arrangement properties which the copolymer shows (28). Igarashi's (29, 30) procedures are used to calculate the fraction of M_1-M_1 , M_2-M_2 and M_1-M_2 units in the copolymers, the data are listed in Table 4.

$$S_{1-1} = m_1 - \frac{2m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \qquad (2)$$

$$S_{2-2} = m_2 - \frac{2m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \qquad (3)$$

$$S_{1-2} = \frac{4m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \qquad (4)$$

where: m_1 (NAA) and m_2 (AA or MA)– the mole fractions in the copolymer, S_{1-1}, S_{2-2}, and S_{1-2} – the mole fractions of 1-1, 2-2, and 1-2 sequences, respectively, r_1 and r_2 – the reactivity ratios.

The following equations were then used to calculate the probabilities of finding the sequence and the average length sequences of NAA, AA, and MA units (31, 32); the data are listed in Table 4.

$$P11 = r_1[A]/(r_1[A]+[B]) \qquad (5)$$
$$P22 = r_2[B]/(r_2[B]+[A]) \qquad (6)$$
$$P12 = [B]/(r_1[A]+[B]) \qquad (7)$$
$$P21 = [A]/(r_2[B]+[A]) \qquad (8)$$
$$\mu_1 = 1/P12 \qquad (9)$$
$$\mu_2 = 1/P21 \qquad (10)$$

where: A (NAA) and B (AA or MA) are the mole fractions in the feed. In these equations P11, P22, P12 and P21– the probability of a NAA or AA or MA unit to be followed by NAA or AA or MA unit.

Table 4.Statistical data of NAA/AA and NAA/MA copolymer.

Sample code	Blockness (mol%)		Alternation (mol%)	Sequence probability				Sequence length	
	M_1-M_1	M_2-M_2	M_1-M_2	P_{11}	P_{22}	P_{12}	P_{21}	μ_1	μ_2
NAA/AA-1	3.63	63.09	33.28	0.005	0.860	0.994	0.139	1.005	7.194
NAA/AA-2	5.41	45.40	49.19	0.015	0.673	0.984	0.326	1.016	3.067
NAA/AA-3	8.33	29.43	62.24	0.045	0.406	0.954	0.593	1.048	1.686
NAA/AA-4	11.53	13.39	75.08	0.125	0.185	0.874	0.814	1.144	1.228
NAA/AA-5	16.47	7.42	76.42	0.301	0.070	0.698	0.929	1.432	1.076
NAA/MA-1	10.71	30.04	59.25	0.006	0.753	0.993	0.246	1.007	4.065
NAA/MA-2	15.57	20.32	64.11	0.019	0.504	0.980	0.495	1.020	2.022
NAA/MA-3	24.33	9.45	66.22	0.056	0.253	0.943	0.746	1.061	1.342
NAA/MA-4	28.24	3.59	68.17	0.152	0.101	0.847	0.898	1.180	1.113
NAA/MA-5	29.28	1.64	69.08	0.350	0.036	0.649	0.963	1.540	1.038

For both copolymers systems (NAA/AA and NAA/MA), $[M_1]$-$[M_2]$, P12 and P21 increase as AA and MA increases. At the same time, these values are higher than $[M_1]$-$[M_1]$ and $[M_2]$-$[M_2]$, P11 and P22, respectively. From these results, AA in (NAA/AA) copolymer and MA in (NAA/MA) copolymer have a tendency to react with other monomer (NAA) rather than themselves in the growing chain to form alternation and block copolymers and these results are in agreement with the values of r_{AA} (0.68) and r_{MA} (0.34) < 1.

For the system of NAA/AA copolymers, the mean sequence length of NAA, μ_1, varied from 1.005 to 1.432. For these copolymer compositions, values of μ_2 were 7.194 and 1.076 respectively, similarly for the system NAA/MA, the μ_1 varied from 1.540 to 1.007, and for those copolymer compositions, values of μ_2 were 4.065 and 1.038.

Thermal Properties

For NAA/AA-1 copolymer, T_g value observed around 112 °C whereas NAA/MA-1 copolymer showed the T_g around 51 °C. It is found that by increasing the amount of NAA content in the copolymers result in increased T_g, this may be due to the presence of rigid amide group in the backbone in NAA side chain. TGA results are presented in Fig. 7. The NAA/AA copolymer is more stable than the copolymer of NAA/MA with 10 % weight loss at about 400 °C of NAA/AA-1 which is higher than 360 °C of NAA/MA-1. This result could be attributed to the presence of methyl group in the backbone in MA side chain which significantly lowers the T_g value and the thermal stability of NAA/MA copolymer. Values of T_g and data of TGA are given in Table 5.

Table 5.Thermal data of NAA/AA and NAA/MA copolymers.

Samples	T_g(°C)	$T_{10\%}$(°C)	$T_{50\%}$(°C)	Residual at 800 °C (wt %)
NAA/AA-1	112	400	460	16
NAA/MA-1	51	360	455	6

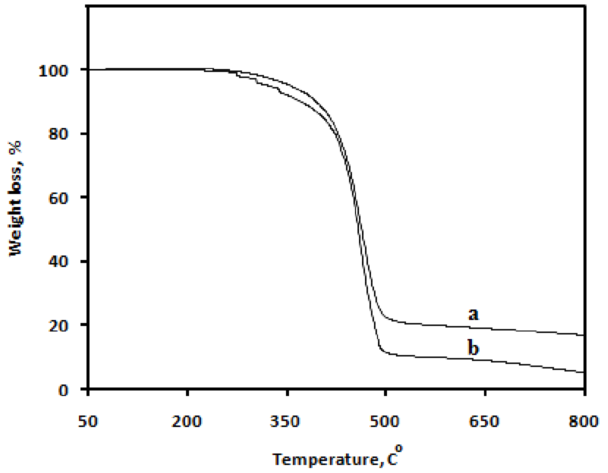


Figure 7. TGA thermogram of: (a) NAA-co-AA, (b) NAA-co-MA.

Conclusions:

The monomer NAA, NAA-co-AA and NAA-co-MA were successfully synthesized. The structure of synthesized monomer and copolymers was confirmed by FT-IR technique. Elemental analysis test was employed to determine the copolymer compositions. Then, the results of N% were used to calculate the reactivity ratios by different methods: Kelen-Tudosand Fineman-Rossmethods and a good agreement was observed between the two procedures. Both copolymers tend to be alternative (r_1 = 0.048, r_2 = 0.34) and (r_1 = 0.066, r_2 = 0.68) respectively. The results of sequence distribution of monomers and microstructure show a good agreement with the obtained reactivity ratios. DSC and TGA analysis were used to study the thermal properties of the copolymers.

Conflicts of Interest: None.

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حساب نسب الفعالية للبوليمر المشترك اكريلويل نفثايل امايد مع حامض الاكريلك والمثيل اكريلات

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الخلاصة :

تم تحضير المونومير اكريلويل نفثايل امايد (NAA) ثم تمت بلمرته بلمرة مشتركة مع كل من حامض الاكريلك (AA) والمثيل اكريلات (MA) في مذيب البنزين الجاف بوجود البادئ بيروكسيد البنزويل)(BPO) بتركيـز ثـابت قدره $10^{-3} \times 1$مولاري عند درجة حرارة ثابتة 70 م°. تم تشخيص المونومر والكوبوليمرات المحضرة بواسطة طيف الاشعة تحت الحمراء ثم درست خواصها الحرارية باستخدام تقنية TGA وDSC. تم حساب نسب الفعالية للمونوميرات الداخلة في تركيب البوليمر المشترك لانظمة البلمرة المشتركة (NAA-CO-AA)، NAA (-CO-MA) باستخدام طريقتين : فايمان وروس Finmman-Ross وطريقة كالين وتودس Kelen-Tudes وكانت قيم (r_1،r_2)، (0.048 ، 0.687)، (0.066 ، 0.346) على التوالي. ثم استخدمت قيم نسب الفعالية لحساب التراكيب المايكروية (الدقيقة).

الكلمات المفتاحية: حامض الاكريلك، المثيل اكريلات، اكريلويل نفثايل امايد، نسب الفعالية