

Dyeability and Mechanical Properties of Acrylonitrile-Diallylamine Salts Copolymers

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ABSTRACT

The dyeability of Acrylonitrile-Diallylamine Acetate (AN-DAA acetate) and Acrylonitrile-Diallylguanidine Acetate (AN-DAGA) copolymers have been studied with both conventional and ultrasonic methods. The results obtained were compared to the parent polyacrylonitrile. The effect of dye concentration, dye bath pH, dyeing time and temperature were studied and the results obtained by dyeing with both techniques were compared. Color strength values were found to be higher with ultrasonic than with conventional method. To identify the structural changes in the dyed copolymers as compared to dyed PAN, during thermal treatment at high temperature, XRD analysis were performed. The XRD patterns of all heated dyed copolymers are similar to the corresponding unheated samples while that of the heated dyed PAN changed dramatically. The mechanical properties of the dyed copolymers had been also studied and compared to those of the dyed PAN.

Keywords: Acrylonitrile, Diallylamine Salts, Copolymerization, Mechanical Properties, Dyeability

1. INTRODUCTION

Acrylonitrile based copolymers have a variety of applications in textile industry. Polyacrylonitrile because of their high melting point, high melt viscosity and poor thermal stability have few application (Abdel-Naby, 2011). Polyacrylonitrile is prepared by addition polymerization of acrylonitrile (Zhou *et al.*, 2011). The pure homopolymer suffers from poor heat stability at high temperature as well as it possesses low dyeability.

Copolymerization of acrylonitrile with suitable comonomers gave the polymer its extra thermal stability and also improved its dyeability (Abdel-Naby and Aboubshait, 2013; Tsai and Lin, 1990; Bahrami *et al.*, 2003; Abdel-Naby, 2011; 2012). Copolymerization of acrylonitrile with acrylic acid in DMF-water matrix showed high thermal stability (Moghadam and Bahrami 2005). Moreover, acrylonitrile copolymers with vinyl acetate or methyl acrylate are used for fiber production in textile industries (Sanderson, 2004).

In our previous work (Abdel-Naby and Al-Harhi, 2013) the copolymerization of acrylonitrile with

diallylamine salts led to thermal stable copolymers as shown from their DSC thermograms and their thermal gravimetric analysis.

The aim of the present work is to investigate the dyeability of the acrylonitrile-diallylamine salts copolymers as compared to PAN homopolymer.

2. MATERIALS AND METHODS

2.1. Experimental

2.1.1. Materials

Acrylonitrile (AN) from (Acros organic). Diallylamine (DAA) 97% from (Acros organic). Cyanamide 95% from (Acros organic). Acetonitrile from (Acros organic). Sodium bisulfate from (Acros organic). Potassium persulphate 99% from (Acros organic). Glacial Acetic Acid (GAA) from (Acros organic). Methanol from (Aldrich). 1-Butanol from (Acros organic). Acetone from (Aldrich). Dimethyl Formamide (DMF) from (Acros organic). The coloring substance (C.I. Arston Basic Red 5BL 200%) was supplied by Dystar Company, Cairo, Egypt. The dye chemical name

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is [2-[[4-(2-cyano-4-nitrophenyl) azo] phenyl] ethylamino] ethyl] triethyl ammonium methyl sulphate.

2.2. Apparatus

A crest ultrasonic, TRU-SWEEPTM ultrasonic bench top cleaner bath, model 575 D with a capacity 5.75 L, was used.

2.3. Synthesis of Diallylamine Salts

Diallylaminesalts were synthesized according to the method described by (Zaikov *et al.*, 2004).

Step 1: Formation of diallylamine acetate.

Glacial acetic acid (1.00 mol) was added with stirring to cooled DAA (1.05 mol) in a one-neck flask (0.5 L) and diallylamine acetate was obtained (**Fig. 1**).

Step 2: Formation of diallylguanidine acetate.

To obtain the diallylguanidine acetate, a cyanamide (1.00 mol) in acetonitrile ($\sim 60 \text{ mL}^{-1}$) was added to the resulting diallylamine acetate. After this reaction mixture was stirred (for about 10 min) without cooling. The prepared mixture was added dropwise to reflux acetonitrile ($25\text{-}250 \text{ mL}^{-1}$) in a three-neck flask (1.00 L) with a reflux condenser and dropping funnel over a period of about 1 h 40 min (crystalline product appeared after addition of half of the mixture), then this mixture was refluxed an additional nearly 1 h 40 min. The precipitate was filtered off, washed many times with

acetonitrile, n-butanol and acetone and dried in vacuum at about (20°C) to give DAGA (m.p. $212\text{-}214^\circ\text{C}$) (**Fig. 2**).

2.4. Copolymerization Procedure

2.4.1. Copolymerization of Acrylonitrile with Diallylamine Acetate

To the diallylamine acetate prepared in three-neck flask acrylonitrile was added in a given concentration, under nitrogen atmosphere, sodium bisulfate and potassium persulphate were added as radical initiators ($4 \times 10^{-2} \text{ mol L}^{-1}$, in distilled water. The mixture was refluxed for (1-2 h) at (45°C). The precipitated pale yellow copolymer was collected and purified by reprecipitation filtered and washed repeatedly with methanol using soxhlet system. The copolymers compositions were calculated on the basis of their nitrogen and carbon-hydrogen contents (Abdel-Naby and Al-Harhi, 2013). **Table 1 and 2** shows the found copolymer compositions of each sample.

2.5. Copolymerization of Acrylonitrile with Diallylguanidine Acetate

Polymerization ampoules of pyrex glass were charged with monomer, water and the initiator sodium bisulfate and potassium persulphate were added as radical initiators ($4 \times 10^{-2} \text{ mol L}^{-1}$). The ampoules were covered with serum caps, cooled and purged with a slow stream of purified nitrogen.

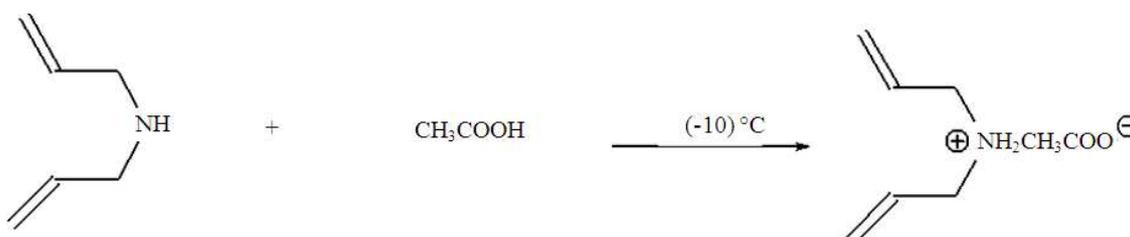


Fig. 1. Synthesis of diallylamine acetate

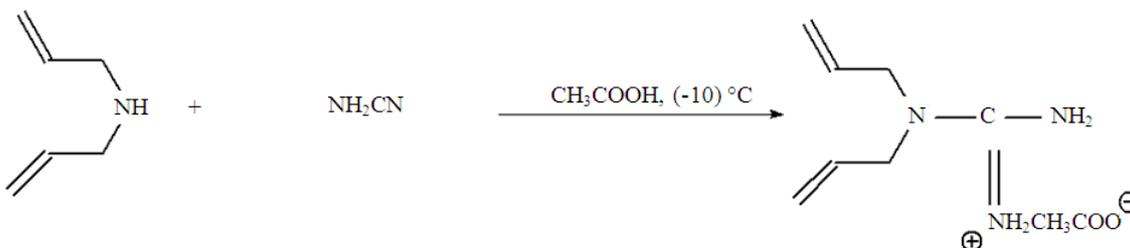


Fig. 2. Synthesis of diallylguanidine acetate

Table 1. The samples compositions data (found) for (AN-DAA acetate) copolymers

No	Sample name	Copolymer compositions	
		M ₁	M ₂
1	(AN-DAA acetate)	35	65
2	(AN-DAA acetate)	60	40
3	(AN-DAA acetate)	78	22

Table 2. The samples compositions data (found) for (AN-DAGA) copolymers

No	Sample name	Copolymer compositions	
		M ₁	M ₂
4	(AN-DAGA)	25	75
5	(AN-DAGA)	45	55
6	(AN-DAGA)	55	45

The polymerization was carried out at (50°C) till the precipitation of the copolymer. The precipitate was then filtered and washed repeatedly with methanol using Soxhlet system. The copolymer compositions were calculated on the basis of their nitrogen and carbon-hydrogen contents (Abdel-Naby and Al-Harhi, 2013).

2.6. Dyeing of Acrylonitrile Copolymers using Conventional and Ultrasonic Methods

0.5 g of the prepared copolymer was dyed with a basic dye at liquor ratio of 1: 50. Dyeing was carried out at pH values (4-7), temperature (40-80°C) at time intervals (30-90 min). In case of ultrasonic for comparison, the same conditions of dyeing were carried out using ultrasonic dyeing with power level 300 Watt. Then the dyed samples were rinsed with cold water and washed for 30 min with warm distilled water (50°C) and dried.

2.7. Measurements

2.7.1. UV/vis Spectroscopy

UV/visible spectra were obtained using Perkin-Elmer Lambda 4 UV/vis spectrophotometer.

2.8. Quantity of Dye Uptake by AN-Diallylamine Salts Copolymers

The quantity of dye uptake was estimated using the following Equation 1 (Kamel *et al.*, 2010):

$$Q = (C_0 - C_f) V / W \quad (1)$$

where, Q is the quantity of dye-uptake (mg/g), C₀ and C_f are the initial and final concentration of the dye solution (mg L⁻¹), respectively. V is the volume of dye bath/(liter) and W is the weight of copolymer (g). The concentration

of the solution was determined using a calibration of the basic dye.

2.9. Color Strength

The color strength of the dyed samples was evaluated by a light reflectance technique using UV/vis spectrophotometer. The relative color strength (K/S values) was calculated using the Kubelka-Munk equation (Kamel *et al.*, 2010):

$$K/S = (1-R)^2 / 2R \quad (2)$$

Where:

R = Observed reflectance

K = Absorption coefficient and

S = Scattering coefficient

2.10. X-Ray Diffraction

X-ray diffraction patterns were recorded using a Rigaku D/max 2500 v/pc X-ray diffractometer. The diffractograms were measured at 2θ in the range of 5-80° using Cu Kα as the monochromatic radiation source (λ = 1.54 Å) by applying a parabolic filter, at a tube voltage of 40 kV and a tube current of 200 mA.

2.11. Atomic Force Microscope

The roughness of the polymeric film has been determined using (AA2000 Atomic force microscope).

2.12. Mechanical Properties

The tenacity and elongation at break of the dyed copolymer films determined using Instron universal testing machine. The test were conducted at a laboratory standard environment. The tenacity was determined using the following equation (Khan *et al.*, 2009):

$$\text{Tenacity} = \frac{\text{Max breaking load (N)}}{\text{Area of the polymeric film (nm}^2\text{)}}$$

2.13. Ultraviolet Fastness of the Dyed Samples

The UV fastness of various dyed samples was performed using low pressure mercury lamp (λ = 250 nm).

3. RESULTS AND DISCUSSION

3.1. Characterization of Monomers

The DAGA and DAA acetate comonomers were prepared according to the method previously described.

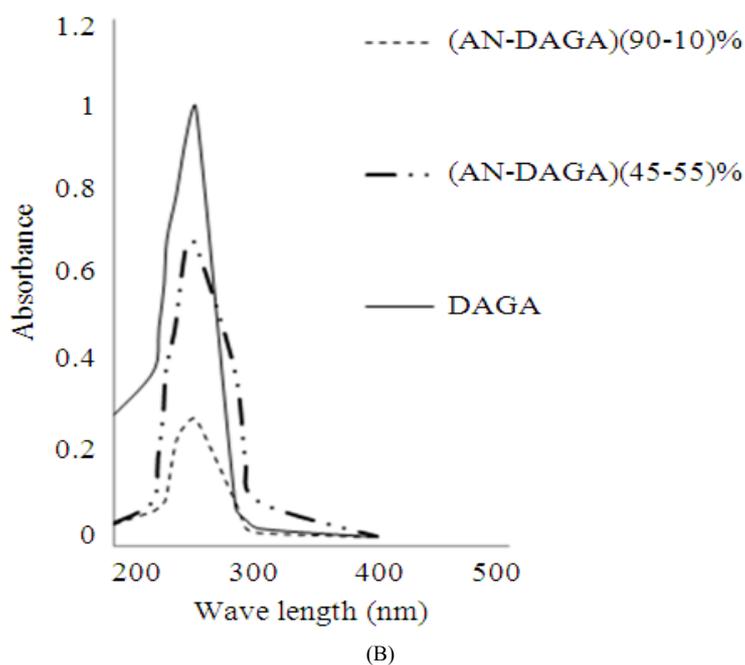
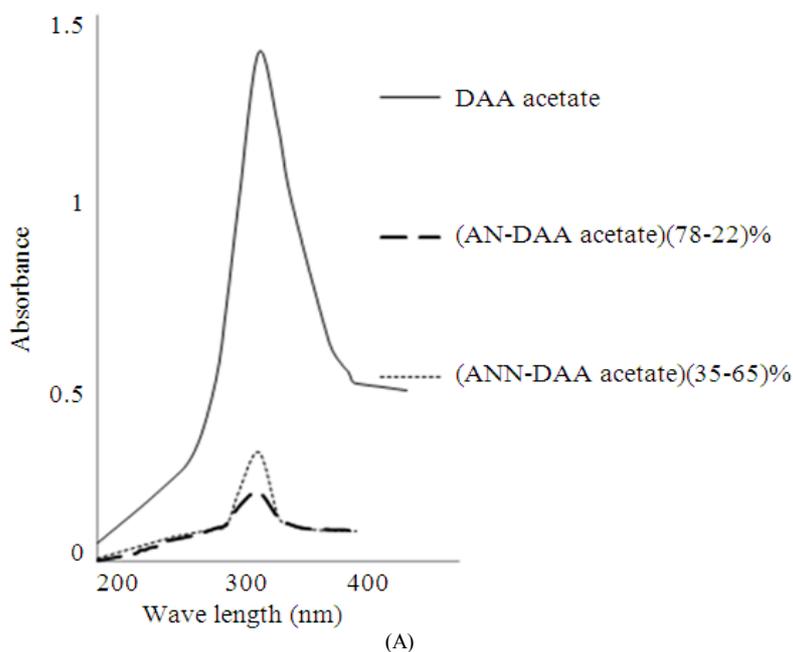


Fig. 3. UV/vis spectra of DAA acetate and its copolymers (A) and DAGA and its copolymers (B)

We had previously confirmed (Abdel-Naby and Al-Harhi, 2013) the structure of the two comonomers as well as the structure of the AN/DAGA and AN/DAA acetate copolymers using FTIR spectroscopy.

Investigation of the prepared copolymer samples in DMF by UV spectrophotometry are shown in (Fig. 3).

Figure 3A illustrates the UV spectra of various compositions of AN-DAA acetate copolymers.

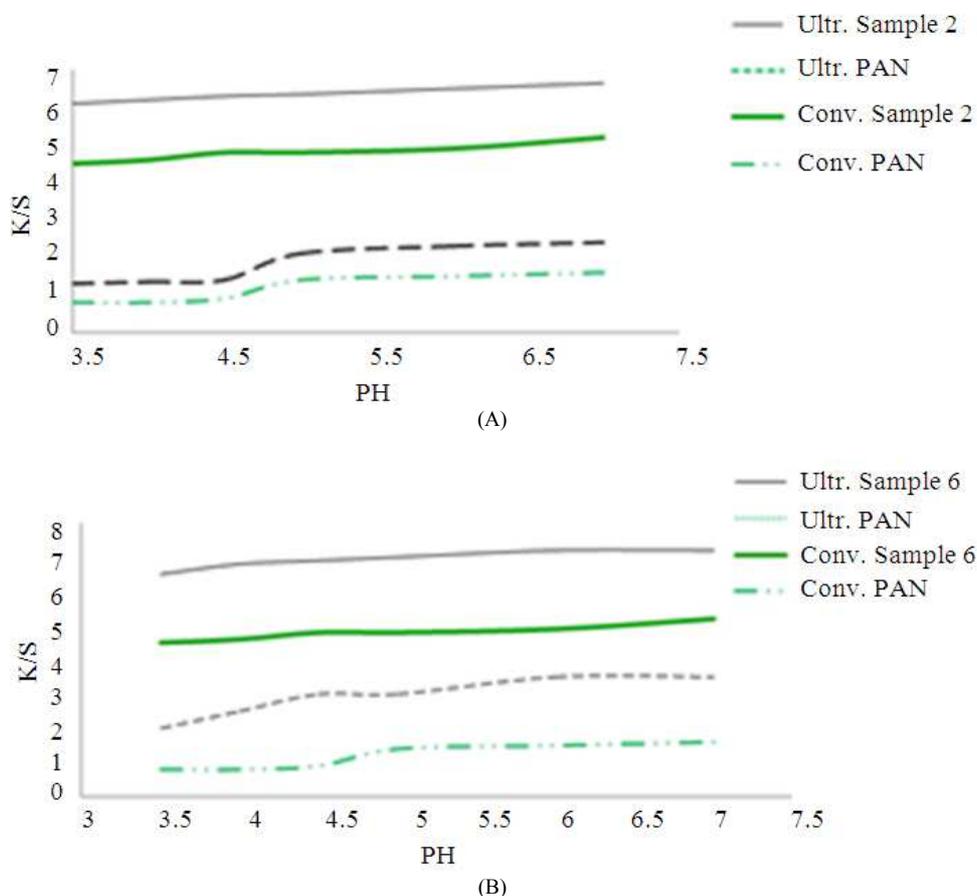


Fig. 4. Effect of dye pH on the color strength of the AN-DAA acetate (A) and AN-DAGA (B) copolymer using C.I. Astrazon Basic Red 5BL 200% as compared to PAN. Dyeing conditions: copolymer 0.5 g, L.R. 1:50, dye conc. 0.5%, at 80 °C for 45 min in case of conventional and ultrasonic methods

A broad peak at 320 nm indicating the presence of the diallylamine acetate in the PAN backbone. Moreover, **Fig. 3B**, which illustrates the UV spectra of various compositions of AN-DAGA copolymers, shows strong peak at 260 nm indicating the presence of DAGA moieties in the PAN matrix.

3.2. Dyeing of AN-DAGA and AN-DAA Acetate Copolymers

The dyeability of Acrylonitrile-Diallylamine Acetate (AN-DAA acetate) and Acrylonitrile-Diallylguanidine Acetate (AN-DAGA) copolymers was studied with both Conventional (CT) and Ultrasonic (US) methods. **Table 3** shows the quantity of the dye up take by each copolymer sample, according to Equation 1.

3.3. Factors Affecting Dyeing Process

In order to study the factors affecting the dyeability of the two AN/ DAA salts copolymers as compared to PAN. Sample 2 (AN-DAA acetate) (60:40)% and sample 6 (AN-DAGA) (55:45)% had been chosen for the study as they possess comparable copolymer composition ratios.

3.4. Effect of pH

Figure 4 shows the color strength (K/S) (Equation 2) for dyed samples using both Conventional (CT) and Ultrasonic (US) methods. It can be seen that the color strength (K/S) exhibits little gradual increasing with the increase of the pH of the dyeing bath from pH 4 to pH 7 irrespective of the method of dyeing, but with a slightly improvement in the dyeability in case of the ultrasonic dyeing process.

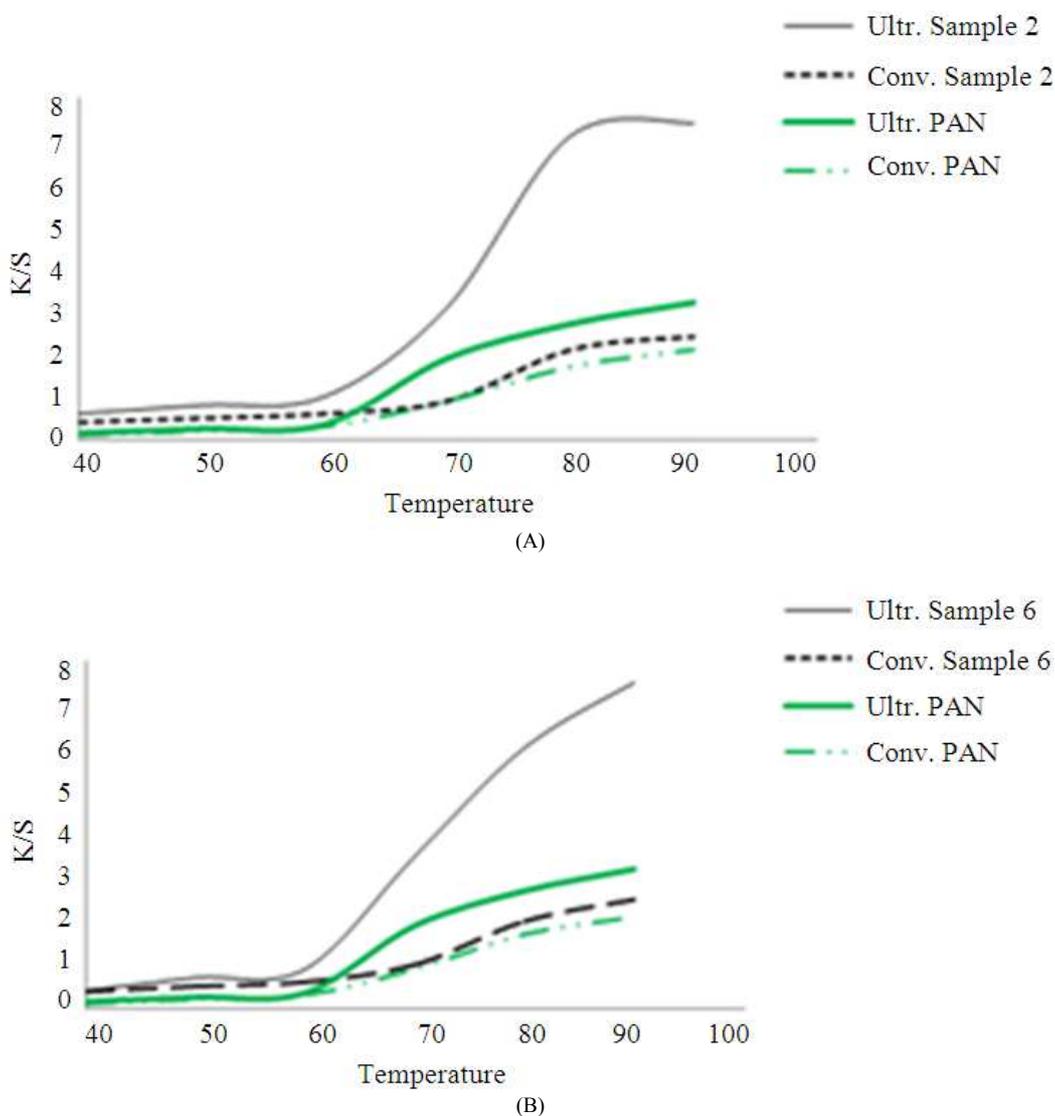


Fig. 5. Effect of temperature on the color strength of the dyed AN-DAA acetate (A) and AN-DAGA (B) copolymer using C.I. Astrazon Basic Red 5BL 200% as compared to PAN. Dyeing conditions: copolymer 0.5 g, L.R. 1:50, dye conc. 0.5%, pH 7 for 45 min in c

Table 3. The quantity of dye up take of AN/ DAA salts copolymers compared to PAN

Sample code	Sample name	Sample compositions %	Q (mg/g) using ultrasonic method	Q (mg/g) using conventional method
1	(AN-DAA acetate)	35:65	65.0	54.0
2	(AN-DAA acetate)	60:40	50.0	36.0
3	(AN-DAA acetate)	78:22	26.0	19.0
4	(AN-DAGA)	25:75	96.0	85.0
5	(AN-DAGA)	45:55	55.0	44.0
6	(AN-DAGA)	55:45	47.0	37.0
-	PAN	100	5.2	2.5

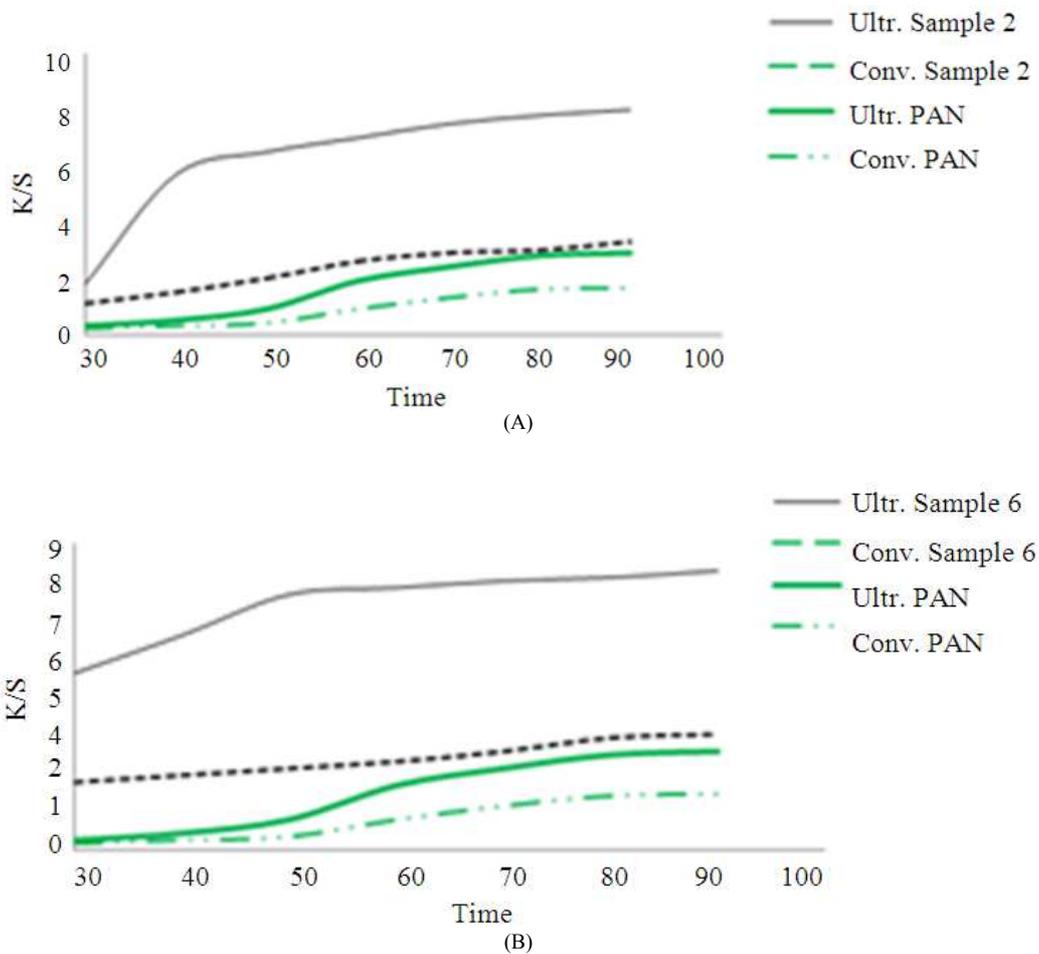
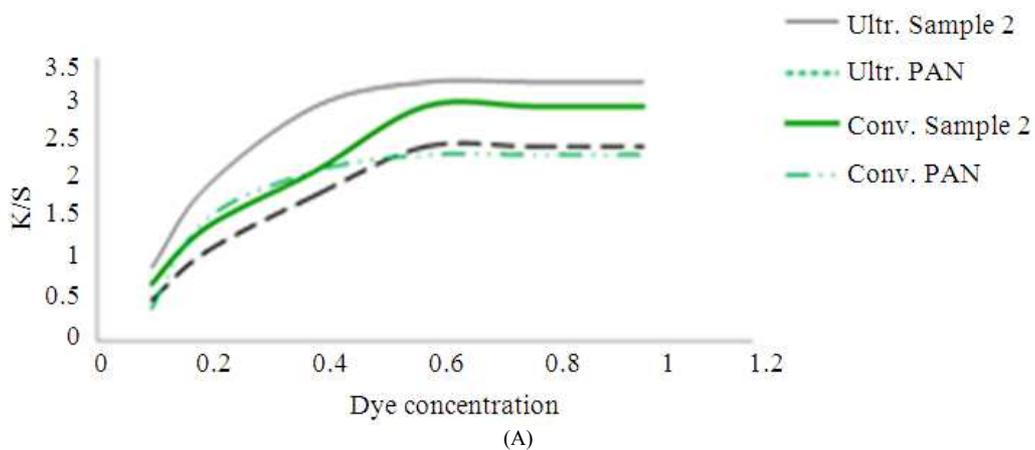


Fig. 6. Effect of time on the color strength of the dyed AN-DAA acetate (A) and AN-DAGA (B) copolymer using C.I. Astrazon Basic Red 5BL 200% as compared to PAN. Dyeing conditions: copolymer 0.5 g, L.R. 1:50, dye conc. 0.5%, pH 7, at 80°C in case of conventional and ultrasonic methods



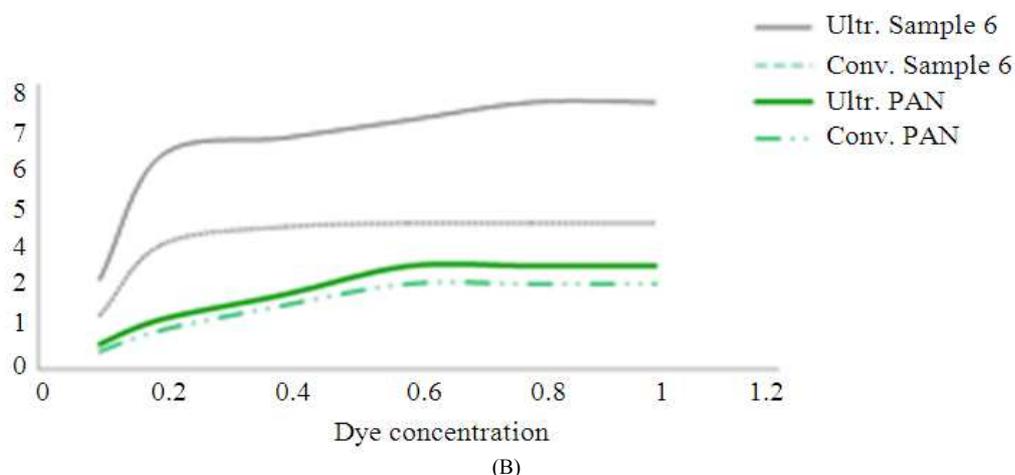


Fig. 7. Effect of dye conc. g/l on the color strength of the dyed AN-DAA acetate (A) and AN-DAGA (B) copolymer using C.I. Astrazon Basic Red 5BL 200% as compared to PAN. Dyeing conditions: copolymer 0.5 g, L.R. 1:50 using pH 4.5, at 80 °C for 45 min in case of conventional and ultrasonic methods

3.5. Effect of Temperature

The effect of dye temperature on the dyeability of AN-DAA salt copolymers was shown in **Fig. 5**. It is clear that the color strength (K/S) value increases with the increase in the dyeing temperature in both the US and CT methods with a more pronounced increase in the second case than the first one. Generally, in case of the US dyeing method, the K/S values increase as the temperature increases from 40 to 80°C. This result may be due to the fact that high temperature enhances the copolymer swelling as well as that it enhances the dye diffusion. Also, the US power provides other additional factor of de-aggregation of the dye molecules.

3.6. Effect of Time

The effect of dyeing time was studied under US and CT conditions for different dyeing time (30-90 min) to reveal the effect of power ultrasonic on the dyeability of the AN/DAA salts copolymers dyed with C.I. Astrazon Basic Red 5BL dye. As shown in **Fig. 6**, the color strength obtained was increased as the time increased for both US and CT methods, with a much higher color strength value at all points in the US case.

3.7. Effect of Dye Concentration

Figure 7 shows the effect of dye concentration on the dyeing process using ultrasonic method as well as CT method, of the AN/DAA salts copolymers as compared to PAN. It was found that the K/S value always increases

with the dye concentration then it levels off because it reaches the equilibrium status. Also, it shows much higher values at all points in US dyeing method as expected. The extra vibration and agitation conferred on the dyeing system upon using the ultrasonic energy method may account for this.

Moreover, for the same dye concentration, the AN/DAGA copolymers (sample 6) exhibits higher K/S value than that of AN/DAA acetate copolymers (sample 2).

From all the above mentioned data it is remarkable that dyeability of PAN is highly improved by the introduction of diallylamine moieties into its matrix.

3.8. X-Ray Diffraction

To investigate the change in the degree of crystallinity of the dyed AN-DAGA copolymers with various DAGA content during thermal treatment, powder XRD analysis were performed (**Fig. 8**). Up to 200°C, the XRD patterns of the heated samples are similar to that of the unheated corresponding copolymers. The XRD pattern of PAN contains two characteristic peaks, strong one at $2\theta = 17^\circ$ and weak one at 25° (**Fig. 8A**) (Boguslavsky *et al.*, 2005).

When the temperature reaches 300°C, the dyed PAN sample's crystal structure changes dramatically (**Fig. 8D**) while the heated copolymers samples XRD patterns were kept unchanged (**Fig. 8B**) as compared to those of the corresponding unheated dyed copolymers (**Fig. 8C**).

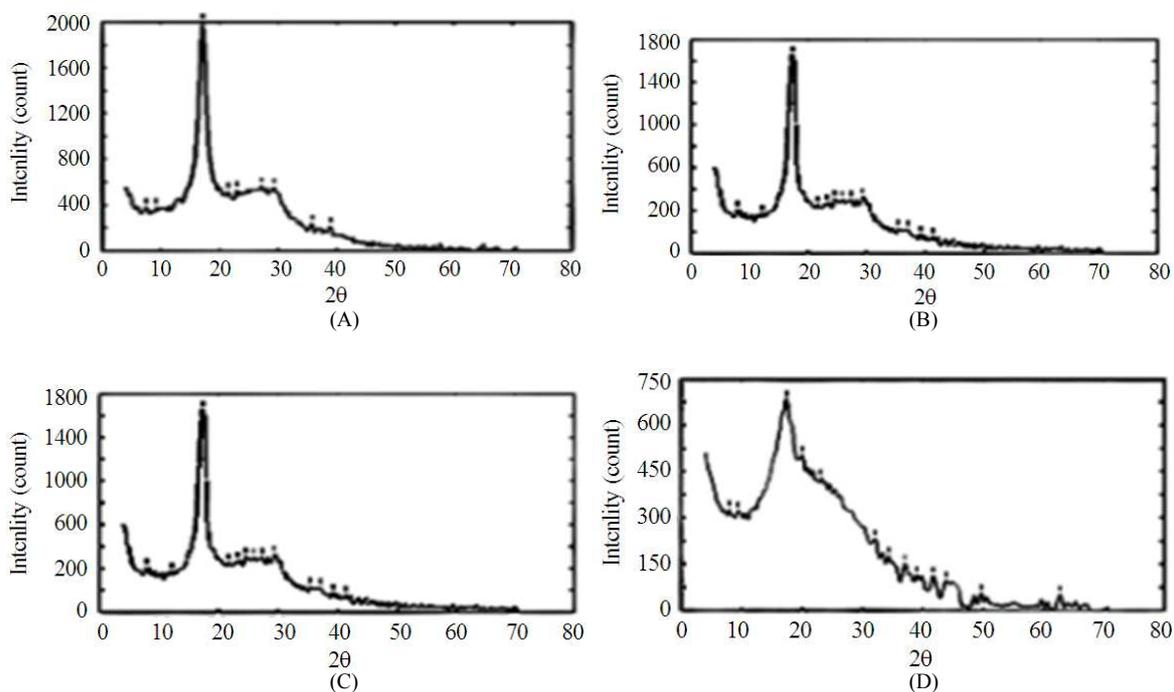


Fig. 8. Change of XRD patterns with temperature of AN/DAGA as compared to PAN

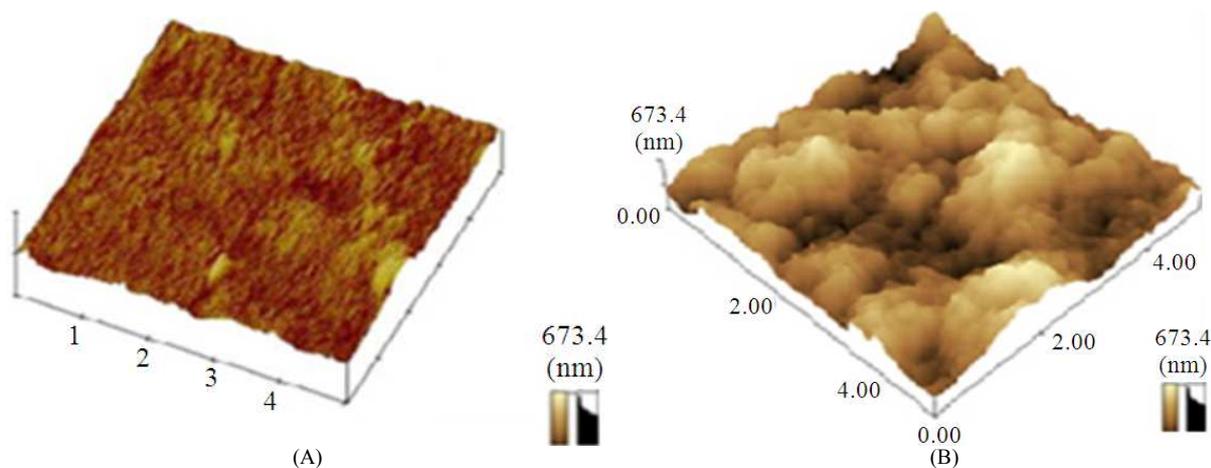


Fig. 9. Atomic force microscopy topographical images of PAN (A) and (AN-DAGA) copolymer sample 4 (B)

Table 4. Tensile properties of the (AN-DAA acetate) copolymer films compared to PAN

Film name	Elastic Young's modulus (MPa)	Tensile strength (MPa)
PAN	1750	30
sample 3	1100	15
sample 2	600	7
sample 1	450	4

Table 5. Tensile properties of the (AN-DAGA) copolymer films compared to PAN

Film name	Elastic Young's modulus (MPa)	Tensile strength (MPa)
PAN	1750	6
sample 6	1250	9
sample 5	800	18
sample 4	450	30

Table 6. Effect of (UV) radiation on the mechanical properties of dyed AN/diallylamine salts copolymers as compared to PAN

Exposed period (h)	(AN-DAA acetate) (60:40)%		AN-DAGA) (55:45) %		PAN	
	Tenacity strength (N/mm ²)	Elongation -at-break (mm)	Tenacity strength (N/mm ²)	Elongation -at-break (mm)	Tenacity strength (N/mm ²)	Elongation -at-break (mm)
0	44.0	0.52	49.3	0.58	24.1	0.37
5	40.5	0.50	44.0	0.57	17.2	0.25
7	34.3	0.42	38.4	0.56	15.3	0.20
9	30.7	0.25	32.9	0.30	11.9	0.18
10	29.4	0.22	26.2	0.27	10.0	0.17
11	20.5	0.20	21.9	0.24	9.2	0.16
12	20.0	0.18	18.9	0.20	8.5	0.15

3.9. Atomic Force Microscopy

As the aforementioned results showed the increase in the dyeability of the copolymers with the increase of diallylamine comonomer content, it was logic to examine the surface of the copolymer films. The examination of the surface of AN-DAGA film (sample 6) (55:45)% by atomic force microscope which showed that the film exhibited high roughness (**Fig. 9B**). This roughness of the surface increased the dyeability of the AN-DAGA copolymer as compared to the smooth PAN film (**Fig. 9A**).

3.10. Mechanical Properties

Table 4 and 5 show that the tensile strength and young's modulus at break of the copolymers' films. All copolymers films possess lower Young's modulus and tensile strength various than PAN film. While, the dyed copolymer films possess higher tenacity and elongation at break as compared to polyacrylonitrile **Table 6**. It was also found that the improvement in the mechanical properties increases with the increase in the diallylamine salt comonomer content. This means that the copolymerization of acrylonitrile with diallylamine salts gave the copolymer its extra strength.

3.11. Effect of (UV) Radiation on the Mechanical Properties of AN/Diallylamine Salts

The dyed copolymer films were kept under prolong exposure to a UV lamp with short wave length ($\lambda = 250$ nm) in air to study the effect of UV radiation on the tenacity and elongation at break of their films as compared to PAN film.

It was found that the loss in tenacity and elongation-at-break of the copolymer films decreased with the increase in exposure time to UV lamp in air, but still these decreases was less remarkable as compared to that in the case of the PAN film.

Therefore, the copolymerization of acrylonitrile with diallylamine salts had improved the mechanical properties before and after the photo oxidation as compared to PAN.

4. CONCLUSION

Acrylonitrile has been copolymerized with various ratios of diallylamine salts to improve the dyeability of the obtained copolymers as compared to PAN homopolymer.

The dyeability of acrylonitrile-diallylamine acetate (AN-DAA acetate) and acrylonitrile-diallylguanidine acetate (AN-DAGA) copolymers have been studied with both conventional and ultrasonic methods. The results revealed that the dyeing process was highly improved in using the ultrasonic method as compared to the conventional method. This is attributed to the extra vibration and agitation conferred on the dyeing system upon using the ultrasonic method.

The examination of the surface of AN-DAGA film (sample 6) (55:45)% by atomic force microscope showed that the film exhibited high roughness. This roughness of the surface increased the amount of the dye molecules diffused through the AN-DAGA copolymer matrix and thus increased its dyeability as compared to the smooth PAN film.

The dyed copolymers films were found to films possess higher tenacity and elongation at break as compared to polyacrylonitrile.

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