Novel Methacrylamide Polymers Based on Thiazole and Styrene: A Study on Synthesis, Characterization, and Determination of Monomer Reactivity Ratios

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Abstract: In this study, firstly, a thiazole methacrylamide (TMAAm) monomer was synthesized from methacryloyl chloride with 2-aminothiazole. Later on, a series of copolymers of 2-thiazole methacrylamide (TMAAm) with styrene (St) using strange compositions in the feed has been prepared in solution via radical at 70 ^{o}C with AIBN as initiator. The structure of the copolymers was elucidated by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy methods. The compositions of the copolymers were determined from the nitrogen (N) difference according to the elemental analysis results. Monomer reactivity ratios; The r_{TMAAm} and r_{St}, Fineman-Ross (FR), Kelen-Tüdös (KT) linear methods, and the error method model in non-linear variables were calculated with the computer program RREVM. The molecular weights and heterogeneity indices of the copolymers were determined by the GPC method. The thermal stability of the copolymers was investigated by thermogravimetry (TG) measurements.

Keywords: Thiazole methacrylamide, monomer reactivity ratios, RREVM.

1. INTRODUCTION

(Meth)acrylamides have been used as a broadly functional vinyl monomer, in academia and industry, from the earliest times in polymer science to the present. Depending on the properties of the monomers added to the functional (meth)acrylamides, polymers with different usage areas are obtained. The monomers are polymerized via radical, anionic, and coordination polymerization, whereas the inclusion of functional moieties is achieved by replacing amide substituents. In recent years, various (meth)acrylamide monomers have been produced academically and commercially [1-3]. Due to their amorphous and water-soluble properties, polyacrylamides constitute a class of polymers that are of great interest and study in agricultural, industrial, and medical fields [4,5]. Due to these interesting properties, polyacrylamides attract attention and studies are continuing in basic research areas such as polymer blends, catalysis, and biomedicine [6-8]. Polyacrylamides are an important area of use in water treatment, mining and paper industry due to their flocculation properties in aqueous suspensions [9,10].

Most monomer designed by adding a spacer maintains polymerization ability between polymerization point and functional group. Conversely, monomer functionalization at the α-position of acrylamides is relatively sparse. In addition to the difficulty of preparing the monomer, direct substitution affects the polymerization behavior of the α-substituent [11-13].

After the 1950s, when polymer chemistry was established as a broad science, scientific and industrial interest in macromolecules gradually shifted to copolymerization reactions. There are various reasons for this. Most of the information on the reactivity of monomers, radicals, carbonium ions, and carbanions in chain polymerizations is based on the study of copolymerization reactions. It is useful to know the behavior of monomers in copolymerization, especially in order to understand the effect of chemical structure on reactivity. Copolymerization is of great technological importance. By utilizing this process, the polymer chemist can design and prepare a polymeric product with desirable features with greater freedom of movement. Because changing the types and relative amounts of the monomers entering the copolymer brings the possibility of making an almost unlimited number of different polymers. The examination of polystyrene is known as a classic example to see the variations brought by the copolymerization process in practice [14,15]. Polystyrene is a plastic that breaks, has low impact resistance, is not resistant to solvents, and is used in very limited places. The polymeric products obtained by the copolymerization of styrene, on the other hand, expand the usage areas of polystyrene and make this polymer one of the most

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useful substances we know. The fact that the annual production is around 5 million tons proves this view. Copolymers (and terpolymers) of styrene are used not only as plastics but also as elastomers. By copolymerization of styrene with acrylonitrile, solvent-resistant polymers with high impact resistance are obtained. The copolymers it gives with butadiene destroy the elastomeric properties. In the terpolymer of styrene with acrylonitrile and butadiene, all three properties can be improved at the same time. In ethylene-propylene copolymers, polymers that change their plastic properties to elastomer properties by changing the amount of the second component are made. Although the application area of copolymers has expanded, the kinetics of copolymerization has not been clarified for a long time. In the 1930s, it was found that monomers show various tendencies to enter the copolymer. Although the kinetics of chain-reaction copolymerization was first developed for radical reactions, the method can also be directly applied to ionic systems. Monomer reactivity ratios are valuable numerical properties used to determine the copolymer type and composition. The rate of conversion of monomers to copolymers and changes in the reaction environment affect monomer reactivity. Among the various methods available to detect monomer reactivity ratios, the methods of Mayo–Lewis (ML), [16] Finemann–Ross (FR), [17] inverted Finemann–Ross (IFR), Kelen–Tüdos (KT), [18] and Tidwell–Mortimer (TM), [19] are suitable processes for the appoint of monomer reactivity ratios at tiny monomer-copolymer conversions (less than 10%).

In this study, an acrylamide monomer containing a thiazole group was synthesized and its structure elucidated. This prepared monomer was copolymerized by the free radical polymerization technique with the styrene commercial monomer. Molecular structures of copolymers elucidated with FT-IR, ^{13}C NMR, and ^{1}H NMR spectral techniques. GPC method was used to determine the molecular weights of the prepared copolymers. The thermal behavior of these copolymers was examined by thermal gravimetric analysis (TGA). The monomer reactivity ratio was evaluated via the FR, KT and RREVM method.

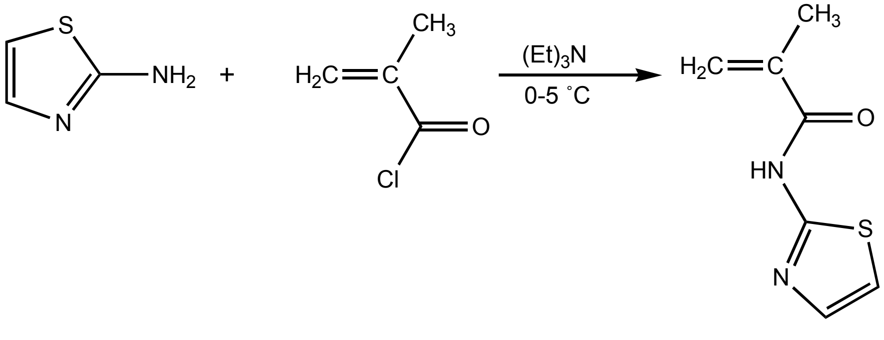
2. EXPERIMENTAL

2.1. Reagents

1,4-dioxane was purchased from Merck. Chloroform, triethylamine, 1,4-dioxane, n-hexane, ethanol, methacryloyl chloride, and 2-aminothiazole were supplied from Sigma-Aldrich. The thiazole methacrylamide monomer used in the copolymerization system was synthesized from 2-aminothiazole and methacryloyl chloride by the amidation reaction according to a literature protocol [20] and in Scheme **1**. Styrene (Aldrich) was dried over CaH_2 and distilled under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was heated in a water bath at 40 °C, dissolved in 50 mL of ethanol, and the solution was filtered while hot. The filtrate was cooled in an ice-water bath and the precipitated AIBN crystals were filtered and dried in a vacuum oven at 25 ^{o}C. The distillation was freshly done of 1,4-dioxane, chloroform, and n-hexane.

2.2. Characterization Technique

The FTIR-ATR spectra were recorded using a Perkin Elmer Spectrum Two (UATR) spectrometer. The samples were analyzed 4000–400 cm^{-1}, operating at a resolution of 4 cm^{-1}. For the copolymers the ATR-diamante device was used, NMR spectra were captured together JEOL JNM-LA400 FT NMR spectrometer using $CDCl_3$ solvent. Molecular weights and heterogeneity index values of the copolymers were appointed by the gel permeation chromatography (GPC) (Agilent 1260 GPC system, Agilent Technologies, Santa Clara, USA) elaborated via a PL gel 5 μm MIXED-C column, and a 410-differential refractometer by GPC grade tetrahydrofuran (THF) as the carrier solvent at a flow rate of 1.0 mL min^{-1}.



Scheme 1: Synthesis reaction of TMAAm monomer.

Thermal degradation behaviors were conducted using a thermogravimetric analyzer (Hitachi 7000 TGA/DTA model thermogravimetry device) at a heating rate of 20 °C min^{-1} under an N_2 atmosphere.

2.3. Copolymerization Study of Thiazole Methacrylamide (TMAAm) and Styrene (St)

The relative amount of monomer used for each copolymerization is given in Table **1**.

1% of the total monomer amount of 2,2'-azobisisobutyronitrile free radical initiator was taken for all copolymerizations. Monomers were dissolved by adding 10 mL of solvent (1,4-dioxane) to each polymerization tube. The solution contained in Pyrex-glass polymerization tubes was degassed using N_2. Copolymerizations were achieved at 343 K until a rise of the viscosity of the solution was fixed (approximately 6 h). The mixture was poured into n-hexane and reprecipitated from 1,4-dioxane/n-hexane at least three times. The copolymers were dried in a vacuum at 313 K to constant weight and stored in colored bottles for analysis. The copolymeric units of TMAAm with St can be represented according to Scheme **2**:

3. RESULTS AND DISCUSSIONS

3.1. FTIR and NMR Characterization of the TMAAm-St Copolymer System

Figure **1** shows the FT-IR spectrum of the copolymer synthesized with TMAAm and St monomers. When Figure **1** is examined, it can be seen that the NH stretching vibration in the copolymer molecules is at 3200 cm^{-1}, the CH stretching vibrations arising from the aliphatic structure are in the range of ~2900-3200 cm^{-1}, the CH bending vibrations are in the range of ~1400-1450 cm^{-1}, the CN stretching vibrations are in the range of ~1200 cm^{-1}, the C=O peak of the amide carbonyl was observed at ~1670 cm^{-1}.

In Figure **2**, ^{1}H-NMR and ^{13}C-NMR spectra and molecular structure evaluations are given on the figüre-spectrum for the copolymer sample [0.59:0.41] synthesized with TMAAm and St monomers.

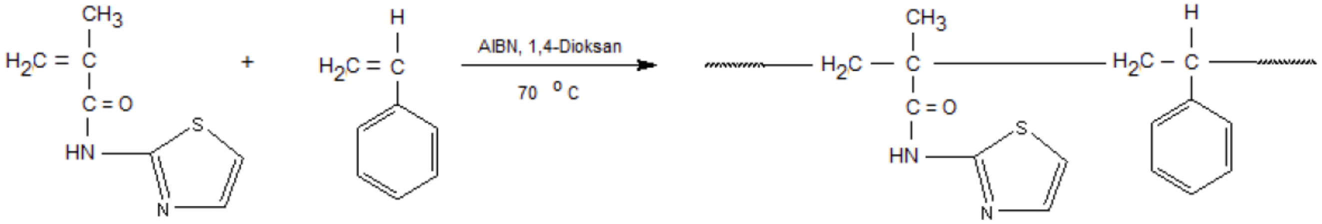
3.2. Molecular Weights of the Copolymers

The molecular weights of the copolymers were appointed by GPC with polystyrene as the standard and tetrahydrofuran as the carrier solvent, respectively.

Table 1: Copolymer Feed Rates, Copolymer Composition and Molecular Weights

Sample No	Monomer Feed Composition in Mole Fraction			Elemental Analysis N (%)	Copolymer Compositions			
	TMAAm(M_1)	St(M_2)	Conversion (%)^a		TMAAm(m_1)	St(m_2)	Mn^b	Mw/Mn^b
1	0.10	0.90	8.8	3.260	0.13	0.87	6840	1.74
2	0.25	0.75	8.1	6.849	0.30	0.70	5350	1.88
3	0.40	0.60	8.4	8.190	0.37	0.63	8500	1.64
4	0.50	0.50	8.5	10.800	0.53	0.47	6690	1.81
5	0.60	0.40	7.6	11.640	0.59	0.41	9640	1.76
6	0.75	0.25	9.8	13.340	0.71	0.29	6620	1.70
7	0.90	0.10	9.2	15.040	0.85	0.15	8460	1.62

Reaction conditions: Solvent: 1,4-dioxane; Conversion < 10% (less than 6 h.); Temperature: 70 ± 1 °C.
^{a}Obtained from gravimetrically.
^{b}Determined by GPC measurement.



Scheme 2: Synthesis reaction of poly(TMAAm-co-St) copolymer.

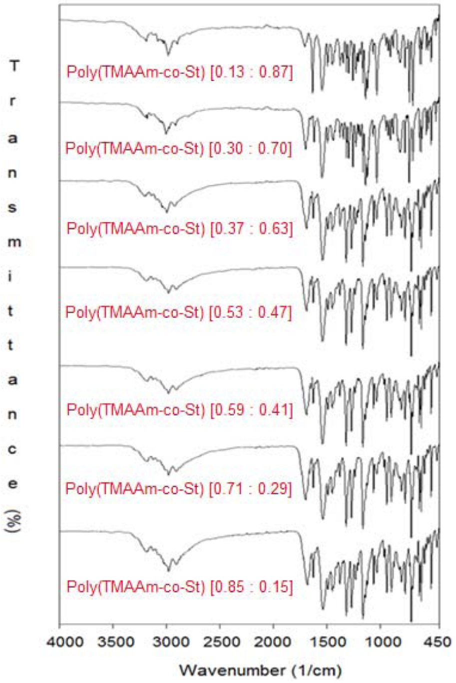


Figure 1: FT-IR spectra of Poly(TMAAm-co-St) in different compositions.

The number average (Mn) and weight average (Mw) molecular weights and the polydispersity indexes (Mw/Mn) of copolymers are given in Table **1**. When the table is examined, it is seen that the polydispersity index values of the copolymers vary between 1.62 and 1.88. İn the literature, the theoretical values of M_w/M_n for polymers synthesized via radical recombination and disproportionation are 1.5 and 2.0, respectively [21]. The polydispersity indices of produced copolymers in this work suggest that the chain termination takes place predominantly by disproportionation outweighs coupling [22].

3.3. Monomer Feed Rates for the TMAAm-St Copolymer System

Fineman-Ross and Kelen-Tüdös values were appointed using the values in Table **1** and given in Table **2**.

3.4. Calculation of Monomer Reactivity Ratios for TMAAm - St Copolymer System

The G versus H values of Fineman Ross parameters were plotted, and η vs. ξ values of Kelen-Tüdös parameters were plotted.

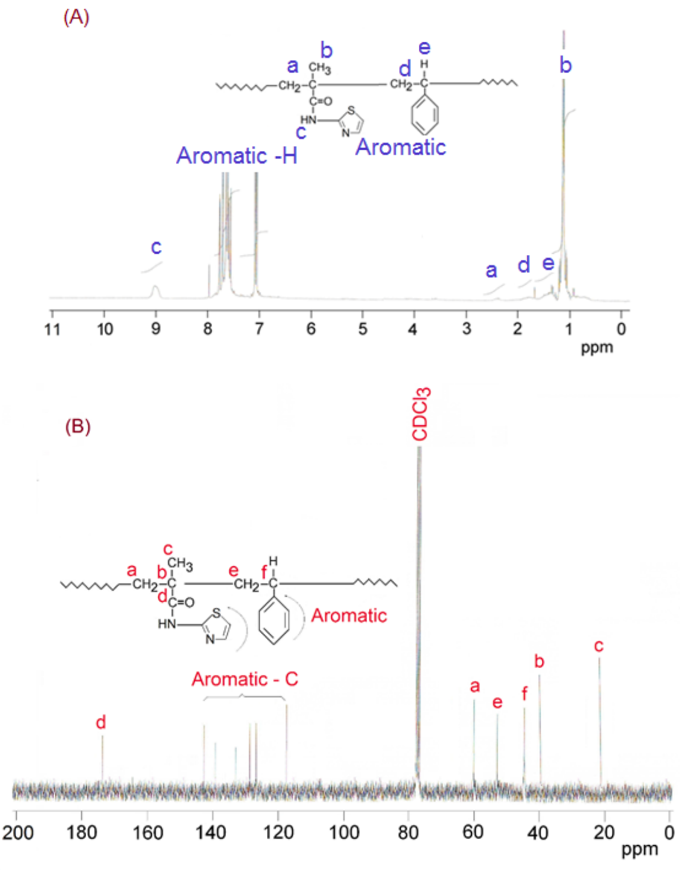


Figure 2: ^{1}H-NMR (**A**) and ^{13}C-NMR (**B**) spectra of Poly(TMAAm-co-St): [0.59:0.41].

Table 2: FR and KT Parameters for the TMAAm-St Copolymer Ssystem

$F=M_1/M_2$	$f=m_1/m_2$	$G=F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
0.111	0.150	-0.629	0.082	-0.542	0.070
0.333	0.432	-0.438	0.257	-0.328	0.192
0.666	0.598	-0.448	0.742	-0.246	0.408
1.000	1.139	0.122	0.878	0.062	0.449
1.500	1.433	0.453	1.570	0.171	0.593
3.000	2.482	1.791	3.626	0.381	0.771
9.000	5.720	7.427	14.161	0.487	0.929

Reaction Conditions; Solvent: 1,4-dioxane; conversion < 10%; α (arbitrary constant) = $(H_{max} . H_{min})^{½}$ = 1,078

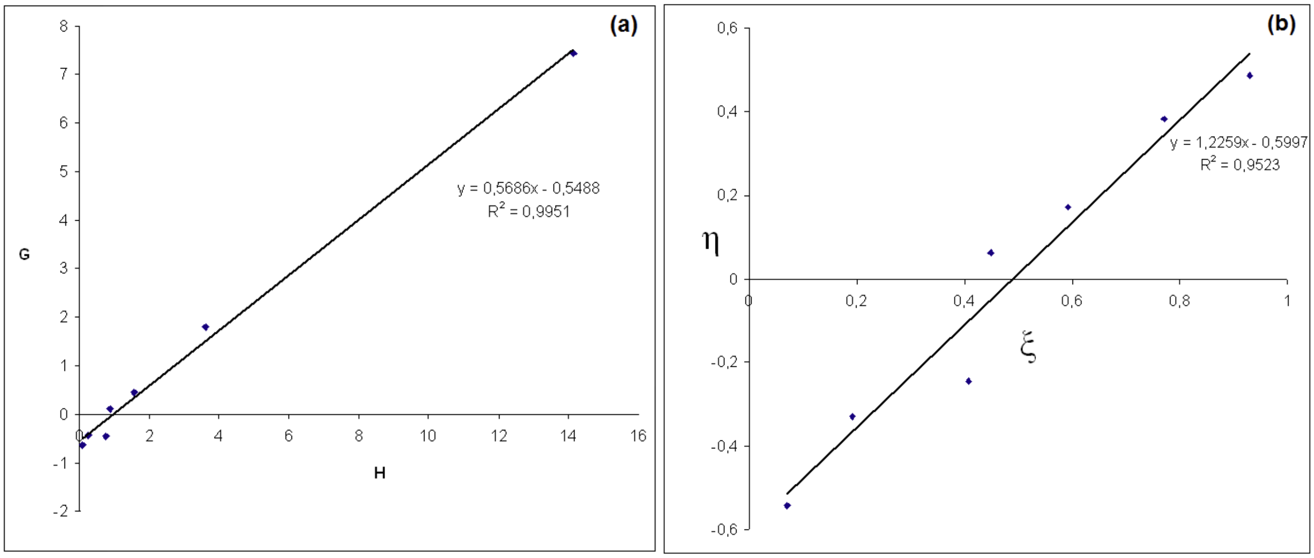


Figure 3: (**a**) FR and (**b**) KT Graphs to determine monomer reactivity ratios for TMAAm(r_1) and St(r_2) copolymerization from elemental analysis results.

a) graph; $G = H r_1 – r_2$ is a straight line by link. The equation of this line was assigned on the graph as y = 0.5686x – 0.5488 and it was calculated as r_1= 0.569 from the slope of this line and r_2 = 0.549 from the cut-off point.

b) graph; η = (r1 + r2 / α) ξ - r2 / α is a straight line by link. The equation of this line was assigned from the graph as y = 1.2259 x – 0.5997. From the equation; from $r_2 / \alpha = 0.5997$ (α = 1.078), $r_2 = 0.646$ and it was calculated from $r_1 + r_2 / \alpha) = 1.2259$ to $r_1 = 0.626$.

These variables and monomer reactivity values were also obtained using a non-linear computational estimation program known as the error of reactivity ratios in the variable model (RREVM) [23].

Calculated reactivity ratios are given in Table **3**.

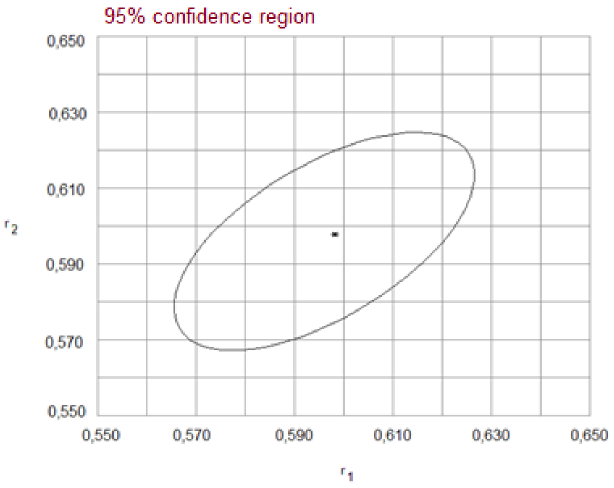


Figure 4: 95% confidence region for r_1 and r_2 values calculated by RREVM method for TMAAm-St copolymer system.

For the copolymer system formed, r_1 (rTMAAm) < 1 and r_2 (rSt,) < 1 are in question. Under these

Table 3: Monomer Reactivity Ratio Values Calculated from Free Radical Copolymerization for the TMAAm-St Copolymer Ssystem.

Method	r_1^a	r_2^b	r_1r_2
Fineman-Ross	0,569	0,549	0,312
Kelen-Tüdös	0,626	0,646	0,404
RREVM	0,597	0,598	0,357

r_1^a and r_2^b: Monomer reactivity ratios of TMAAm and St.

conditions, there is a tendency for an optional copolymer to form [24]. In the copolymer chain, random units from each monomer are attached to the copolymer formation and optional copolymers are formed.

3.5. Thermal Analysis Results for TMAAm – St Copolymer System

The thermal stability of the copolymers was reviewed by TGA and measured by heating with a heating rate of 10 °C/min. From the thermograms, it is seen that the degradation steps are similar to each other and the degradation takes place in three steps. In a previously published study [25], in the analysis of the thermogravimetric curve of polystyrene, it was seen that the decomposition temperature started at 250 °C, the decomposition took place in a single step and was completed at 400 °C, leaving a residue of 8%. As can be seen in Figure **5**, it is seen that the initial decomposition temperatures of poly(TMAAm-co-St) copolymers start around 200 °C, the decompositions take place in three steps and they end at around 430 °C, leaving around 15% residue. It can be said that with the increase in the mole fraction of TMAAm, the decrease in the initial decomposition temperature and the increase in the final decomposition temperature and residue are due to the presence of the thiazole group in the copolymer.

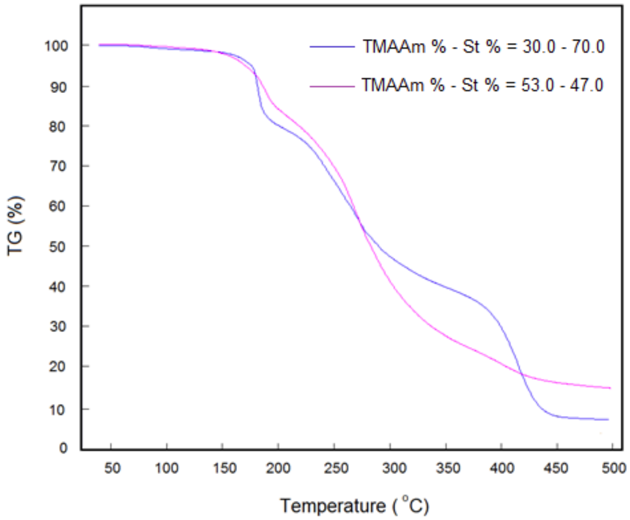


Figure 5: TG curves of poly(TMAAm-co-ST) in different compositions.

CONCLUSIONS

This study aims to prepare a series of copolymers based on varying initial molar ratios of TMAAm and St monomers and to elucidate their structures. The molecular structures of the obtained copolymers were confirmed by the spectra obtained from FT-IR and NMR spectroscopic analyzes. The monomer reactivity ratios for the investigated monomer pair were appointed by the FR, KT linear method, and the non-linear RREVM method. The calculated values of copolymerization composition and monomer reactive ratios showed that the monomers showed random and optional reactivity behavior in copolymerization and random copolymers were obtained. The M_w/M_n values of the copolymers confirm that the copolymers were produced by the free radical polymerization method. TGA analysis showed that copolymers have three decomposition steps. Thiazole and its derivatives are biologically important compounds found such as in the vitamin B1 molecule and coenzyme cocarboxylase [26]. Penicillin is another compound that contains a thiazolidine ring in its molecule. 2-Aminothiazoles are known as biologically active molecules with a wide spectrum of activity used as intermediates in the production of antibiotics and dyes [27]. From this point of view, thiazole and styrene-based new methacrylamide copolymers, whose kinetic properties we have determined in this study, will form the basis for new projects and research in this field.

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