Synthesis, Characterization and Thermal Decomposition Kinetics of a Novel Benzofuran Ketoxime Derived Polymer

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Abstract

A novel benzofuran ketoxime derived polymer, poly(benzofuran-2-yl-methylketoxime-O-methacrylate) [poly(BMK-MA], was firstly synthesized by free radical polymerization method. Its thermal degradation studies were performed by thermogravimetric analysis (TGA) in order to determine the actual reaction mechanisms of the decomposition process. The activation energy of the solid-state process was determined by using Flynn-Wall-Ozawa method, which resulted to be 235.9 kJ/mol. The activation energies of different mechanism models were determined by Coats-Redfern, Madhusudanan and Van Krevelen kinetic methods. Compared with the Ozawa method, the actual reaction mechanism obeyed deceleration type, phase boundary controlled reaction (R_1).

Keywrds: Synthesis, characterization, benzofuran, ketoxime, activation energy, thermogravimetric analysis.

1. Introduction

Heterocyclic polymers are useful materials due to their scientific and technologic importance such as biological, medicinal, chemical, physical and mechanical potentials.[1–9] These properties shift depend on the heterocyclic group at the side chain of polymer. A class of very important heterocyclic compounds is benzofurans and their derivatives existing widely in natural products and unnatural compounds with physiological, pharmacological, toxic and optical potentials. Thus, much attention has been paid to the development of these compounds.[10–12] Some different benzofuran derivative polymers have been successfully synthesized in recent years.[13–16] In one of our previous studies, we synthesized and characterized a polymer containing benzofuran side group, poly(2-(5-bromo benzofuran-2-yl)-2-oxoethyl methacrylate), and we also investigated its thermal degradation kinetics.[13] In another study, Yonezumi and co-workers[14] studied the living cationic polymerization of benzofuran and some dihydrofurans using base-stabilized initiating systems with various Lewis acids. Xu and coworkers[15] reported the electro-syntheses of poly(2,3-benzofuran) films in boron trifluoride diethyl etherate

containing poly(ethylene glycol) oligomers and some properties. Banihashemi and Atabaki[16] reported the synthesis and characterization of thermally stable polybenzimidazoles derived benzofuran group. Pokladko and coworkers[17] also studied on the synthesis and polymerization of novel methacrylates with benzofuranyl pendant groups for photovoltaic applications. Erol et al.[18] reported the synthesis, characterization, monomer reactivity ratios and biological activity of new methacrylate copolymers based on the benzofuran ring.

Besides, thermogravimetric analysis (TGA) is widely used to investigate the thermal decomposition of polymeric materials.[19–21] The TGA technique determines the amount and rate of change in the mass of a polymer sample as a function of temperature or time in a controlled atmosphere. The TGA measurements are used primarily to determine the thermal stabilities of polymers as well as their compositional properties. Its measurements provide valuable information that can be used for selection of polymeric materials to predict product performance, improve product quality and certain end-use applications. Thermal decomposition stabilities of methacrylate polymers change depending on cyclic groups on the polymer chains, which lead to increasing thermal

stability.[22] In the literature, it seems that there has not been enough work on the investigation of thermal degradation kinetics of methacrylate polymers with benzofuran and ketoxime derivatives so far. Therefore, the present study aims to synthesis, characterization and thermal decomposition process of poly(benzofuran-2-yl-methylketoxime-O-methacrylate), which is a new methacrylate polymer containing both benzofuran and ketoxime side groups.

2. Theory

The application of dynamic TGA methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer degradation. The kinetics of polymer degradations is usually described by the basic kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $f(\alpha)$ and $k(T)$ are functions of conversion and temperature, respectively. $f(\alpha)$ depends on the particular decomposition mechanism and $k(T)$, the temperature dependence of the rate of weight loss, t is time and α represents the fraction of conversion. The value of α is experimentally determined by TGA as a relative mass loss. In many cases, the temperature dependence of $k(T)$ can be defined by the Arrhenius equation, whose substitution into *Eq. 1* yields:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}$$

where E is the activation energy, A is the preexponential factor, T is the absolute temperature, and R is the universal gas constant. The last equation is integrated with the initial condition of $\alpha = 0$ at $T = 0$ to any condition of $\alpha = \alpha_p$ at $T = T_p$ to obtain the following expression:

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} e^{-\frac{E}{RT}} \, dT \tag{3}$$

Different expressions of integral function of conversion for solid-state reaction mechanisms may be seen in literature.[13] In order to estimate the thermal degradation mechanism, these functions can be applied to thermogravimetry.[23]

2. 1. Flynn-Wall-Ozawa Method

Flynn-Wall-Ozawa method[24,25] is one of the integral methods that can determine the activation energy without

a knowledge of reaction order and differential data of TGA. It is used to determine the activation energy for given values of conversion. Flynn-Wall-Ozawa method uses the following equation:

$$\log \beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457\,E}{RT} \tag{4}$$

where β is the heating rate. The activation energy, E, is calculated from the slope of a plot of $\log \beta$ versus $(1000/T)$, which is equal to $(-E/R)$.

2. 2. Coats-Redfern Method

Coats–Redfern method[26] is also an integral method, and it involves the thermal degradation mechanism. Using an asymptotic approximation for resolution of *Eq. 3*, the following equation can be obtained:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \tag{5}$$

According to the different degradation processes, E and A can be determined from a plot of $\ln[g(\alpha)/T^2]$ versus 1000/T.

2. 3. Madhusudanan Method

As well as the Coats-Redfern method, the most probable mechanism may also be determined providing that *Eq. 3* is solved in different ways. Thus, the accuracy of calculation may be increased. One of these solutions is suggested by Madhusudanan et al.[27] as represented with a kinetic *Eq. 6*:

$$\ln\left[\frac{g(\alpha)}{T^{1.921503}}\right] = \left[\ln\frac{AE}{\beta R} + 3.772050 - 1.921503 \ln E\right] - 1.000955716 \frac{E}{RT} \tag{6}$$

A plot of $\ln[g(\alpha)/T^{1.921503}]$ versus $1000/T$ and fitting to a straight line would give a slope of $-1.000955716E/R$.

2. 4. Van Krevelen Method

Van Krevelen[28] method was also used to verify the solid state thermodegradation mechanism of polymer. *Eq. 7* to determine the activation energies and correlations by Van Krevelen method is as below:

$$\log g(\alpha) = \log B + \left(\frac{E}{RT_r} + 1\right) \log T \tag{7}$$

where T_r is a reference temperature. It was taken as the

maximum temperature rate determined from derivative thermogravimetry in this work. The activation energies of every *g(α)* function were calculated from the slope of lines of log *g(α)* versus log *T* plots.

3. Experimental

3. 1. Instrumental Techniques

Infrared spectra were recorded on a Perkin Elmer Spectrum 100. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Avence II 400 MHz NMR spectrometer at room temperature using $CDCl_3$ as a solvent and TMS as an internal standard. Thermogravimetric analysis was performed using a Shimadzu TG-50 system. The thermal stability measurements were carried out from ambient temperature to 400 °C with different heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min. All the experiments were carried out in a nitrogen atmosphere. The optimum gas flow rate was 25 ml/min.

3. 2. Materials

All chemicals and solvents used in this study were analytical grade. Calicylaldehiyde, chloroacetone, hydroxylamine hydrochloride, pyridine, methacryloyl chloride, anhydrous magnesium sulfate and potassium carbonate, tetrahydrofuran, 1,4-dioxane, acetone were received from Merck.

3. 3. Synthesis of Benzofuran-2-yl-methylketone Compound (1)

1-Chloroacetone (9.253 gr, 7.96 mL, 0.1 mol) in acetone (15 mL) was successively added to a mixture of calicylaldehyde (12.82 gr, 10.96 mL, 0.105 mol) and anhydrous K_2CO_3 (20.7 gr, 0.15 mol). The reaction mixture was stirred and refluxed for 70 minutes. Then, the reaction mixture was cooled to room temperature, precipitated in water, filtered and washed with water by several times, respectively. The compound (1) was crystallized from ethanol (yield: 62%).

^{1}H-NMR (CDCl$_3$, δppm): 7.23–7.68 (aromatic ring protons and furan =CH proton), 2.67 (3H, methyl protons).

^{13}C-NMR (CDCl$_3$, δppm): 190.53 (ketone carbonyl carbon), 157.64 (ipso carbon in aromatic ring next to furan oxygen), 154.64 (ipso carbon in furan ring), 130.22–114.40 (aromatic ring carbons and =CH carbon in furan ring), 28.40 (methyl carbon).

FTIR (cm^{-1}, the most characteristic bands): 3130–3078 cm^{-1} (aromatic C-H stretching), 2980–2935 cm^{-1} (aliphatic C–H stretching),1669 cm^{-1} (sharp, ketone C=O stretching), 1605 cm^{-1} (C=C stretching in aromatic ring), 1076 cm^{-1} (C-O-C stretching).

3. 4. Synthesis of Benzofuran-2-yl-methylketoxime Compound (2)

To a 250 mL round-bottom flask, Benzofuran-2-yl-methylketone (9.00 gr, 0.056 mol), hydroxylamine hydrochloride (4.69 gr, 0.067 mol) and 75 mL of pyridine were respectively added, and the solution was refluxed about 40 minutes. After this time, the mixture was cooled, precipitated in water, filtered, washed with excessive water, and dried, respectively (yield: 95%).

^{1}H-NMR (CDCl$_3$, δppm): 7.29–8.26 (aromatic ring protons and furan =CH proton), 3.38 (methyl protons).

^{13}C-NMR (CDCl$_3$, δppm): 171.18 (C=N carbon), 155.72 (ipso carbon in aromatic ring next to furan oxygen), 151.32 (ipso carbon in furan ring), 127.30–114.05 (aromatic ring carbons and =CH carbon in furan ring), 13.40 (methyl carbon).

FTIR (cm^{-1}, the most characteristic bands): 3223 (O-H stretching), 3129–3075 cm^{-1} (aromatic C-H stretching), 2980–2933 cm^{-1} (aliphatic C-H stretching), 1626 (C=N stretching), 1603 cm^{-1} (C=C stretching in aromatic ring).

3. 5. Synthesis of Benzofuran-2-yl-methylketoxime-O-methacrylate Monomer (3)

The solution of methacryloyl chloride (4.942 gr, 4.58 mL, 0.0473 mol) in THF was drop wised to the solution of benzofuran-2-yl-methylketoxime (8.20 gr, 0.0468 mol) in THF (65 mL) at 0–5 °C. Then, the mixture was stirred at the room temperature for 3 hours. At the end of the reaction, THF was evaporated and the organic residue was dissolved in chloroform. Then, it was extracted with dilute NaHCO$_3$ solution several times. The organic phases were collected and dried over anhydrous MgSO$_4$. After the chloroform had evaporated, benzofuran-2-yl-methylketoxime-O-methacrylate monomer (BMKMA) was obtained at the yield of 80%. The synthesis of monomer was shown in Scheme 1.

3. 6. Free Radical Polymerization of BMKMA Monomer

Appropriate amounts of the BMKMA monomer (1.5 g), 1,4-dioxane (4.5 mL) and benzoyl peroxide (0.003 g, 0.2% of the monomer) were placed in a polymerization tube and purged with Ar for 10 min. After the tube had been kept at 65 °C for 25 h, the contents were poured into a large amount of methanol. The polymer, poly(BMK-MA), was purified by reprecipitation with methanol several times, and finally dried in a vacuum.

4. Results and Discussion

The molecular structure of benzofuran-2-yl-methylketoxime-O-methacrylate, BMKMA, was cha-
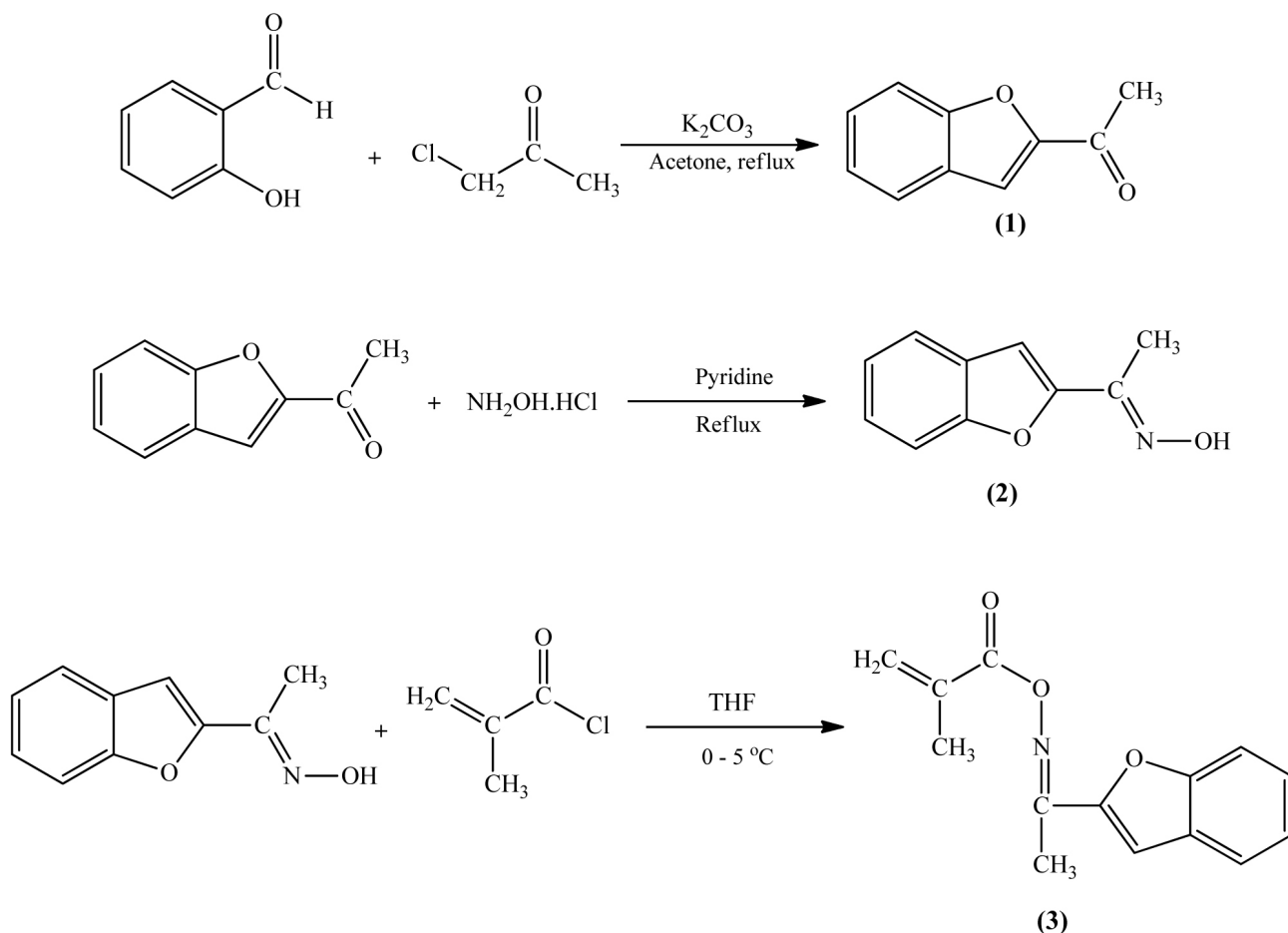
Scheme 1. Synthesis of BMKMA monomer

racterized by FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. Fig. 1a shows the FTIR spectrum of BMKMA monomer, in which the absorption peaks at 3130–3076 cm^{-1} are characteristic for aromatic C-H stretching. The peaks at 2981–2930 cm^{-1} are due to C-H stretching of aliphatic methylene and methyl groups. The strong absorbance at 1737 cm^{-1} is attributed to a vibration characteristic of methacrylic ester carbonyl. BMKMA monomer was especially characterized from the aliphatic and aromatic C=C stretching bands observed at 1634 cm^{-1} and 1600 cm^{-1}, respectively. The absorption at 1600 cm^{-1} is also attributed to C=N stretching. As it can be seen in Fig. 1a, the presence of stretching of both carbonyl and C=C bands proves the formation of BMKMA monomer.

Fig. 2a shows the ^{1}H-NMR spectrum of BMKMA monomer. The multiplet resonance absorptions between 7.57 ppm and 7.17 ppm are characteristic for aromatic protons on the benzene group and furan =CH proton. The singlets at 6.13 ppm and 5.53 ppm are due to the protons in vinyl group. The resonances at 2.37 ppm and 1.97 ppm are attributed to methyl protons next to vinyl group and furan ring, respectively.

The ^{13}C-NMR spectrum of BMKMA monomer which shown in Fig. 3 is also compatible with its structure, where the signal at 163.89 ppm corresponds to metha-
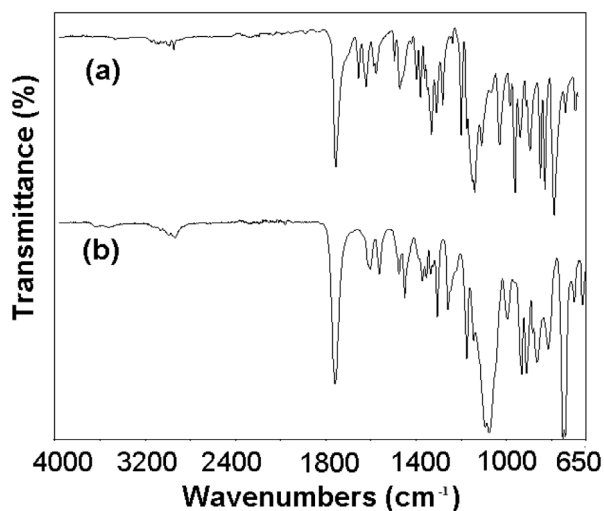

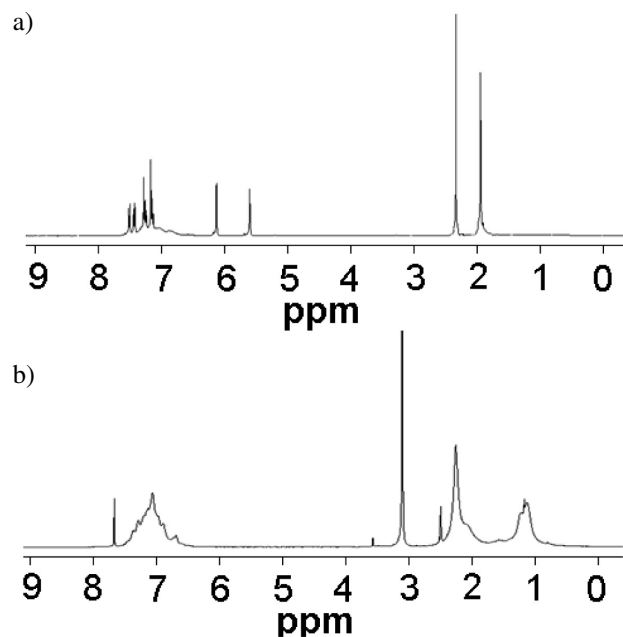**Fig. 1.** FTIR spectra of a) BMKMA monomer, b) poly(BMKMA) homopolymer.

a)

b)

Fig. 2. ¹H-NMR spectra of a) BMKMA monomer, b) poly(BMK-MA) homopolymer.

cm⁻¹ are due to aromatic and aliphatic C-H stretching vibrations, respectively. The absorption peak for ester carbonyl is observed at the vibration frequency 1758 cm⁻¹. The band at 1611 cm⁻¹ is attributed to C=N stretching. In the frequency region of C=C stretching, only the absorption band at 1602 cm⁻¹ for aromatic C=C stretching was observed whereas the aliphatic C=C stretching wasn't. The disappearance of aliphatic C=C stretching is one of the main evidences that the homopolymerization of BMKMA is accomplished by free radical polymerization method. The band at 1071 cm⁻¹ is also attributable to symmetric C-O-C stretching vibration. On the ¹H-NMR spectrum of the poly(BMKMA) shown in Fig. 2b, the resonances between 7.69 ppm and 6.92 ppm are assigned to =CH protons on the benzofuran ring. The backbone methylene protons are observed at the resonances between 2.51–2.16 ppm while the methyl protons are between 1.24–1.14 ppm. The another main evidence that the homopolymerization is accomplished is disappearance of two singlet resonances at 6.13 ppm and 5.53 ppm assigned to vinylic protons of BMKMA monomer, and is also appearance of new broad signals at chemical shifting of 2.51–2.16 ppm and 1.24–1.14 ppm, which are due to methylene and methyl protons on the homopolymer backbone.

crylic ester carbonyl carbon. The signal at 155.43 ppm is attributed C=N carbon. The signals at 154.84 ppm and 149.77 ppm correspond to ipso carbon in aromatic ring next to furan oxygen and ipso carbon in furan ring. The other signals of benzofuran group observed between 134.88 ppm and 111.85 ppm. The signals at 127.40 ppm and 121.81 ppm, which are due to vinylic ipso carbon next to ester carbonyl and vinylic methylene carbon (=CH₂), respectively. The resonances for methyl carbons next to vinylic and furan groups are observed at 18.35 ppm and 13.32 ppm, respectively.

The spectral characterization of poly(BMKMA) was also performed with FTIR and ¹H-NMR methods. The FTIR spectrum of poly(BMKMA) was illustrated in Fig. 1b. The most characteristic absorption bands for polymer are as follows: The bands at 3131–3076 and 2983–2930
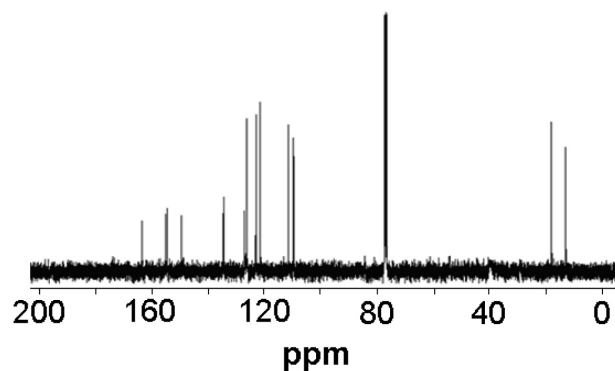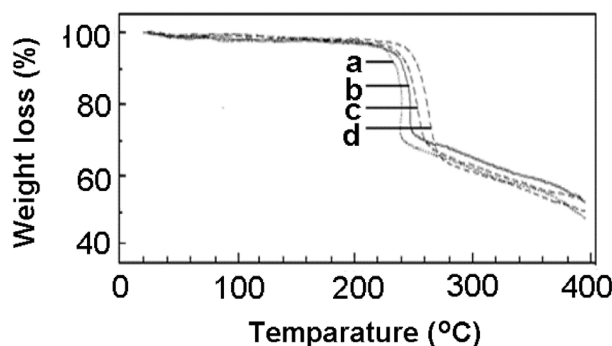

Fig. 4. TGA curves of poly(BMKMA) homopolymer at different heating rates: a) 5 °C/min, b) 10 °C/min, c) 15 °C/min, d) 20 °C/min

Kinetic parameters and thermal characteristics of poly(BMKMA) samples were determined by thermogravimetric analysis (TGA) under conditions of non-isothermal heating. The dynamic experiments of degradation were performed increasing the temperature up to 400 °C at heating rates of 5, 10, 15 and 20 °C/min in an inert atmosphere of argon. The weight loss curves showed that decomposition of poly(BMKMA) took place in one stage in the 30% weight loss area attributed to the formation of volatile hydrocarbons in the first decomposition temperature range up to approximately 270 °C.[13] TGA curves and peak temperatures shift to higher values with an increase in the heating rate. This alteration has been recorded in the

Fig. 3. ¹³C-NMR spectrum of BMKMA monomer.

case of thermal degradation of different types of polymers.[19,29,30] From thermogravimetric data, the fractional decomposition (α) values were also calculated for each heating rate, and those values continuously increased as the temperature was increased. Fig. 4 illustrates the alteration of the weight loss curves of poly(BMKMA) samples in relation to heating rate from room temperature to 400 °C. In this thermogram, there was a lateral shift to higher temperatures for initial decomposition temperatures for all samples as the heating rates are increased. The initial
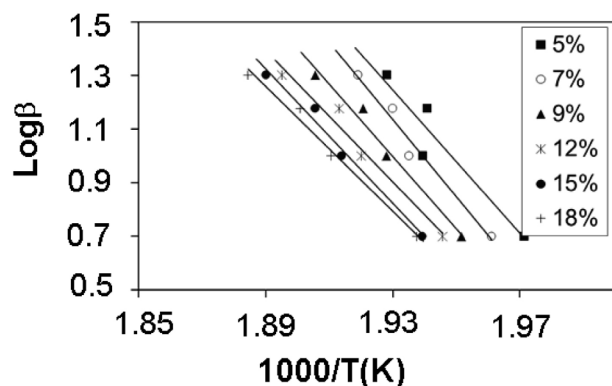
decomposition temperatures at heating rates of 5, 10, 15 and 20 °C/min were determined as 203, 210, 213 and 215 °C, respectively.

In the present study, we determined the decomposition activation energies and the solid state thermodegradation mechanism of polymer for only the first decomposition range that corresponds to initial decomposition range at different heating rates. For this purpose, we used different integral and differential methods to evaluate the kinetic information of poly(BMKMA). The Flynn-Wall-Ozawa method[24,25] is one of the integral methods to determine the activation energy without knowledge of reaction order. It is used to determine the activation energy for given values of conversion using *Eq. 4*. Fig. 5 shows the plots of log β against $1000/T$ where the fitting straight lines are nearly parallel. This is a important information that the applicability of Flynn-Wall-Ozawa method to thermal degradation of poly(BMKMA) polymer at applied conversions may be valid. The activation energies estimated at different conversions are listed in Table 1. The mean activation energy value in Table 1 was found to be 235.9 kJ/mol.

Coats-Redfern method[26] was used in order to determine the most probable thermal degradation mechanism of poly(BMKMA). If the correct $g(\alpha)$ is used, a plot of $\ln[g(\alpha)/T^2]$ against $1000/T$ will give a straight line, and the values of the apparent activation energy E can easily be determined from its slope. In the case of polymers, the degradation process usually continues as either a sigmoidal (nucleation and growth) or a deceleration (phase boundary reaction or diffusion) function. The apparent activation energies and correlations are tabulated in Tables (2 to 5) for heating rates of 5, 10, 15 and 20 °C/min, respectively. In this study, we have compared the apparent activation energies obtained with the Coats-Redfern method to the method of Flynn-Wall-Ozawa to determine the thermal degradation mechanism of poly(BMKMA) polymer. The reason of chosen the Flynn-Wall-Ozawa method for

Fig. 5. Typical plots of Logβ versus ($1000/T$) for poly(BMKMA)

Table 1. Activation energies obtained using the Flyn-Wall-Ozawa method.

α (%)	E (kJ/mol)	r
5	243.4	0.897
7	262.3	0.973
9	245.9	0.980
12	222.9	0.970
15	229.0	0.983
18	212.1	0.986
Mean	235.9	

Table 2. Activation energies obtained for several solid state processes at a heating rate of 5 °C/min

Mechanism	Coats-Redfern Method		Madhusudanan Method		Van Krevelen Method	
	E (kJ/mol)	r	E (kJ/mol)	E (kJ/mol)	E (kJ/mol)	r
A_2	140.9	0.986	141.1	0.986	146.9	0.988
A_3	91.1	0.985	91.3	0.985	96.5	0.988
A_4	66.2	0.984	66.5	0.984	71.3	0.987
R_1	277.5	0.989	277.7	0.989	285.4	0.990
R_2	283.8	0.987	283.9	0.987	291.7	0.989
R_3	285.9	0.987	286.1	0.987	293.8	0.988
D_1	563.7	0.989	563.5	0.989	574.9	0.990
D_2	571.9	0.988	571.8	0.988	583.1	0.989
D_3	580.4	0.987	580.2	0.987	591.7	0.988
D_4	574.8	0.988	574.5	0.988	586.1	0.989
F_1	290.2	0.986	290.3	0.986	298.2	0.987
F_2	17.2	0.751	17.6	0.758	21.8	0.872
F_3	43.0	0.824	43.3	0.826	47.8	0.872

comparison is due to the independent from a particular mechanism. Analyzing of Table 4, it should be noted for all the samples studied that the activation energy value of polymer corresponding to a mechanism of R_1 was 236.9 kJ/mol at heating rate 15 °C/min. This value is very close 235.9 kJ/mol by Flynn-Wall-Ozawa method. These results strongly suggest that the thermal degradation mechanism of poly(BMKMA) is a deceleration type, phase boundary controlled reaction (R_1).

As well as the Coats-Redfern method, the most probable mechanism may also be determined providing that *Eq. 3* is solved in different ways. Thus, the accuracy of calculation may be increased. Two methods, which are Madhusudanan method[27] and Van Krevelen[28] method, were used to verify the solid state thermodegradation mechanism of polymer. The decomposition activation energies and correlations for thermal degradation of poly(BMKMA) polymer at different heating rates are also summarized in Tables (2 to 5). When the activation energies and correlation coefficients of linear regression were calcula-

ted according to the Madhusudanan method (*Eq. 6*) using integral functions, the activation energy value was obtained at the heating rate of 15 °C/min corresponding to a deceleration R_1 mechanism in Table 4, which was found to be 237.0 kJ/mol with the best correlation (0.994). These values are in good agreement with the value obtained with the Flynn-Wall-Ozawa method.

To corroborate that poly(BMKMA) polymer follows phase boundary controlled reaction of deceleration type (R_1) of thermal decomposition mechanism, we have also used the Van Krevelen method. The activation energies of every $g(\alpha)$ function were calculated from the slope of lines of log $g(\alpha)$ versus log T plots using *Eq. 7*. The activation energies and correlations at the conversion range are given in Tables (2 to 5) for different heating rates. The best agreement was determined for R_n reaction mechanisms in all heating rates. In particular, the activation energy calculated for R_1 process given in Table 4 at a heating rate of 15 °C/min is 244.6 kJ/mol, which is in good agreement with the Flynn-Wall-Ozawa method that of 235. 9 kJ/mol.

Table 3. Activation energies obtained for several solid state processes at a heating rate of 10 °C/min

Mechanism	Coats-Redfern Method		Madhusudanan Method		Van Krevelen Method	
	E (kJ/mol)	r	E (kJ/mol)	E (kJ/mol)	E (kJ/mol)	r
A_2	147.6	0.977	147.8	0.978	153.8	0.981
A_3	95.5	0.976	95.8	0.976	101.1	0.981
A_4	69.5	0.975	69.8	0.975	74.7	0.981
R_1	290.5	0.981	290.6	0.981	298.5	0.982
R_2	297.1	0.980	297.2	0.980	305.2	0.982
R_3	299.3	0.979	299.4	0.979	307.4	0.981
D_1	589.6	0.981	589.5	0.981	601.3	0.982
D_2	598.3	0.980	598.1	0.980	610.0	0.982
D_3	607.2	0.980	607.1	0.980	619.1	0.981
D_4	601.3	0.980	601.1	0.980	613.0	0.982
F_1	303.8	0.979	303.8	0.979	311.9	0.981
F_2	18.4	0.763	18.8	0.770	23.1	0.876
F_3	45.5	0.830	45.8	0.832	50.5	0.876

Table 4. Activation energies obtained for several solid state processes at a heating rate of 15 °C/min

Mechanism	Coats-Redfern Method		Madhusudanan Method		Van Krevelen Method	
	E (kJ/mol)	r	E (kJ/mol)	E (kJ/mol)	E (kJ/mol)	r
A_2	119.6	0.992	119.8	0.992	125.7	0.993
A_3	76.9	0.991	77.1	0.991	82.3	0.993
A_4	55.5	0.991	55.8	0.991	60.7	0.993
R_1	236.9	0.994	237.0	0.994	244.6	0.995
R_2	242.3	0.993	242.4	0.993	250.1	0.994
R_3	244.1	0.993	244.2	0.993	251.9	0.994
D_1	482.3	0.994	482.3	0.994	493.4	0.995
D_2	489.4	0.994	489.4	0.994	500.8	0.995
D_3	496.8	0.993	496.7	0.993	508.3	0.994
D_4	491.9	0.993	491.8	0.993	503.0	0.994
F_1	247.8	0.992	247.9	0.992	255.7	0.993
F_2	13.6	0.750	13.9	0.759	18.2	0.890
F_3	35.9	0.838	36.2	0.840	40.8	0.890

Table 5. Activation energies obtained for several solid state processes at a heating rate of 20 °C/min

Mechanism	Coats-Redfern Method		Madhusudanan Method		Van Krevelen Method	
	E (kJ/mol)	r	E (kJ/mol)	E (kJ/mol)	E (kJ/mol)	r
A_2	89.9	0.959	90.1	0.959	97.7	0.967
A_3	57.0	0.955	57.3	0.956	63.7	0.967
A_4	40.6	0.951	40.9	0.951	46.6	0.967
R_1	180.2	0.966	180.3	0.966	191.5	0.971
R_2	184.2	0.964	182.9	0.964	195.7	0.969
R_3	185.8	0.964	185.8	0.964	197.1	0.969
D_1	369.0	0.968	369.0	0.968	387.4	0.971
D_2	374.4	0.966	374.3	0.967	393.0	0.970
D_3	379.9	0.965	379.9	0.965	398.7	0.969
D_4	376.2	0.966	376.2	0.966	394.9	0.969
F_1	188.3	0.962	188.5	0.963	200.0	0.827
F_2	8.0	0.522	8.4	0.542	12.9	0.827
F_3	24.7	0.719	25.0	0.725	30.2	0.827

5. Conclusions

Thermal degradation mechanism and activation energies for initial decomposition process under non-isothermal conditions of a novel benzofuran ketoxime polymer, poly(benzofuran-2-yl-methylketoxime-O-methacrylate), were determined by integral approximation methods from the thermogravimetric study. The activation energy of the solid-state process was determined using Flynn-Wall-Ozawa method, which resulted to be 235.9 kJ/mol. The study of kinetic equations showed that the reaction mechanism of the decomposition process in the conversion range studied progressed with R_1 mechanism, phase boundary controlled (one-dimensional movement) of deceleration type of solid state mechanism. The best conformity in all integral methods and heating rates to that of the Flynn-Wall-Ozawa model was obtained in the case of the Coats-Redfern method ($E = 236.9$ kJ/mol) at a heating rate of 15 °C/min.

6. Acknowledgment

7. References

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Povzetek

S prostoradikalsko polimerizacijo smo sintetizirali poli(benzofuran-2-il-metilketoksime-O-metakrilat) [poly(BMK-MA]. Mehanizem procesa razpada tega polimera smo proučevali s termogravimetrično analizo (TGA). Z metodo Flynn-Wall-Ozawa smo v trdnem določili aktivacijsko energijo 235.9 kJ/mol. Vrednosti aktivacijskih energij smo določili tudi s kinetičnimi modeli Coats-Redferna, Madhusudanana in van Krevelena ter s primerjavo vrednosti sklepali, da je dejanski mehanizem razpada reakcija, kontrolirana s procesi na fazni meji.