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The Study of Kinetics of Poly[(*R*,*S*)-3-hydroxybutyrate] Degradation Induced by Carboxylate

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Summary: The carboxylate induced degradation of the poly[(*R*,*S*)-3-hydroxybutyrate] (PHB) has been investigated with non-isothermal measurements. The apparent activation energies for PHB degradation have been determined. Application of the Kissinger's and Flynn-Wall-Ozawa's method for TG and DSC derived data gave good correlation of the results proving applicability of the non-isothermal DSC measurements for the study. Moreover, dependence of the apparent activation energies on the activity of the carboxylate has been found.

Keywords: activation energy; biodegradable; degradation; thermal properties; thermogravimetric analysis (TGA)

Introduction

Polyhydroxyalkanoates (PHA)s have attracted a great deal of attention because of their biodegradability and thermoplastic properties. Besides intensive studies on their biodegradability, understanding of their thermal stability and thermal degradation behavior has importance for processing and application.

One of the PHAs representative is poly[(*R*)-3-hydroxybutyrate] which is well known as typical biodegradable polyester in practical applications. Thermal degradation of PHB was studied by many researchers[1–11] and it was suggested to occur almost exclusively by a non-radical random chain scission reaction (cis-elimination) involving a six-member ring transition state.[1–3] It was also reported that under the heating conditions, the low degradation products may enhance the production of the volatile products[12] or the degradation can be enhanced by the presence of Ca or Mg ions due to coordinative mechanism.[13] Apart from the degradation mechanism activation energies (E_a) were determined for cis-elimination degradation process.[12,13]

Recently we have reported the E1cB mechanism of base catalyzed PHB degradation proceeding via deprotonation of α- carbon.[14,15] In present paper study of E_a of this process is shown. Degradation of synthetic PHB in the presence of different acetic acid salts has been investigated and respective E_as have been determined in order to compare with previously reported for other PHB degradation mechanisms.[12,13] In this study, thermal degradation of PHB has been studied under non-isothermal conditions.

Experimental Part

Materials

Synthetic poly[(*R*,*S*)-3-hydroxybutyrate] (PHB, $M_n = 10\,000$; $M_w/M_n = 1.06$) has been obtained as previously reported.[16,17] For thermal degradation experiments samples of crude and acidified PHB with –COONBu$_4$ and –COOH end groups respectively have been used. Samples of the acidified PHB containing desired

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acetate have been prepared by mixing of chloroform solutions of the known amount of PHB with desired amount of methanol solution of known concentration of the respective acetate. Next, the solvent has been evaporated and samples have been dried under vacuum at room temperature till constant weight. All the prepared mixtures have contained $9.57 \cdot 10^{-5}$ mol of acetate/g of sample. In case of crude PHB – carboxylate are inherited from initiator and their concentration has been also equal to $9.57 \cdot 10^{-5}$ mol/g.

Potassium acetate, (KAc) (Aldrich), lithium acetate (LiAc) (Aldrich) have been used as received. 18-crown-6 ether (18C6) (Aldrich) has been dried under vacuum at 50 °C for 72 hours. KAc/18C6 complex has been prepared by adding the crown ether to the solution of the potassium acetate in dry methanol. Molar ratio of the acetate to the crown ether has been 1:1.05. After stirring overnight methanol has been evaporated and the complex has been dried under the vacuum.

Thermal Degradation Test

A TA Instruments 2910 DSC has been used for studying the thermal properties of PHB samples. The PHB samples have been placed in aluminum hermetic pans. Sample size has been of 1 mg has been employed for these experiments. Temperature range has been 25–300 °C. Dry, oxygen-free nitrogen has been used to purge the DSC at a rate of 50 $cm^3 \cdot min^{-1}$. Heat flow for each of the mixtures have been scanned at heating rates of 2.5, 5, 10 and 20 $deg \cdot min^{-1}$. Temperature and heat flow calibrations using indium and gallium standards have been performed prior to the experiments according to ASTME967[18] and ASTM E968,[19] respectively.

To confirm a single process degradation thermogravimetric analyses (TGA) have been performed for the same as for DSC samples. TG experiments have been run on Thermogravimeter TGA/SDTA 851^e Mettler Toledo with heating rates 5, 10, 20 and 40 $deg \cdot min^{-1}$ under a nitrogen flow 60 $cm^3 \cdot min^{-1}$. The samples (each of about 8 mg) have been heated in range 25–300 °C.

Kinetic Methods

The data from dynamic DSC measurements have been analyzed using two kinetic models: Kissinger's[20] (differential) and Flynn-Wall-Ozawa's[21,22] (integral). These methods have been applied since it is not necessary to have a prior knowledge of the reaction mechanism. Both methods are based on the Arrhenius equation and on an assumption that the amount of energy consumed in a reaction or a process is proportional to number of moles substance that reacted.

According to Kissinger's method, the rate of thermal reaction can by written as Arrhenius equation:

$$r = \frac{d\alpha}{dt} = Ae^{(E/RT_p)}(1-\alpha)^n$$

where α is the lost fraction of the material decomposed, n the reaction order, R the gas constant, T the temperature [K], A is a pre-expotentional constant that is the property of the material and E_a.

If the sample temperature is changed by a controlled and constant heating rate, $\beta = dT/dt$, the variation in the degree of conversion can be analyzed as a function of temperature which depends on the time of heating. The reaction can be written as follows:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = \beta\frac{d\alpha}{dT}$$

Combination of the above equations is a background for the applied methods.

Since the maximum rate of decomposition occurs when dr/dt is equal to zero, differentiating previous equation with respect to time and equating resulting expression with zero gives, equation witch can be written in the natural logarithm form:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{E}{R}\right) - \ln(A) - (n-1)\ln(1-\alpha)_p + \frac{E}{RT_p}$$

where T_p is the temperature of maximum rate of a degradation and β is a heating rate.

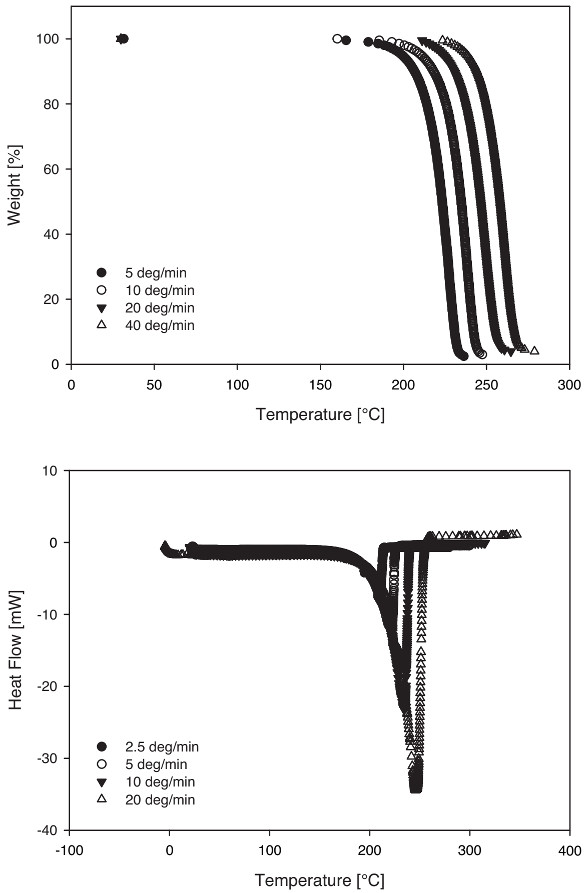

Figure 1.
Example experimental a)TG and b) DSC curves at different heating rates for PHB/KAc.

The activation energy can be calculated, by Kissinger's method, from the slop from the plot of ln(β/T$_p^2$) versus 1000/T$_p$ and fitting to a straight line.

$$\frac{d\left[\ln\left({}^{\beta}\!/_{T_p^2}\right)\right]}{d\left({}^{1}\!/_{T_p}\right)} = -\frac{E_a}{R}$$

This equation is independent of reaction order n however, calculation of the pre-expotentional factor is on assumption of a first-order reaction as follows:

$$A = \beta\frac{E}{RT_p^2}\exp\left(\frac{E}{RT_p}\right)$$

Flynn-Wall- Ozawa's method is a second theoretical treatment and this method is based on Doyle's approximation:

$$\begin{aligned}\log\beta &= \frac{1}{2.303}\ln\beta\\ &= -0.4567\frac{E}{RT}\\ &\quad + \left(\log\frac{AE}{R} - \log F(x) - 2.315\right)\end{aligned}$$

Where β is the same heating rate, E$_a$ is the activation energy, R is the gas constant and F(x) is the conversion-dependent term.

In this method a plot of lnβ versus 1/T$_p$ should give straight line with a slope of 1.052 Ea/R.

$$\frac{d(\ln\beta)}{d\left({}^{1}\!/_{T_p}\right)} = -1.052\frac{E_a}{R}$$

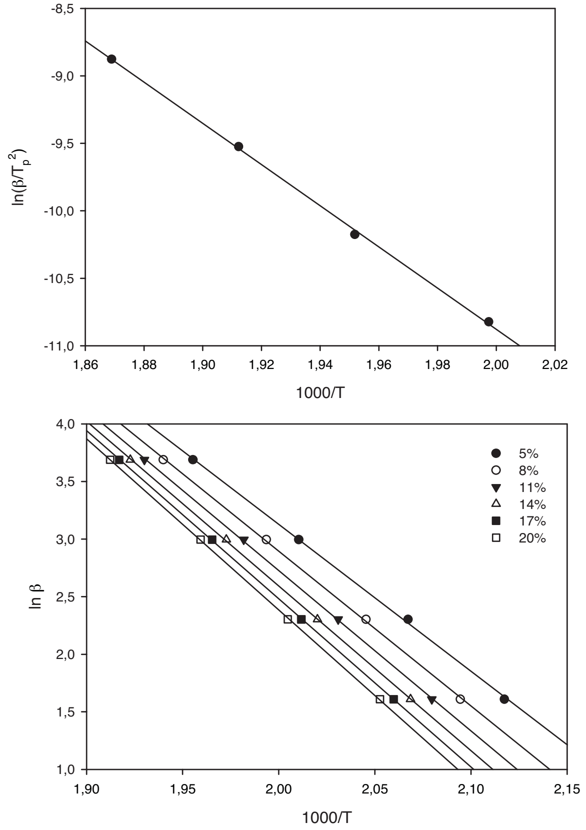

Figure 2.
Typical plots of a) Kissinger's method and b) Flynn-Wall-Ozawa's method applied to TG experimental data of mixture PHB with potassium acetate (KAc).

The activation energy can by calculate for different levels of conversion but in this article for DSC-based calculations the method has been applied only to the maximum rate of the degradation (top of the peak).

Table 1.
The comparison of the derived activation energies for PHB with potassium acetate (KAc).

$\alpha^{a)}$ [%]	E_a [kJ/mol]	$R^{2\ b)}$
5	100.8408	0.9993
8	106.2619	0.9996
11	110.0545	0.9998
14	113.0069	0.9999
17	115.3826	0.9999
20	117.4255	0.9999
average:	110.50	

[a)] initial weight loss.
[b)] linear regression coefficent.

Results and Discussion

The thermogravimeric analyses of PHB/acetates have been performed prior to confirm single-stage decomposition (Figure 1a). Moreover, procedural (initial and final temperature) are well defined. In case of the PHB/KAc inflection points of TG curves have been found at 227.5, 239.2, 249.8, and 261.9 °C for the heating rates 5, 10, 20 and

Table 2.
The comparison of the derived activation energies for PHB/KAc

Experimental method	Calculation method	E_a [kJ/mol]
TG	Kissinger	126.96
	Flynn-Wall-Ozawa	110.50
DSC	Kissinger	108.46
	Flynn-Wall-Ozawa	111.00

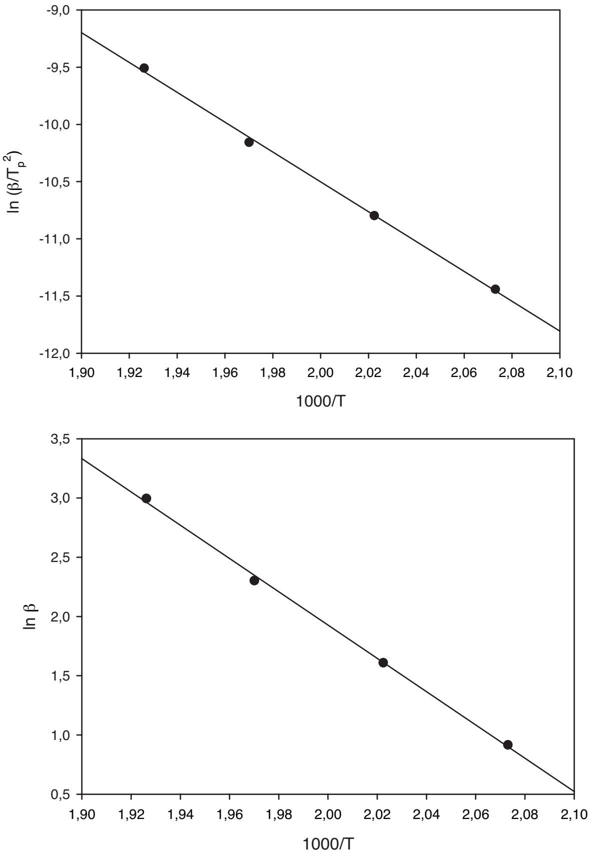

Figure 3.
Typical plots of a) Kissinger's method and b) Flynn-Wall-Ozawa's method applied to DSC experimental data of PHB/KAc.

40 deg · min^{-1}, respectively. Next step has been DSC experiment with various but constant heating rate (Figure 1b). These data for the PHB/KAc reveal peaks at temperatures (T_p) 246.0, 234.4, 221.3 and 209.2 °C for the heating rates 2.5, 5, 10 and 20 deg · min^{-1}, respectively.

Using Kissinger's method as well as the obtained TG data the activation energy of the decomposition of PHB has been calculated from a straight line fit of a plot of $\ln(\beta/T_p^2)$ versus $1000/T_p$ (Figure 2a). The value obtained from Figure 2a for the activation energy is 126.96 kJ/mol.

The activation energy has been also determined using the Flynn-Wall-Ozawa's method from a linear fitting of $\ln\beta$ versus 1000/T at different conversions. The activation energy has been calculated for conversions of 5, 8, 11, 14, 17 and 20%. The result of this analysis is given at Figure 2b. The depicted best straight line fitted are nearly parallel indicating a constant activation energy range of conversion analyzed and confirming the validity of the approach applied. The calculated activation energies of PHB/KAc are listed in Table 1.

The DSC data have been proceeded similarly. The only difference is application of the T_p in Flynn-Wall-Ozawa's method since determination of the exact conversion is impossible. Respective plots of Kissinger's method and Flynn-Wall-Ozawa's method for DSC data have been depicted in Figure 3. The calculated Ea for these data are 108.46 kJ/mol and 111.00 kJ/mol respectively.

Table 3.
The apparent activation energies of PHB/acetate calculated by Kissinger's and Flynn-Wall-Ozawa's method from DSC data.

Entry	Sample	β [deg · min^{-1}]	T_p [°C]	Kissinger		Flynn-Wall-Ozawa
				E_a [kJ/mol]	A [10^{10}min^{-1}]	E_a [kJ/mol]
1.	PHB	2.5	270.1	137.66	244.59	137.85
		5	280.8			
		10	294.6			
		20	307.2			
2.	PHB/LiAc	2.5	210.8	111.52	15.50	113.94
		5	223.0			
		10	234.3			
		20	247.3			
3.	PHB/KAc	2.5	209.2	108.46	7.68	111.00
		5	221.3			
		10	234.4			
		20	246.0			
4.	PHB/(KAc/18C6)	2.5	205.9	99.77	0.99	102.18
		5	218.1			
		10	231.5			
		20	245.8			
5.	PHB-COO$^-$ $^+$NBu$_4$	2.5	204.6	94.29	0.25	96.30
		5	216.7			
		10	232.0			
		20	246.4			

The comparison of the determined apparent activation energies obtained from TG and DSC data using Kissinger's method and Flynn-Wall-Ozawa's method (Table 2) shows good correlation of the results. Furthermore, it indicates that DSC measurements are applicable in the study of the investigated degradation process. The E_as obtained from TG data analysis have been expected to be higher from the DSC obtained due to contributed evaporation enthalpy of the volatile products of the degradation and the Kissinger's method has shown expected behavior. Surprisingly, the integral method result has been in better correlation with DSC obtained E_as. It is explained by proceeding the calculations on relatively low degree of the degradation and due to this fact contribution evaporation enthalpy of volatile products is very low.

Applying above calculation procedure E_as of all the other PHB/acetate mixtures has been calculate using DSC data and sorted in order of decreasing activation energy (Table 3).

Analysis of the obtained results reveals two very important facts: (i) activation energy of the carboxylate induced degradation of PHB is lower than activation energy of the degradation via cis-elimination mechanism making the E1cB process useful tool for low molecular weight compounds preparation; (ii) the decreasing activation energy values correlate with increasing radius of the counter-ion and activity of the acetate used which is dependent on the increase of the counter-ion size. The E_a dependence on acetate activity is another proof for ionic mechanism of this type of the degradation. Furthermore, basing on the above data the degradation rate constant as well as the half life time of the PHB can be estimated from Arrhenius equation.

Conclusion

The quantitative approach for describing carboxylate induced degradation of PHB has been presented. Moreover, applicability of non-isothermal measurements for investigation of the kinetics of the degradation of PHB has been proved. The most important conclusion is that the carboxylate induced degradation occurs also in moderate temperatures due to lower activation energy of the process.

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