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RESEARCH ARTICLE - CHEMISTRY

Cyclocopolymerization of *N*,*N*-Diallylammonium and *N*,*N*-Diallylguanidinium Acetate with Acrylonitrile Characterization, Thermal and Morphological Properties

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Abstract

Two diallylamine salts, diallylammonium acetate (DAA acetate) and diallylguanidinium acetate (DAGA) were cyclocopolymerized in water with acrylonitrile (AN) using power ultrasound in order to prepare acrylonitrile copolymers involving thermally stable heterocyclic rings in their polymeric matrix. The structural characterization of the copolymers was performed using FTIR, ^{13}C NMR, UV/Vis spectroscopy and elemental analysis. The results revealed that the diallyl amine salts cyclopolymerized to form pyrrolidine and not piperidine rings throughout the polymeric chains. The thermal behavior of the copolymers prepared under nitrogen atmosphere was investigated using thermogravimetry, differential thermal analysis (TGA/DTA) and differential scanning calorimetry. The morphological property was also discussed using scanning electron microscopy (ESEM). The results revealed that the thermal stability of the copolymers was improved by the increase in the content of *N*,*N*-diallylammonium and *N*,*N*-diallylguanidinium acetate. The power of ultrasonic waves enhanced the homogeneity of the copolymers blend films irrespective of the copolymer compositions.

Keywords Acrylonitrile · Diallylammonium and diallylguanidinium acetate · Copolymerization · Thermal properties · Morphology

1 Introduction

Polyacrylonitrile (PAN) is known to suffer from poor heat stability at high temperatures and weak dyeability because of its high percentage of crystallinity. The copolymerization of acrylonitrile with different comonomers has been used as an effective method to improve the properties of the polymer [1–4]. Acrylonitrile–maleimide copolymers were found to exhibit high thermal stability due to the presence of the thermally stable maleimide moieties in the PAN matrix [5,6]. Divinyl monomers normally yield highly cross-linked and insoluble polymers. However, Butler and Ingley found that these monomers could occasionally yield soluble, gel-free, polymers. They suggested that the cyclopolymerization of *N*,*N*-diallylammonium and *N*,*N*- diallylguanidinium acetate might lead to the formation of either pyrrolidine or piperidine ring [7–10]. Butler et al. also suggested a new type of alternative intra-/inter-molecular propagation for the cyclopolymerization of diallyl quaternary ammonium salts to form five-membered ring (pyrrolidine). Following this suggestion, free radical cyclopolymerization was extended to many symmetric and asymmetric divinyl monomers. The copolymerization of symetric, non-conjugated diolefins (diallylamine salts) were found to be possible in the presence of ultrasound and peroxodisulfate [11,12]. The ultrasonic energy is known to enhance chemical reaction such as the improvement in dyeability of acrylonitrile copolymers [6,13,14].

Diallylammonium acetate (DAA acetate) and diallylguanidinium acetate (DAGA) have the ability to polymerize in water and organic solution in the presence of a radical initiator with very small yield % [11]. The introduction of the (DAA) and (DAGA) into the PAN matrix would decrease the crystallinity as compared to PAN which would increase the dyeability of the copolymers with respect to the parent PAN [14].

The aim of this work is to cyclocopolymerize diallylamine salts with acrylonitrile through free radical initiation. To increase the reactivity of (DAA) and (DAGA) comonomers,

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ultrasonic waves will be used. The structural characterization, as well as the determination of the copolymer crystallinity, will be discussed. Moreover, the investigation of the thermal stability of the copolymers will be investigated to adjust the copolymer for fiber applications.

2 Experimental

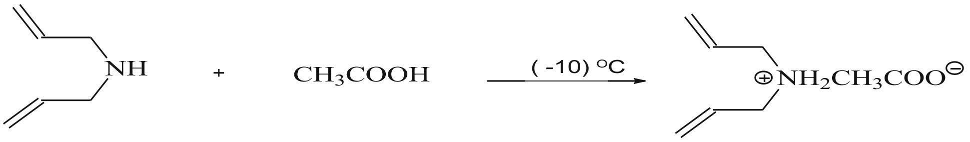
2.1 Materials

Acrylonitrile (AN) was supplied by Acros organic and was purified by distillation before polymerization. Diallylamine (DAA) 97% was obtained from Acros organic and was used as received. Cyanamide 95% was purchased from Acros organic. Acetonitrile, sodium bisulfite, potassium persulfate 99%, and glacial acetic acid (GAA) were supplied by Acros organic. Other reagents and solvents were of analytical grade and were used as received.

2.2 Synthesis of Diallylamine Salts

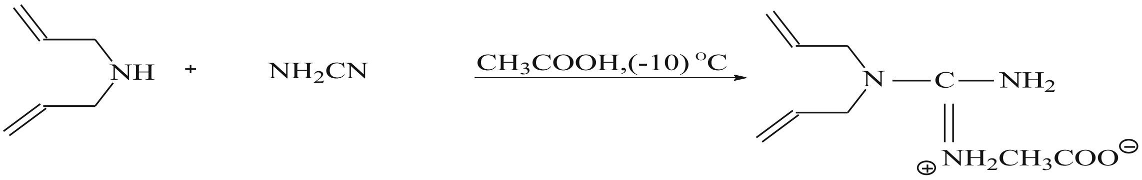
The diallylamine salts were synthesized according to the method described in our previous work Eqs. (1) and (2) [14].

synthesis of diallylammonium acetate



(1)

synthesis of diallylguanidinium acetate



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2.3 Copolymerization Procedure

2.3.1 Copolymerization of Acrylonitrile with Diallylammonium Acetate Using the Ultrasonic Technique

Polymerization ampoules of Pyrex glass were charged with monomer and water. Sodium bisulfite and potassium persulfate were added as radical initiators (2×10^{-2} mol/l). The ampoules were covered with serum caps, cooled, and purged with a slow stream of purified nitrogen. The polymerization was conducted in ultrasonic bath with a power level of 300 W at 50 °C until the precipitation of the copolymer. The precipitate was then filtered and washed repeatedly with methanol using a soxhlet system. The copolymer compositions were calculated on the basis of their nitrogen and carbon-hydrogen contents [15].

2.4 Measurements

2.4.1 FTIR

Infrared spectra were obtained using a Perkin spectrophotometer FTIR 1650. The spectrum resolution was 4 cm^{-1}, and the scanning range was 600–4000 cm^{-1}.

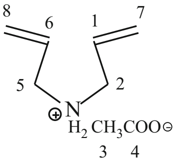
2.4.2 UV/Visible Spectroscopy

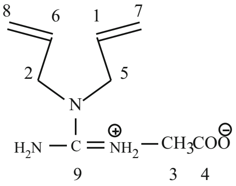
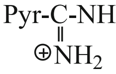
UV/visible spectra were obtained using a Perkin-Elmer Lambda 4 UV/Vis spectrophotometer.

2.4.3 ^{13}C NMR Spectroscopy

^{13}C NMR spectra were recorded using (Mercury-200 MHz, DMSO-d_6, δ) (Varian) or (ARX400 MHz, DMSO-d_6, δ) (BRUKE R) spectrometers.

Table 1 (A) ^{13}C NMR spectral characteristics of DAA acetate monomer. (B) ^{13}C NMR spectral characteristics of DAGA monomer

DAA acetate monomer	Carbon atom in DAA acetate	^{13}C NMR δ ppm
A		
	$-CH_2N$ (5,2)	50.5
	$=CH_2$ (7,8)	126.6
	$=CH-$ (1,6)	125.8
	$-CH_3$ (3)	20.6
	C=O (4)	175

DAGA Monomer	Carbon atom in DAGA	^{13}C NMR δ ppm
B		
	$-CH_2N$ (5,2)	50.17
	$=CH_2$ (7,8)	114
	$=CH_2-$ (1,6)	131
	 $\text{Pyr-}\underset{\overset{\|}{\oplus NH_2}}{C}\text{-}NH_2$	153
	$-CH_3$ (3)	20.65
	C=O (4)	175

2.4.4 Thermal Analysis TGA/DTA and Differential Scanning Calorimetry (DSC)

The thermal stability was examined, under nitrogen, using a Perkin-Elmer (TGA/DTA) thermogravimetric analyzer from room temperature to 500 °C at a heating rate of 10 °C. The glass transition temperature (T_g) was measured on a Perkin-Elmer differential scanning calorimeter (Model DSC 2010, USA) by heating from 20 to 500 °C at a scanning rate of 20 °C min^{-1}, under nitrogen atmosphere. The differential scanning calorimetry (DSC) curves were recorded.

2.4.5 Morphology (ESEM)

The samples were examined using FEG-ESEM Q400 SEM. The ESEM was operated at 10 kV, 0.23 to 0.68 torr water vapor pressure and a working distance of approximately 11 mm. Backscattered and secondary electron images together with EDS spectra were acquired from different parts of the samples.

3 Results and Discussion

3.1 Characterization of Monomers

Diallylammonium acetate (DAA acetate) and diallylguanidinium acetate (DAGA) were synthesized according to the methods previously described. The structures of the two monomers were confirmed by ^{13}C NMR spectroscopy.

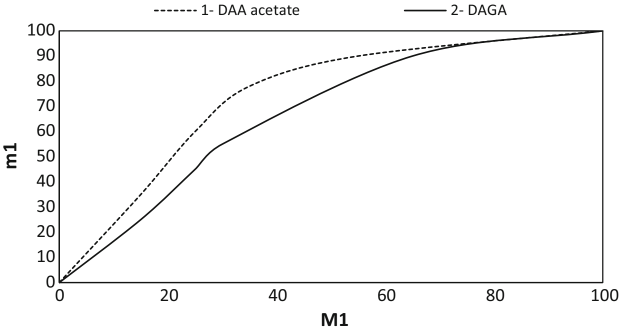


Fig. 1 Copolymer compositions diagram of AN [M_1, in monomer feed and m_1, in the synthesized copolymer] with 1-DAA acetate, 2-DAGA

The data from ^{13}C NMR of the DAA acetate and DAGA are given in Table 1a and b, respectively.

3.1.1 Reactivity Ratio

The composition of the initial monomer feed mixtures and that of the copolymers are compiled in Fig. 1.

The results clearly indicate that the reactivity of the DAA acetate was less than that of AN. The data in the tables showed that DAGA possessed a slightly higher reactivity than DAA acetate, which may be attributed to the less steric hindrance around the double bonds in the case of the DAGA monomer compared with DAA acetate. The results also revealed that the use of power ultrasound led to the formation of copolymers with higher (DAA) and (DAGA) content than conventional method used (Table 2). This is attributed to the fact that the power ultrasound can enhance the reactivity

Table 2 In-feed and found copolymer compositions of the prepared AN/ DAA salts copolymers with and without using power ultrasound (300 W)

Sample name (M1/ M2)	In-feed monomer compositions M1/ M_2	Found copolymer compositions without using power ultrasound M1/M2	Found copolymer compositions using power ultrasound 300 W M1/ M_2
(AN-DAA acetate)	15/85	60/40	35/65
(AN-DAA acetate)	35/65	88/12	78/22
(AN-DAA acetate)	25/75	74/26	60/40
(AN-DAGA)	30/70	68/32	55/45
(AN-DAGA)	25/75	64/36	45/55
(AN-DAGA)	15/85	55/45	25/75

of the diallylamine radicals, mainly due to the phenomenon known as cavitation in a liquid medium, thus the growth and explosive collapse of these bubbles can generate localized high temperature, high pressure, shock waves and sever shear force capable of breaking chemical bonds [6,13].

3.1.2 Characterization of the Copolymers Produced

The most convenient methods for the elucidation of structural features of acrylonitrile/diallylamine salts copolymers are FTIR, UV/visible, and ^{13}C NMR spectroscopy.

3.1.3 FTIR Spectroscopy

Figure 2 illustrates the IR spectra of PAN (spectrum C), the AN/DAGA copolymer (spectrum B), and DAGA (spectrum A).

For the structure of the counterion core, two stable structures having different binding types could be supposed for diallylguanidinium acetate (Scheme 1): either with hydrogen bonding of a charged amino group with delocalized acetate ion (structure B) or with participation of delocalized system of two nitrogen atoms and an acetate counterion (structure A) [15]. Spectrum A, representing the FTIR spectrum of DAGA, showed the following peaks:

1. N–H stretching vibration gives rise to two broad bands with maximum at 3250 cm^{-1} and 3013 cm^{-1}.
2. Absence of the bands of C=N bonds at 1660-1680 cm^{-1} in the DAGA spectrum confirms the structure (A).
3. The acetate ion bands are shows asymmetric stretching at 1580 cm^{-1} and symmetric one at 1411 cm^{-1}.

The IR spectrum (B) shows the FTIR of the AN/DAGA copolymer which involves an intense broad band at 1620 cm^{-1} related to C=N stretching. The intensity of this band indicates the overlap of this band with the asymmetric C=O stretching band of the acetate counterion. Also the presence of a shoulder inflexion at 1580 cm^{-1} indicates the presence of NH_2 angle deformation.

Moreover, the symmetric C=O band is present at 1453 cm^{-1} which indicates a lower degree of delocalization in ($^{-}$O–C = O) than the case of monomer which leads to a shorter wave number. The two asymmetric and symmetric stretching bands of NH_2 appear at 3407 cm^{-1} and 3250 cm^{-1}.

From the aforementioned spectral features, one can suppose that the first type of counterion bonding (structure B) of DAGA moieties is realized in the AN/DAGA copolymer.

Moreover, the AN/DAGA spectrum (B) also involves the stretching at 2245 cm^{-1} related to the acrylonitrile moieties.

3.1.4 UV/Vis Spectroscopy

The investigation of the copolymers samples prepared in DMF, AN/DAA acetate, and AN/DAGA by UV spectrophotometry showed the peaks corresponding to (DAA) and (DAGA), which confirmed the presence of their moieties in the PAN matrix [14].

3.1.5 ^{13}C NMR

It was recognized that the cyclopolymerization of (DAA) and (DAGA) might led to the formation of either pyrrolidine or piperidine ring [7,8].

To confirm the size of the heterocyclic ring in the prepared AN/ DAA salts copolymers, ^{13}C NMR was used. If five-member, pyrrolidine ring was formed, the copolymerization of acrylonitrile with DAA acetate and DAGA should lead to the following copolymers (Scheme 2).

Each diallylammonium and diallylguanidinium acetate comonomer moiety exhibits symmetric structure with respect to the nitrogen atom of the ring and also two aliphatic CH_2 groups to the pyrrolidine ring (unlike the piperidine ring structure which exhibits only one aliphatic CH_2 group α to the ring from the opposite side of the acrylonitrile moiety). Moreover, the ^{13}C NMR of AN/DAA acetate showed comparable δ value for the two -CH- groups of the ring (C_2, C_3) (46.8, 38.8). Also for the two $-CH_2$ groups of the ring (C_1, C_4) (21.9, 24.4) and finally for the two $-CH_2$ groups of the nitrogen atom of the ring (C_8, C_9) (48.89, 49.58). Compara-

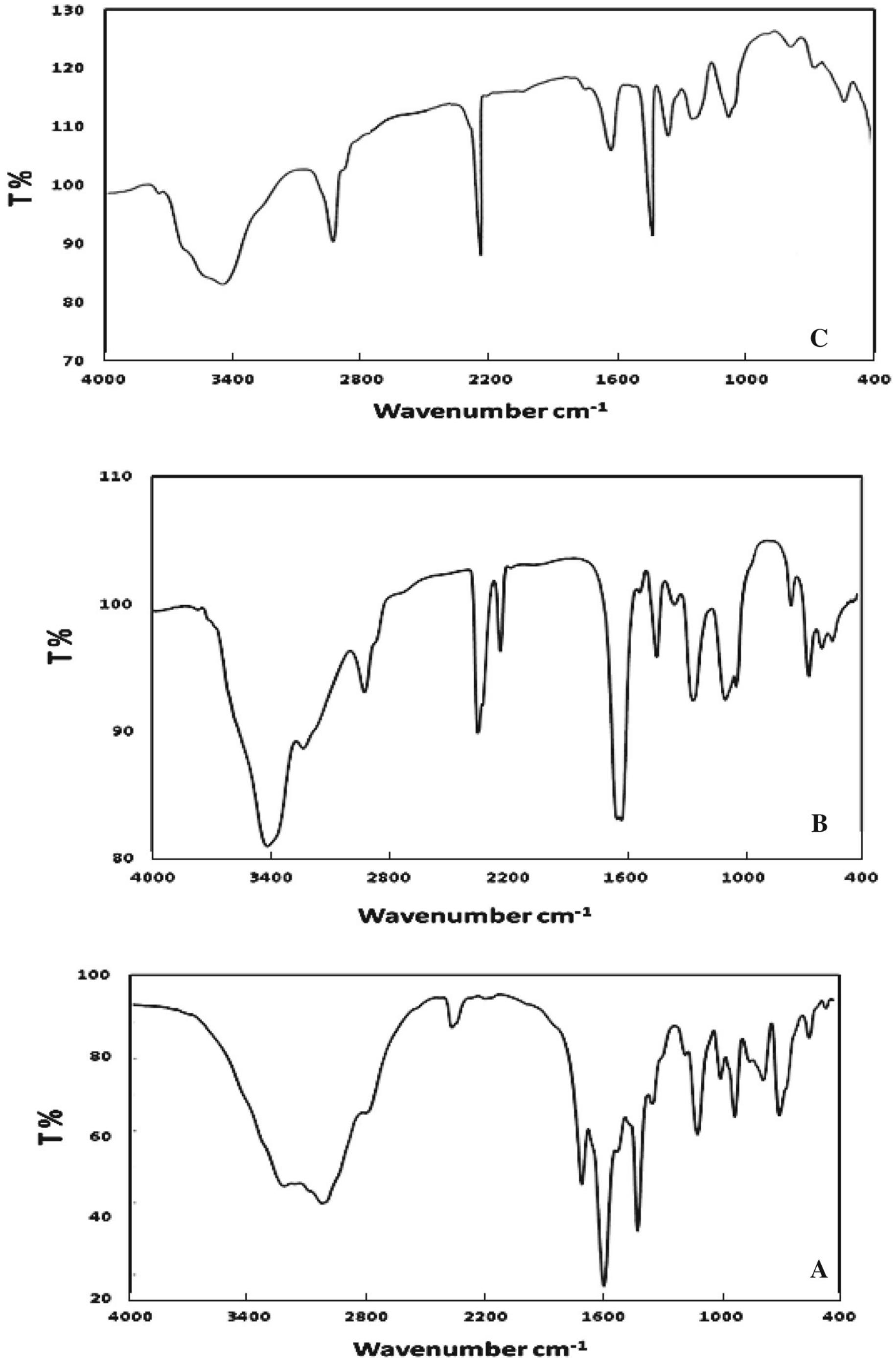


Fig. 2 FTIR spectra of (DAGA) (**a**), (AN-DAGA) copolymer (**b**), and PAN (**c**)

ble results were obtained in case of AN/DAGA copolymers (Table 3).

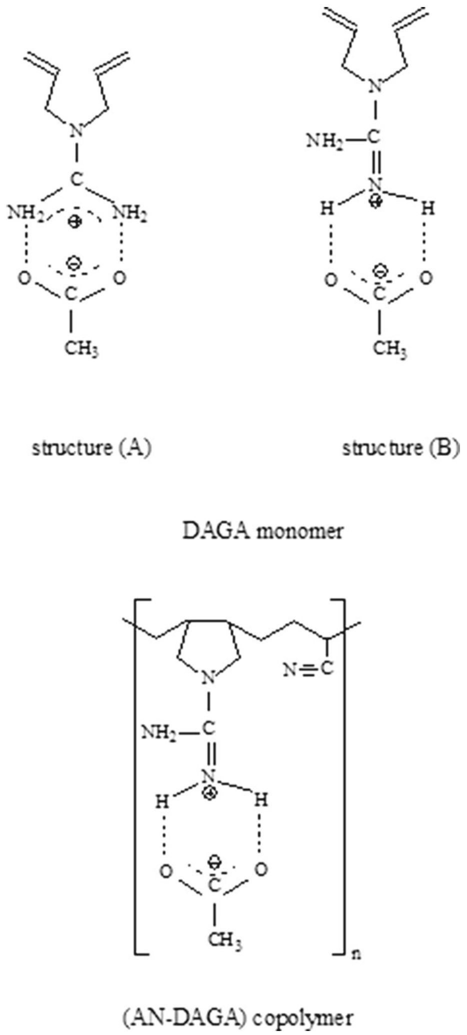
As the ^{13}C NMR spectrum of typical PAN shows three groups of peaks centered approximately $\delta = 27, 32$, and 120 ppm which correspond to the CH_2, CH, and nitrile carbon atoms, respectively, and the ^{13}C NMR of the AN/diallylamine salts spectra showed these peaks, then each copolymer structure involves the nitrile groups in its matrix.

Thus, the ^{13}C NMR spectra of all copolymers confirmed the formation of the pyrrolidine ring in the copolymer matrix as shown in Fig. 3a and b.

3.1.6 Thermal Behavior of the Copolymers

a. Thermogravimetry TGA / DTA

This work aims to improve the thermal stability of PAN at high temperatures through the copolymerization of acry-



Scheme 1 .

lonitrile with diallylamine salts as comonomers. The thermal stability was examined using thermal gravimetric analysis (TGA / DTA). The initial decomposition temperature T_{o} and the weight loss percentage (wt loss %) values of PAN and its copolymers are compiled in Table 4.

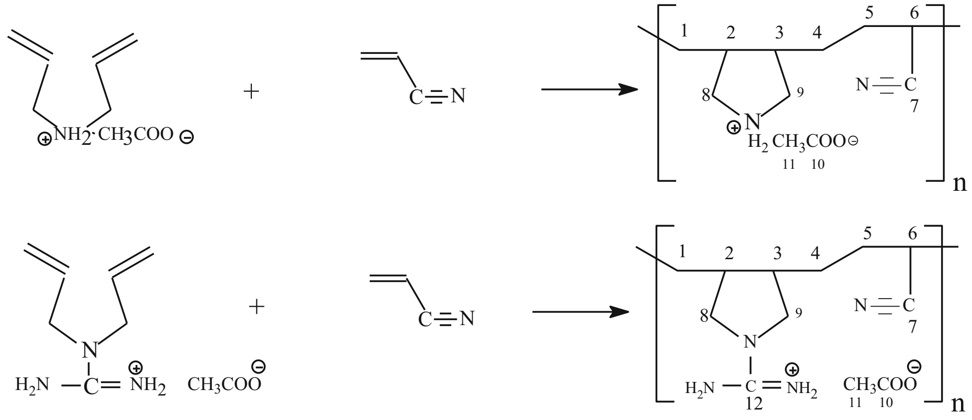
Table 3 ^{13}C NMR chemical shifts (δ ppm) characteristics of (AN-DAA acetate and AN-DAGA copolymers)

Carbon atom in AN/DAA acetate	^{13}C NMR δ ppm	Carbon atom in AN/DAGA	^{13}C NMR δ ppm
1	21.9	1	20.94
2	46.8	2	34.16
3	38.8	3	29.07
4	24.4	4	26.07
5	31.4	5	32.24
6	29.4	6	27.17
7	122.4	7	122.4
8	48.89	8	50.34
9	49.58	9	51.03
10	175	10	175
11	20.65	11	20.65
–	–	12	154.78

The data indicate that the thermal stability of each of the copolymers investigated is improved, as shown by the decrease in weight loss% at (500 °C) and the increase in the initial decomposition temperature T_{o} compared with those of the PAN homopolymer, where ($T_{\mathrm{o}} = 250\,^{\circ}\mathrm{C}$) and the weight loss is approximately half of its weight at 500 °C (− 48%). The data also indicate that AN/DAGA copolymers possessed higher thermal stability than the AN/DAA acetate copolymers. The thermogravimetric analysis (TGA) of various compositions of AN/DAGA and that of PAN homopolymer are illustrated in Fig. 4.

The results clearly show that the initial decomposition temperature T_{o} increases with the increase in the DAGA composition in the copolymer. Moreover, it was determined that all AN/DAGA and AN/DAA acetate copolymers possessed a lower total weight loss percentage at high temperatures 500 °C, compared to PAN homopolymer, as shown in Table 5, regardless of the composition ratios of the copolymer or the

Scheme 2 .



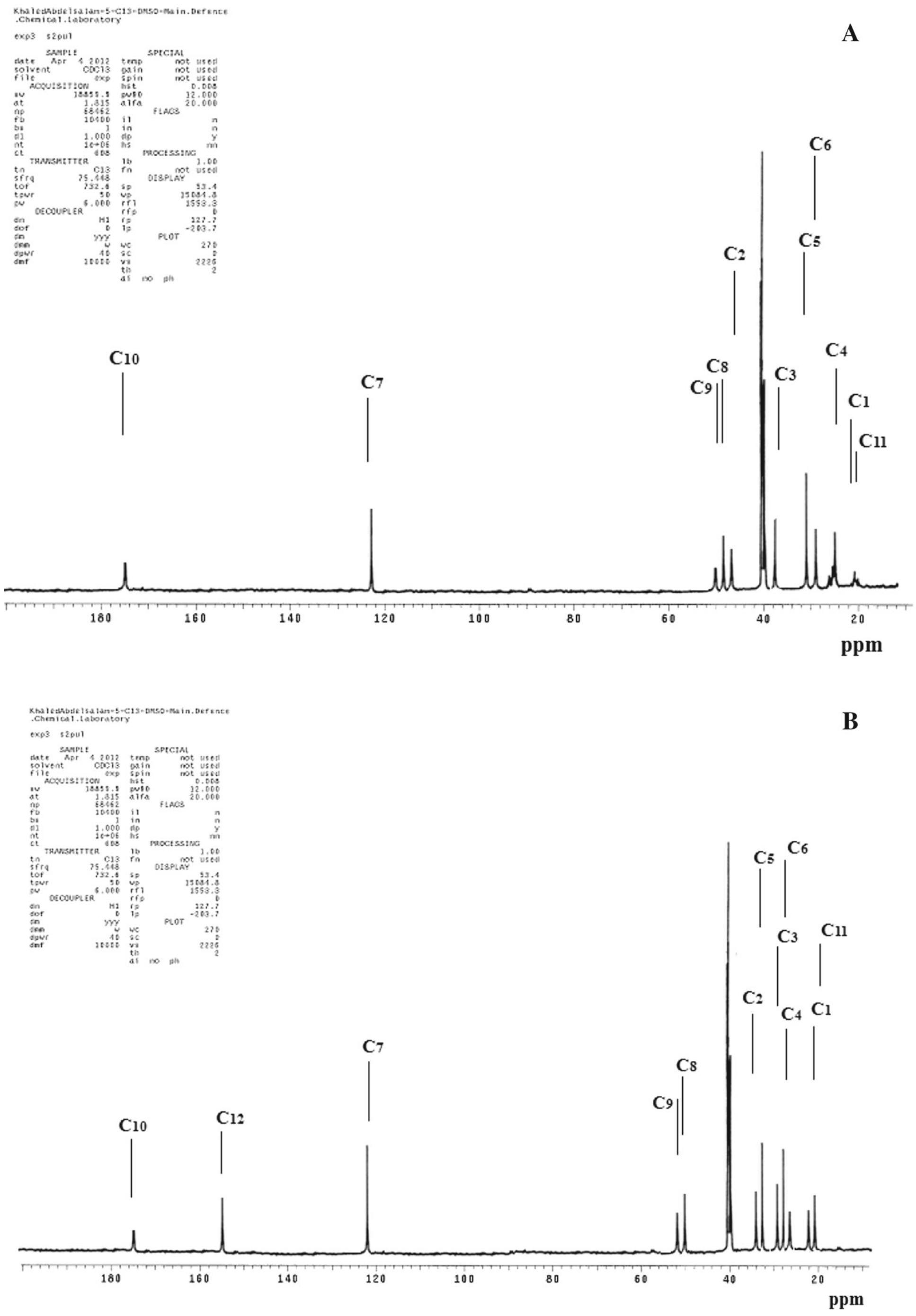


Fig. 3 ^{13}C NMR spectra (**a**) of (AN-DAA acetate) copolymer, sample 1 and (**b**) of (AN-DAGA) copolymer, sample 4

Table 4 Decomposition temperature (T_o) and total weight loss percentage of PAN and its copolymers

Sample code	Sample name	T_o (°C)	Total weight loss% at 500 °C (%)
1	(AN-DAA acetate) (35:65)	320	− 28.2
2	(AN-DAA acetate) (60:40)	300	− 34.8
3	(AN-DAA acetate) (78:22)	280	− 40.8
4	(AN-DAGA) (25:75)	400	− 18.85
5	(AN-DAGA) (45:55)	365	− 28.3
6	(AN-DAGA) (55:45)	280	− 33.4
–	PAN	250	− 48

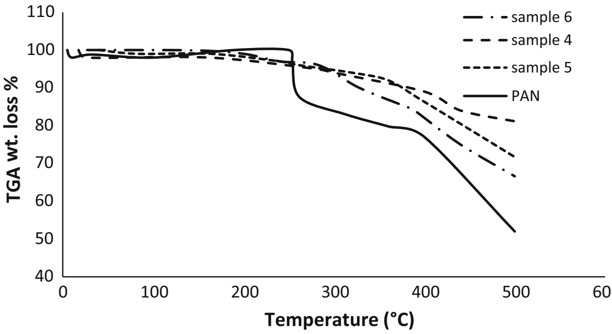


Fig. 4 The thermogravimetric analysis (TGA) of various compositions of (AN-DAGA) copolymers compared to PAN under nitrogen atmosphere

type of diallylamine comonomer. The improvement in the thermal stability of the acrylonitrile copolymers is mainly attributed to the stability of the five-membered pyrrolidine ring. This stable five-membered ring gave the copolymer its extra thermal stability. Conversely, the DTA curve of each AN/DAGA or AN/DAA acetate copolymer shows a large exotherm peak near 300 °C, as shown in Fig. 5, which is related to the crystal structure. PAN possesses the highest peak, while the copolymers with the highest contents of diallylamine salts showed the lowest degree of crystallinity. This result implies that the degree of crystallinity of the copolymer decreases with the increase in the (DAA) and (DAGA) content. This is attributed to the disturbance of the ladder structure formation in PAN matrix by the pyrrolidine rings.

b. Differential Scanning Calorimetry (DSC)

The data from the differential scanning calorimetry (DSC) of AN/(DAA) and (DAGA) copolymers are shown in Table 5. The data show that each copolymer exhibits only one glass transition temperature T_g. The single T_g confirmed the formation of the new copolymer. The T_g values of all copolymers are less than those of PAN homopolymer, which agree with what is recognized about the copolymerization effect on the highly ordered fiber [13,16].

3.1.7 Morphological Characterization

0.5 g of AN / DAA salt copolymer was dissolved in (DMF / THF) solvent mixture and was allowed to blend in water bath or ultrasonic bath of power 300 W, at 60 °C until a clear solution is obtained. The mixture was then poured into a suitable Petri dish. Then, it later was put in a vacuum oven at 50 °C to evaporate the solvent (checked by UV spectrum) and obtain the film. All films were 0.5 mm thick.

The morphology of the surface of PAN and that of AN/DAA acetate and AN/DAGA copolymers films are showed that. A homogeneous morphology is only observed for AN/(DAA) and (DAGA) films with limited diallylammonium and diallylguanidinium acetate content, either using ultrasonic or conventional bath. However, a homogeneous morphology is observed for AN/(DAA) and (DAGA) films with high diallylammonium and diallylguanidinium acetate content only with the assistance of the ultrasound power.

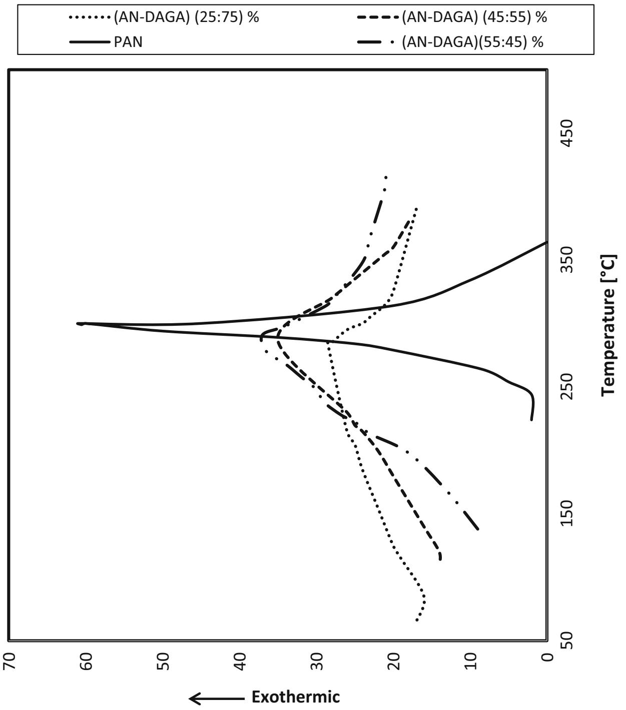


Fig. 5 The differential thermal analysis (DTA) of (AN-DAGA) copolymers compared to PAN, under nitrogen atmosphere

Table 5 Glass transition temperature of various compositions of (AN-DAA acetate) and (AN-DAGA) copolymers as compared to PAN

Sample code	Sample name	Sample compositions (%)	Tg (°C)
1	(AN-DAA acetate)	35:65	108
2	(AN-DAA acetate)	60:40	112
3	(AN-DAA acetate)	78:22	116
4	(AN-DAGA)	25:75	101
5	(AN-DAGA)	45:55	107
6	(AN-DAGA)	55:45	110
–	PAN	100	120

4 Conclusions

1. Diallylammonium acetate and diallylguanidinium acetate were cyclocopolymerized with acrylonitrile, using power ultrasound to improve the thermal stability of PAN. The structures of the suggested copolymers were determined using FTIR spectroscopy, and those of prepared copoly-

mers were determined using ^{13}C NMR. The investigation of thermal stability of both types of copolymers showed that they exhibit higher thermal stability than PAN. Moreover, the AN/DAGA exhibits higher thermal stability than AN/DAA acetate as shown from their TGA curves. The thermal stability of the copolymer depends on the diallylammonium and diallylguanidinium acetate comonomer content. Their extra stability was attributed to the formation of five-membered pyrrolidine rings throughout the copolymer chains. The ultrasound power enhanced preparation of acrylonitrile/diallylammonium and diallylguanidinium acetate copolymer with high (DAA) and (DAGA) content.

2. A homogeneous morphology is only observed for AN/diallylammonium and diallylguanidinium acetate films with limited (DAA) and (DAGA) content, either using an ultrasonic or a conventional bath. However, a homogeneous morphology is observed for AN/ diallylammonium and diallylguanidinium acetate films with high (DAA) and (DAGA) content only with the assistance of the ultrasound power.
3. The percentage of crystallinity decreased with the increase in the diallylammonium and diallylguanidinium acetate content in the prepared copolymer, as shown by the DTA data.

Thus, the cyclocopolymerization of diallylammonium and diallylguanidinium acetate with acrylonitrile is greatly enhanced by the use of power ultrasound, leading to high thermally stable copolymers. The power ultrasound also enhances the homogeneity of their copolymer films.

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