

Thermal Decomposition Kinetics of Copolymers Derived from *p*-dioxanone, L-lactide and Poly(ethylene glycol)

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(Received May 24, 2004; Revised October 19, 2004; Accepted October 26, 2004)

Abstract: The kinetic parameters, including the activation energy E , the reaction order n , and the pre-exponential factor Z , of the degradation of the copolymers based on the poly(L-lactide) (PLLA) or poly(*p*-dioxanone-co-L-lactide) (PDO/PLLA) and diol-terminated poly(ethylene glycol) (PEG) segments have been evaluated by the single heating methods of Friedman and Freeman-Carroll. The experimental results showed that copolymers exhibited two degradation steps under nitrogen that can be ascribed to PLLA or PDO/PLLA and PEG segments, respectively. However, copolymers exhibited almost single degradation step in air. Although the values of initial decomposition temperature were scattered, copolymers showed the lower maximum weight loss rate and degradation-activation energy in air than in nitrogen whereas the higher value of temperature at the maximum rate of weight loss was observed in air.

Keywords: Biodegradable, Poly(*p*-dioxanone-co-L-lactide)-b-poly(ethyleneglycol), Thermogravimetric analysis, Activation energy, Friedman method, Freeman-Carroll method

Introduction

As a part of developing biodegradable copolymer, a novel block copolymers of poly(*p*-dioxanone-co-L-lactide)-b-poly(ethyleneglycol) [poly(PDO/PLLA)-b-PEG] has been synthesized [1,2]. With the view of various applications of the biodegradable polymers [3,4], such as molding procedures involving various thermal treatments [5-9] have been developed. Also, the study of the thermal degradation behavior has importance from the view of processing, application and thermal recycling. The susceptibility to thermal degradation of various types block copolymers consisting of PDO, PLLA or PDO/PLLA and PEG segments has been studied using thermogravimetric analysis (TGA) in our previous paper [10]. In this article, we have attempted to investigate the thermal degradation behavior of the block copolymers with three important kinetic parameters by performing thermogravimetric (TG) and derivative thermogravimetry (DTG) analyses in nitrogen and air.

Experimental

Instrumental

Themogravimetric measurements (TG/DTG) were conducted with a TA 2010 type thermogravimetric analyzer in platinum pans at heating rate of 15 °C/min in the range of ambient temperature to 550 °C under a steady flow of nitrogen or air [10].

Materials

The copolymers LLA-b-PEG- or PDO/PLLA-b-PEG were

synthesized by ring opening melt polymerization according to previous method [1]. The chemical composition and molecular parameters of the copolymers used for the study are given in Table 1.

Weight Loss Kinetics

There are several methods (proposed by Friedman, Freeman and Carroll, Chang, Flynn and Wall, Chatterjee and Conrad, Horowitz and Metzger, Kissinger, Coats and Redfern, Van Krevelen, Reich and Ozawa [11-21]) for calculating kinetic parameters, which depend not only on the experimental conditions but also on the mathematical treatment of the data. We have used the Friedman and Freeman-Carroll methods to evaluate the activation energy E , reaction order n , and frequency

Table 1. Molecular weight parameters of copolymers

Sample code	Com- position	$M_n^c \times 10^{-3}$	$M_w^d \times 10^{-3}$	D^e
PDO/PLLA-b-PEG1500 (1A)	19/64/17 ^a	24	33	1.4
PDO/PLLA-b-PEG1500 (1C)	20/58/22 ^a	18	24	1.3
PDO/PLLA-b-PEG1500 (1F)	30/30/40 ^a	8	11	1.2
PDO/PLLA-b-PEG10000 (b16)	10/20/70 ^a	29	38	1.3
PLLA-b-PEG10000 (LPL1)	50/50 ^b	17	18	1.3
PLLA-b-PEG10000 (LPL3)	70/30 ^b	30	37	1.2
PLLA-b-PEG10000 (LPL5)	95/5 ^b	61	152	2.4

^{a, b}Mole ratios of PDO:LLA:PEG and LLA:PEG, respectively calculated from the ¹H-NMR spectra, ^cnumber average molecular weight evaluated by GPC using polystyrene narrow standard, ^dweight average molecular weight evaluated by GPC using polystyrene narrow standard, ^epolydispersity index, M_w/M_n .

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factor Z based on a single heating rate measurement without making any assumptions. Detailed descriptions of these methods are not given because the techniques for evaluating the kinetic parameters from TG/DTG traces are easily available from the literature [11,12]. The equations employed in the methods are listed below.

The thermal decomposition kinetics related to TG weight loss data was attributed to the kinetic equation:

$$da/dt = Z \cdot (1-a)^n \cdot e^{-E/(R \cdot T)} \quad (1)$$

Where a is the weight loss of the polymer undergoing degradation at time t , da/dt denotes the decomposition rate or weight-loss rate, Z is the frequency factor, n represents the decomposition reaction order, E stands for the activation energy, R is the gas constant ($8.3136 \text{ J mol}^{-1} \text{ K}^{-1}$) and T symbolizes the absolute temperature (K).

Friedman technique is a single heating-rate treatment method for TG and DTG curves to find the kinetic parameters of thermal decomposition, which is

$$\ln(Z) = \ln(da/dt) - n \cdot \ln(1-a) + E/(R \cdot T) \quad (2)$$

This is just the natural logarithmic differential form of equation (1). From a plot of $\ln(da/dt)$ or $\ln(1-a)$ against $1/T$, the value of $-E/R$ or $E/(n \cdot R)$ could be determined from the slope. Then Z can be calculated from equation (1).

Freeman-Carroll technique is another single heating-rate treatment method for TG and DTG curves to obtain the kinetic parameters of thermal decomposition. The equation is as follows:

$$\Delta \ln(da/dt)/\Delta \ln(1-a) = n - (E/R)\Delta(1/T)/\Delta \ln(1-a) \quad (3)$$

By plotting $\Delta \ln(da/dt)/\Delta \ln(1-a)$ against $\Delta(1/T)/\Delta \ln(1-a)$, a straight line was obtained with the slope and intercept equal to $-E/R$ and n , respectively. The values of $\Delta \ln(da/dt)$ and $\Delta \ln(1-a)$ are taken at regular small intervals of $\Delta(1/T)$. In addition, the Z can be gained using equation (1).

Results and Discussion

Thermogravimetric Analysis

Copolymers with different composition ratio and with different lengths of segments were considered to investigate the influence of structure on the degradative behavior of these materials. The weight loss (TGA) curve and differential weight loss (DTG) curve of the copolymers were discussed in the previous paper [10]. Qualitative characterization of the degradation process is illustrated by initial weight loss temperature (T_d), maximum weight loss temperature (T_{dm}), maximum weight loss rate ($(da/dt)_m$), total weight loss percentage at the end of the step (W) and final decomposition temperature (T_{df}) obtained from DTG and TGA traces. The characteristic temperatures of degradation for these polymers at heating rate of $15 \text{ }^\circ\text{C}/\text{min}$ are listed in Tables 2 and 3.

Thermal Degradation in Nitrogen

The characteristic degradation parameters T_d , T_{dm1} , T_{dm2} , ΔW_1 , ΔW_2 , T_{df} , $(da/dt)_{m1}$ and $(da/dt)_{m2}$ are listed in Table 2. All the copolymer samples exhibited two overlapping decomposition process. The decomposition tendency is varied with copolymer composition, since all copolymer samples are block type. The degradation parameter results suggest that the first degradation step is due to the blocks from LLA or PDO/PLLA and the second due to the PEG portion. As mentioned previously [1], the terminal groups of the copolymer are

Table 2. Results obtained from TGA and DTG of the copolymers^a in nitrogen

Polymers	T_d^b	1st step		2nd step		T_{df}^e ($^\circ\text{C}$)	$(da/dt)_m^f$ (%/min)	
		T_{dm1}^{c1} ($^\circ\text{C}$)	ΔW^{d1} (wt%)	T_{dm1}^{c2} ($^\circ\text{C}$)	ΔW^{d2} (wt%)		1st step	2nd step
1A	154	311	95	408	4	433	43	2
1C	179	317	89	420	9	443	31	4.7
1F	175	301	82	417	17	442	33	7.6
b16	157	285	30	427	68	457	5.2	29
LLA/PEG 50:50	195	303	40	419	58	447	15	25.7
LLA/PEG 70:30	221	303	69	412	30	440	33	13
LLA/PEG 95:5	271	326	93	415	5	435	24	1.8
PLLA	290	388	98	-	-	417	38	-
PPDO	157	320	94	-	-	353	35	-
PEG 1500	276	418	-	-	98.2	449	-	31
PEG 10000	326	420	-	-	97	454	-	36

^aAnalysis conditions: sample of about 20 mg heated into platinum pan from ambient to $550 \text{ }^\circ\text{C}$ at $15 \text{ }^\circ\text{C}/\text{min}$, ^bdegradation temperature, ^{c1}, ^{c2}temperature at the maximum rate of weight loss corresponding to 1st and 2nd step degradation, respectively, ^{d1}, ^{d2}total weight loss percentage at the end of the steps, ^efinal decomposition temperature, ^fmaximum weight loss rate.

Table 3. Results obtained from TGA and DTG of the copolymers^a in air

Polymers	T_d^b	1st step		2nd step		T_{df}^e (°C)	$(d\alpha/dt)_m^f$ (%/min)	
		T_{dm1}^{c1} (°C)	ΔW^{d1} (wt%)	T_{dm1}^{c2} (°C)	ΔW^{d2} (wt%)		1st step	2nd step
1A	175	341	99	-	-	423	17	-
1C	180	334	97	-	-	421	16	-
1F	159	338	80	420	17	452	24	6.2
b16	156	283	98.1	-	-	459	13.5	-
LLA/PEG 50:50	174	327	98	-	-	430	13	-
LLA/PEG 70:30	199	327	97	-	-	426	20	-
LLA/PEG 95:5	224	350	98	-	-	428	19	-
PLLA	310	386	97	-	-	412	33	-
PPDO	160	333	95	-	-	414	20	-
PEG 1500	199	267	24	418	68	453	4	21
PEG 10000	216	270	25	421	74	457	3	27

^aAnalysis conditions: sample of about 20 mg heated into platinum pan from ambient to 550 °C at 15 °C/min, ^bdegradation temperature, ^{c1, c2}temperature at the maximum rate of weight loss corresponding to 1st and 2nd step degradation, respectively, ^{d1, d2}total weight loss percentage at the end of the step, ^efinal decomposition temperature, ^fmaximum weight loss rate.

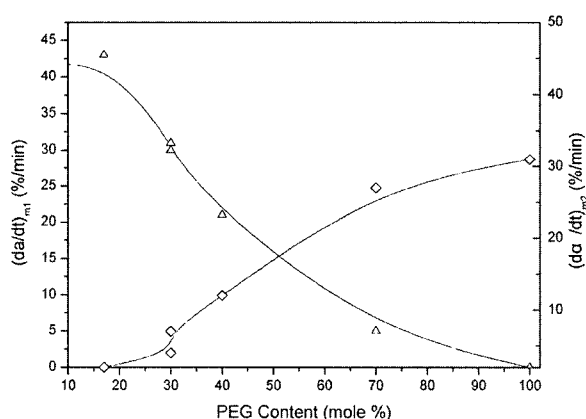


Figure 1. Effect of PEG unit content in triblock copolymer PDO/PLLA-b-PEG- on the maximum weight loss rate corresponding to two weight loss steps in TGA curves under nitrogen at 15 °C/min heating rate. \triangle $(da/dt)_{m1}$ for PDO/PLLA segment and \diamond $(da/dt)_{m2}$ for the PEG segment. $(da/dt)_{m1}$ value at 0 % PEG corresponds to PLLA homopolymer and $(da/dt)_{m2}$ value at 100 % PEG corresponds to PEG1500.

hydroxyl, so the shorter the chain, the more the end hydroxyl groups in the material. The thermostability of end hydroxyl groups in the copolymer could be relatively poor. It has been found for poly(L-lactide) and poly(*p*-dioxanone) that the hydroxyl groups initiate their thermal degradation, specially, for the intra-molecular transesterification (between ester groups and hydroxyl groups) forming oligomeric cyclic rings [9,22]. So the thermostability enhances with increasing the molecular weight and the effect of molecular weight on T_d and T_{dm1} is significant. There is a linear increase of the $(da/dt)_{m1}$ as the PEG content decreased (Figure 1) which is higher in order

than the $(da/dt)_{m2}$ even in case of 100 % PEG. This phenomenon can be explained as being due to the higher heat instability of PDO/PLLA units as compared with PEG units in the copolymer. The degradation of a polymer consisting of hydroxyl ends and carbonyl groups in the backbone chain might be to the formation of more volatile products, thus resulting in a decreasing amount of carbonaceous mass and faster degradation. Results of total weight loss percentage (Table 2) at the end of the steps for the copolymers are almost quantitative to the copolymer composition.

Further information on the thermal degradation of the copolymers can be obtained from the kinetic parameters calculated by the Friedman and Freeman-Carroll methods using single heating rate. Figures 2, 3, and 4 show the relationship given by equation (2) of Friedman technique, whereas the Figures 5, 6, and 7 show the relationship given by the equation (3) of Freeman-Carroll technique. All these representative plots for the thermal decomposition reaction generally show good linearity although some scatter were possibly detected due to the difficulties for accurate measurements at the beginning and end of the plots as frequently encountered in kinetic analysis. Three kinetic parameters derived from the above mentioned linear plots are summarized in the Tables 4 and 5. The values E , n , and $\ln(Z)$ obtained from the 1st step weight loss in TGA curves corresponding to the PDO/PLLA or LLA and PEG blocks in the copolymer are given in Tables 4 and 5, respectively. Kinetic parameters of both types of copolymer (i.e., PDO/PLLA-b-PEG- or LLA-b-PEG) are changed with their compositions. E values obtained from 1st step weight loss in TGA curve derived from both Friedman and Freeman-Carroll technique are roughly depended with molecular weight, but no clear dependency of n and $\ln(Z)$ values on the molecular weight is

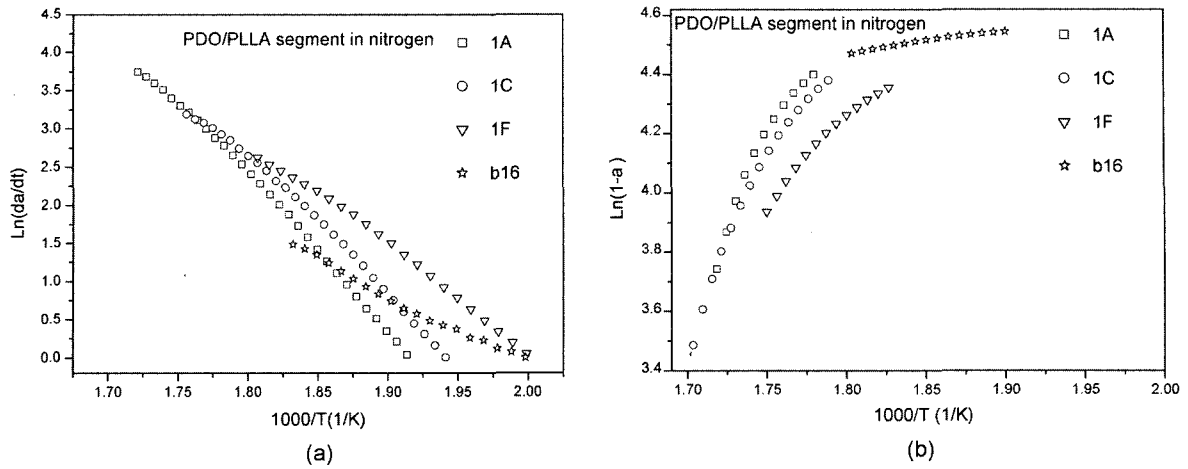


Figure 2. Friedman plots of (a) $\ln(da/dt)$ versus reciprocal temperature and (b) $\ln(1 - a)$ versus reciprocal temperature of the direct calculation of E and n value of thermal degradation of the PDO/PLLA-b-PEG- type copolymer in nitrogen at heating rate of $15\text{ }^\circ\text{C}/\text{min}$.

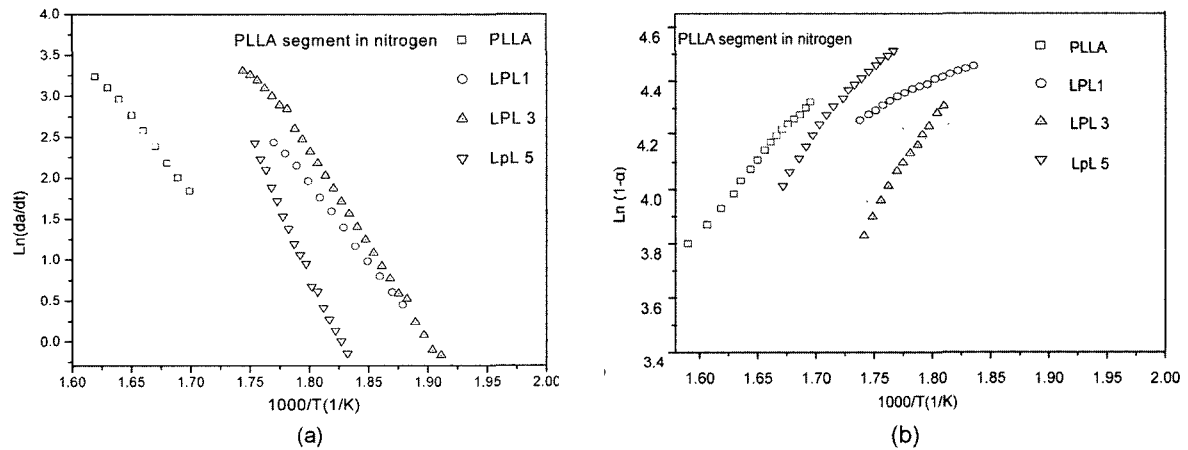


Figure 3. Friedman plots of (a) $\ln(da/dt)$ versus reciprocal temperature and (b) $\ln(1 - a)$ versus reciprocal temperature of the direct calculation of E and n value of thermal degradation of the PLLA-b-PEG- type copolymer in nitrogen at heating rate of $15\text{ }^\circ\text{C}/\text{min}$.

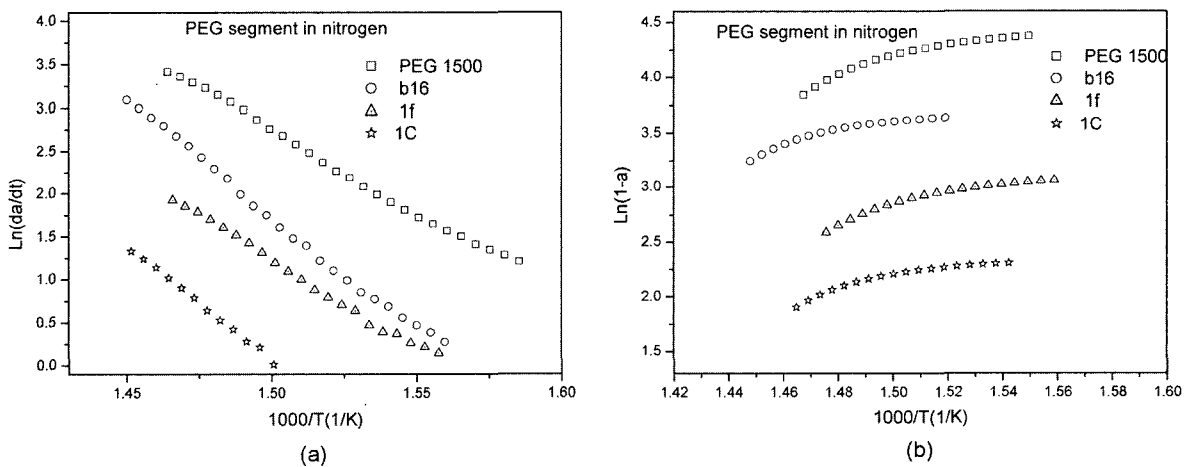


Figure 4. Friedman plots of (a) $\ln(da/dt)$ versus reciprocal temperature and (b) $\ln(1 - a)$ versus reciprocal temperature for the direct calculation of E and n value of thermal degradation of PEG segment of the PDO/PLLA-b-PEG- type copolymer in nitrogen at heating rate of $15\text{ }^\circ\text{C}/\text{min}$.

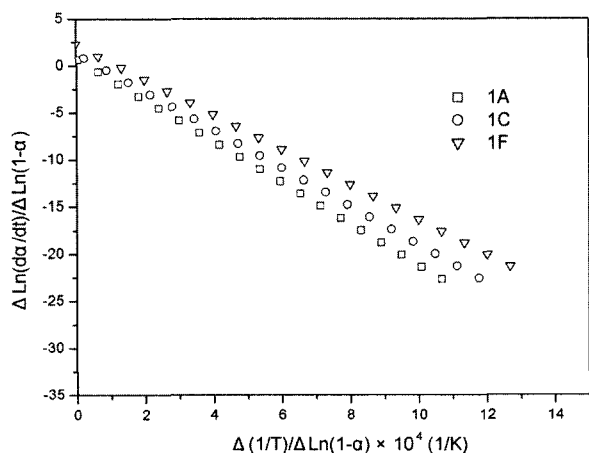


Figure 5. Freeman-Carroll plots of $\Delta \text{Ln}(da/dt)/\Delta \text{Ln}(1-a)$ versus $\Delta(1/T)/\Delta \text{Ln}(1-a)$ for the block copolymers (PDO/PLLA-b-PEG-type) in nitrogen at heating rate of 15 °C/min.

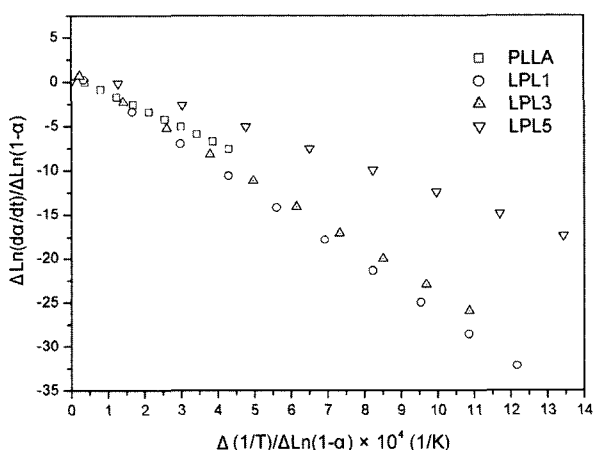


Figure 6. Freeman-Carroll plots of $\Delta \text{Ln}(da/dt)/\Delta \text{Ln}(1-a)$ versus $\Delta(1/T)/\Delta \text{Ln}(1-a)$ for the block copolymers (PLLA-b-PEG-type) in nitrogen at heating rate of 15 °C/min.

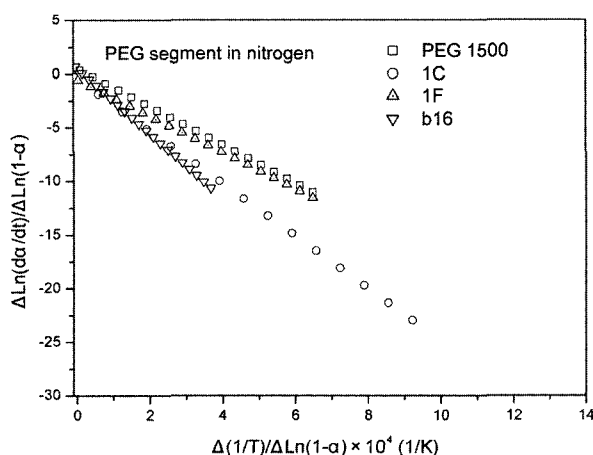


Figure 7. Freeman-Carroll plots of $\Delta \text{Ln}(da/dt)/\Delta \text{Ln}(1-a)$ versus $\Delta(1/T)/\Delta \text{Ln}(1-a)$ for the block copolymers (PDO/PLLA-b-PEG-type) in air at heating rate of 15 °C/min.

Table 4. Kinetic parameters of the first stage of thermal degradation of copolymers under nitrogen at 15 °C/min. The units of E and $\text{Ln}(Z)$ are kJ/mol and min^{-1}

Sample code	Friedman			Freeman-Carroll		
	E	n	$\text{Ln}Z$	E	n	$\text{Ln}Z$
1A	157	2.3	27	171	0.2	33
1C	124	1.6	25	166	1	37
1F	100	2	16	149	2	30
B16	75	2.3	10	91	1	20
PLLA	116	1.8	19	166	0.6	31
LPL5	180	4	24	170	1.1	32
LPL3	174	4	18	190	1.2	37
LPL1	141	3.2	19	193	0.9	24
PDO	130	0.98	20	145	0.7	22

Table 5. Kinetic parameters of the second stage of thermal degradation of copolymers under nitrogen at 15 °C/min. The units of E and $\text{Ln}(Z)$ are kJ/mol and min^{-1}

Sample code	Friedman			Freeman-Carroll		
	E	n	$\text{Ln}Z$	E	n	$\text{Ln}Z$
PEG1500	132	2	19	144	0.5	28
^a 1C	157	3	32	155	0.6	30
^a 1F	151	2.2	24	141	0	25
PEG10000	207	2.2	33	232	0.2	42
^b LPL1	215	2.5	34	207	0.2	37
^b LPL3	212	3	32	215	0.8	34
^b b16	199	2.8	31	207	0	39

^aCopolymers consisting of PEG1500, ^bcopolymers consisting of PEG1500.

observed. In general, E means the lowest energy needed for reaction (degradation) and n indicates the exponential relation between the concentration of reactants $(1-a)$ and the weight loss rate da/dt described in equation (1). A decomposition order of zero characterizes the most rapid decomposition reaction. As the order increases, the decomposition reaction becomes slower.

Kinetic parameters (Table 5) of two types PEGs ($M_n = 1,500$ and $10,000$) with their different compositions in the copolymer are derived from the 2nd step weight loss in the TGA curves. Although the numerical values are different with that of parent PEG, and variation with the calculation methods, the kinetic parameters obtained are roughly constant and irrespective with the composition in the copolymer. But $(da/dt)_{m2}$ values are changed with the composition of PEG (Table 2). The decomposition behavior of the PDO/PLLA segment of the copolymer (PDO/PLLA-b-PEG-type) under nitrogen is quite different from that of the respective homopolymer PPDO or PLLA [9,22]. The results obtained of the first step weight loss in TGA curve and discussed so far could be

taken as the random sequence of PDO and LLA units at the two ends of PEG block because no distinct peaks representative of thermal decomposition of individual PPDO and PLLA homopolymers are observed during the thermal decomposition of the tri-component type triblock copolymer. In the case of random sequence, generally step wise degradation of individual homopolymer segments merge into single step [23,24].

Three kinetic constants of the thermal degradation summaries for the block copolymers (Tables 4 and 5), E and $\ln(Z)$ values obtained by Friedman technique are smaller but the n value is larger than the Freeman-Carroll technique. Clearly there are tremendous variations in the calculated E and $\ln(Z)$ depending on the mathematical approach for the thermal degradation behavior in different temperature ranges. As a matter of fact, kinetic parameters change more or less with temperature, even though we assume that they do not vary

with temperature in every mathematical technique. Freeman-Carroll describes the behavior of thermal degradation in the temperature range from $(T_{dm}-[30\sim60]K)$ to T_{dm} . However, the E value given by Friedman technique mainly indicates the thermal decomposition behavior in the temperature range from $(T_d-(20\sim40)K)$ to T_d , in which the linear relation between $\ln(da/dt)$ and $1/T$ is available.

Thermal Degradation in Air

The thermal degradation behavior (TGA and DTG curves) of the copolymers in air was different from that in nitrogen [10]. The characteristic degradation parameters are listed in Table 3. The results indicated that the single step weight loss takes place in most of the copolymers (except 1F), compared to the corresponding analysis under nitrogen.

It is obvious from Table 3 that T_d and $(da/dt)_{m1}$ values are

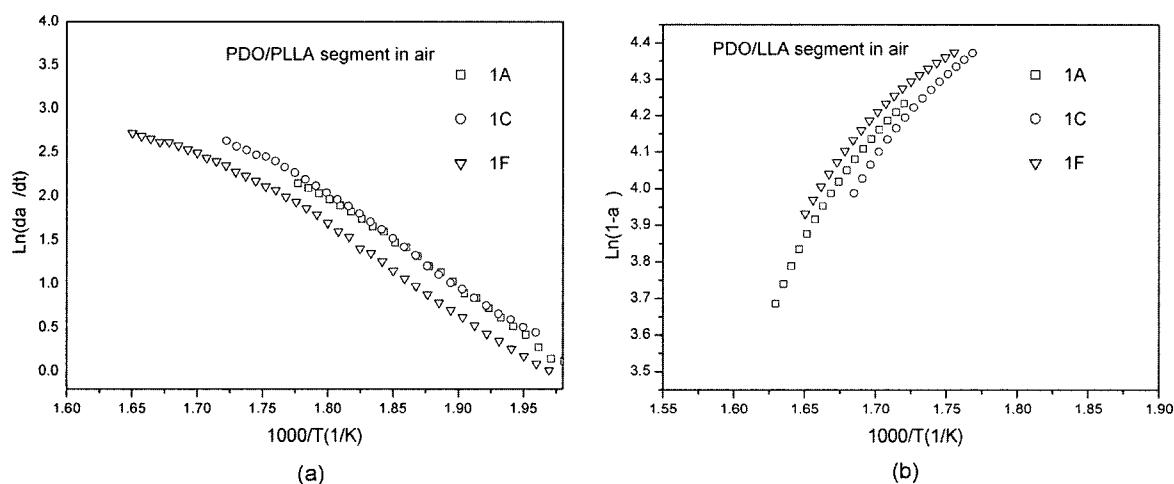


Figure 8. Friedman plots of (a) $\ln(da/dt)$ versus reciprocal temperature and (b) $\ln(1-a)$ versus reciprocal temperature of the direct calculation of E and n value of thermal degradation of the PDO/PLLA-b-PEG- type copolymer in air at heating rate of $15^\circ\text{C}/\text{min}$.

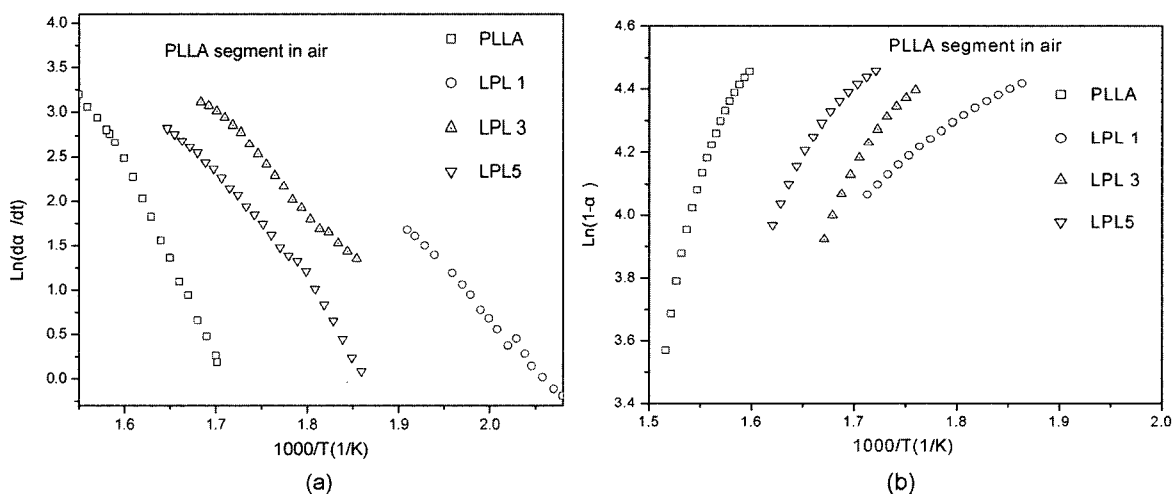


Figure 9. Friedman plots of (a) $\ln(da/dt)$ versus reciprocal temperature and (b) $\ln(1-a)$ versus reciprocal temperature of the direct calculation of E and n value of thermal degradation of the LLA-b-PEG- copolymer in air at heating rate of $15^\circ\text{C}/\text{min}$.

smaller than that of in nitrogen, but T_{dm} values are higher than that of in nitrogen. Two degradation steps were detected in the TGA traces of PEG in air. It should be noticed that besides the single volatilization step, another degradative process takes place at lower temperature compared to the corresponding analysis run under nitrogen. So that the overall stability of PEG in air is decreased. The first step weight loss of PEG in air may correspond to the degradation of PEG chain into smaller fragments of oxygenated products by random chain scission process and the second step may be attributed to the thermodegradation of small fragments into volatile products [25,26]. The reason for higher T_{dm} values in air (Table 3) than in nitrogen may be the corresponding weight loss might arise not only from the degradation of PLLA or PDO/PLLA segments of the block copolymer, but also from the oxidative degradation of the PEG blocks which is located

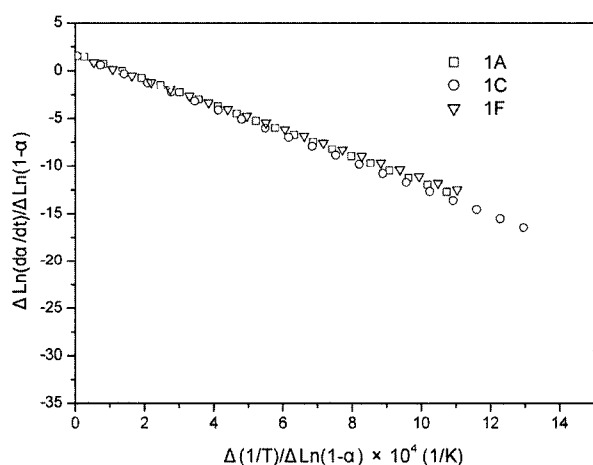


Figure 10. Freeman-Carroll plots of $\Delta \text{Ln}(da/dt)/\Delta \text{Ln}(1-a)$ versus $\Delta(1/T)/\Delta \text{Ln}(1-a)$ for the block copolymers (PDO/PLLA-b-PEG-) in air at heating rate of 15 °C/min.

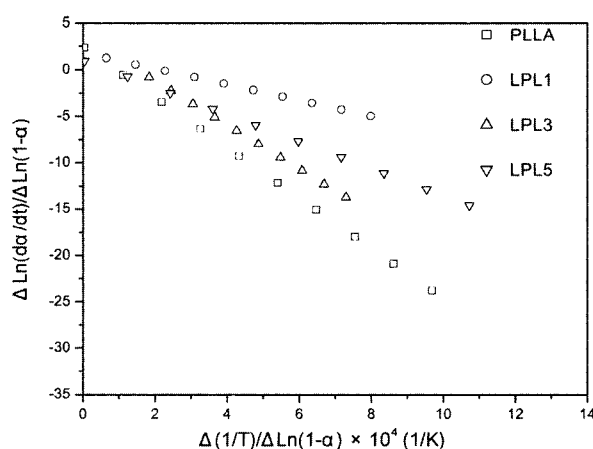


Figure 11. Freeman-Carroll plots of $\Delta \text{Ln}(da/dt)/\Delta \text{Ln}(1-a)$ versus $\Delta(1/T)/\Delta \text{Ln}(1-a)$ for the block copolymers (PLLA-b-PEG- type) in air at heating rate of 15 °C/min.

Table 6. Kinetic parameters of the first stage of thermal degradation of copolymers in air at 15 °C/min. The units of E and $\text{Ln}(Z)$ are kJ/mol and min^{-1}

Sample code	Friedman			Freeman-Carroll		
	E	n	$\text{Ln}Z$	E	n	$\text{Ln}Z$
1A	58	1.1	10	108	1.2	20
1C	66	1.6	10	111	1	20.6
1F	75	1.8	11	100	0.8	19
b16	60	2	12	80	0.9	18
PLLA	157	2.1	25	208	2.5	33
LPL5	91	2.2	13	116	1.2	21
LPL3	83	2.5	12	119	1.3	18
LPL1	75	2.2	9	83	1.5	14
PDO	64	1.6	9	100	2	15

in the same range of temperature. The disappearance of the lower temperature volatilization step observed in PEG when they inserted into the block copolymers would suggest that the corresponding oxidative process may involve hydroxyl end groups [25,27].

The relationship given by equation (2) of Friedman technique for the copolymer in air are shown in Figures 8 and 9 and the relationship given by equation (3) of Freeman-Carroll technique for the decomposition process in air are shown in Figures 10 and 11. Almost linear relations were obtained similar to test runs under nitrogen. The kinetic parameters including E , n and $\text{Ln}(Z)$ reported in Table 6 are mostly smaller than those obtained in nitrogen under the same condition. E and $\text{Ln}(Z)$ values are also smaller in Friedman technique than in Freeman-Carroll technique. All the kinetic parameters are varied with the copolymer compositions like in nitrogen. Irrespective to the degradation behavior of PDO/PLLA segments of the copolymer consisting of relatively higher fraction of PLLA, all kinetic parameters for PLLA degradation were higher in air than in nitrogen, although T_d , T_{dm} and $(da/dt)_{m1}$ values were smaller in air. Two degradation steps were observed in PLLA under nitrogen (lower temperature degradation peak obtained in DTG curve [10]), indicated the two dominating decomposition pathways (i.e., tin-catalyzed PLLA depolymerization and intramolecular ester exchange [28]). Probably, the PLLA degradation in air is mainly caused by the thermo-oxidative decomposition and the higher stability may be due to the residual catalyst-oxygen interactions [29].

These degradation behaviors are quite different than the previous studies for poly(ether ether ketone) [30], chlorinated atactic polypropylene poly. vinyl chloride [31] and poly (p-oxy benzoate-co-ethylene terephthalate) [32].

Conclusions

Some important thermal degradation kinetic parameters

such as activation energy, degradation orders and frequency factors of two co-polymers viz PLLA-b-PEG and PDO/PLLA-b-PEG were calculated using Friedman and Freeman-Carroll method by taking the account of results derived from TGA and DTG in a single heating rate. Results show that the decomposition temperature, kinetic parameters of the co-polymers basically depended on the composition, testing environment and calculation methods. Higher volatilization temperature was obtained from the TGA curve in air for most of the co-polymers at 1st step weight loss in spite of the scattered initial weight loss temperature. It was concluded that the decomposition order and activation energy of the co-polymers was higher under nitrogen environment relative to the open aerial environment. Aerial environment may facilitate the cleavage of chemical bonds that leads the generation of volatility in co-polymers so that they come to have low activation energy and decomposition orders.

Acknowledgement

We express our appreciation to the Korea Health 21 R & D project (01 PJ1 PG3 31400-0013), Ministry of Health and Welfare for supporting this work.

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