Copolymerization of Acrylonitrile-acrylic Acid in DMF-water Mixture

Sharareh Shaari Moghadam and S. Hajir Bahrami*

Textile Engineering Department, Amir Kabir University of Technology, P.O. Box: 15875/4413, Tehran, I.R. Iran

A B S T R A C T

Copolymerization of acrylonitrile (AN) with acrylic acid (AA) carried out by solvent (DMF)- water suspension method, at 60°C, using azobisisobutyronitrile (AIBN) as an initiator. The effects of mole fraction variation of acrylic acid and concentration variation of water in reaction medium, on the properties of synthesized copolymers were investigated by FTIR, viscometry, and DSC techniques. The reactivity ratios were calculated using Fineman-Ross and Kelen-Tudos methods. The results obtained show that by increasing the mole fraction of acrylic acid in the feed up to 0.0756, the conversion percentage decreases. However, the molecular weight increases in this range of feed ratio. In the samples prepared by keeping the feed ratio of comonomers constant and varying the ratio of the solvent/nonsolvent, the molecular weight increases by increasing nonsolvent amount. The reactivity ratio of AA is 6.5 times greater than that of AN. DSC Exothermic peak of homopolymer shows a single peak whereas, for copolymers it appears as doublets, due to more distinction of dehydrogenation, oxidation, and cyclization reactions.

INTRODUCTION

Acrylonitrile based copolymers have a variety of applications in textile industry, house wares, and custom moulding products. Acrylonitrile polymers, because of their high melting point, high melt viscosity, and poor thermal stability have few applications [1]. Copolymers of acrylonitrile with vinyl acetate or methyl acrylate are used for fibre production in textile industries. Commercially, copolymers are produced by radical polymerization, much of them in aqueous slurry

(∗) To whom correspondence should be addressed.
E-mail: Hajirb@aut.ac.ir

processes using various water-soluble free radical initiators [2]. Various polymerization parameters, such as comonomers type, temperature, initiator system, polymerization media etc., affect the properties of the final polymer [3].

Bajaj et al. [4] studied the solution copolymerizations of acrylonitrile with various vinyl acids, i.e., acrylic acid, methacrylic acid and itaconic acid, in DMF, at 70ºC, using azobisisobutyronitrile (AIBN) as initiator. They also studied some of the characteristics of synthesized copolymers using FTIR, CHN analysis, ^{1}H and ^{13}C NMR. The reactivity ratios of the comonomers were calculated. Similar investigations were carried out on the copolymers synthesized by water suspension method, At 40ºC, using ammonium persulfate and sodium metabisulphite as the redox initiator. The reactivity ratios of copolymer system were calculated by Finemann-Ross and the Kelen-Tudos methods [5]. The influence of comonomers concentration on the molecular weight, tacticity and number average sequence lengths were studied using NMR technique. Copolymers with approximately 2 mol % of acrylic acid have a greater percentage (> 30%) of isotactic content than homopolyacrylonitrile.

Ebdon et al. [6] reported the structural investigation of free radical (ammonium persulphate/sodium metabisulphite) aqueous slurry polymerization of acrylonitrile. The polymer has shown to contain small quantities of acrylamide and acrylic acid units and to possess predominantly sulphonate and non-sulphur containing end groups derived principally from transfer to bisulphite ion during the polymerization. Mechanism of copolymerization of acrylonitrile-methacrylic acid has been investigated in bulk using FTIR and NMR technique. The reactivity ratios for the system was calculated to be $r_1(M)= 3.7$ and $r_2(A)= 0.19$ [7].

Kinetic of polymerization of acrylonitrile initiated by manganese (III)-glycine redox initiator system has been investigated by Rai et al. [8]. The rate of polymerization and the rate of manganese disappearance have been measured. The effects of some water miscible organic solvents, surfactants, and complexing agents on the rate of polymerization were investigated.

DMSO-water mixture was used to study the effect of solvent on the chain propagation and termination reaction rates in the radical polymerization of acrylamide, methacrylamide and acrylic, methacrylic, and fluoroacrylic acids [9]

Li and Shan [10] studied the effect of the mixed solvent of DMF-water on the polymerization behaviour and the properties of poly (acrylonitrile-methylacrylate itaconic acid) terpolymer. They started the copolymerization in a known amount of DMF and water and after polymerizing for a given time, the required amount of solvent was added. With increasing DMF content of the medium, the molecular weight of the polymer decreases whereas, when the content of DMF in the medium increases up to about 35% the conversion increases and then decreases. The molecular weight distribution however, broadens with decreasing DMF content in the medium. Bajaj et al. [11] reported the effect of reaction medium on the copolymerization of acrylonitrile vinyl acids. They used itaconic and methacrylic acids. The rate of reaction is reported to decrease with increase in the DMF content of the medium.

Pichot et al. [12] investigated the emulsion copolymerization of acrylonitrile-methacrylic acid at 35ºC using potassium persulfate and sodium metabisulfite as initiator. The reactivity ratios calculated were $r_1(AN)=0.128$ and $r_2(MAA)=2.40$. The copolymers were characterized by ^{1}H and ^{13}C NMR. By increasing the mole fraction of the methacrylic acid in the copolymer feed up to 0.145 the intrinsic viscosity increases up to 924 mLg[-1].

During the heat treatments of acrylic fibres, instead of melting, some exothermic reactions, such as cyclization of nitrile groups, takes place, which lead to formation of ladder like structure. Thermal behaviour of acrylonitrile homo and copolymers has always been a subject of great interest, since polyacrylonitrile and its copolymers are used as precursors for the production of high strength carbon fibres. The demand for high quality carbon fibres in composite materials has intensified the interest in he thermal characterization of acrylic polymers particularly under programmed conditions. The oligomerization of nitrile groups, an important step in the manufacture of carbon fibres from polyacrylonitrile, is influenced by the method of polymerization, nature of comonomers, additives, as well as pre-heat treatment [13-17].

The influence of methyl methacrylate, acrylamide, vinyl acetate, vinyl chloride, and itaconic, acrylic and, methacrylic acids, etc., on the nitrile oligomerization reported by various authors [18-20].

Grassie and McGuchan [21] reported that 20% acrylate or methylacrylate content in polyacrylonitrile copolymer exhibits as a diluent effect without inhibiting the reaction, while comonomers with styrene type structures behave differently; showing a marked inhibiting effect on the nitrile oligomerization. Ferguson et al. showed the role of acrylic acid comonomer as accelerator in cyclization, while *N*-vinyl pyrrolidone acts as an inhibitor [17].

Grassie and McGuchan [22] also reported that acrylic, methacrylic, and itaconic acids and acrylamide have a strong initiation effect on the exothermic nitrile group oligomerization. As the acid content increases, the exotherm becomes broader and less intense with lower initiation and peak temperature. The methacrylic and itaconic acid copolymers show more complex and broaden exotherms than the AN-AA copolymer. Guyot et al. [23] investigated pyrolysis of acrylonitrile methacrylic acid (MAA) copolymers having 2 to 10 mol % of MAA and their sodium salts under inert atmosphere at various heating rates using thermogravimetric analysis coupled with gas liquid chromatography, thermal volatilization analysis and DSC techniques. According to them, nitrile oligomerization, which is not directly related to any loss in weight, can be initiated through a molecular mechanism by the carboxylic group of the acid.

Polyacrylonitrile (PAN) and copolymer of acrylonitrile-vinyl acids prepared by solution polymerization technique have been characterized by DSC (under dynamic as well as isothermal conditions), thermograviemetric analysis (TGA), and on-line DSC-FTIR spectroscopy. The initiation temperature of PAN homopolymer is higher than that of the copolymers. For instance, the initiation temperature of PAN in air was 244ºC , whereas, the onset of exothermic reaction was in the range of 172-218ºC for acrylonitrile-vinyl acid copolymers [24]. Recently Devasia et al. investigated the cyclization reaction of acrylonitrile-itaconic acid copolymers [25].

As stated earlier one of the most important applications of copolymers of acrylonitrile carboxylic acids is in the production of carbon fibres. However, obtaining high molecular weight with lower molecular defects are of prime importance in the production of high quality carbon fibres. Solution polymerization will result in lower molecular defects with comparatively lower molecular weight polymer. On the other hand aqueous suspension polymerization will produce higher molecular weight but with more molecular defects [13]. Combining these two methods will produce copolymers with high molecular weight and lower molecular defects. Combined solvent (DMF)-water suspension polymerization technique has not been reported previously for copolymers of acrylonitrile with acrylic acid. In this work, an attempt was made to investigate the effects of mole fraction variation of AA and concentration of water in reaction medium, on some of the properties of synthesized copolymers by solvent (DMF) - water suspension method.

EXPERIMENTAL

Materials

AN Was freed from inhibitor by washing with sodium hydroxide solution and then with distilled water to remove traces of sodium hydroxide and dried over calcium chloride. AA Was purified by distillation. AIBN Was purified by recrystalization from methanol. DMF Was dried over calcium oxide and distilled at 153ºC.
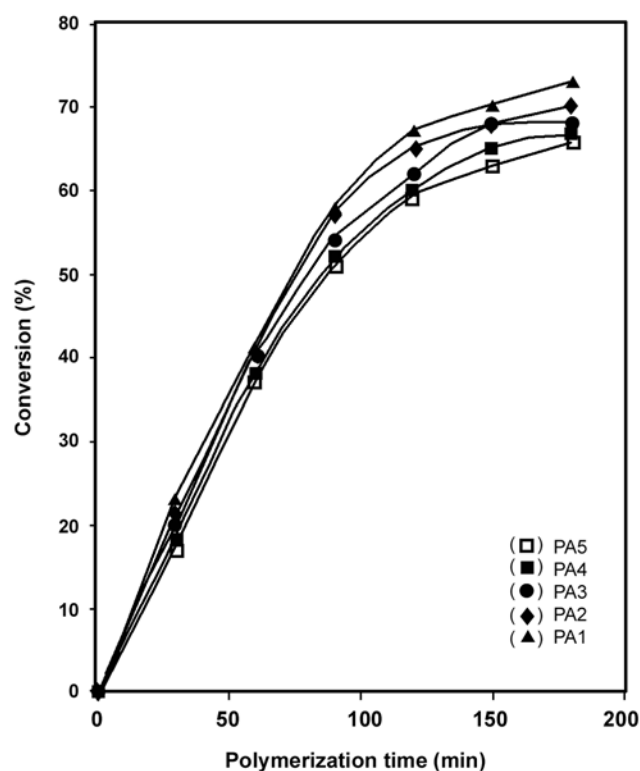
Polymerization

Copolymerizations of AN with AA were carried out in a four - necked glass reactor, using mixture of deionized water and DMF as a reaction medium, at 60ºC, under pure nitrogen atmosphere. The total weight of H_2O and DMF was 3 times greater than that of the monomers. AIBN (2 % wt on the basis of the monomers) was used as initiator. Poly(AN-AA) copolymers were synthesized using different ratios of AA (0 to 10 % wt on the basis of the monomers) in feed, and mixed deionized water-DMF (50-50 % wt) as a reaction medium. In another set of experiment, to investigate the effect of polymerization medium, i.e., solvent/non-solvent ratio, copolymers were synthesized using different ratios of DMF (20-100 % wt on the basis of the reactions medium), and 5 % wt of AA comonomer. The reactions were stopped after 3 h. The copolymers were washed with excess of distilled water and filtered and dried in oven at 50ºC over night. To determine the reactivity ratios, copolymers with different feed ratios of monomers (0-100 %) were synthesized and the reaction medium kept constant (50:50

water/DMF). These copolymerizations were stopped at conversion of less than 30%. It has been reported that the reactivity ratios can be calculated using Kelen-Todus method even at high conversion of 50% [26].

Intrinsic viscosity [η] of copolymers were measured in DMF solution using an Ubbelohde viscometer in constant temperature water bath at 25±1°C. FTIR Spectra of the copolymers were recorded on FTIR 4300 Shimadzu spectrophotometer using KBr pellets. It also was used to calculate the composition of the copolymers. DSC thermograms of the copolymers were recorded on DSC V4.0B Dupont 2000, at a heating rate of l0°C/min under air atmosphere.

RESULTS AND DISCUSSION

The results of the copolymerization of AN-AA are given in Table 1. From time vs. conversion curve (Figure.1) it is clear that the addition of the AA comonomer decreases the percentage of conversion of the copolymer. However, the intrinsic viscosity of the copolymers increases as the comonomer content increases in the feed. This is probably because the copolymer radicals with AA units at the chain ends are considerably more

Figure 1. Time vs. conversion of Polyacrylonitrile and copolymers of AN-AA.

active than the polyacrylonitrile growing radicals. This

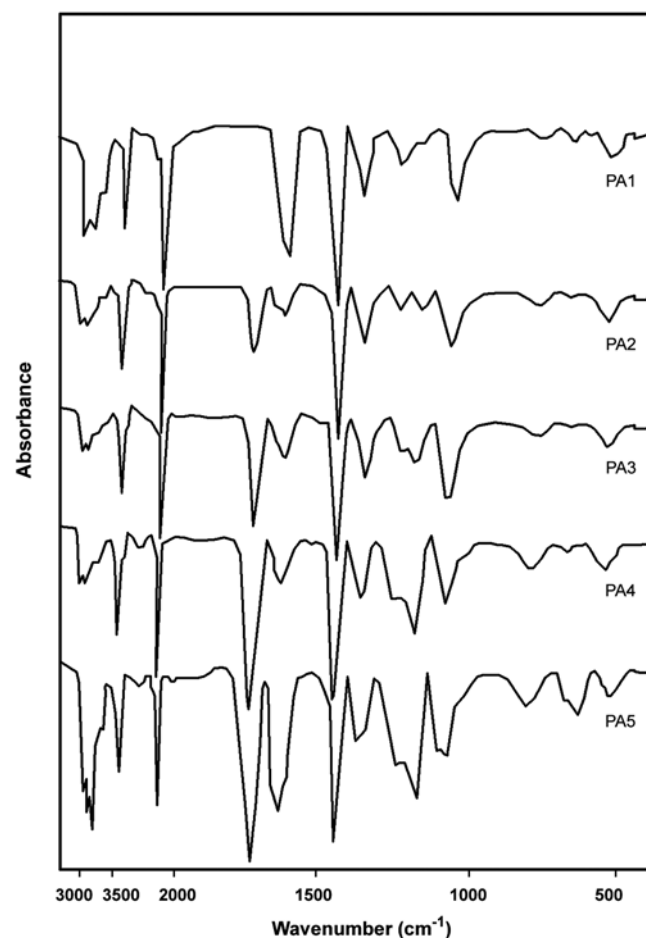**Table 1.** Polymerization of AN with AA.

Polymer code	Monomer feed (wt%)		Reaction medium (wt%)		Mole fraction of AA			Conversion (%)	[η] (dLg⁻¹)
	AA	AN	DMF	H$_2$O	Feed	Copolymer			
						FTIR	CHN		
PA1	0	100	50	50	0	0	0	72.12	1.11
PA2	2	98	50	50	0.0148	0.0205	0.0210	70.86	1.79
PA3	5	95	50	50	0.0373	0.0543	0.0532	68.08	1.85
PA4	7	93	50	50	0.0533	0.0792	0.0803	66.04	2.18
PA5	10	90	50	50	0.0756	0.0984	0.1015	65.86	2.67
PB1	5	95	100	0	0.0373	0.0430	0.0486	42.42	0.50
PB2	5	95	90	10	0.0373	0.0487	0.0490	45.50	0.65
PB3	5	95	80	20	0.0373	0.00529	0.0504	50.76	0.93
PB4	5	95	60	40	0.0373	0.0542	0.0524	62.82	1.43
PB5	5	95	50	50	0.0373	0.0528	0.0532	68.08	1.85
PB6	5	95	40	60	0.0373	0.0553	0.0542	70.20	2.04
PB7	5	95	20	80	0.0373	0.0593	0.0573	74.04	3.29
PB8	5	95	0	100	0.373	0.0592	0.0609	87.6	4.6

means that the addition of the monomer will be more rapid than the case of radical termination in an AN unit [27]

In the case of copolymers prepared by changing solvent/non-solvent ratio (Table 1), it can be seen that polymers prepared in DMF, i.e., in solution had lowest conversion and molecular weight. This is due to the chain transfer effect of the solvent, which is quite high. The chain transfer constant of water is almost zero whereas, that of DMF is 2.8×10^4 at 50°C [28]. However, with incorporation of non-solvent (water) into the medium, the polymerization system changes and conversion increases. The polymer prepared in completely suspension system, i.e., PB8 has the highest molecular weight which is due to the low chain transfer constant of water.
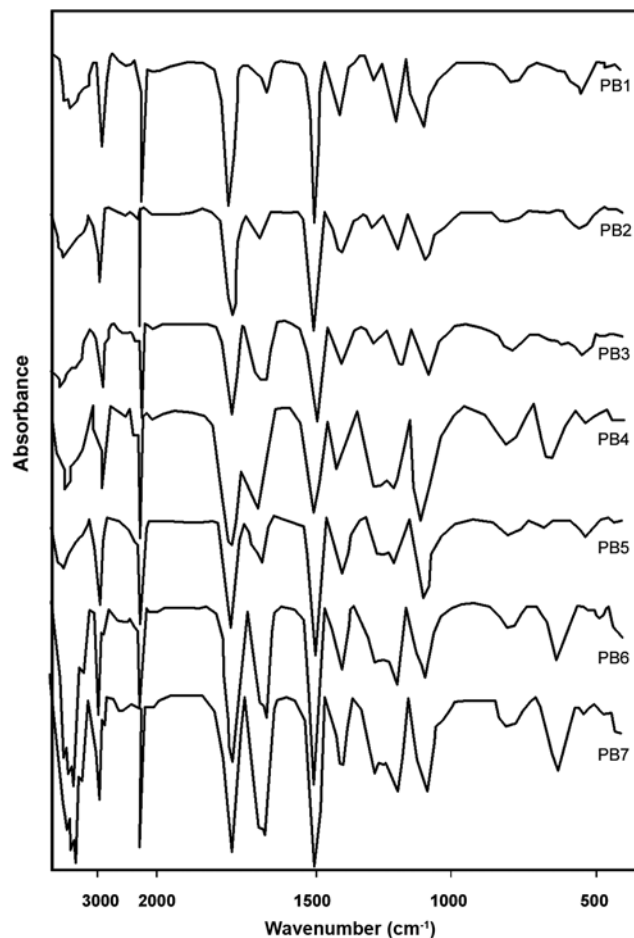
FTIR Spectra

IR Spectra of the copolymers are shown in Figures 2-4.

The absorption band at 530 cm^{-1} is due to C-C≡N. The l075 cm^{-1} band is assigned to the CH vibration mode. The absorption band at 1250 cm^{-1} is due to the bending mode of the methine (-CH) group coupled with the rocking mode of the methylene (CH$_2$) group. The bands appear at 1220-1270, 1345-1375, and 1465 cm^1 are assigned to C-H vibrations modes.

Bands at 1640 cm^{-1} are due to the hydrolysis of AN units during the polymerization process. In the IR spectra of the copolymers, the absorption bands at 1000-1300 cm^{-1} might be due to C-O, also the strong band at 1730 cm^{-1} is due to the carboxyl (C=O) stretching vibration of the acrylic acid. The strong band appears at 2240 cm^{-1} is assigned to nitrile (C≡N) group. The band at 2850-2960 cm^{-1} is due to stretching vibration of CH$_2$ and the absorption bands at 3500-3560 cm^{-1} are assigned to stretching vibration of OH. The composition of copolymers were calculated by considering the

Figure 2. FTIR Spectra of copolymers of (AN-AA) with different feed ratio of monomers.

Figure 3. FTIR Spectra of copolymers of (AN-AA) prepared in different composition of DMF- H$_2$O.
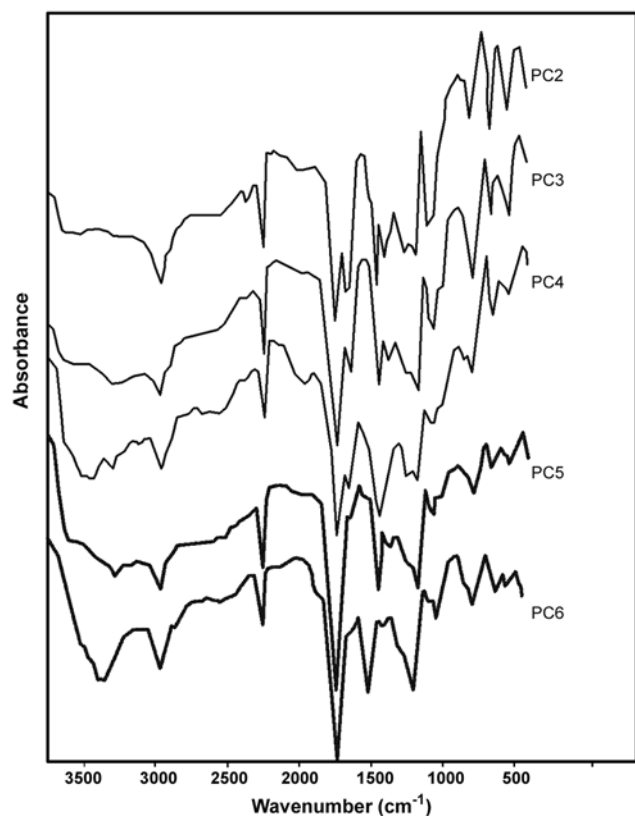
Figure 4. FTIR Spectra of copolymers of (AN-AA) prepared at low conversion percentage for reactivity ratio calculations.

bands at 2240 cm^{-1} due to C≡N, and 1730 cm^{-1} due to C=O. The intensities of absorbtion of C=O and C≡N were used to estimate the AA content in the copolymers:

$$\text{ODR} = \frac{(\text{Absorbance ratio})\nu_{(C=O)}}{(\text{Absorance ratio})\nu_{(C \equiv N)}} = \frac{\log(I_\circ/I)\nu_{(C=O)}}{\log(I_\circ/I)\nu_{(C \equiv N)}}$$

Where, I and I_0 represent the intensities of the transmitted and incident radiants, respectively. Having the optical density ratio (ODR), the copolymers compositions were calculated using the following equation [29]:

$$X = 16.3\,Y - 8.5Y^2 + 2.24\,Y^3 - 1.78$$

Where, X and Y are the percentage of comonomer in the copolymer and the ODR, respectively. This equations was given by Pandey to determine the amount of comonomers in the Poly(acrylonitrile-vinyl acetate) system. However, other investigators used this equation to determine the amount of comonomers in other copolymers of acrylonitrile.

Table 2. Data for reactivity ratios calculation.

Polymer code	Monomer content in feed (mole fraction)		Copolymer composition (mole fraction)	
	AA	AN	AA	AN
PC 1	1	0	1	0
PC 2	0.9244	0.0756	0.876	0.124
PC 3	0.8445	0.1555	0.714	0.286
PC 4	0.6719	0.3281	0.430	0.570
PC 5	0.5759	0.4241	0.325	0.675
PC 6	0.4752	0.5248	0.206	0.794
PC 7	0.2534	0.3466	-	-
PC 8	0.1311	0.8689	-	-
PC 9	0	1	0	1

Reactivity Ratios

Reactivity ratios of these monomers in the copolymer system were measured by these methods to compare the obtained values with the reported valued of the other systems.

For calculating reactivity ratios, copolymers of AN-AA were prepared using DMF-water of equal ratio (50:50) at 60ºC and the reaction was stopped at low conversion (%). The results are given in Table 2. The composition of copolymers was determined by CHN analysis and FTIR. The reactivity ratios were calculated using Kelen-Tudos [30] and Fineman-Ross method [31] (Table 3).

Kelen and Tudos proposed a graphical equation for calculating reactivity ratios.

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$$

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha}\right)\frac{F}{\alpha + F} - \frac{r_2}{\alpha}$$

Where G and F are represented by :

$$G = \frac{x(y-1)}{y} \quad \text{and} \quad F = \frac{x^2}{y}$$

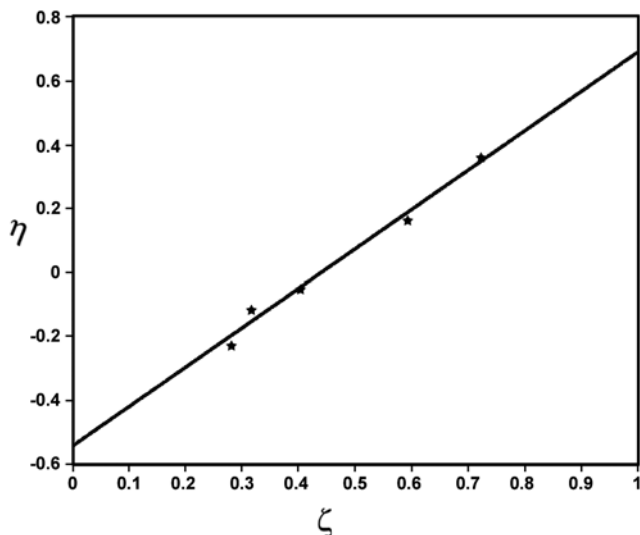in which x and y are the ratios of the mole fraction of the monomers in the feed and in the copolymer, respectively.

Figure 5. Keken-Tudos plot of AN-AA copolymers.

Figure 6. Finemann- Ross plot of AN-AA copolymers.

α is given by:

$$\alpha = (F_m F_M)^{-1/2}$$

where F_M and F_m represent the highest and the lowest F values calculated from the series of measurements. The plot of η vs. ξ gives a straight line. Extrapolation of the line to $\xi=1$ gives r_1 and to $\xi=0$ gives r_2/α. Kelen-Tudos plot for calculating the reactivity ratios is shown in Figure 5.

Finemann and Ross proposed the following equation for calculating reactivity ratios of copolymers.

$$G = r_1 H - r_2$$

Where,

$$G = \frac{f_1}{f_2}\left(1 - \frac{F_2}{F_1}\right) \quad \text{and} \quad H = \left(\frac{f_1}{f_2}\right)^2 \frac{F_2}{F_1}$$

in which, f_1 and F_1 are the mole fractions of AN in the feed and the copolymers and f_2 and F_2 represent the mole fraction of acidic comonomer in the feed and in the copolymer, respectively.

The plot of G vs. H gives a straight line with the slope as r_1 and the intercept as r_2. Finemann-Ross plot for calculating the reactivity ratios is shown in Figure 6. The values of r_1(AN) and r_2(AA) are given in Table 3. The reactivity ratios reported by aqueous and solution methods are also reported in this table. It can be seen
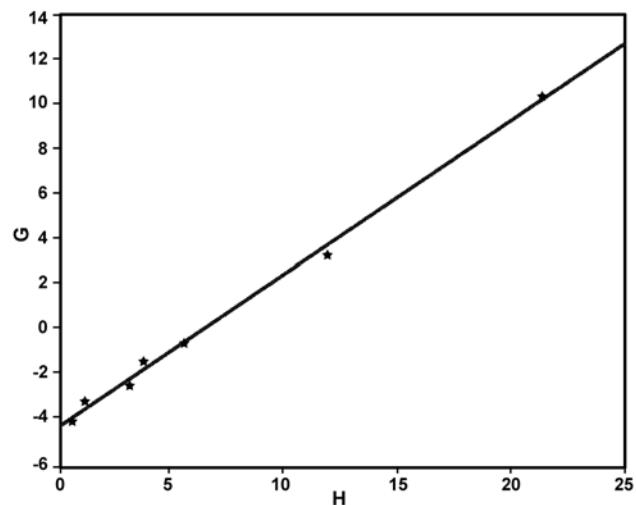
from this data that the value of r_2/r_1 in aqueous system is 9.56 whereas, in solution it is 4.89. This indicates that in the later system due to chain transfer termination, the propagation of polymer chain are affected by it. However in solvent water suspension method the value of r_2/r_1 equles 6.48 which is quiet acceptable.

The value of $r_1<1$ and $r_2>1$ means that the propagation reaction $\sim\sim M_2 M_2^\circ$ and $\sim\sim M_1 M_2^\circ$ will be preferred over $\sim\sim M_2 M_1^\circ$ and $\sim\sim M_1 M_1^\circ$. Hence, the probability of entering M_2(AA) to the copolymer chain is higher than the entering of M_1(AN).

The reactivity ratios of AN and AA comonomers, in solution and water suspension methods, are also given in Table 4. It is obvious that irrespective of the method of polymerization, AA is more active than AN. Beside it can be seen that by increasing the concentration of water in reaction medium, the value of r_2/r_1 increases too.

DSC Studies
DSC Thermograms of PAN homopolymer (PA1) and, PA3 and PA5 copolymers are shown in Figure 7, and that of the PB2, PB4 and PB7 copolymers are shown in Figure 8. The various paramenters obtained from these

Table 3. Reactivity ratios of AN and AA.

Method	r_1 (AN)	r_2 (AA)
Kelen-Tudos	0.693	4.509
Fineman-Ross	0.699	4.532

Table 4. Comparing the reactivity ratios of AN-AA in different methods of copolymerization.

Copolymerization method	Kelen-Tudos method			Fineman-Ross method		
	r_1 (AN)	r_2 (AA)	r_2/r_1	r_1 (AN)	r_2 (AA)	r_2/r_1
Aqueous suspension	0.36	3.25	11.37	0.27	3.07	9.56
Solvent water suspension	0.693	4.509	6.51	0.699	4.532	6.48
Solution in DMF	0.495	2.502	5.05	0.531	2.60	4.89

thermograms, including the temperature of initation (T_i), temperature of termination (T_f), width of the exothermic peaks ($\Delta T = T_f - T_i$) and peak temperature (T_{pk}), are listed in Table 5.

Exothermic peaks of copolymers appear as doublets. Whereas, that of homopolymer appears rather as a single peak. This is probably due to mere separation of the temperature range of occurring exothermic reactions (including dehydrogenation, oxidation and cyclization) in the copolymers. The T_i values for all the copolymers are lower than the T_i value for the homopolymer. This indicates a much easier initiation of the exothermic process in presence of AA. ΔT Values for all the copolymers are greater than ΔT value for the homopolymer. The reason is that in the PAN homopolymer the cyclization initiates through a radical mechanism, where as in poly(AN-AA) copolymers it follows an ionic mechanism. Cyclization reaction initiated through radical mechanism is faster than the cyclization, which is initiated through ionic mechanism.

It appears that increasing the mole fraction of AA in copolymer, leads to decreasing the intensity of the first peak of the doublets, and increasing that of the second one. The first peak can be assigned to the primary oxidative (including dehydrogenation and cyclization) reactions, and the second one can be assigned to the secondary oxidative reactions leading to the evolution of HCN, CO_2, and CO. The extent of the primary

oxidative reactions decreases with increase in the AA content. This observation suggests that the acidic comonomer reduces the extent of cyclization reactions. This may be attributed to the interruption in the sequence of CN unit. Thereby adversely affecting the process of cyclization reaction. The acidic comonomer promote the secondary oxidative reactions. This is probably due to the increase in the amorphous phase in the polymer by incorporation of the comonomer units, which may provide greater opportunity for the molecules to come in to contact with air. It appears that increasing the water concentration in reaction medium during polymerization, has no considerable effect on

Table 5. DSC data obtained from AN-AA copolymers.

Polymer code	T_i (°C)	T_f (°C)	ΔT (°C)	T_{PK} (°C)	
PA 1	229	385	156	-	344
PA 3	217	410	193	282	331
PA 5	214	414	200	267	333
PB 2	217	409	192	280	328
PB 4	217	409	192	282	330
PB 7	217	410	193	287	333
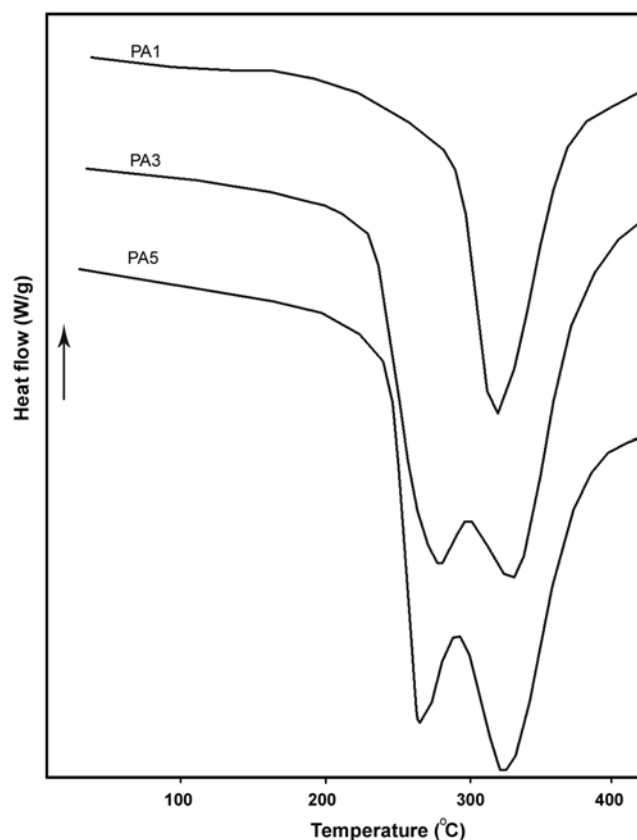
Figure 7. DSC Thermogram of polyacrylonitrile PA1 and AN-AA copolymers PA3 and PA5.
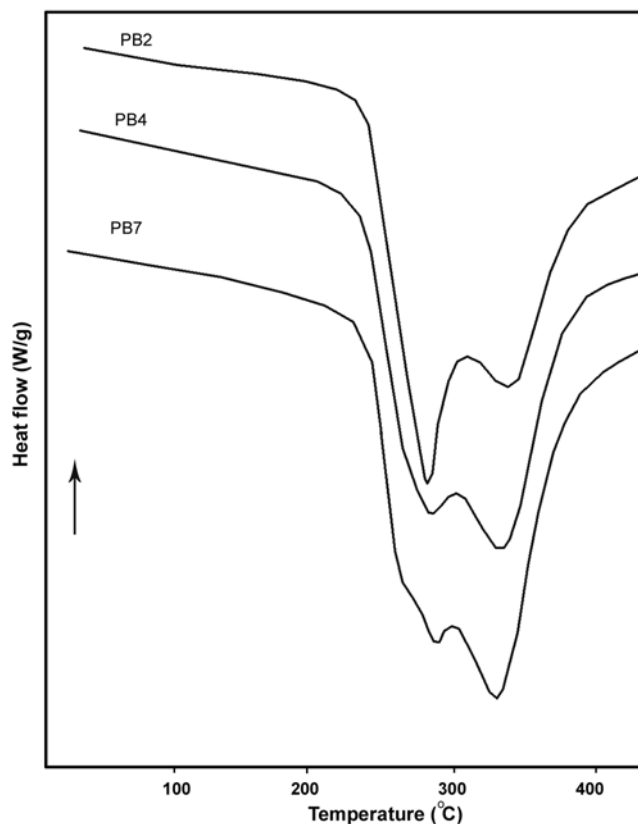
Figure 8. DSC Thermogram of AN-AA copolymers PB2, PB4, and PB7.

ΔT and T_i, but it decreases the intensity of the first peak of the doublets and increases that of the second one. Besides, shape of the doublet approaches triplet. This is probably due to more separation of the occurring range of the exothermic reactions.

CONCLUSSION

Solvent water suspension polymerization technique was used for copolymerization of AN with AA. It is concluded that increasing the amount of AA in the feed up to 10 weight % will reduce the conversion percentage and increase the molecular weight. The reactivity ratios of these monomers were calculated using Kelen-Tudos and Fineman-Ross methods in order to compare the values with the values available in the literature for other copolymerization systems. It is found that reactivity ratio of acrylonitrile is much lower than that of acrylic acid. Thermal behaviour of these copolymers shows that with increasing the comonomer content, the

onset of exothermic reaction falls to a lower temperature. The DSC thermograms show that the difference between temperature of initiation of the reaction and the final temperature of the reaction increases with increasing the comonomer content. It indicats that the heat of reaction can be dissipated in larger time and have less damage on the polymer during the heat treatment.

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