RESEARCH ARTICLE

Thermal decomposition kinetics of a coumarin based copolymer: poly(3-benzoyl coumarin-7-yl-methacrylate:0.54-co-methyl methacrylate:0.46)

Adnan Kurt [a,*], Ahmet Faruk Ayhan [a], Murat Koca [b]

[a] Department of Chemistry, Faculty of Arts and Science, University of Adiyaman, 02040, Adiyaman/Turkey
[b] Department of Pharmaceutical Chemistry, Pharmacy Faculty, University of Adiyaman, 02040, Adiyaman/Turkey

* Corresponding author: adnkurt@gmail.com

Abstract

In present study, thermal decomposition studies of a copolymer based the coumarin containing monomer 3-benzoyl coumarin-7-yl-methacrylate (BCMA) and methyl methacrylate [poly(BCMA:0.54-co-MMA:0.46)] were performed by thermogravimetric analysis (TGA). The temperature for maximum rate losses was increased from 384.81 °C to 407.45 °C with the increasing in heating rate from 5 °C/min to 20°C/min. The thermal decomposition activation energies of copolymer in the conversion range of 9% - 21% were resulted to be 212.98 kJ/mol and 210.30 kJ/mol by Kissinger's and Flynn–Wall–Ozawa methods, respectively. The study of kinetic equations such as Coats-Redfern, Tang, Madhusudanan and Van-Krevelen methods exhibited that the thermal decomposition process of the studied copolymer was followed with a D_3 mechanism, a three-dimensional diffusion type deceleration solid state mechanism, at the optimum heating rate of 20 °C/min.

Keywords: Coumarin copolymer, methyl methacrylate, thermal decomposition kinetics, activation energy, reaction mechanism

INTRODUCTION

Heterocyclic compounds with six-membered ring containing oxygen as a heteroatom exist commonly in nature with a lot of benefits for the life cycle [1]. Coumarin is a member of these heterocylic compounds and consists of a large class of phenolic substances found in natural plants [2]. As chemical structure, it is made of fused benzene and α-pyrone rings to form a heterocyclic skeletal structure [2]. Therefore, coumarin and its derivatives contribute to a versatile class of compounds accompanying an important place in the different branches of natural or synthetic chemistry [3] for many years due to their versatile applications in various fields of science and technology; shifting from electronic and photonic applications such as electro-optic materials, light storage/energy transfer materials, organic-inorganic hybrid materials, liquid crystal materials [4-8] to additives in food, perfumes, cosmetics, pharmaceuticals and to the preparation of insecticides [2]. Futhermore, these compounds exhibit important pharmacological properties such as anti-biotic, anti-bacterial, anti-tumor, anti-viral, anti-coagulants, anti-psoriatic, anti-HIV, anti-inflammatory, anti-fungal, anti-hypertensive, anti-tubercular, anti-oxidant, anti-convulsant, anti-adipogenic, anti-hyperglycemic, enzyme inhibitor, neuroprotective activity, etc. [9-15].

On the other hand, in recent years, a large number of polymers from heterocyclic organic compounds have been synthesized and tested in different application areas as mentioned above. These polymers are used in specific applications due to not only for their macromolecular properties but also for their functional properties [16]. In this framework, due to their existing heterocyclic structures, the coumarin compounds may also be converted into their own polymers in accordance with suitable reactions or polymerization

methods [17]. Thus, these compounds have been able to place to a new member position, which is highly remarkable in the class of reactive functional polymers. In recent years, there have been some studies on the synthesis, characterization and investigation of various properties based on the some coumarin polymers [16,18-21]. Among these properties, thermal properties have acquired an importance and reported in some papers. Patel and coworkers have reported that the synthesis and characterization of a new functional acrylic monomer, 7-acryloxy 4-methyl coumarin, and its copolymerization with vinyl acetate. They have also studied their thermal behavior and found that the coumarin polymers showed moderate thermal stability [16]. Venkatesan and friends have also synthesized and characterized a coumarin containing monomer, 7-methacryloyloxy-4-methylcoumarin and copolymerized it with butoxyethylmethacrylate in order to study their thermal behavior and anti-microbial activity. Thermogravimetric analysis and differential scanning calorimetry measurements of the studied polymers have shown moderate thermal stability and higher glass transition temperature values [22]. Besides, our research group have published some papers regarding the coumarin derived polymers in previous studies [17,23,24]. In one study, we have synthesized and spectral characterized a copolymer series of 3-benzoyl coumarin-7-yl-methacrylate monomer with methyl methacrylate at different compositions in which the glass transition temperature of copolymers was decreased to 165 °C with the decreasing of coumarin monomer composition to 23% level [17].

In addition, the knowledge in thermal degradation process of any polymeric material offers many advantages regarding that polymer such as the selection of suitable polymer for certain end-use applications, prediction in material performance, improvement in material quality, kinetic information, etc. [25]. Especially, kinetic analysis is a useful and highly preferred subject for many applications

in the field of thermal analysis. These kinetic studies are also being helpful in the calculation of the Arrhenius parameters such as activation energy, reaction order, pre-exponential factor and to determine the mechanism of decomposition reaction [26]. However, within our literature knowledge, there is not enough work on the thermal decomposition kinetics of coumarin containing polymers except in our previous publications [23,24]. Apart from our previous works and in addition to them, in present study, we have investigated the thermal decomposition kinetics of the copolymer of 3-benzoyl coumarin-7-yl-methacrylate (BCMA) monomer and methyl methacrylate (MMA) at the chemical composition of 54% coumarin monomer, poly(BCMA:0.54-co-MMA:0.46), by various kinetic models such as Kissinger's, Flynn–Wall–Ozawa, Coats–Redfern, Tang, Madhusudanan and Van Krevelen models using thermogravimetric analysis (TGA) in the studied conversion range.

EXPERIMENTAL

Instrumental techniques

The infrared characterization of the copolymer was performed using a Perkin Elmer Spectrum 100 model FTIR instrument. Nuclear magnetic resonance (^{1}H-NMR) characterization was carried out on a Bruker 300 Mhz Ultrashield TM instrument model NMR spectrometer. NMR spectra were recorded at room temperature in the presence of deuterated dimethyl sulfoxide (d-DMSO) solvent and trimethylsilane (TMS) standard. On the other hand, Seiko SII 7300 TG/DTA system was used for thermogravimetric analysis of the copolymer. For this purpose, TGA analysis was performed by applying a controlled heating program at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min from ambient temperature to 500 °C under a dynamic nitrogen atmosphere.

Materials

Ethyl benzoyl acetate, 2,4-dihydroxybenzaldehyde, piperidine, methacryloyl chloride, triethylamine (TEA), methyl methacrylate (MMA), anhydrous magnesium sulphate and the solvents of N,N-dimethylformamide (DMF), acetone, chloroform, tetrahydrofuran (THF), methanol, ethanol were purchased from Sigma-Aldrich. Azobisisobutyronitrile (AIBN) as initiator was obtained from Merck, and it was purified by dissolving in chloroform and recrystallizing from ethanol just before polymerization. In addition, the copolymerization of 3-benzoyl coumarin-7-yl-methacrylate (BCMA) and methyl methacrylate (MMA) was re-achieved by free radical polymerization method according to our previous study [17] as briefly as follows: BCMA (0.4175 g), MMA (0.1250 g), AIBN initiator (0.0325 g, 6 wt% of the total amount of monomers) and DMF solvent (2.71 mL) were added into a polymerization tube and degassed with argon gas for 10 minutes. The polymerization tube was then closed with a rubber septum and placed in an oil bath preheated to 60 ºC. After the polymerization time for 48 hours, the copolymer (Scheme 1) was precipitated in ethanol two times, then filtrated and dried overnight in a vacuum oven at 40 ºC for 24 hours.
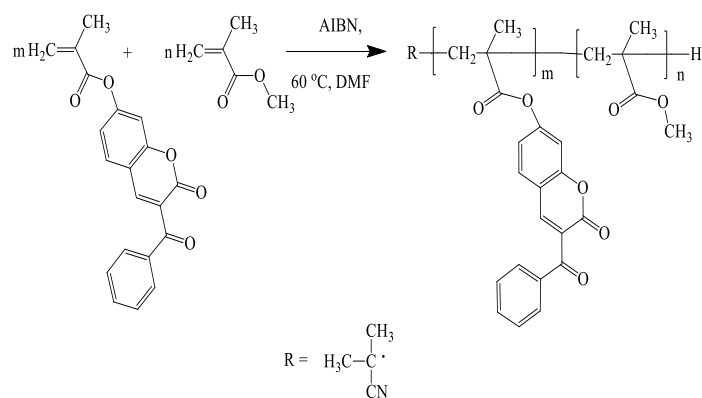
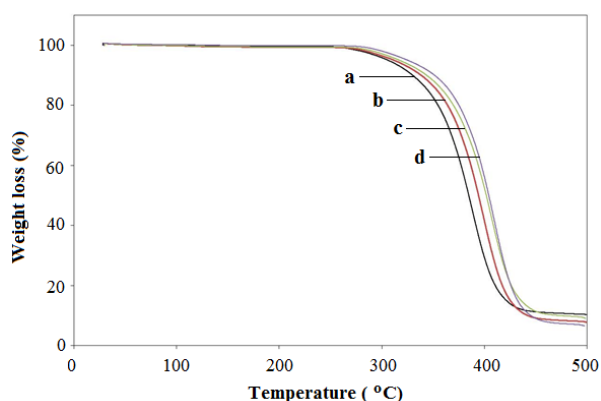**Scheme 1** Synthesis of poly(BCMA:0.54-co-MMA:0.46) copolymer [17].

RESULTS AND DISCUSSION

The characterization of poly(BCMA:0.54-co-MMA:0.46) copolymer was re-performed by FTIR and ^{1}H-NMR spectra according to reference [17], however, it was briefly referred to below. Fig. 1a shows the FTIR spectrum of copolymer in which the most characteristic bands were due to coumarin methacrylate C=O stretching at 1753 cm^{-1}, methyl methacrylate C=O stretching at 728 cm^{-1}, coumarin lactone ring C=C stretching at 1666 cm^{-1} and aromatic C=C stretching at 1614 cm^{-1}. Besides, in ^{1}H-NMR spectrum (Fig. 1b), the signal at 8.30 ppm was attributed to =CH- proton in coumarin lactone ring while the resonances between the 7.86–7.22 ppm were observed for aromatic =CH- protons in benzoyl and coumarin rings. The other signals were recorded for –OCH$_3$ protons in MMA units at 3.54 ppm and methylene and methyl protons in polymer main chains at 1.86 - 0.74 ppm, respectively. 3.35 ppm and 2.50 ppm were also due to DMSO solvent. By using ^{1}H-NMR spectrum data, the monomer composition of the copolymer has been determined by the ratios of the integration height of the signal group at 8.30-7.22 ppm that corresponding to the 9 protons reasoned from BCMA units and that of the 3.54 ppm signal attributed to MMA units that corresponding to the 3 protons. Thus, the ratio of BCMA units in copolymer was found to be 54% whereas for the MMA units was 46%.
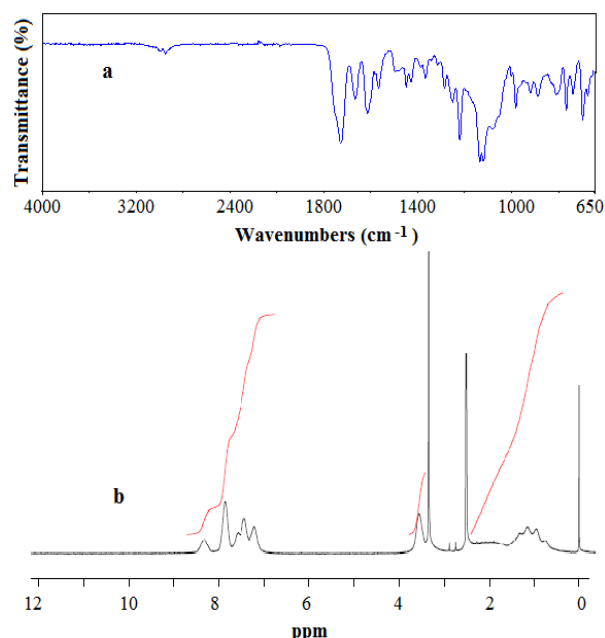
Fig. 1 FTIR (a) and ^{1}H-NMR (b) spectra of poly(BCMA:0.54-co-MMA:0.46) copolymer.

Thermal decomposition of the coumarin derived copolymer poly(BCMA:0.54-co-MMA:0.46) was determined using thermogravimetric analysis (TGA) by applying a controlled heating program at the various heating rates under a dynamic nitrogen atmosphere. The obtained TGA curves were illustrated in Fig. 2. From the corresponding thermograms, it was observed that the decomposition of copolymer occurred at a single stage between approximately 310°C-450°C of temperature range. This decomposition range was in accordance with the recorded values for the coumarin-derived polymers in the literature. For example, Patel and coworkers reported that the thermal degradation of a series of polyacrylates with 4-methyl coumarin side group has been occurred in a single step at a temperature range of 263°C-458°C [27]. Also, in one of our previous published studies, we found that the initial decomposition temperature of a coumarin containing polymer poly(3-acetyl coumarin-7-yl-methacrylate) was at 281°C whereas the final decomposition temperature was about 460°C [23].

Fig. 2 TGA curves of poly(BCMA:0.54-co-MMA:0.46) copolymer at different heating rates of a: 5 °C/min, b: 10 °C/min, c: 15 °C/min, d: 20 °C/min under nitrogen atmosphere.

Table 1 shows some thermal characteristics of poly(BCMA:0.54-co-MMA:0.46) copolymer at different heating rates such as the temperatures of 5% and 50% weight loses, the decomposition percentages at the temperatures of 350 °C and 400 °C, and the residues at 500 °C. The initial decomposition (accepted as 5%) temperatures of copolymer at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min were determined to be 306.05 °C, 311.88 °C, 317.14 °C and 325.25 °C, respectively. As seen from Table 1, by depending on the increase at the heating rate, the peak temperatures of the curves showed a change in the positive direction. This change was observed for many polymers and the information about that has been reported in the literature [23,24,28].

Table 1 Thermal behaviors of poly(BCMA:0.54-co-MMA:0.46) copolymer at different heating rates.

Reaction rate (°C/min)	T_a (°C)	T_b (°C)	%Weight loss at 350 °C	%Weight loss at 400 °C	Residue at 500 °C (%)
5	306.05	384.81	17.35	70.56	10.29
10	311.88	394.33	13.52	58.37	7.74
15	317.14	401.87	11.75	47.39	9.05
20	325.25	404.33	9.63	43.72	6.56

T_a and T_b: Decomposition temperatures at the weight losses of 5% and 50%, respectively

Thermal decomposition reactions of solid state materials were defined by the following expression [29]:

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

(1)

where k(T) is a temperature-dependent rate constant, f(α) is the particular reaction model describing the dependence of the reaction rate on the extent of reaction, α represents the extent of reaction which can be determined from TGA runs as a fractional mass loss, t is time, A and E are being the pre-exponential factor and the activation energy, respectively.

Besides, g(α) was defined as the integral function of conversion as expressed by following equation:

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

(2)

In this equation, R is the ideal gas constant, β is the heating rate and T is the absolute temperature. Thermal decomposition of polymeric materials was generally followed one of the decomposition processes of sigmoidal and deceleration type mechanism [30]. Various statements of g(α) integral functions were reported in literature and by using these functions, thermal decomposition

mechanisms might easily be determined by thermogravimetric analysis [31].
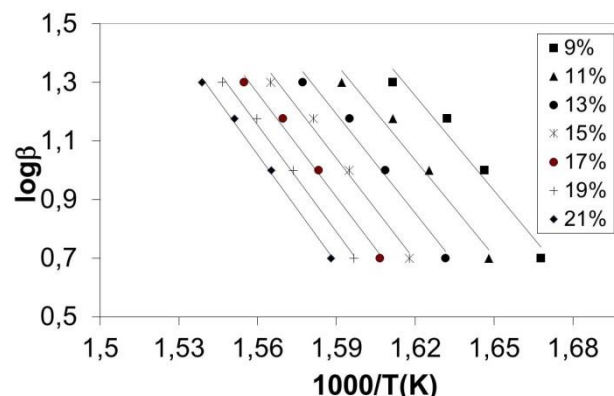
Fig. 3 The plots of log β versus (1000/T) at different conversion values used for Flynn Wall Ozawa method.

The kinetic analysis of our synthesized coumarin derived copolymer poly(BCMA:0.54-co-MMA:0.46) was accomplished by using various kinetic methods in literature such as Flynn–Wall-Ozawa [32,33], Kissinger [34], Coats–Redfern [35], Tang [36], Madhusudanan [37] and Van Krevelen [38] methods. In present study, we have calculated the thermal decomposition activation energy in the first step of the kinetic analysis of the copolymer and in the subsequent step, we have determined the thermal decomposition mechanism. Therefore, in the first step, thermal degradation activation energies of the copolymer have been determined according to the Flynn-Wall-Ozawa and Kissinger methods using the data from the degradation curves recorded at various heating rates. Especially, the main purpose of using these two methods was that both methods were integral methods for determining activation energies without having to know the reaction order or the decomposition mechanism [31]. The kinetic equation of the Flynn-Wall-Ozawa method was expressed as:

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

(3)

where E is the activation energy and may be determined from the slope of the plots of log β versus (1000/T). Another integral method to determine the thermal decomposition activation energies of copolymer was the Kissinger method and described by the following expression

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}}$$

(4)

where T_{max} is the temperature corresponding to the maximum reaction rate, α_{max} is the maximum conversion at T_{max}, n is the reaction order. The activation energy, E, can be calculated from the slope of a plot of $\ln(\beta/T_{max}^2)$ versus $1000/T_{max}$.

Table 2 Activation energies of poly(BCMA:0.54-co-MMA:0.46) copolymer calculated by Flynn-Wall-Ozawa method.

α (%)	E (kJ/mol)	R
9	196.04	0.9648
11	198.86	0.9749
13	204.76	0.9812
15	211.23	0.9876
17	215.65	0.9926
19	220.91	0.9962
21	224.64	0.9971
Mean	210.30	

The dynamic measurements at different conversion values such as 9%, 11%, 13%, 15%, 17%, 19% and 21% were taken for the Flynn-Wall-Ozawa method. The plots of log β against 1000/T according to

the corresponding values of these conversions were plotted as shown in Fig. 3. The activation energy value corresponding to each conversion was separately calculated and summarized in Table 3. Among these values, the average activation energy value for the poly(BCMA:0.54-co-MMA:0.46) copolymer was determined to be 210.30 kJ/mol. The closest activation energy to this mean value was obtained for 15% decomposition rate with a value of 211.23 kJ/mol as seen in Table 2.
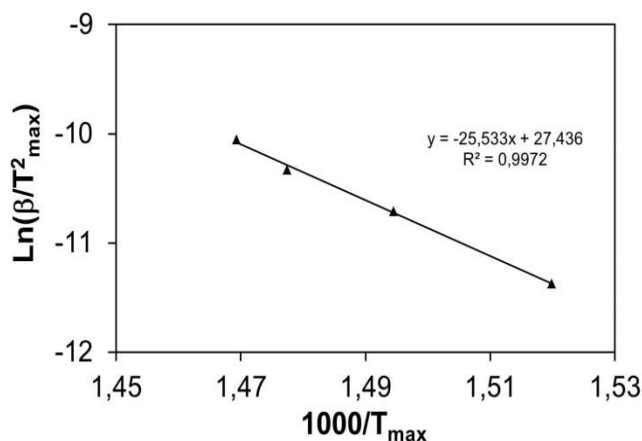

Fig. 4 The plots of $\ln(\beta/T^2_{max})$ versus $1000/T_{max}$ obtained from Kissinger method.

The temperatures corresponding to the maximum reaction rate (T_{max}) required to calculate the activation energy value according to Kissinger's method were determined from the derivative thermogravimetry (DTG) to be 384.81 °C, 395.98 °C, 403.72 °C and 407.45 °C at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively. The plots of $\ln(\beta/T^2_{max})$ versus $1000/T_{max}$ for poly(BCMA:0.54-co-MMA:0.46) copolymer were shown in Fig. 4. By fitting these plots to a straight line and from its slope ($-E/R$), the decomposition activation energy was calculated to be 212.28 kJ/mol by Kissinger's method. A fairly good agreement was found between the calculated thermal degradation activation energies obtained from both methods when they were compared to each other. There was only a 1.98 kJ/mol energy gap between the activation energies that were calculated according to Flynn-Wall-Ozawa and Kissinger's methods.

Table 3 Activation energies obtained for several solid state processes at different heating rates using Coats-Redfern Method.

| Mechanism | Heating Rate | | | | | | | |
| | 5 °C/min | | 10 °C/min | | 15 °C/min | | 20 °C/min | |
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	37.25	0.9980	36.40	0.9963	36.45	0.9974	41.92	0.9953
A_3	21.43	0.9974	20.81	0.9952	20.82	0.9966	24.42	0.9941
A_4	13.52	0.9965	13.02	0.9934	12.99	0.9953	15.68	0.9921
R_1	77.65	0.9991	76.20	0.9982	76.37	0.9988	86.59	0.9975
R_2	81.14	0.9988	79.63	0.9977	79.81	0.9984	90.44	0.9969
R_3	82.32	0.9986	80.79	0.9975	80.98	0.9982	91.74	0.9967
D_1	165.52	0.9992	162.77	0.9984	163.18	0.9989	183.75	0.9977
D_2	170.10	0.9990	167.28	0.9981	167.71	0.9987	188.81	0.9974
D_3	174.86	0.9988	171.96	0.9977	172.41	0.9984	194.06	0.9970
D_4	171.68	0.9989	168.84	0.9980	169.28	0.9986	190.56	0.9972
F_1	84.72	0.9984	83.16	0.9971	83.35	0.9979	94.39	0.9962
F_2	4.32	0.7648	3.94	0.7081	3.91	0.7212	5.47	0.7738
F_3	18.86	0.9376	18.24	0.9266	18.26	0.9320	21.51	0.9280

In order to determine the most probable thermal decomposition mechanism of coumarin copolymer, the kinetic methods of Coats-Redfern, Tang, Madhusudanan and Van Krevelen methods have been used in present study. The thermal decomposition activation energies and linear regressions determined in the range of 9% to 21% were summarized in Tables (3 to 6) for these kinetic methods at the heating rates of 5, 10, 15 and 20 °C/min. We have compared the activation energies from these methods to the Kissinger's and Flynn-Wall-Ozawa methods in order to appoint the thermal decomposition mechanism of the copolymer. For this purpose, the following kinetic equations which defined in various names were obtained by dissolving the Eq. 2 in different ways. Thus, the accuracy of calculations was confirmed by this way.

One of these solutions was suggested by Coats-Redfern as represented with a kinetic Eq. 5:

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

(5)

According to the various decomposition processes, the apparent activation energies of each $g(\alpha)$ function could be determined from a plot of $\ln[g(\alpha)/T^2]$ versus $1000/T$.

Besides the Coats-Redfern method, thermal decomposition mechanism of copolymer was defined by Tang method using the following equation:

$$\ln\left[\frac{g(\alpha)}{T^{1.89466100}}\right] = \left[\ln\frac{AE}{\beta R} + 3.63504095 - 1.89466100 \ln E\right] - 1.00145033\frac{E}{RT}$$

(6)

In this equation, the activation energy was calculated from the slope of the plots of $\ln[g(\alpha)/T^{1.89466100}]$ versus $1000/T$ for every $g(\alpha)$ functions.

Table 4 Activation energies obtained for several solid state processes at different heating rates using Tang Method.

| Mechanism | Heating Rate | | | | | | | |
| | 5 °C/min | | 10 °C/min | | 15 °C/min | | 20 °C/min | |
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	37.74	0.9980	36.89	0.9964	36.95	0.9974	42.42	0.9955
A_3	21.94	0.9975	21.33	0.9954	21.34	0.9967	24.95	0.9943
A_4	14.04	0.9967	13.55	0.9938	13.53	0.9956	16.21	0.9926
R_1	78.08	0.9992	76.65	0.9982	76.81	0.9988	87.03	0.9975
R_2	81.57	0.9988	80.07	0.9977	80.25	0.9984	90.87	0.9969
R_3	82.75	0.9987	81.24	0.9975	81.42	0.9983	92.18	0.9967
D_1	165.83	0.9992	163.09	0.9984	163.52	0.9990	184.05	0.9977
D_2	170.41	0.9990	167.59	0.9981	168.03	0.9987	189.11	0.9974
D_3	175.16	0.9988	172.27	0.9977	172.73	0.9984	194.35	0.9970
D_4	171.99	0.9989	169.15	0.9980	169.60	0.9986	190.85	0.9972
F_1	85.14	0.9984	83.59	0.9971	83.79	0.9979	94.82	0.9963
F_2	4.85	0.8039	4.48	0.7582	4.45	0.7704	6.02	0.8055
F_3	19.38	0.9407	18.76	0.9304	18.79	0.9355	22.04	0.9313

In another method proposed by Madhusudanan, as following Eq. 7:

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

(7)

The slope obtained from the plots of $\ln[g(\alpha)/T^{1.921503}]$ versus $1000/T$ gave the $-1.000955716E/R$ value and from that, the activation energy of each $g(\alpha)$ function was calculated.

In addition to above kinetic models, Van Krevelen method was also used to verify the thermal decomposition mechanism of copolymer and followed the following equation:

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

(8)

where T_r is a reference temperature which represents the maximum temperature rate obtained DTG. The decomposition activation energy for each $g(\alpha)$ function was calculated from the slope of the plots log $g(\alpha)$ versus log T.

When the activation energy values calculated from the above-mentioned kinetic methods were analyzed, the deceleration type dimensional diffusion mechanisms (D_n) were said to be remarkable for all methods. So, the activation energies calculated for these deceleration-type mechanisms were very close to the activation energies calculated from the Flynn-Wall-Ozawa (E = 210.30 kJ/mol) and Kissinger (E = 212.28 kJ/mol) methods. Especially, the activation energies corresponding to D_3 three-dimensional diffusion type deceleration mechanism at the heating rate of 20 °C/min have the best agreement with the activation energies of Kissinger and Flynn-Wall-Ozawa methods. When it was considered for the Coats-Redfern method as given in Table 3, at the heating rate of 20 °C/min, the activation energy corresponding to D_3 mechanism was 194.06 kJ/mol with a well linear regression (R=0.9970). This was close to 210.30 kJ/mol by Flynn-Wall-Ozawa method and also in good agreement with the value obtained by the Kissinger method (212.28 kJ/mol). Thus, three-dimensional diffusion mechanism of D_3 could be the probable thermodegradation kinetic mechanism of copolymer according to Coats-Redfern method.

Table 5 Activation energies obtained for several solid state processes at different heating rates using Madhusudanan Method.

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	37.62	0.9980	36.78	0.9964	36.83	0.9974	42.29	0.9954
A_3	21.81	0.9975	21.20	0.9954	21.21	0.9967	24.82	0.9942
A_4	13.91	0.9966	13.42	0.9937	13.39	0.9955	16.08	0.9925
R_1	77.98	0.9992	76.55	0.9982	76.71	0.9988	86.93	0.9975
R_2	81.47	0.9988	79.97	0.9977	80.15	0.9984	90.78	0.9969
R_3	82.65	0.9987	81.14	0.9975	81.32	0.9983	92.08	0.9967
D_1	165.77	0.9992	163.03	0.9984	163.45	0.9990	184.04	0.9977
D_2	170.36	0.9990	167.54	0.9981	167.98	0.9987	189.06	0.9974
D_3	175.11	0.9988	172.22	0.9977	172.67	0.9984	194.30	0.9970
D_4	171.94	0.9989	169.10	0.9980	169.54	0.9986	190.81	0.9972
F_1	85.05	0.9984	83.50	0.9971	83.69	0.9979	0.9473	0.9963
F_2	4.72	0.7949	4.34	0.7466	4.31	0.7590	5.88	0.7981
F_3	19.25	0.9400	18.63	0.9295	18.66	0.9346	21.91	0.9305

To verify D_3 mechanism determined by Coats-Redfern method, we used the other integral methods of Tang, Madhusudanan and Van Krevelen methods, and the obtained results for the activation energies and correlations were given in Tables 4, Table 5 and Table 6, respectively. According to Tang method as given in Table 4, the activation energy (E) and the linear regression (R) values were matched to D_3 mechanism at the heating rate of 20 °C/min and found to be E=194.35 kJ/mol and R= 0.9970, respectively, which in good agreement with the Kissinger (212.28 kJ/mol) and Flynn-Wall-Ozawa (210.30 kJ/mol) methods. In addition to these two integral methods, the activation energies and linear regressions for D_3 mechanism at the heating rate of 20 °C/min were calculated according to Madhusudanan method (Table 5) to be E = 194.30 kJ/mol (R = 0.9970) and according to Van Krevelen method (Table 6), E = 213.68 kJ/mol (R = 0.9979).

From analyses of these tables, the best conformity in all kinetic models and heating rates to that of the Flynn-Wall-Ozawa (E = 210.30 kJ/mol) and Kissinger (E = 212.28 kJ/mol) methods was obtained in the case of the Van Krevelen method (E=213.68 kJ/mol) for D_3 mechanism at a heating rate of 20 °C/min. Hereby, it could be said that the thermal decomposition mechanism of copolymer was a D_3 three-dimensional diffusion type deceleration mechanism and the optimum heating rate value was 20 °C/min.

Table 6 Activation energies obtained for several solid state processes at different heating rates using Van Krevelen Method.

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	45.37	0.9991	44.67	0.9983	44.89	0.9988	50.59	0.9976
A_3	28.42	0.9991	27.93	0.9983	28.05	0.9988	31.85	0.9976
A_4	19.95	0.9991	19.55	0.9983	19.63	0.9988	22.47	0.9976
R_1	88.62	0.9996	87.43	0.9990	87.88	0.9994	98.48	0.9985
R_2	92.37	0.9994	91.11	0.9987	91.59	0.9992	102.61	0.9981
R_3	93.64	0.9993	92.37	0.9986	92.85	0.9991	104.01	0.9979
D_1	182.72	0.9996	180.41	0.9990	181.39	0.9994	202.62	0.9985
D_2	187.64	0.9995	185.26	0.9988	186.26	0.9993	208.05	0.9982
D_3	192.74	0.9993	190.29	0.9986	191.34	0.9991	213.68	0.9979
D_4	189.34	0.9994	186.94	0.9987	187.95	0.9992	209.93	0.9981
F_1	96.21	0.9991	94.91	0.9983	95.41	0.9988	106.85	0.9976
F_2	10.12	0.9743	9.81	0.9704	9.85	0.9729	11.55	0.9679
F_3	25.70	0.9743	25.19	0.9704	25.33	0.9729	28.75	0.9679

CONCLUSION

Thermal decomposition kinetics of poly(BCMA:0.54-co-MMA:0.46) coumarin derived copolymer were studied by integral approximation methods under non-isothermal conditions. The temperatures for maximum rate losses were increased from 384.81 °C to 407.45 °C with increasing heating rate. Thermal decomposition activation energies in the conversion range of 9% - 21% were found to be 212.98 kJ/mol and 210.30 kJ/mol by Kissinger's and Flynn–Wall–Ozawa methods, respectively. The analysis of kinetic models showed that the thermal decomposition mechanism of poly(BCMA:0.54-co-MMA:0.46) copolymer was followed D_3 mechanism, a three-dimensional diffusion type deceleration solid state mechanism. Also, the best conformity between the all kinetic models and heating rates to Flynn-Wall-Ozawa and Kissinger's models was defined by the Van Krevelen method (E=213.68 kJ/mol) for D_3 mechanism at a heating rate of 20 °C/min.

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