

Thermal Decomposition Kinetics of Poly(*n*ButMA-*b*-St) Diblock Copolymer Synthesized by ATRP

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ABSTRACT: The reaction mechanism of decomposition process and the kinetic parameters of the poly(*n*-butyl methacrylate-*b*-styrene), poly(*n*ButMA-*b*-St), diblock copolymer synthesized by atom transfer radical polymerization (ATRP) were investigated by thermogravimetric analysis (TGA) at different heating rates. TGA curves showed that the thermal decomposition occurred in one stage. The apparent activation energies of thermal decomposition for copolymer, as determined by the Kissinger's, Flynn–Wall–Ozawa and Tang methods, which does not require knowledge of

the reaction mechanism (RM), were 112.52, 116.54, and 113.41 kJ/mol, respectively. The experimental results were compared with master plots, in the range of the Doyle approximation. Analysis of experimental results suggests that in the conversion range studied, 3–18%, the actual RM is an A_2 sigmoidal type. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 624–629, 2009

Key words: thermogravimetric analysis (TGA); activation energy; diblock copolymers; thermal properties

INTRODUCTION

Thermal degradation studies of polymers are necessary as many applications depend on their thermal stability. To accomplish this goal, thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information afforded by a simple thermogram.¹ In the thermal degradation of homo polymers or block copolymers, depolymerization is one of the main patterns of breakdown.^{2,3} During depolymerization, the distinctive feature is the absence of residues at high temperatures, i.e., all the degrading products, e.g., monomers, dimers, chain fragments, have essentially the same composition as the repeating unit.^{4,5} In most cases, the polymer molecular weight will fall rapidly as degradation proceeds and often, but not invariably, there is only one stage of degradation as the temperature is gradually raised.⁶

The synthesis, characterization, and product identification studies of thermal degradation of poly(*n*-butyl methacrylate-*b*-styrene), poly(*n*ButMA-*b*-St), diblock copolymer synthesized by atom transfer radical polymerization (ATRP), using poly(*n*ButMA) C-Br-end-group as macroinitiator were reported by Demirelli et al.⁷ In that study, the thermal degradation behavior of the block copolymer was studied using thermo gravimetric analysis (TGA) and a single line vacuum system consisting of a degradation

tube with a condenser for product collection and a liquid nitrogen trap (-196°C). The block copolymer was heated from ambient temperature to 500°C . The products of degradation were collected at two different fractions, which are cold ring fraction (CRF) and volatile liquid fraction (VLF) trapped at -196°C . *n*-butyl methacrylate and styrene are given as major products of degradation determined by means of IR, ^1H NMR, and GC-MS techniques.⁷ On the other hand, the most important minor products such as benzene, ethyl benzene, ethyl methacrylate, and toluene are among products of degradation. They are reported by McNeill et al.⁸ from the degradation of the styrene chain units of the copolymer prepared free radical polymerization.

Thermogravimetric analysis (TGA) was also used to investigate the activation energies. The thermal degradation expression results change according to different assumptions and derivatives, for example, bulk or powder, carrier gas, flow rate, would directly affect the results of parameters.⁹ The different analysis methods are described. These methods require several TGA curves at different heating rates. Many studies of curing and thermogravimetric kinetic mechanism of polymers^{10–13} have employed reference theoretical curves known as master curves. These curves are characteristic curves, independent of the conditions of measurements, which are easily obtained from kinetic or thermogravimetric experimental data.

In this article, the thermal decomposition kinetics of diblock copolymer system of *n*-butyl methacrylate (*n*ButMA) with styrene [poly(*n*ButMA-*b*-St)] was reported.

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TABLE I
Algebraic Expressions for $g(\alpha)$ for the Most Frequently Used Mechanisms of Solid-State Processes

Symbol	$g(\alpha)$	Solid-state processes
Sigmoidal curves		
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami eq. (1))
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami eq. (2))
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami eq. (3))
Deceleration curves		
R_1	α	Phase boundary controlled reaction (One-dimensional movement)
R_2	$[1 - (1 - \alpha)^{1/2}]$	Phase boundary controlled reaction (contraction area)
R_3	$[1 - (1 - \alpha)^{1/3}]$	Phase boundary controlled reaction (contraction volume)
D_1	α^2	One-dimensional diffusion
D_2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	Two-dimensional diffusion
D_3	$[1 - (1 - \alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1 - 2/3\alpha)(1 - \alpha)^{2/3}$	Three-dimensional diffusion (Ginstling-Brounshtein equation)
F_1	$-\ln(1 - \alpha)$	Random nucleation with one nucleus on the individual particle
F_2	$1/(1 - \alpha)$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1 - \alpha)^2$	Random nucleation with three nuclei on the individual particle

EXPERIMENTAL

Instrumental techniques

Thermogravimetric analysis was performed using a Shimadzu TGA 50 analyzer. The thermal stability and the decomposition activation energy measurements were carried out from ambient temperature to 500°C with heating rate of 5, 15, 25, and 35°C/min⁻¹. All the experiments were carried out under a nitrogen atmosphere. The optimum gas flow rate was used 25 ml/min for TGA 50 analyzer.

Thermal degradation kinetics

The application of dynamic thermogravimetry (DTG) methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer degradation. The rate of solid-state isothermal decomposition reactions is expressed as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (1)$$

where T is absolute temperature (K), A is the preexponential factor (min⁻¹), E is the activation energy (kJ/mol), R is the gas constant (8.314 J mol⁻¹ K⁻¹). Rearranging eq. (1) and integrating both sides of the equation leads to the following expression

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} e^{-\frac{E}{RT}} dT \quad (2)$$

where $g(\alpha)$ is the integral function of conversion. In the case of polymers, the degradation process follows either a sigmoidal function or a deceleration function. Table I shows different expressions of $g(\alpha)$ for the different solid-state mechanisms.¹⁴⁻¹⁶

Kissinger's method

The activation energy can be determined by Kissinger's method¹⁷ without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}} \quad (3)$$

where β is the heating rate, T_{\max} is the temperature corresponding to the maximum reaction rate, A is the preexponential factor, α_{\max} is the maximum conversion, and n is the reaction order. From a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ and fitting to a straight line, the activation energy E can be calculated from the slope.

Flynn-Wall-Ozawa method

This method was derived from the integral method that can determine the activation energy without knowledge of reaction order.^{18,19} It is used to determine the activation energy for given values of conversion. Using the Doyle approximation,²⁰ eq. (2) may then be integrated to give the following in logarithmic form:

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

where β , A , E , and T have the known meanings. The activation energy for different conversion values can be calculated from a $\ln \beta$ versus $1000/T$ plot.

Tang method

With the logarithms of side taken and an approximation formula for the solution of eq. (2) used,²¹ the following equation can be obtained

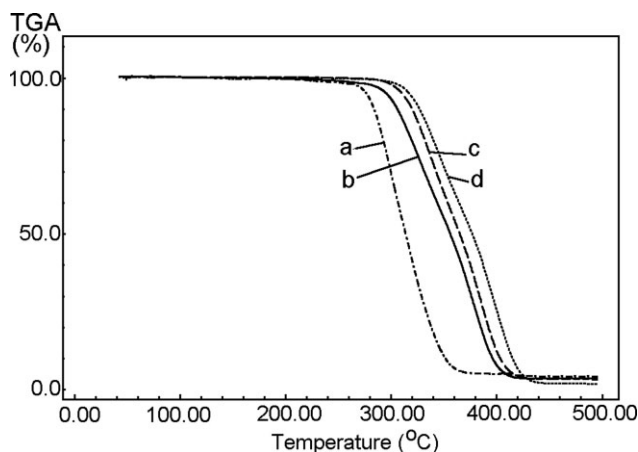


Figure 1 Experimental TG curves at different heating rates (a) 5°C/min, (b) 15°C/min, (c) 25°C/min, and (d) 35°C/min.

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left(\frac{AE}{Rg(\alpha)}\right) + 3.635041 - 1.894661 \ln E - \frac{1.001450E}{RT} \quad (5)$$

The plots of $\ln(\beta/T^{1.894661})$ versus $1/T$ give a group of straight lines. E can be obtained from the slope $-1.001450 E/R$ of the regression line.

Coats–Redfern method

The Coats–Redfern method²² is also an integral method, and it involves the thermal degradation mechanism. With an asymptotic approximation for resolution of eq. (2), the following equation can be obtained:

$$\ln \frac{g(\alpha)}{T_2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (6)$$

Activation energy for every degradation process listed in Table I can be determined from a plot of $\ln g(\alpha)$ versus $1000/T$.

Van Krevelen and Horowitz-Metzger methods

Van Krevelen et al.²³ made the first serious theoretical treatment of thermogravimetric data. These

authors approximated the exponential integral to obtain a final equation in logarithmic form:

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

where

$$B = \frac{A}{\beta} \left(\frac{E}{RT_r} + 1\right)^{-1} \left(\frac{0.368}{T_r}\right)^{\frac{E}{RT_r}}$$

and T_r is a reference temperature. Horowitz and Metzger²⁴ simplify the exponential integral using an approximation similar to Van Krevelen et al., defining a characteristic temperature θ such that $\theta = T - T_r$ where T_r is a reference temperature. Making the approximation

$$\frac{1}{T} = \frac{1}{T_r + \theta} \cong \frac{1}{T_r} - \frac{\theta}{T_r^2}$$

they finally obtain for $n = 1$;

$$\ln g(\alpha) = \frac{E\theta}{RT_r^2} \quad (8)$$

In this study, to obtain reproducible results, the reference temperature was taken as that corresponding to the maximum temperature rate. Using any of these two methods, the activation energy can be determined without the precise knowledge of the thermodegradation kinetics.

Determination of reaction mechanism by the master plot method

If the value of the activation energy is known, the kinetic model of the process can be found in the following way. Criado et al.¹⁵ define the function

$$z(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)}{\beta} \pi(x) T \quad (9)$$

where $x = E/RT$; and $\pi(x)$ is an approximation of the temperature integral, which cannot be expressed in a

TABLE II
TGA Data for Diblock Copolymer at Different Heating Rates

Reaction rate (°C/min)	^a T_i	^b T_f	^c T_{50}	% Weight loss at 300°C	% Weight loss at 350°C	Residue at 450°C (%)
5	264	371	314	29	89	5
15	274	416	356	13	45	4
25	283	425	365	2	36	3
35	294	436	377	1	29	2

^a Initial decomposition temperature.

^b Final decomposition temperature.

^c Decomposition temperature at 50%.

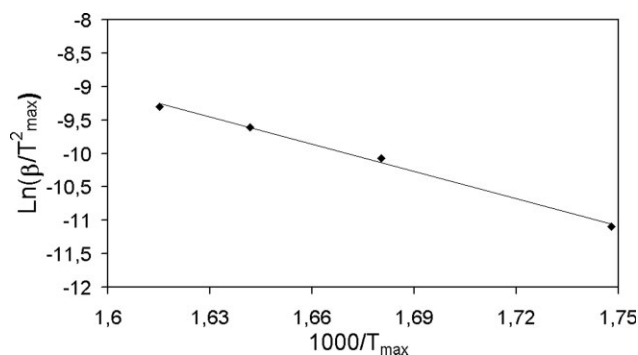


Figure 2 Kissinger Method applied to experimental data at different rates.

simple analytical form. In this study, it was used the fourth rational expression proposed by Senum et al.²⁵

$$z(\alpha) = f(\alpha)g(\alpha) \quad (10)$$

This equation was used to obtain the master curves as a function of the reaction degree corresponding to the different models listed in Table I.

RESULTS AND DISCUSSION

Thermal decomposition curves of poly(nButMA-*b*-St) diblock copolymer carried out at different heating rates 5, 15, 25, and 35°C/min showed in Figure 1. The initial decomposition temperature (T_i), decomposition temperature at 50% weight loss, the weight loss (%) at 300°C and 350°C, and residual mass at 450°C after complete degradation can be determined from these curves and are shown in Table II. From the corresponding DTG profiles, the temperatures related to the maximum decomposition rates were found to be 299, 322, 336, and 346°C. Analysis of these curves shows that, at 450°C, the residue diminished 2% with a 35°C/min heating rate. The 10°C/min intervals between measurements have chosen to avoid the overlapping of inflection point temperatures.¹⁶

According to Kissinger's method, the activation energy can be calculated from a plot of $\ln(\beta/T_{\max}^2)$

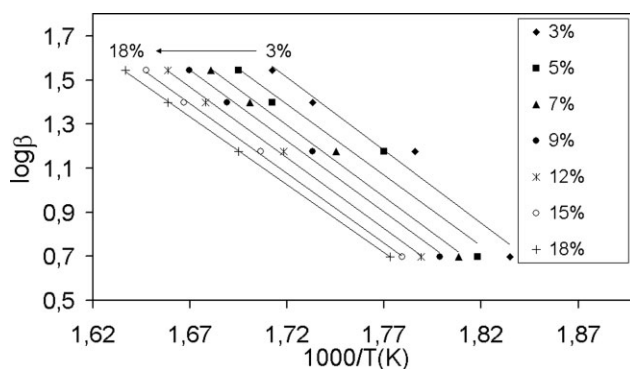


Figure 3 Flynn-Wall-Ozawa Method applied to experimental data (3–18%).

TABLE III
Activation Energies Obtained Using the Flynn-Wall-Ozawa and Tang Methods

α (%)	Flynn-Wall-Ozawa method		Tang method	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
3	119.97	0.9665	117.19	0.9613
5	116.94	0.9599	113.93	0.9524
7	118.30	0.9926	115.30	0.9913
9	117.08	0.9944	113.96	0.9934
12	116.31	0.9983	113.11	0.9979
15	115.06	0.9987	111.74	0.9985
18	112.14	0.9998	108.62	0.9998
Mean	116.54		113.41	

versus $1000/T_{\max}$ and fitting to a straight line using eq. (3). From Figure 2, the activation energy obtained using this method is 112.52 kJ/mol. The activation energy can also be determined using the method of Flynn-Wall-Ozawa, eq. (4), from a linear fitting of $\log \beta$ versus $1000/T$ at different conversions. Because of the fact that this equation was derived using the Doyle approximation, only conversions values in the range 5–20% can be used. For this study, the conversion values 3, 5, 7, 9, 12, 15, and 18% have used. Figure 3 shows that the fitting straight lines are nearly parallel, thus indicating the applicability of this method to poly(nButMA-*b*-St) diblock copolymer in the conversion range studied. Table III shows the activation energies corresponding to the different conversions calculated by Flynn-Wall-Ozawa method. A mean value 116.54 kJ/mol was found from these values. Table III also shows that the activation energy corresponding to 18% conversion (112.14 kJ/mol) is very close to the value obtained using Kissinger's method (112.52 kJ/mol).

Tang method was also used for determining of activation energy. eq. (5) was used to obtain E , which could be calculated from the plot of $\ln(\beta/T^{1.894661})$ versus $1000/T$ fit to a straight line shown in Figure 4. The mean value of the E of the thermal degradation of poly(nButMA-*b*-St) diblock

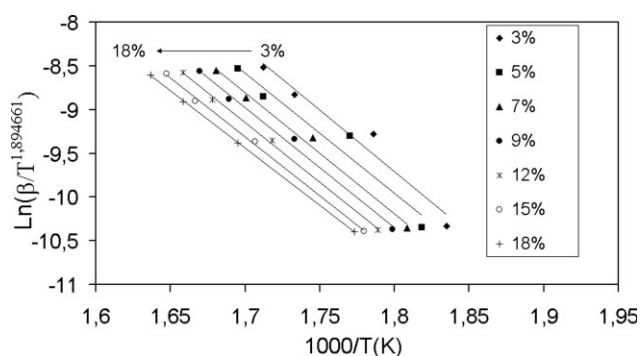


Figure 4 Tang Method applied to experimental data (3–18%).

TABLE IV
Activation Energies Obtained Using the Coats-Redfern Method for Several Solid-State Processes at Heating Rates of 5°C/min and 15°C/min

Mechanism	Heating rate 5°C/min		Heating rate 15°C/min	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
A_2	116.21	0.9982	73.24	0.9888
A_3	74.40	0.9981	45.65	0.9871
A_4	53.49	0.9979	6.90	0.9851
R_1	230.65	0.9974	148.77	0.9889
R_2	236.09	0.9979	152.37	0.9895
R_3	237.94	0.9981	153.58	0.9897
D_1	470.52	0.9975	307.09	0.9896
D_2	477.71	0.9979	311.85	0.9990
D_3	485.09	0.9982	316.73	0.9904
D_4	480.18	0.9980	313.48	0.9901
F_1	241.64	0.9984	147.72	0.9901
F_2	13.75	0.8609	5.26	0.8607
F_3	35.57	0.9179	20.07	0.8859

copolymer was 113.41 kJ/mol that is very close to the value obtained using two method mentioned above. The calculated results are summarized in Table III. Compared with other methods, these three methods present the advantage that they do not require previous knowledge of the reaction mechanism for determining of activation energy. To check thermodegradation mechanism models, these methods were used by some authors.^{10,16,26}

The activation energy for every $g(\alpha)$ function listed in Table I was proposed by Coats and Redfern²² using eq. (6). These values were obtained at constant heating rates from fitting of $\ln(g(\alpha)/T^2)$ versus $1000/T$ plots. The same conversion values are used for this study. Tables IV and V show activation energies and correlations for conversions in the range 3–18% at heating rate values 5, 15, 25, and 35°C/min,

TABLE V
Activation Energies Obtained Using the Coats-Redfern Method for Several Solid-State Processes at Heating Rates of 25°C/min and 35°C/min

Mechanism	Heating rate 25°C/min		Heating rate 35°C/min	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
A_2	94.86	0.9984	93.19	0.9952
A_3	59.97	0.9982	58.82	0.9946
A_4	42.53	0.9979	5.0074	0.9938
R_1	190.37	0.9976	187.23	0.9940
R_2	194.72	0.9981	191.74	0.9949
R_3	196.45	0.9983	193.26	0.9952
D_1	390.57	0.9978	384.39	0.9943
D_2	396.57	0.9981	390.35	0.9949
D_3	402.71	0.9984	396.45	0.9954
D_4	398.61	0.9982	392.38	0.9951
F_1	199.54	0.9986	196.33	0.9957
F_2	8.86	0.7889	8.61	0.8319
F_3	27.54	0.9043	27.15	0.9237

TABLE VI
Activation Energies Obtained Using the Van Krevelen et al. Method for Sigmoidal Processes at Different Heating Rates

Heating rate (°C/min)		Mechanism		
		A_2	A_3	A_4
5	E_a (kJ/mol)	124.59	81.47	59.91
	R	0.9981	0.9981	0.9981
15	E_a (kJ/mol)	80.76	52.19	37.91
	R	0.9908	0.9908	0.9908
25	E_a (kJ/mol)	102.95	66.95	48.95
	R	0.9983	0.9983	0.9983
35	E_a (kJ/mol)	101.68	66.01	48.26
	R	0.9953	0.9953	0.9953

respectively. Analysis of these tables show that, at all the heating rate values, the activation energies in better agreement with that obtained using Kissinger's method correspond to an A_n type mechanism. Kissinger's, Flynn-Wall-Ozawa, and Tang methods for comparison have chosen because they are independent of a particular kinetics mechanism. From these tables, it can be seen that the optimum heating rate value is 5°C/min, at which the activation energy corresponding to a mechanism A_2 is 116.21 kJ/mol, very close to 116.54 kJ/mol obtained by Flynn-Wall-Ozawa method and 112.52 kJ/mol by Kissinger's method. These facts strongly suggest that the solid-state thermodegradation mechanism followed by this copolymer is a sigmoidal (A_n) type.

The activation energies and correlations were calculated using the Van Krevelen et al.²³ and Horowitz-Metzger²⁴ methods to confirm this sigmoidal behavior. The activation energy is obtained through a linear fitting of $\log g(\alpha)$ versus $\log T$ plots using eq. (7). Table VI shows activation energies and correlation values for A_n mechanisms at different constant heating rate values. From this table, as can be seen, the mechanism A_2 , at heating rate 5 and 25°C/min, gives results in better agreement with that obtained using Flynn-Wall-Ozawa method. At the same time, the best correlation (0.9981) is that corresponding to

TABLE VII
Activation Energies Obtained Using the Horowitz-Metzger Method for Sigmoidal Processes at Different Heating Rates

Heating rate (°C/min)		Mechanism		
		A_2	A_3	A_4
5	E_a (kJ/mol)	135.14	90.19	67.64
	R	0.9978	0.9978	0.9978
15	E_a (kJ/mol)	91.88	61.25	45.94
	R	0.9902	0.9902	0.9902
25	E_a (kJ/mol)	114.35	76.23	57.17
	R	0.9978	0.9978	0.9978
35	E_a (kJ/mol)	113.70	75.45	56.58
	R	0.9944	0.9944	0.9944

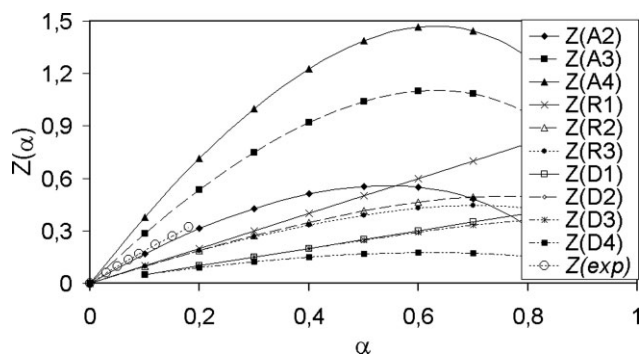


Figure 5 Theoretical $Z(\alpha)$ and experimental $Z(\text{exp})$ (3–18%) master plots.

5°C/min, in good agreement with the value obtained using the Coats–Redfern method. Table VII shows activation energies and correlations obtained using sigmoidal mechanisms and the Horowitz and Metzger model, which uses $\ln g(\alpha)$ versus $(T - T_r)$ plots by eq. (8). Again the best agreement with Flynn–Wall–Ozawa method corresponds to a sigmoidal A_2 mechanism and heating rate 5 and 25°C/min with best correlation (0.9978) at 5°C/min.

According to Criado et al.¹⁵ method, the determination of mechanism of a solid-state process may be easy and precise. This method used reference theoretical curves called master plots, which are compared with experimental data. Experimental results are obtained from eq. (9) at a heating rate of 5°C/min, which is considered the optimum through studies based on integral methods. Figure 5 shows master curve plots $z(\alpha)$ versus α . Because the Doyle approximation has used, only conversion values in the range 3–18% are considered for discussion. As can be seen in Figure 5, in this range of conversion, experimental results show better agreement with the $z(A_2)$ master curve, which corresponds to a sigmoidal A_2 mechanism.

CONCLUSIONS

The kinetics of the thermal degradation of poly (nButMA-*b*-St) diblock copolymer were investigated by thermogravimetric analysis at different β values. The E values of the thermal degradation of copoly-

mer in N_2 obtained by the Kissinger's, Flynn–Wall–Ozawa, and Tang methods were 112.52, 116.54, and 113.41 kJ/mol, respectively, for the decomposition stage. The study of master curves and integral methods indicated that thermodegradation mechanism, in the conversion range considered, followed a sigmoidal A_2 mechanism that is a nucleation and growth solid-state process.

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