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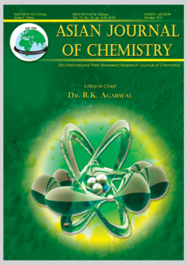

Synthesis and Thermal Characteristics of *N*-(Thiazol-2-yl)methacrylamide-Acrylonitrile Copolymers

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N-(Thiazol-2-yl)methacrylamide monomer has been prepared by the reaction of 2-aminothiazole either with methacryloyl chloride in the presence of triethylamine as catalyst or with methacrylic acid in the presence of *N,N*-dicyclohexyl carbodiimide as a dehydrating agent. The prepared monomer was copolymerized with acrylonitrile in dimethyl formamide using azobisisobutyronitrile as initiator. The homopolymer and also the copolymers were characterized by a variety of spectral and thermal methods. The thermal behaviour in nitrogen of the homopolymer as well as the copolymers was investigated using thermogravimetric and differential thermal analysis techniques. *N*-(Thiazol-2-yl)methacrylamide was found to initiate the nitrile oligomerization in the copolymers upon heating. A mechanism for the degradation and initiation of the methacryloyloxy units in the nitrile copolymers is proposed. This was confirmed by interpreting the fragmentation patterns of the obtained mass spectra of the monomer, as well as the FT-IR spectra of the copolymers after heating.

Key Words: *N*-(Thiazol-2-yl)methacrylamide, Acrylonitrile, Copolymerization, Thermal properties, Cross-linking.

INTRODUCTION

The technological importance of polyacrylonitrile (PAN) is known to suffer from several disadvantages such as weak moldability, colour instability and poor dyeability. The main solution of these problems was achieved by introduction of comonomers into the polyacrylonitrile chains. Coleman and coworkers[1,2] investigated the thermal degradation of polyacrylonitrile and its copolymers in air as well as in nitrogen. Intramolecular cyclization, intermolecular cross-linking and water elimination have been proposed[3-8]. Oxidative reactions were a major factor with subsequent heating. Grassie and McGuchan[9,10] showed that as the comonomer is an integral part of the copolymer chain, it may affect the cyclization reaction either by initiation, participation or inhibition. Thus, to avoid these problems, several monomers have been used as comonomers for the production of acrylonitrile (AN) with copolymers with improved thermal stability[11-16]. In this work, a high conversion of *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymers have been prepared and characterized by spectral, analytical and thermal methods. The aim was to find out the effect of introducing a methacryloyloxy unit into the polymer chain of polyacrylonitrile. It was expected that the thermal properties of polyacrylonitrile would be affected and, consequently, it is necessary to investigate the thermal behaviour of the copolymers produced.

EXPERIMENTAL

2-Aminothiazole was provided by M & T chemical inc. (Rahway, NJ). Acrylonitrile and methacrylic acid were obtained from BDH (Toronto, Canada) and were purified by distillation at reduced pressure and the middle fractions were retained for use. Methacryloyl chloride and *N,N*-dicyclohexyl carbodiimide (DCCI) were purchased from Aldrich (Milwaukee, WI). Azobisisobutyronitrile was from Merk (Darmstadt, Germanty) and was recrystallized from ethanol. The solvents used were of reagent grade and were purified according to the standard method.

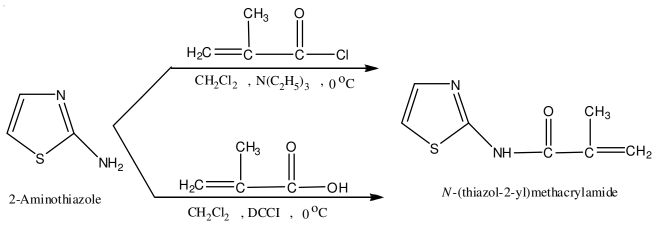
Synthesis process: *N*-(Thiazol-2-yl)methacrylamide monomer was synthesized either by the acid chloride method or by the *N,N*-dicyclohexyl carbodiimide method, as described in previous work[17]. P-*N*-(thiazol-2-yl)methacrylamide and its copolymers with acrylonitrile, were obtained by solution polymerization of predetermined quantities of *N*-(thiazol-2-yl)methacrylamide and acrylonitrile in DMF (1.5 mol, 11) under N_2 at 70 ºC in the presence of 1 mol % azobisisobutyronitrile. After the required time, the polymers were precipitated in excess methanol and then filtered off, washed and dried in vacuum at 50 ± 1 ºC to constant weight. The overall conversions were restricted to less than 10 % in every case[18]. The copolymer compositions of *N*-(thiazol-2-yl)methacrylamide with acrylonitrile were calculated on the basis of sulphur content in the copolymer samples.

Solubility studies: Both the monomer and the polymers were tested against solubility in solvents with different polarity. About 6-8 mg of the tested compound was put in a test tube containing 7 mL of the solvent and kept overnight with the tube tightly closed. The solubility was observed after 1 day[18].

The sulphur analysis was measured using oxygen flask combustion and multi-dosimate E 415. Fourier transform infrared (FTIR) spectra were measured using Nicolet Impact-400D on carefully dried samples embedded in KBr pellets. The proton magnetic resonance (in DMSO as a solvent and using TMS for internal reference) were recorded at room temperature with a Varian EM-390 spectrometer operating at 90 MHz. The mass spectrum was measured on a Hewlett Packard MS 5988 spectrometer at 15 eV. Differential thermal analysis was performed at a heating rate of 15 °C min^{-1} using a Shimadzu X-D-30 thermal analyzer. Thermogravimetric thermograms were obtained at a heating rate of 10 °C min^{-1}, using a DT-30B thermal analyzer (Shimadzu, Kyoto, Japan). The analysis were performed at the Micro Analytical Center, Faculty of Science, Cairo University, Egypt.

RESULTS AND DISCUSSION

N-(Thiazol-2-yl)methacrylamide (TMA) monomer was prepared by two methods according to **Scheme-I**. The prepared monomer was a pale yellow solid, sparingly soluble in most organic solvents, but easily soluble in dimethyl formamide and dimethyl sulfoxide. The meting point of the *N*-(thiazol-2-yl)methacrylamide monomer is 82-83 °C (yield 85 %). The ^{1}H NMR and FTIR spectra of this monomer have been discussed previously according to previous work[17]. The mass spectrum of *N*-(thiazol-2-yl)methacrylamide monomer is shown in Fig. 1. The fragmentation patterns are represented in **Scheme-II**, which illustrates the most abundant fragments of *N*-(thiazol-2-yl)methacrylamide monomer.



Scheme-I: Preparation of *N*-(thiazol-2-yl)methacrylamide monomer

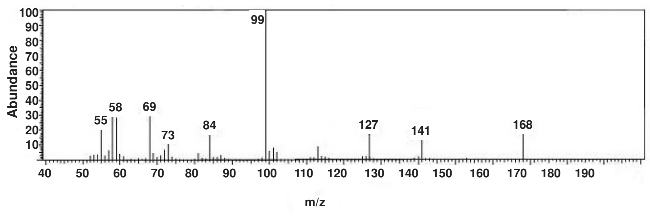
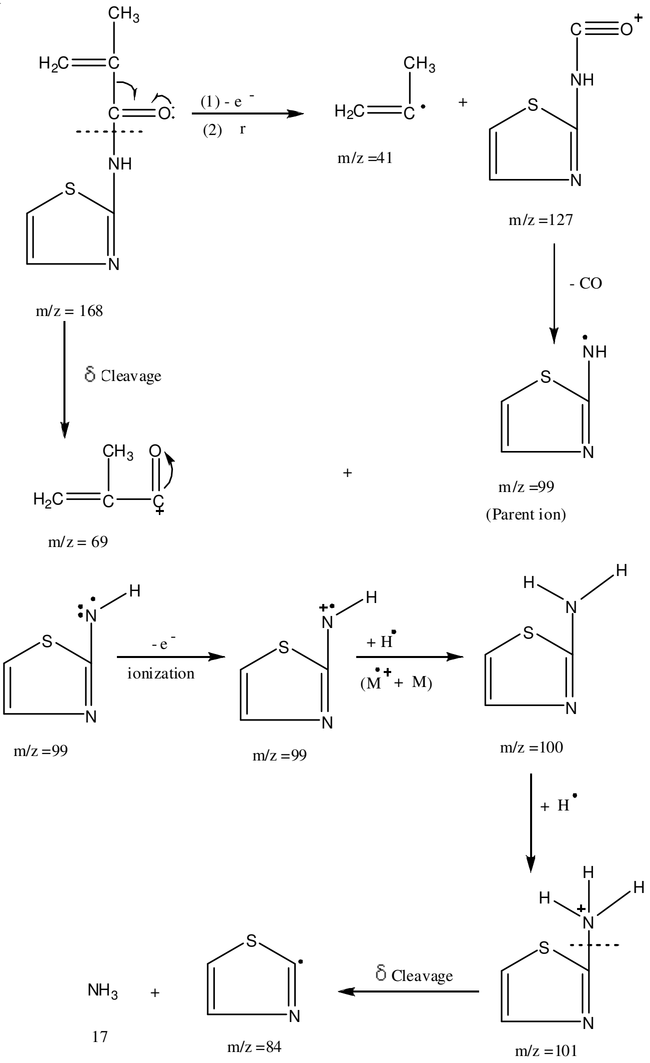


Fig. 1. Mass spectrum of *N*-(thiazol-2-yl)methacrylamide monomer



Scheme-II: Fragmentation of *N*-(thiazol-2-yl)methacrylamide monomer

Homopolymerization: *N*-(Thiazol-2-yl)methacrylamide monomer was polymerized in DMF at 70 °C, using azobisisobutyronitrile as initiator and gave the homopolymer P-*N*-(thiazol-2-yl)methacrylamide (yield 65 %). P-*N*-(thiazol-2-yl)methacrylamide was a pale yellow solid polymer, sparingly soluble in most organic solvents but soluble only in DMF or DMSO. FTIR spectrum of P-*N*-(thiazol-2-yl)methacrylamide polymer was characterized by absence of the band that appears at 1640 cm^{-1} (related to aliphatic ν(C=C) indicating a complete homopolymerization.

Copolymerization: The copolymerization data of *N*-(thiazol-2-yl)methacrylamide with acrylonitrile in DMF at 70 °C were obtained by sulfur analysis and summarized in Table-1. The reactivity ratios for the comonomers were calculated using the Kelen-Tüdös method[19,20] and were found to be r_1 (TMA) = 0.769 ± 0.063 and r_2 (acrylonitrile) = 1.987 ± 0.036 according to Fig. 2. FTIR spectrum of *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymer wasn't only characterized by absence of olefinic C=C band (1640 cm^{-1}), but also by presence of ν(C≡N) band (2240 cm^{-1}) and thus leading to a successful copolymerization.

Thermal behaviour: The thermal behaviour of any polymer may be affected appreciably by the introduction of a comonomer in the polymer chain. Thus, it is important to investigate the thermal behaviour of the synthesized copolymers. For this aim, four *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymers consist of 10, 20, 30 and 40 % *N*-(thiazol-2-yl)methacrylamide were prepared. The thermal characteristics of polyacrylonitrile have been studied in detail by Grassie[21].

TABLE-1
ANALYTICAL DATA FOR COPOLYMERIZATION OF *N*-(THIAZOL-2-YL)METHACRYLAMIDE WITH ACETONITRILE

Feed composition		Conversion	S*	Copolymer composition	
a	f_1	(%)	(%)	b	F_1
0.1111	0.1004	7.75	2.9	0.0567	0.0541
0.2500	0.1990	8.71	5.8	0.1382	0.1173
0.4286	0.3001	6.92	8.1	0.2336	0.1908
0.6666	0.3999	5.89	10.3	0.3718	0.2757
1.0000	0.4987	9.02	12.4	0.5891	0.3730
1.5000	0.6003	7.38	14.2	0.9251	0.4827
2.3333	0.7002	6.33	15.8	1.5365	0.6039

* Determined by elemental analysis of sulfur
a = M_1/M_2 in the feed composition
f_1 = mole fraction of M_1 in the feed composition
b = M_1/M_2 in the copolymer composition
F_1 = mole fraction of M_1 in the copolymer composition

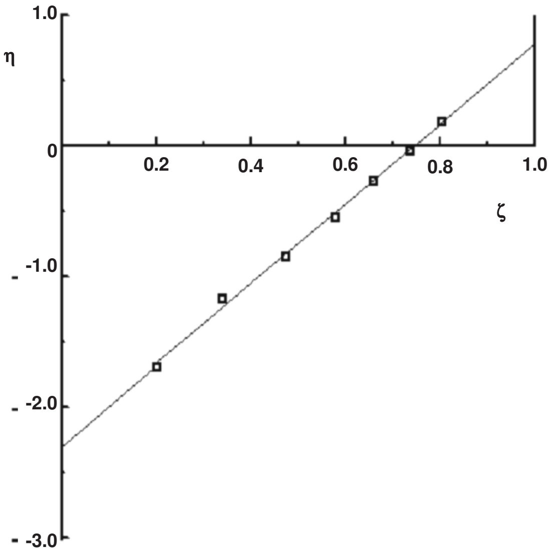


Fig. 2. Kelen-Tüdös plot for copolymerizations of *N*-(thiazol-2-yl)methacrylamide monomer with acetonitrile: $\zeta=[a^2/(\alpha b+a^2)]$ and $\eta=\{[a(b-1)]/(\alpha b + a^2)\}$, where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively; and $\alpha = [(a_{min} \times a_{max})/(b_{min} \times b_{max})]^{1/2}$

Herein, present investigation the thermal analysis of polyacrylonitrile is given as a reference, so the comparison of differential thermal analysis and thermogravimetric data of polyacrylonitrile and those of the corresponding P-*N*-(thiazol-2-yl)methacrylamide and copolymers will show the effect of these comonomers on the thermal behaviour of the products.

The differential thermal analysis curves of polyacrylonitrile, P-*N*-(thiazol-2-yl)methacrylamide and those of the corresponding copolymers with acrylonitrile are represented in Fig. 3. The thermal analysis of polyacrylonitrile in nitrogen shows the usual thermogram with an initial decomposition at 295 ºC and a sharp exotherm peak with a maximum at 324 ºC, which results from the oligomerization of the C≡N groups and formation of some aromatic structures[21]. On the other hand, the differential thermal analysis curve of P-*N*-(thiazol-2-yl)-methacrylamide show exotherm with maximium at 210 and 468 ºC, which may represent the homolytic scission and complete decomposition. The proposed homolytic scission of P-*N*-(thiazol-2-yl)methacrylamide was suggested from the fragmentation patterns obtained from the mass spectrum of *N*-(thiazol-2-yl)methacrylamide monomer (Fig. 1). As shown in **Scheme-II**, the most abundant fragmentation is cleavage of the C-N bond, giving a parent ion of m/z = 99. The exotherm at 468 ºC represent a complete decomposition and about 80 % weight loss. Moreover, in a separate experiment, when P-*N*-(thiazol-2-yl)methacrylamide was heated at 250 ºC, a black soluble solid remained, indicating that no cross-linking reaction occurred.

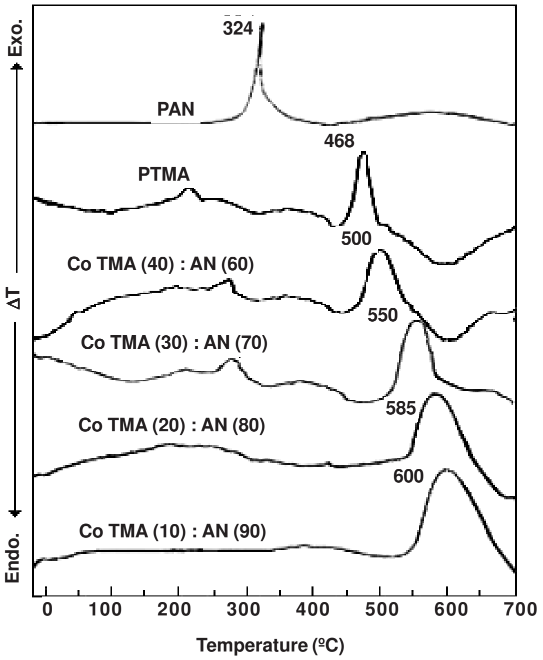


Fig. 3. DTA curves for PTMA, PAN and copolymers (TMA-AN) in nitrogen

The differential thermal analysis curves of acrylonitrile-*N*-(thiazol-2-yl)methacrylamide copolymers in N_2 atmosphere (Fig. 3) show exotherms with maxima at (270 and 500 ºC for 40 % *N*-(thiazol-2-yl)methacrylamide), (275 and 550 ºC for 30 % *N*-(thiazol-2-yl)methacrylamide), (585 ºC for 20 % *N*-(thiazol-2-yl)methacrylamide) and finally (600 ºC for 10 % *N*-(thiazol-2-yl)methacrylamide). Theses curves reflect many processes probably including scission, cyclization, cross-linking and decomposition at the higher temperature exotherm. The first stage of degradation may be attributed to scission in the C-N bond (similar in manner to the suggested degradation of homopolymers), followed by cyclization and cross-linking. The differential thermal analysis peaks of the copolymers were shifted to lower temperatures relative to that of polyacrylonitrile, indicating an initiating effect of *N*-(thiazol-2-yl)methacrylamide comonomers by the cyclization process.

The FTIR spectra of the unheated and heated *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymer 1 (40:60) (Fig. 4) show bands for the unheated copolymer at 3375, 2243, 1689 and 1254 cm^{-1} which are related, respectively, to ν(NH), ν(C≡N), ν(C=O) of the methacryloyl amide and ν(C-O). By contrast, there is an observed decrease in the intensity of the C≡N band at 2243 cm^{-1}, when *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymer was heated to 250, 350, 450 and 600 ºC. The carbonyl band at 1689 cm^{-1} merges with the band at 1640 cm^{-1} which characteristic to the imino group (C=N) and then the two bands were enlarged and broadened. Therefore, these spectral changes reflect radical changes in the copolymer structure and should also be the result of a direct interaction between the nitrile group and the carbonyl group of the comonomer to be a part of a conjugated system through an initiation of cyclization and cross-linking reactions.

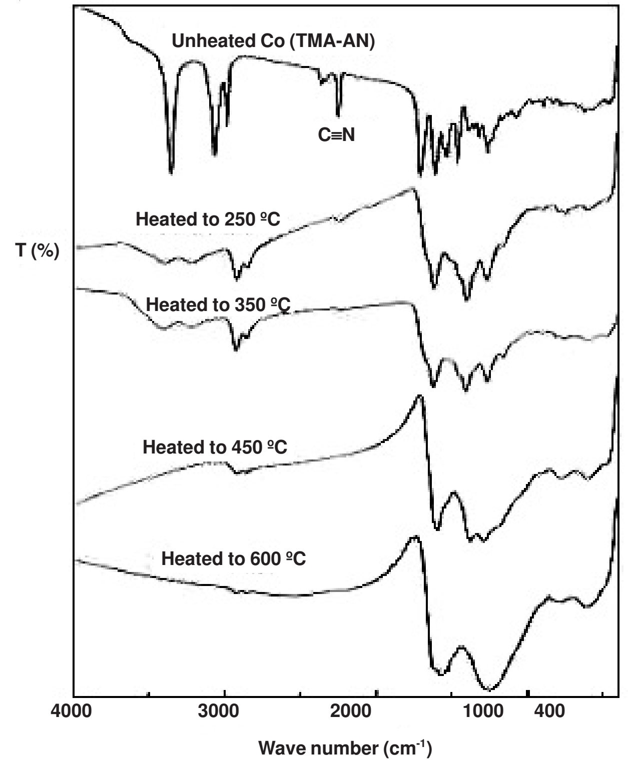


Fig. 4. FTIR spectra of heated and unheated copolymer 1 (TMA-AN) at different temperatures

The thermogravimetric thermograms for polyacrylonitrile, P-*N*-(thiazol-2-yl)methacrylamide and one of the copolymers (*N*-(thiazol-2-yl)methacrylamide:acrylonitrile = 40:60) are performed in nitrogen atmosphere and given in Fig. 5. The analysis shows more than one decomposition step, reflecting the presence of more than one process during the thermal degradation reaction. Also, the thermogravimetric curves show an increase in the weight loss of the copolymer relative to that of polyacrylonitrile. This could be confirmed when the copolymer *N*-(thiazol-2-yl)methacrylamide-acrylonitrile was heated for about 6 min at 350 ºC; where, a black insoluble mass remained, indicating an appreciable cross-linking reaction attributed to the cyclization process.

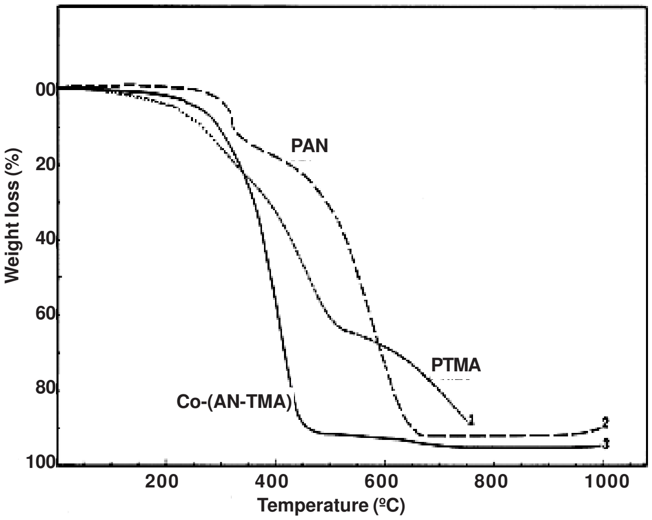
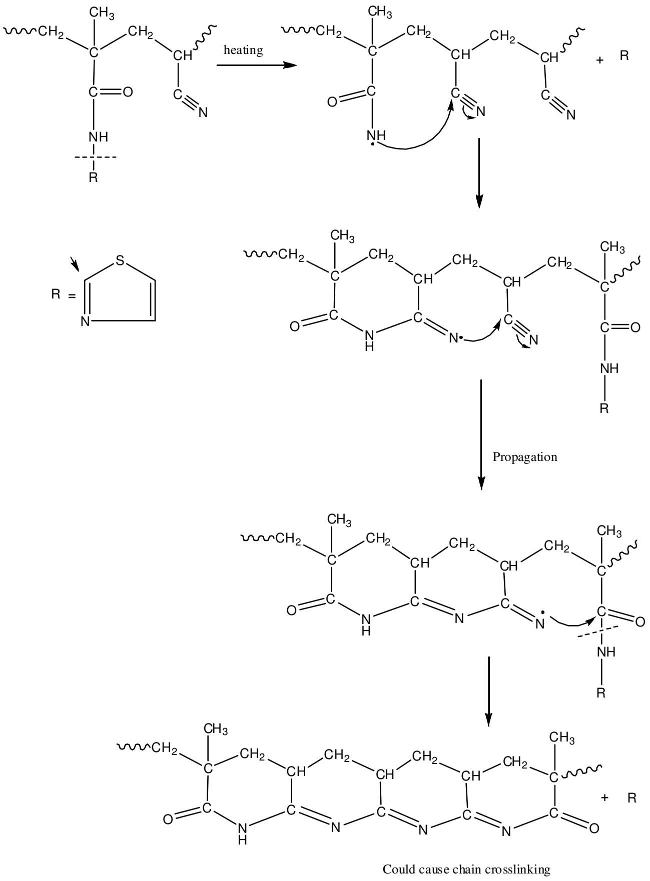


Fig. 5. TG curves in nitrogen for PTMA (1), PAN (2) and TMA-AN [40-60] copolymer (3)

From the mass spectrum fragmentation mechanism (**Scheme-II**) mentioned above, it is clear that the lower ionization potential of the C-N bond may be responsible for its fission. This confirms our suggested mechanism as represented in **Scheme-III**.



Scheme-III: Thermal degradation of *N*-(thiazol-2-yl)methacrylamide-acetonitrile copolymer

Conclusion

N-(Thiazol-2-yl)methacrylamide monomer was synthesized by two different methods. The homopolymer (P-*N*-(thiazol-2-yl)methacrylamide) and the copolymers of *N*-(thiazol-2-yl)methacrylamide with acrylonitrile were synthesized by free radical solution polymerization techniques. Characterization of *N*-(thiazol-2-yl)methacrylamide monomer and the produced polymers were performed by several spectral and thermal techniques such as FTIR, Mass, differential thermal analysis and thermogravimetric. Solubility studies showed that: *N*-(thiazol-2-yl)methacrylamide, P-*N*-(thiazol-2-yl)methacrylamide and *N*-(thiazol-2-yl)methacrylamide-acrylonitrile were pale yellow solids, sparingly soluble in most organic solvents, but easily soluble in DMF and DMSO. The monomer reactivity ratios for *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymers were determined by the Kelen-Tüdös method[19] and were found to be r_1(*N*-(thiazol-2-yl)methacrylamide) = 0.769 ± 0.063 and r_2 (acrylonitrile) = 1.987 ± 0.036. The thermal stability of *N*-(thiazol-2-yl)methacrylamide-acrylonitrile copolymers showed that the *N*-(thiazol-2-yl)methacrylamide monomer initiates the nitrile oligomerization reaction in the copolymers upon heating and gives some aromatic compounds.

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