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Research Article

A study on copolymers of styrene with a methacrylamide containing benzofuran side group: Their monomer reactivity ratios, thermal stabilities, thermal degradation kinetics

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ABSTRACT

The aim of this study was to determine the monomer reactivity ratios, thermal properties and thermal degradation behavior of new P(N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide-co-styrene) polymers synthesized at different compositions. For this purpose, novel copolymers of N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide (NBBM) monomer with styrene (St) monomer were prepared using free radical polymerization method. The ^{1}H-NMR spectra was used to calculate the compositions of the copolymers. The reactivity ratios of monomers were calculated in line with the universal copolymerization equation using Kelen-Tüdös and Finemann-Ross linearization methods, and found to be r_1:0,62 r_2:1,09 and r_1:0,61, r_2:1,07 respectively (where r_1 is reactivity ratio of NBBM). DSC, TGA and DTG were used to study the thermal behaviors of the copolymers. The Tg value of P(NBMM) was found to be 211 °C and the Tg values of the studied copolymers were determined to increase from 144 °C to 184 °C with increasing concentration of NBMM units. Thermal data showed that the maximum degradation temperatures increased from 349 °C to 391 °C as the St units increased in the copolymer system. The activation energy (Ea) values of P(NBBM) and the studied copolymer were determined from the TGA curves obtained at different heating rates and the Flynn-Wall-Qzawa, Kissinger, Tang isoconversional methods were used. Solid state reaction mechanisms were also calculated by being used the Van Krevelen method, a non-isoconversion model. The Ea values obtained with isoconversion models for P(NBBM) and copolymer were found very close to the values obtained from non-isoconversion models. Moreover, the R3 mechanism was proposed for the homopolymer and copolymer.

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INTRODUCTION

Polymers containing functional groups with different properties have been used in various applications as functional materials. In this regard, polymethacrylates with benzofuran ring in the side group have gained more and more interest lately. One of the most frequently used methods to produce materials with desired properties using monomers containing these functional groups is copolymerization. Functional methacrylate copolymers have many biomedical applications in industry. Drug delivery systems, dental and knee prosthesis, biosensors are some of these areas of applications. Studies have aimed to improving properties such as biocompatibility, bioactivity and long-lasting durability in their areas of use [1-4]. Benzofuran and its derivatives have been investigated for their biological activities [5-8], optical properties [9, 10], thermal properties [11] and these studies are still ongoing. For example, one study reported that 2-acetyl benzofurans can be used for anti-cancer treatment [12]. In another study, anticancer, antibacterial and antioxidant properties of some benzofuran modified compounds were investigated. As a result of the study, it was reported that these compounds showing antiproliferative effect are promising [13]. Some researchers who have studied the effect of benzofurane structures containing bromine for a long time against cancer have found that these structures exhibit quite important effects against leukemia [14]. For these reasons, the synthesis of methacrylamides containing benzofuran groups and further investigation of such polymers will lead to promising results. But when synthesizing a copolymer, it is important to have information about the reactivity ratios of the monomer of the copolymer to be synthesized [15-17]. These reactivity ratio values provide an insight into the design and composition of the product.. As a result, copolymer composition is critical for some applications [18, 19]. In this context, the knowledge of monomer reactivity ratios in methacrylate copolymers containing benzofuran structure synthesized in our study and having many properties enables the use of these copolymers in various application areas. For example, this use could be the production of disposable materials such as gloves, vials and pipettes made from styrene-based polymers containing benzofuran in their structure. In order to determine monomer reactivity ratios, which is such important information, linear and nonlinear mathematical methods as well as some experimental kinetic data are frequently preferred [20-23].

One of the important properties of polymers is their thermal behavior. The fundamental thermal data are significant in terms of the use of polymer materials. The change in mass of a polymer as a function of time and temperature is determined by thermogravimetric analysis [24]. From this analysis it is possible to obtain information about the thermal stability of a polymer, the degree of thermal degradation reaction and the activation energy of thermal degradation [11]. These properties change drastically according to the groups found in the structure of the material [25]. The change in the thermal stability of methacrylate polymers due to the addition of side groups, especially heterocyclic groups, has attracted the interest of researchers [26]. The thermal behavior of some methacrylate copolymers containing benzofuran has also been studied and reported to exhibit high thermal stability. For example, Demirelli et al. examined methacrylate polymers with different benzofuran concentration and reported that thermal stability increased with increasing benzofuran units in the structure. In addition, they reported that the composites of these structures made with graphite oxide have semiconducting properties at all temperatures studied [27].

Styrene is one of the most important monomers for copolymers and composites, which are used today in an increasingly wide range of applications. Therefore, polystyrene is found in many commonly used products. Polystyrene is used in the medical field, especially in the production of implants and devices [28, 29]. It is also widely used in disposable materials such as gloves and vials. Polystyrene is also preferred in the production of laboratory equipment such as petri dishes, pipettes and sterilization trays [30, 31]. In addition to its low cost and thermal stability, its durability, lightness, and ease of processing make polystyrene a suitable candidate for these uses. Due to the recent increasing demand for single-use medical materials, the need for such medical polymers continues to increase significantly. In many studies in the literature, poly(styrene-block-isobutylene-block-styrene) block copolymers have been frequently used for biomedical applications due to their processability, biocompatibility and stability. [32,33]. In addition, the thermal stability, biological, optical and electrical properties of new polymers containing styrene units in their structure have been frequently studied in the literature [34-38].

The benzofuran ring is a fundamental structure found in many medically important compounds. But a vast majority of studies on benzofurans are aimed at synthesising new benzofuran derivatives with small molecular weight by various organic synthesis reactions and investigating their biological properties. When the literatures are examined, studies on the synthesis and properties of benzofuran containing polymers are quite limited [27, 39-41]. Due to the properties mentioned above, P(NBMM-co-St) copolymers can be used in various manufacturing and medical fields, especially in biomedical applications. Therefore, in our study, the monomer reactivity ratios of P(NBMM-co-St) copolymers with functional and characteristic properties to be used for the desired purpose were determined. At the same time, the thermal behaviors of these polymers, which reveal their properties such as processability and resistance to high temperatures, were investigated and their thermal degradation kinetics were studied.

EXPERIMENTAL PROCEDURES

Materials and Characterization

The monomer namely, N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide (NBBM) was synthesized through a method from the literature [42]. Methanol, ethanol, triethylamine, acetone and methacryloyl chloride (Sigma-Aldrich) were commercial products with analytical grade and were used as received. The comonomer styrene (Sigma-Aldrich) was cleaned up from inhibitor first by being washed with aq. NaOH (5%). Later, it was dried over MgSO4. Azobisisobutyronitrile (AIBN) (Merck) was purified by recrystallisation using the chloroform-methanol mixture.

A Perkin Elmer Spectrum FT-IR spectrometer was used for the FT-IR measurements. A 600 MHz Avance III HD 600 NMR spectrometer with $CDCl_3$ as the solvent was used for the NMR measurements. The molecular weights (Mn and Mw) of the polymers were determined using an Agilent 1100 series gel permeation chromatograph equipped with an RI detector and calibrated to poly(methyl methacrylate) standards. Thermal data were obtained using a Perkin Elmer DSC-8000 instrument at a heating rate of 20 °C min^{-1} in an N_2 atmosphere and a Perkin Elmer SII 7300 model TGA/DTA device at a heating rate of 10 oC min-1 in an N2 atmosphere.

Synthesis of NBBM-ST Copolymers

Conventional free radical polymerization method was applied for the synthesis of copolymers. The typical example for synthesizing copolymers here is as the following. The N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide was placed in a polymerization tube with a commercial monomer styrene (St) at certain ratios by mole. The monomers were dissolved in the 1,4-Dioxane: tetrahydrofuran (3:2) solvent which is 3 times the total weight taken for polymerization. As initiator, AIBN in the ratio of 1% by weight of the total amount of monomers was added. The tube was flushed with nitrogen gas for 10 minutes in order to remove the air from the polymerization tube and was then allowed to polymerize in an oil bath at a temperature of 70 °C. The polymerization reaction was stopped

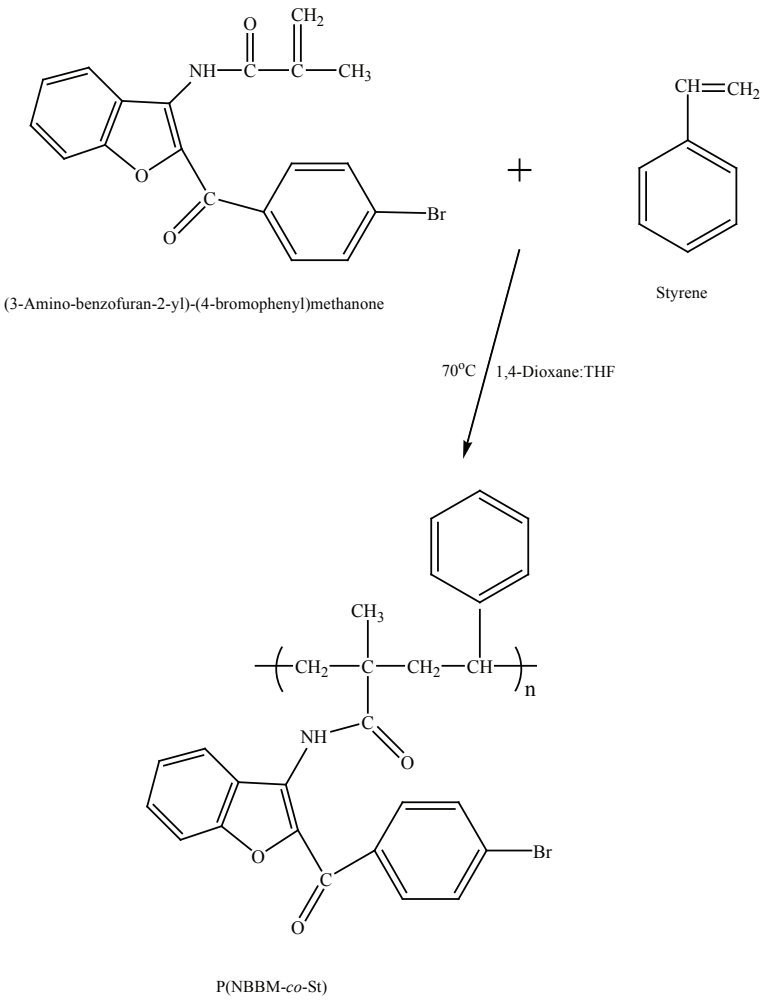

Figure 1. Synthesis of P(NBBM-co-St) copolymers.

after 12 hours. The mixture was precipitated dropwise in ethyl alcohol, filtered and dried under vacuum at 40 °C for 24 hours. The solid product (polymer) was then dissolved in dichloromethane, precipitated again in ethyl alcohol and dried. This purification process was repeated 3 times. Using NBBM and St monomers, a series of copolymers composed of five different compositions by mole was also synthesized by this method. Figure 1 shows the scheme for copolymer synthesis.

RESULTS AND DISCUSSION

Characterization of Copolymers

The copolymerization of the NBBM monomer with styrene has been carried out using the free radical polymerization method. The percentage compositions of NBBM and St copolymers were experimentally calculated from ^{1}H-NMR spectra and NBBM: St mole ratios are found as; Co-1: 18/82, Co-2: 30/70, Co-3: 43/47, Co-4: 59/41, Co-5: 73/27, respectively. FT-IR and ^{1}H-NMR measurements were used to identify the structures of the copolymers. Figure 2 shows the FT-IR spectra of the copolymers. The peaks related to amide carbonyl (NHC═O) at 1700 cm^{-1}, ketone carbonyl (C═O) [43] at 1612 cm^{-1} and mono-substituted benzene derived from St monomer at 700 cm^{-1} have been clearly seen from the FT-IR spectra of copolymers. Additionally, the direct proportional variation of the relative intensity of the peak at 700 cm^{-1}, depending on the molar ratio of the St monomer used in the copolymers, demonstrates clearly the effectuation of the synthesis of the copolymers at different monomer ratios.

In the ^{1}H-NMR spectra of NBBM-St copolymers (Fig. 3), the disappearance of the signals of monomeric vinylic protons at 5.68-6.17 ppm demonstrates clearly the completion of copolymerization reaction. In addition, the presence of aromatic protons of the styrene monomer with the other aromatic protons in the structure at 6.23-8.40 ppm, aliphatic protons at 0.43-2.61 ppm and *NH* proton at 10.58 ppm in the spectrum supported the expected copolymer structures. Both FT-IR and ^{1}H-NMR results were found to agree with the predicted chemical structure of the copolymers [41, 43].

Determination of the Monomer Reactivity Ratios

The ^{1}H-NMR spectra were used to calculate the percentage compositions of the NBBM-St copolymers. The NH protons at 10.58 ppm in the PNBBM units and the aromatic protons at 6.23-8.40 ppm in the NBBM-St units were taken as a basis for the calculation of composition percentages (Table 1).

Copolymer compositions were calculated from the following Equations.

$$C = \frac{Integral\ values\ of\ NH\ protons}{Integral\ values\ of\ aromatic\ CH\ protons} = \frac{m_1}{5m_2 + 8m_1} \quad (1)$$

If it is to simplify;

$$C = \frac{5C}{1 - 3C} \quad (2)$$

Where m_1 and m_2 are the mole fractions of NBBM and St, respectively in the copolymer. Since the total mole fraction is always equal to 1, m_2=1-m_1 if m_1+m_2=1. The calculation method of the copolymer compositions for the Co-1 polymer sample is as follows.

$$\frac{m_1}{5(1 - m_1) + 8m_1} = \frac{31.00}{31.47} \quad (3)$$

It is calculated as % m_1 = 0.18 and % m_2 = 1 - m_1 = 0.82

For the other samples, compositions were determined by similar calculations using the peak heights obtained

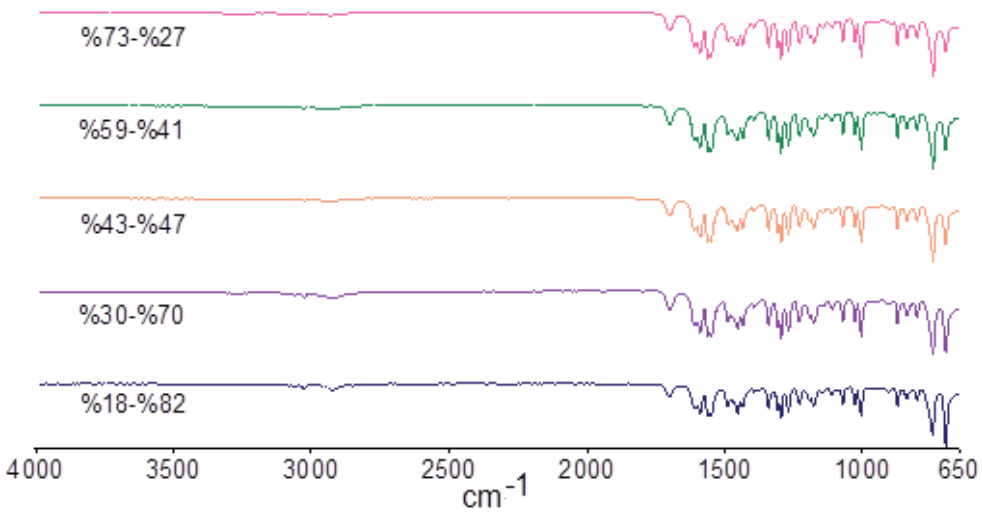

Figure 2. FT-IR spectra of P(NBBM-co-St) copolymers.

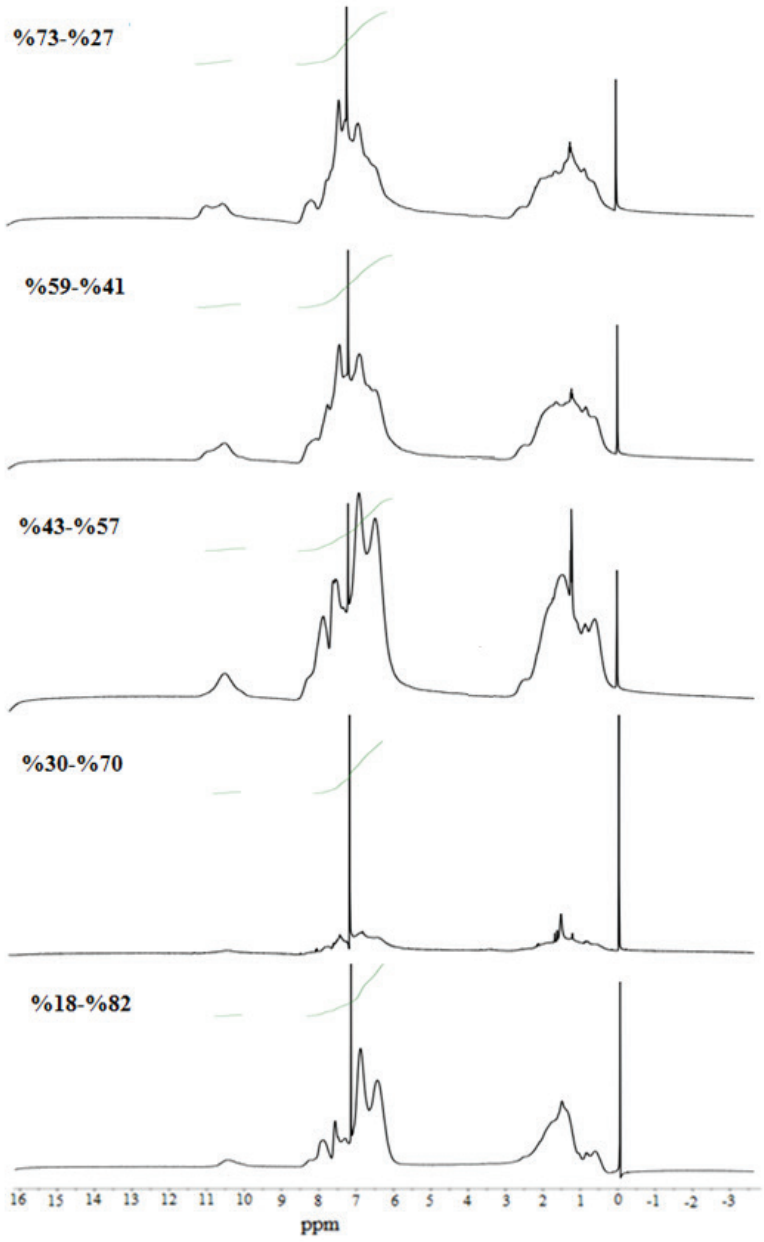

Figure 3. [1]H-NMR spectra of P(NBBM-co-St) copolymers.

Table 1. Monomer compositions in feed and in the copolymer

Sample	Feed composition (mole fraction)					Copolymer composition (mole fraction)	
	NBBM (M_1)	St (M_2)	Conversion (%)	*I*Ara	*I*NHb	NBBM (m_1)	St (m_2)
Co-1	0.20	0.80	11	31.47	1.00	0.18	0.82
Co-2	0.35	0.65	9	19.66	1.00	0.30	0.70
Co-3	0.50	0.50	13	14.60	1.00	0.43	0.57
Co-4	0.65	0.35	10	11.52	1.00	0.59	0.41
Co-5	0.80	0.20	15	9.83	1.00	0.73	0.27

[a]Integral values of aromatic C*H* protons
[b]Integral values of N*H* protons

through the ^{1}H-NMR spectra. The copolymer conversions were calculated gravimetrically [44].

The parameters r_1 and r_2, known as monomer reactivity ratios, represent the reactivity ratio of NBBM and St, respectively. Both the feed composition and the reactivity ratio of the monomers affect the composition of the copolymers. Therefore, knowing these ratios is important for synthesizing copolymers with desired properties.

To estimate the monomer reactivity ratios of the synthesized copolymers were used the Kelen Tüdös (K-T) [45] and Fineman-Ross (F-R) [46] Equations 4-5. The Notations in the equations were described in Table 2.

$$(Kelen-Tüdos\ equation)\ \eta = \left(r_1 + \frac{r_2}{\propto}\right)\xi - \frac{r_2}{\propto} \quad (4)$$

$$(\text{Fineman} - \text{Ross equation})\ G = r_1 \text{H} - r_2 \quad (5)$$

Graphs of η versus ξ and G versus H were plotted for Kelen-Tüdös and Finemann-Ross methods, respectively (Fig. 4,5). From the straight line slope and intercept, monomer reactivity ratios of NBBM and St were determined and presented in Table 2.

When the calculated r_1 and r_2 values are examined; the r_1 value of NBBM is smaller than the r_2 value of St monomer, indicating that the NBMM monomer has a lower reactivity than the St monomer and the polymer chain has a higher tendency to add St monomer. That is, there are more St monomers and fewer NBBM monomers in the copolymer chain. The reason of this can probably be interpreted as that the NBBM monomer with large-volume groups have sterically difficulty in adding its own monomer and so tends to add the other monomer, styrene.

Gel Permeation Chromatography (GPC)

The GPC chromatograms of NBBM-St copolymers are monodispers (Fig. 6). The average molecular weights (Mn and Mw) and polydispersities (PI) of the copolymers, given in Table 3, were determined from the GPC measurements. It is known that *PI* value for natural polymers is 1, and this value is close to 1 for living and controlled polymers. The copolymers we synthesized were synthetic and their *PI* values ranged from 1.51 to 1.26 in GPC measurements.

Thermal Properties

The glass transition temperatures of the NBBM-St copolymers have been determined from the DSC curves

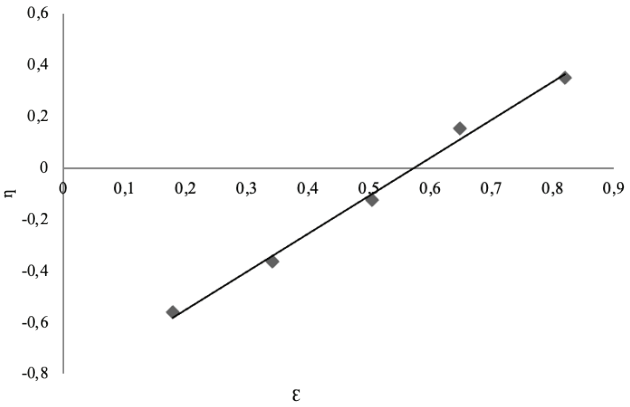

Figure 4. Kelen-Tüdös (K-T) plot for P(NBBM-co-St).

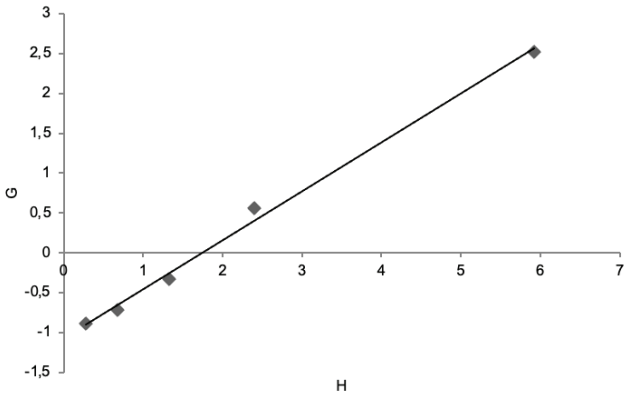

Figure 5. Finemann-Ross (F-R) plot for P(NBBM-co-St).

Table 2. K-T and F-R parameters for P(NBBM-co-St)

Sample	M_1	M_2	m_1	m_2	$F=M_1/M_2$	$f=m_1/m_2$	$G= F(f-1)/f$	$H= F^2/f$	$\eta = \frac{G}{(\alpha + H)}$	$\xi = \frac{H}{(\alpha + H)}$
Co-1	20	80	18	82	0.25	0.219	-0.888	0.284	-0.561	0.179
Co-2	35	65	30	70	0.539	0.428	-0.717	0.676	-0.363	0.342
Co-3	50	50	43	57	1	0.754	-0.325	1.325	-0.124	0.505
Co-4	65	35	59	41	1.858	1.439	0.566	2.396	0.153	0.648
Co-5	80	20	73	27	4	2.703	2.520	5.917	0.349	0.820

α=√Hmax.Hmin=0.817
M_1; Mole fraction of NBBM in the feed
M_2; Mole fraction of St in the feed
m_1; Mole fraction of NBBM in the copolymer
m_2; Mole fraction of St in the copolymer

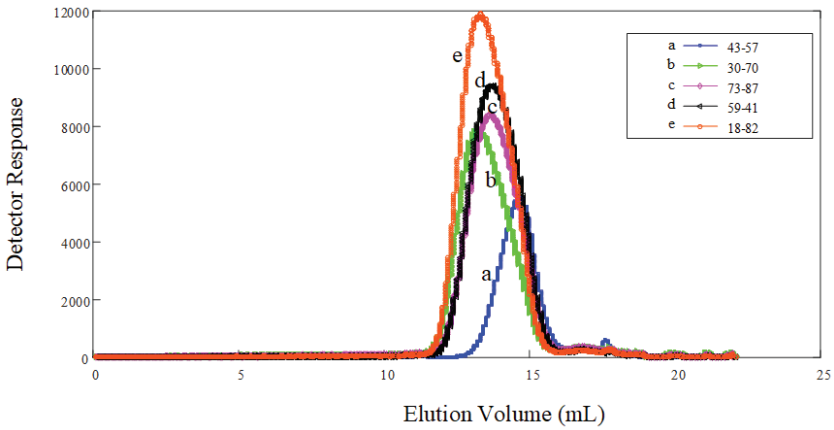

Figure 6. GPC curves of synthesized copolymers.

Table 3. Molecular weights and polydispersity index values of copolymers

Sample	Mn	Mw	HI
Co-1	8 677	13 144	1.51
Co-2	8 396	12 594	1.49
Co-3	6 695	9 979	1.49
Co-4	6 695	9 618	1.47
Co-5	6 515	4 852	1.26

(Fig. 7). The curves were recorded by heating the samples to 300 °C in a nitrogen atmosphere at a heating rate of 20 °C/min. Table 4 shows the glass transition temperatures (Tg) for the NBBM-St copolymers. The Tg value of styrene homopolymer is 105 °C [47] and that of P(NBBM) is 211 °C. The Tg values of the copolymers have been found in the range of the Tg values of the homopolymers. According to these results, an increase in Tg values from 144 °C to 184 °C was observed as the molar fraction of NBBM monomer in the copolymer increased. The cyclic benzofuran structure

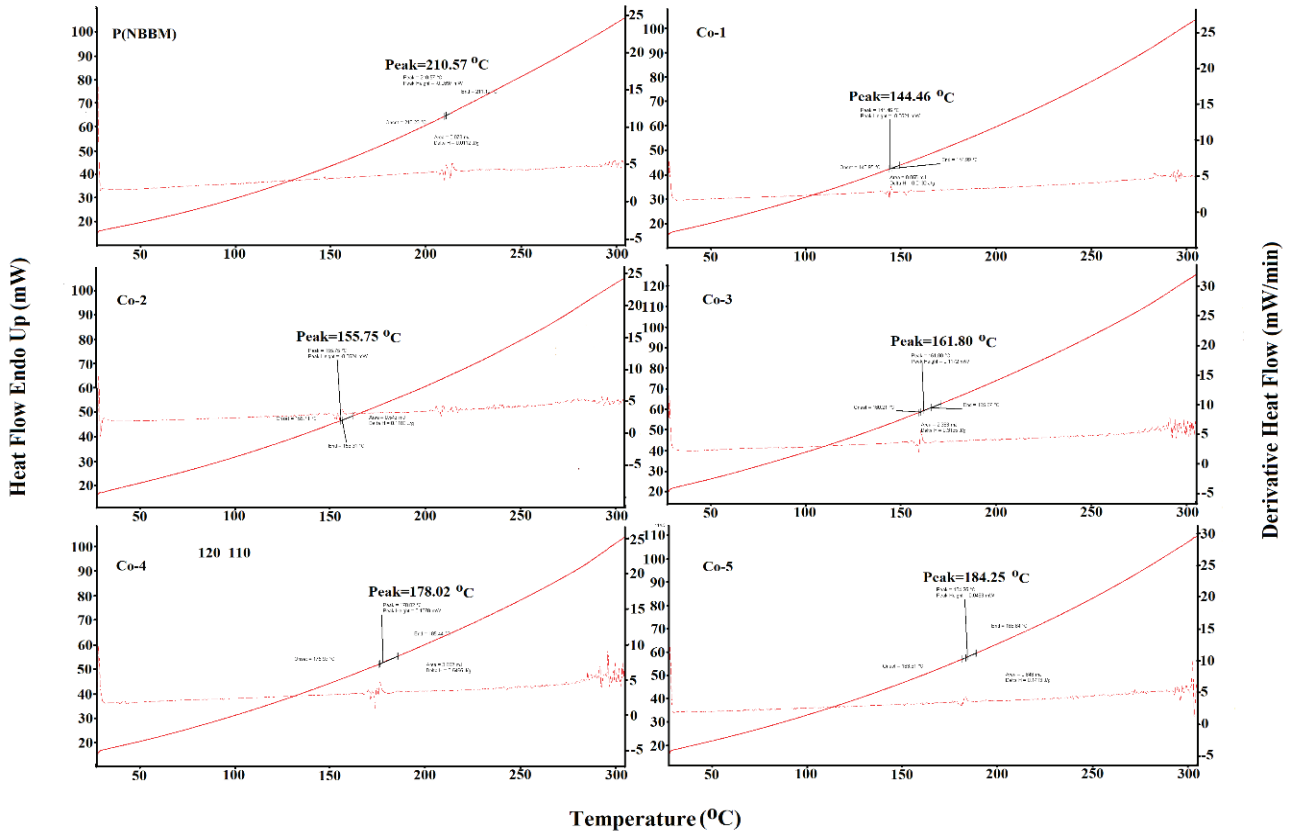

Figure 7. DSC curves of P(NBBM) and its copolymers.

resulting from the NBBM units in the polymer chain gives rigidity to the polymer chain. This restricts the mobility and flexibility of the chain, leading to an increase in the Tg value [47].

Table 4. Tg values of P(NBBM) and its copolymers

Sample	NBMM / St (mol)	Tg (°C)
P(St)	0 / 100	105
Co-1	18 / 82	144
Co-2	30 / 70	156
Co-3	43 / 57	162
Co-4	59 / 41	178
Co-5	73 / 27	184
P(NBBM)	100 / 0	211

The TGA curves of NBBM-St copolymers in a nitrogen atmosphere were recorded from room temperature up to 500 °C at a heating rate of 10 °C/min (Fig. 8). The mass losses of these curves at different temperatures are given in Table 5. When the TGA curves of the copolymers are examined, it was seen that the most heat-resistant polymer is polystyrene P(St), and the least heat-resistant polymer is the P(NBBM). The temperature at which 50% weight loss occurs in polymeric materials can be taken as a measure to determine the thermal stability of materials [48]. While these temperatures were determined as 423 °C for P(St) and 377 °C for P(NBBM), these values were found between their homopolymers for the copolymers studied. The thermal stability of copolymers with St units in their structure was seen to be higher than that of P(NBBM). This is due to the fact that P(St) is more

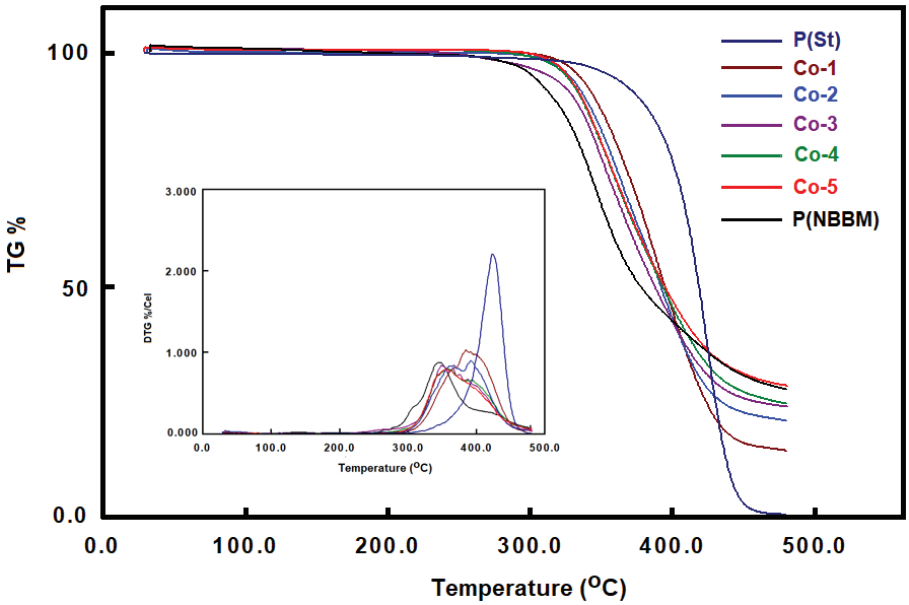

Figure 8. TGA and DTG curves of P(NBBM) and its copolymers.

Table 5. Decomposition temperatures of the copolymers at various compositions

Sample	m_1 [a]	$T_{int.}$ [b] (°C)	T_{max} [c] (°C)	%10 [d]	%30 [d]	%50 [d]	%70 [d]	%90 [d]
PNBBM	1.00	279	347	318	347	377	453	-
PSt	1.00	323	423	378	406	419	428	440
Co-1	0.18	301	385	347	374	394	416	-
Co-2	0.30	305	391	340	367	392	420	-
Co-3	0.43	308	349	332	360	388	427	-
Co-4	0.59	310	357	337	364	393	434	-
Co-5	0.73	293	355	338	364	395	458	-

[a] m_1 Weight fraction of NBBM in the copolymer
[b]: Initial decomposition temperature
[c] Temperature corresponding to maximal mass loss
[d] Temperatures at which the weight loss was respectively 10%, 30%, 50%, 70% and 90%

thermally stable. The initial degradation temperatures ($T_{int.}$) of P(St), P(NBBM) homopolymers were 323 °C and 279 °C, respectively, and $T_{int.}$ values of P(NBBM-co-St) copolymer systems were observed in the range of these two values. The maximum degradation temperatures (Tmax) of the polymer were obtained from derivative of mass loss (DTG) curves were given in Figure 8. Thermal decomposition of both homopolymers and copolymers were occurred in one step. Considering the data obtained from the TGA curves of the copolymers, St units in the copolymer systems studied compared to P(NBBM) caused an increase in Tmax. values.

Thermal Decomposition Kinetics

Thermogravimetric analysis (TGA) is based on mass loss measurement by heating the sample in an environment with inert gas flow at a constant heating rate. This method has an important role in elucidating the mechanism of physical and chemical events that occur during the degradation of polymers under the influence of heat. The rate of an isothermal decomposition reaction in the solid state can be described by the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (6)$$

In equation 6*;* α is the degree of conversion, T is the absolute temperature in Kelvin (K), A is the preliminary exponential factor (min^{-1}), E is the activation energy, (kj mol^{-1}), R is the gas constant, (8.314 $Jmol^{-1}K^{-1}$) and $f(\alpha)$ is a function that depends on the reaction mechanism.

The solid state reaction mechanism in non-isothermal TG experiments was determined from equation 7, which was obtained by rearranging by integrating both sides. In this equation, $g(\alpha)$ is the integral function of the transformation, αp is the degree of transformation at the peak temperature, and Tp depends on the peak temperature. The differential expression of g(a) for different solid state mechanisms is shown in Table 6 [49-51].

$$g(\alpha) = \int_0^{\alpha p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{Tp} e^{-E/RT} \mathrm{dT} \quad (7)$$

In this study, thermal stability and activation energy measurements of decomposition have been performed at different heating rates (10, 15, 20 and 25 °C min^{-1}) between room temperature and 500 °C under a nitrogen atmosphere. Kissinger [52], Flynn-Wall-Ozawa (FWO) [53, 54], Tang [55] methods were chosen, which are integral and isoconversional techniques that do not require any mechanism for activation energy calculation. In addition, calculations were made with the non-isoconversial method, the Van Krevelen method [56], and the type of degradation mechanism was determined. In the calculations carried out by these methods, the decomposition rate (α), temperature (T), and heating rate (β) do not change depending on the reaction model. The proposed reaction model remains the same throughout the reaction. The following are the final equations of the methods for calculating the activation energy:

$$\text{KISSINGER}: \ln\left(\frac{\beta}{Tmax2}\right) = \{ln\frac{AR}{E} + ln[\text{n}(1\text{-}\alpha\ \text{max})\text{n-}1]\} - \frac{E}{RTmax} \quad (8)$$

$$\text{FWO}: \log(\beta) = \log[\frac{AE}{g(\alpha)R}] - 2.315 - \frac{0.457E}{RT} \quad (9)$$

Table 6. Algebraic Expressions for g(α) for the most frequently used mechanisms of solid-state processes

Symbol	g(α)	Solid-state processes
Sigmoidal curves		
A2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami eq. (1))
A3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami eq. (2))
A4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami eq. (3))
Deceleration curves		
R1	α	Phase boundary controlled reaction (One-dimensional movement)
R2	$[1-(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (contraction area)
R3	$[1-(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (contraction volume)
D1	α^2	One-dimensional diffusion
D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D4	$(1-2/3\alpha)(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling-Brounshtein equation)
F1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F2	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F3	$1/(1-\alpha)^2$	Random nucleation with three nuclei on the individual particle

$$\text{TANG: } \ln\left(\frac{\beta}{T1.894661}\right) = \ln\left(\frac{AE}{Rg(\alpha)}\right) + 3.635041 - 1.894661\ln E - \frac{1.001450E}{RT} \quad (10)$$

$$\text{VAN KREVELEN: } \log g(\alpha) = \log \beta + \left(\frac{E}{RTr} + 1\right) + \log T \quad (11)$$

Where; R gas constant, A pre-exponential factor, g(α) differential conversion function, α degradation ratio (α=(-wi-wt)/(wi-wf)), E activation energy.

To evaluate the thermal degradation kinetics of the studied copolymer systems, the copolymer containing 30% NBMM and 70% styrene (Co-2) was chosen as a reference copolymer. The activation energy for P(NBBM) and copolymer (Co-2) was calculated from the slope of the ln(β/T^2max) versus 1000/Tmax plot according to the Kissinger method. The activation energy of P(NBBM) and Co-2 for this method were calculated as 146.66 and 158.52 kj mol^{-1}, respectively (Fig. 8a,b).

The activation energy was calculated from the 1000/T plot against log β at different % conversions using the Flynn-Wall-Ozawa method (Fig. 10a,b) and the results (Ea values) are given in Table 7. Using this method, the average activation energies for P(NBBM) and Co-2 were calculated as 150.7 and 160.89 kj mol^{-1}, respectively.

With the Tang method, activation energies were calculated by using Equation 10 and drawing $\ln(\beta/T^{1.894661})$ and 1/T graphs (Fig. 11a,b) for different conversion percentages, and the results are given in Table 8. With this method, the average activation energy of P(NBBM) and Co-2 were calculated as 142.33 and 151.326 kj mol^{-1}, respectively. The activation energy values obtained by Tang are very close to those calculated by the other two methods. In many studies, the activation energy of polystyrene has been reported as approximately 200 kj mol^{-1} [57, 58]. Activation energy values are higher for copolymers than for homopolymers. In other words, the added styrene units increased the activation energy. There are studies in the literature confirming this result.

These methods, which are in use by some authors for the control of models of the degradation mechanism, have also been used in our study [51, 59].

Using the Van Krevelen Equation (11), the activation energy for each g(α) function listed in Table 8 was obtained from a constant heating rate in the range log[$g(\alpha)$/T2] - log$T$.

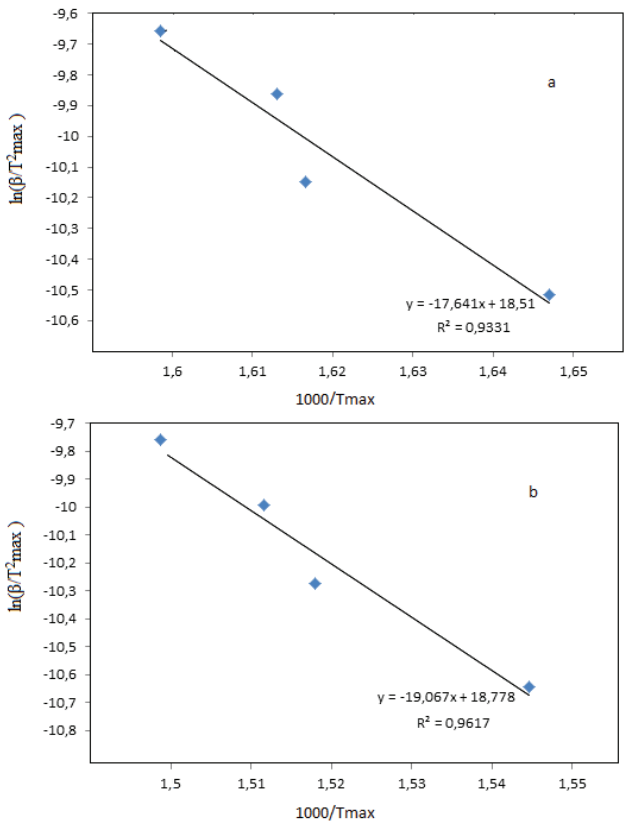

Figure 9. Kissinger method applied to the experimental data at different heating rates (a:P(NBBM), b: P(NBBM-co-St)).

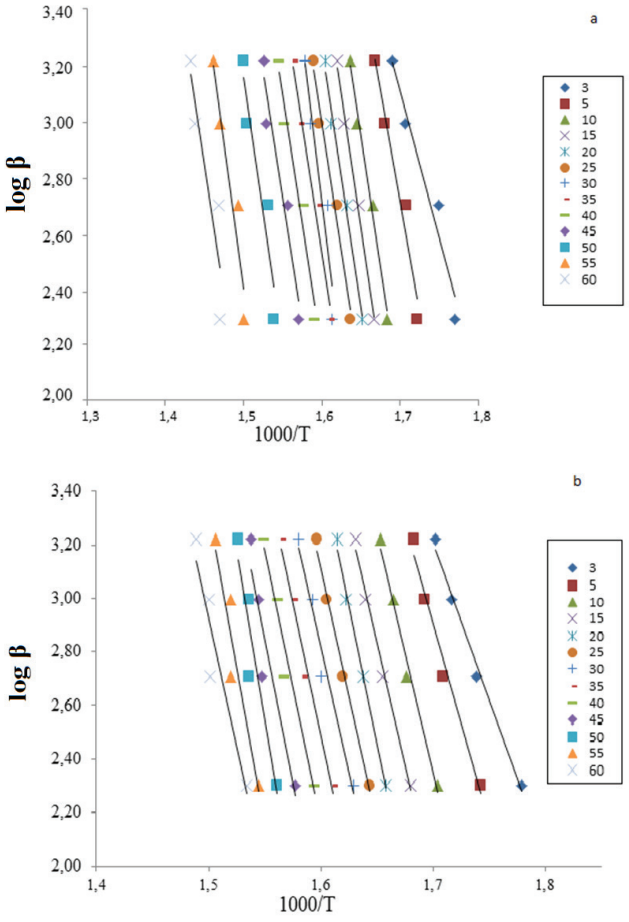

Figure 10. Flynn–Wall–Ozawa method applied to the experimental data (3–60%),(a:P(NBBM), b: P(NBBM-co-St)).

Table 7. Activation energy (Ea) values obtained with the Flynn– Wall–Ozawa method for P(NBBM) and P(NBBM-co-St)

	P(NBBM)		P(NBBM-co-St)	
α (%)	E (kj mol^{-1})	R2	E (kj mol^{-1})	R2
3	86,374	0,9511	96,73339	0,9905
5	130,8707	0,9599	124,2943	0,9811
10	156,378	0,9857	150,5167	0,9858
15	155,9041	0,993	153,2686	0,9933
20	153,0691	0,9851	174,4194	0,9932
25	153,9337	0,9756	157,2261	0,9915
30	185,9177	0,9127	155,5799	0,9747
35	152,1462	0,97	166,2052	0,975
40	152,7781	0,9603	169,431	0,9663
45	149,6271	0,9406	178,2688	0,8887
50	158,5729	0,8941	210,1447	0,8924
55	171,4014	0,9202	196,1356	0,9138
60	152,2543	0,8303	159,3461	0,887
AVERAGE	150,7		160,89	

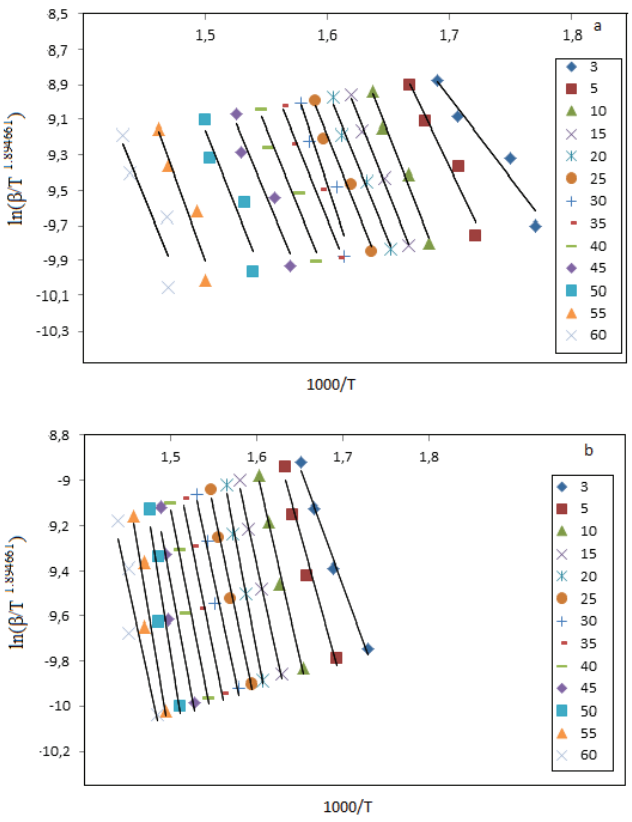

Figure 11. Tang method applied to the experimental data (3–60%),(a:P(NBBM), b: P(NBBM-co-St)).

The activation energies and the correlation between 3% and 60% conversion at different heating rates (10, 15, 20 and 25 °C/min) are shown in Tables 9 and 10. The activation energy values obtained are compatible with those computed by the Kissinger method. From these tables it can be seen that the P(NBBM) at an optimum heating rate of 10 °C/min occurs with the R3 mechanism (Ea: 143.29 kj mol^{-1} (phase boundary controlled reaction (contraction volume)). These values are close to the values obtained from FWO (150.7 kj mol^{-1}) and Kissinger (146.66 kj mol^{-1}) which are methods that do not depend on the mechanism. In addition to the calculation made for the Co-2 for termodegaraditon mechanism of copolymer, at an optimum heating rate of 10 °C/minute takes place with the R3 mechanism (Ea: 151.46 kj mol^{-1}). These values are close to the values obtained from FWO (160.89 kj mol^{-1}) and Kissinger (158.52 kj mol^{-1}) which are methods that do not depend on the mechanism. However, the strong correlation (0.976) is the correlation that corresponds to 10 °C/min for Co-2 at the preferred site with the value obtained by the Van Krevelen method.

CONCLUSION

Copolymer systems were successfully synthesized by free radical polymerization using N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide and styrene monomers in five different ratios. The structures of the copolymers were characterized by FT-IR and ^{1}H-NMR spectroscopic methods and found to be in accordance with the expected structure. Experimentally, the percentage compositions of P(N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide-co-Styrene) copolymers were calculated through ^{1}H-NMR spectra. The glass transition temperatures of the copolymers were determined from DSC curves. The glass transition temperature of P(NBMM) is 211 °C, which is a high temperature. It was observed that the glass transition

Table 8. Activation energy (Ea) values obtained with the Tang method for P(NBBM) and P(NBBM-co-St)

	P(NBBM)		P(NBBM-co-St)	
α (%)	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2
3	97,141	0,9885	97,141	0,9885
5	121,3995926	0,9534	114,6583993	0,9534
10	146,6707654	0,9279	140,6435409	0,9279
15	146,106232	0,9389	143,250357	0,9389
20	143,1839413	0,9497	164,2543212	0,9497
25	143,9560238	0,9613	146,977938	0,9613
30	175,7857467	0,9677	145,2428279	0,9677
35	142,0133646	0,9748	155,7365081	0,9748
40	142,5280863	0,9804	158,8663478	0,9804
45	139,2405093	0,983	167,59171	0,983
50	147,9824754	0,9809	199,3218094	0,9809
55	160,5350422	0,9792	185,2001718	0,9792
60	141,1914704	0,9794	148,3643657	0,9794
AVERAGE	142,133		151,326	

Table 9. Activation energy (Ea) values obtained for P(NBBM) with the Van Krevelen method for several solid-state processes at heating rates of 10, 15, 20 and 25 °C min^{-1}

Symbol	10 (°C min^{-1})		15 (°C min^{-1})		20 (°C min^{-1})		25 (°C min^{-1})	
	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2
A2	75,57	0,9381	78,89	0,9442	78,87	0,9199	80,99	0,906
A3	50,41	0,9381	52,61	0,9442	52,58	0,9199	53,99	0,906
A4	37,81	0,9381	39,45	0,9441	39,43	0,9199	40,49	0,906
R1	128,62	0,9106	134,36	0,9183	133,68	0,8866	137,04	0,8704
R2	139,47	0,9251	145,61	0,932	145,22	0,904	149,00	0,8889
R3	143,29	0,9296	149,58	0,9363	149,28	0,9095	153,21	08948
D1	257,26	0,9106	268,71	0,9183	267,37	0,8866	274,1	0,8704
D2	271,14	0,92	283,13	0,9272	282,14	0,8979	289,39	0,8824
D3	286,58	0,9296	299,16	0,8948	298,58	0,96095	306,53	0,8948
D4	59,93	0,9623	62,21	0,9582	63,78	0,9822	66,08	0,9848
F1	151,24	0,9381	157,83	0,9442	157,75	0,9199	161,98	0,9606
F2	48,96	0,9588	50,80	0,9541	52,14	0,9801	54,08	0,9839
F3	97,93	0,9588	101,62	0,9541	104,29	0,94801	108,11	0,9839

temperature increased from 144 °C to 184 °C depending on the increase in the molar ratio of N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide in the copolymer. This increase in the glass transition temperatures was due to the decrease in the free volume caused by the rather large benzofuran ring in the N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide monomer. When the TGA curves were examined, it was determined that the thermal stabilities of the copolymers of NBBM with St were higher than the thermal stability of P(NBBM). It is clear that the increase in the thermal stability of the copolymers is due to the styrene units in the polymer chain. Because polystyrene was found to have the highest thermal stability among the polymers studied. While the maximum degradation temperature of Poly(N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide) was 347 °C, the maximum degradation temperature of Polystyrene was 423 °C. A similar situation was seen in the maximum decomposition temperatures. It was determined that the maximum decomposition temperatures increased in copolymers with St units compared

Table 10. Activation energy (Ea) values obtained for P(NBBM-co-St) with the Van Krevelen method for several solid-state processes at heating rates of 10, 15, 20 and 25 °C min^{-1}

Symbol	10 (°C min^{-1})		15 (°C min^{-1})		20 (°C min^{-1})		25 (°C min^{-1})	
	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2	Ea (kJ mol^{-1})	R2
A2	79,79	0,9815	81,14	0,9684	89,12	0,9721	88,63	0,9647
A3	53,12	0,9815	54,11	0,9684	59,41	0,9721	59,09	0,9647
A4	39,82	0,9815	40,58	0,9680	44,56	0,9721	44,31	0,9647
R1	136,43	0,9626	138,41	0,9647	152,121	0,9505	151,09	0,9406
R2	147,55	0,973	149,9	0,9575	164,66	0,9621	163,66	0,9536
R3	151,46	0,976	153,94	0,9614	168,08	0,9656	169,08	0,9575
D1	272,86	0,9626	276,82	0,9447	304,23	0,9502	302,20	0,9407
D2	286,13	0,9695	291,55	0,9531	320,33	0,958	318,31	0,9492
D3	302,93	0,976	307,89	0,9614	338,16	0,9656	336,17	0,9575
D4	61,35	0,9494	63,45	0,9664	69,28	0,9593	69,37	0,9652
F1	159,59	0,9815	162,34	0,9684	178,25	0,9721	177,35	0,9647
F2	50	0,9397	51,70	0,9577	56,426	0,9499	56,52	0,9563
F3	100,01	0,9397	103,4	0,9577	112,85	0,9499	113,04	0,9563

to P(NBBM). The reactivity values for the P(N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide-co-Styrene) system are calculated for Kelen-Tüdõs as; r1:0.62, r2: 1.09 and for Finemann-Ross as; r1:0.61, r2: 1.07. r2 value of styrene monomer being larger than r1 value of N-[2-(4-brombenzoyl)-benzofuran-3-yl]-2-methacrylamide monomer means that both monomers prefer styrene radicals. This indicates that there is a tendency towards random copolymerization where the styrene units in the copolymer are more [60, 61]. For the activation energy calculation, the well-known equivalent Kissinger, Flynn-Wall-Ozawa, Tang and Van Krevelen integral techniques were selected. In many studies, the activation energy of polystyrene has been reported to be approximately 200 kj mol^{-1} [57, 58]. The presence of styrene units in the copolymer structure synthesized in the study caused an increase in activation energy values compared to the homopolymer. This increase is an expected result when similar studies are examined in the literature. Calculation results for the analysis of the thermodegradation mechanism showed that the copolymer follows the slowdown (R3) type solid state thermodegradation mechanism. The R3 mechanism calculated by Van Krevelen is compatible with the results obtained by Kissinger and Flynn-Wall-Ozawa methods at heating rates of 10 and 15 °C min^{-1}.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

STATEMENT ON THE USE OF ARTIFICIAL INTELLIGENCE

Artificial intelligence was not used in the preparation of the article.

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