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Kinetic of thermal degradation of poly(isobornyl methacrylate)

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The kinetic of the thermal degradation of poly(isobornyl methacrylate) (PIBORNMA) was investigated by thermo gravimetric (TG) analysis at different heating rates. TG curves showed that the thermal decomposition of PIBORNMA occurred in one stage. The apparent activation energies of thermal decomposition of PIBORNMA was determined by Tang, Flynn-Wall-Ozawa (FWO), Kissenger–Akahira–Sunose (KAS) and Coats-Redfern methods and the values were 80.30, 84.69, 79.81 and 84.413 kJ/mol, respectively. The mechanism function and pre-exponential factor was determined by master plots method.

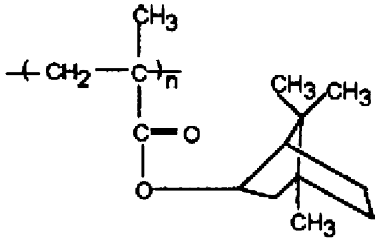
KEY WORDS: poly(isobornyl methacrylate); thermal analysis; apparent activation energies of thermal decomposition.

1. Introduction

Poly(isobornyl methacrylate) (PIBORNMA) is a novel transparent polymer resin, which can be used as optical material. The glass transition temperature (T_g) of PIBORNMA is higher than many of the general transparent polymer resins. The use of PIBORNMA is widely and its degradation is an important aspect of polymer science, so it is interesting for this manuscript to investigate the degradation of PIBORNMA. Kinetic of thermal degradation of solids has been investigated from thermo gravimetric (TG) thermograms at linear rates of temperature rise in a number of studies. Thermogravimetry is widely used as a method to investigate the thermal degradation of polymers and to determine the kinetic parameters such as activation energy, pre-exponential factor, and reaction order. Many studies have been carried out on thermal stability of methacrylate polymers containing various ester residues [1–5]. The thermal stability and degradation depend on the composition [6–8]. The thermal degradation of methacrylate polymers containing the isobornyl moiety in the side chain has not been much studied. In this work, the thermal degradation in one stage of poly(isobornyl methacrylate) was investigated by various methods of TG analysis.

2. Experimental

2.1. Materials



Scheme 1. The structure of PIBORNMA.

Poly(isobornyl methacrylate) (Scheme 1) was supplied by Aldrich in powder form and Registry No. 64114-51-8. The average molecular weight, M_w is ~554.000 by GPC.

2.2. Thermo gravimetric analysis

The TG curves were obtained using a Shimadzu TGA-50 thermo balance. The measurements were performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 mL min^{-1} up to 1273 K. The heating rates were 5, 10, 15 and 20 °C min^{-1} and sample sizes ranged in mass from 8 to 10 mg. Platinum crucible is used as sample container.

2.3. Kinetics methods

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer degradation. In this paper, Integral isoconversional methods have been used to analyze the non-isothermal kinetics of PIBORNMA.

The rate of solid-state non-isothermal decomposition reactions is expressed as

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$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{A}{\beta}\right)\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{1}$$

Rearranging equation (1) and integrating both sides of the equation leads to the following expression.

$$g(\alpha) = \left(\frac{A}{\beta}\right)\int_{T_0}^{u}\exp\left(\frac{-E}{RT}\right)\mathrm{d}T = \left(\frac{AE}{\beta R}\right)p(u) \tag{2}$$

Where $p(u) = \int_{\infty}^{u} -\left(\frac{e^{-u}}{u^2}\right)\mathrm{d}u$ and $u = \mathrm{E/RT}$.

2.3.1. *Flynn–Wall–Ozawa method [9, 10]*

This method is derived from the integral method. The technique assumes that the A, $f(\alpha)$ and E are independent of T while A and E are independent of α, then equation (2) might be integrated to give the following in logarithmic form:

$$\log g(\alpha) = \log(AE/R) - \log\beta + (E/RT) \tag{3}$$

Using Doyle's approximation [11] for the integral which allows for $E/RT > 20$, equ. (3) now can be simplified as

$$\log\beta = \log(AE/R) - \log g(\alpha) - 2.315 - 0.4567E/RT \tag{4}$$

2.3.2. *Coats–Redfern method [12]*

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

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

The expressions of $g(\alpha)$ for different mechanism [13,14] have been listed table 1, and apparent activation energy of thermal decomposition for degradation mechanism can be obtained from the slope of a plot of $\ln\left[g(\alpha)/T^2\right]$ versus $1000/T$

2.3.3. *Tang method [15]*

Taking the logarithms of sides and using an approximation formula for resolution of equation (2), the following equation can be obtained:

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left(\frac{AE}{Rg(\alpha)}\right) + 3.635041 - 1.894661\ln E - \frac{1.001450E}{RT} \tag{6}$$

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

2.3.4. *Kissenger–Akahira–Sunose method [16]*

This method is integral isoconversional methods as FWO.

$$\ln\left[\frac{\beta}{T^2}\right] = \ln\left[\frac{AR}{Eg(\alpha)}\right] - \frac{E}{RT} \tag{7}$$

The dependence of ln (β/T^2) on $1/T$, calculated for the same α values at the different heating rates β can be used to calculate the activation energy.

2.3.5. *Determination of the kinetic model by master plots method*

Using a reference at point $\alpha = 0.5$ and according to equation (2), one gets

$$g(\alpha) = \left(\frac{AE}{\beta R}\right)p(u_{0.5}) \tag{8}$$

where $u_{0.5} = E/RT$. When equation (2) is divided by equation (8), the following equation is obtained

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(u)}{p(u_{0.5})} \tag{9}$$

Plots of $g(\alpha)/g(0.5)$ against α correspond to theoretical master plots of various $g(\alpha)$ functions [17, 18]. To draw the experimental master plots of $P(u)/P(u_{0.5})$ against α from experimental data obtained under different heating rates, an approximate formula [19] of $P(u)$ with high accuracy was used $P(u) = \exp(-u)/\ [u(1.00198882u + 1.87391198)]$. Equation (9) indicates that, for a given α, the experimental value of $g\ (\alpha)/g(\alpha_{0.5})$ are equivalent when an appropriate kinetic model is used. Comparing the experimental master plots with theoretical ones can conclude the kinetic model [20].

3. Results and discussion

3.1. *Thermal decomposition process*

The thermal decomposition of PIBORNMA is selected for the kinetic study. The apparent activation energies of thermal decomposition of the decomposition process were determined by multiple heating rate kinetics. The typical dynamic TG thermograms of PIBORNMA in a dynamic nitrogen atmosphere are shown in figure 1, where the TG curves for the decomposition of 8–10 mg PIBORNMA sample are shown with 5, 10, 15 and 20 °C min^{-1} under 60 mL min^{-1} nitrogen gas. All TG curves of PIBORNMA show that the thermal decomposition took place mainly in one stage and the curves shift to the right-hand side with the increasing.

3.2. *Determination of apparent activation energy of thermal decomposition (E), kinetic model g(α), and pre-exponential factor A*

Several techniques using different approaches have been developed for solving the integral of equation (2). The four methods investigated in this work are those of

Table 1
Algebraic expression for the most frequently used mechanisms of solid state process

No	Mechanisms	Symbol	Diferantial form, f(α)	Integral form, g(α)
Sigmoidal curves				
1	N and G (n = 1)	A_1	$(1-\alpha)$	$[-\ln(1-\alpha)]$
2	N and G (n = 1.5),	$A_{1.5}$	$(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
3	N and G (n = 2)	A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
4	N and G (n = 3),	A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
5	N and G (n = 4),	A_4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Deceleration curves				
6	Diffusion, 1D	D_1	$1/(2\alpha)$	α^2
7	Diffusion, 2D	D_2	$1/(\ln(1-\alpha))$	$(1-\alpha)\ln(1-\alpha)+\alpha$
8	Diffusion, 3D	D_3	$1.5/[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
9	Diffusion, 3D	D_4	$[1.5(1-\alpha)^{2/3}][1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
10	Diffusion, 3D	D_5	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$
11	Contracted geometry shape (cylindrical symmetry)	R_2	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracted geometry shape (sphere symmetry)	R_3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Acceleration curves				
13		P_1	1	α
14		P_2	$2\alpha^{1/2}$	$\alpha^{1/2}$
15		P_3	$(1.5)\alpha^{2/3}$	$\alpha^{1/3}$
16		P_4	$4\alpha^{3/4}$	$\alpha^{1/4}$
17		$P_{3/2}$	$2/3(\alpha)^{-1/2}$	$\alpha^{3/2}$
18		$P_{2/3}$	$3/2(\alpha)^{1/3}$	$\alpha^{2/3}$
19		$P_{3/4}$	$4/3(\alpha)^{-1/3}$	$\alpha^{3/4}$

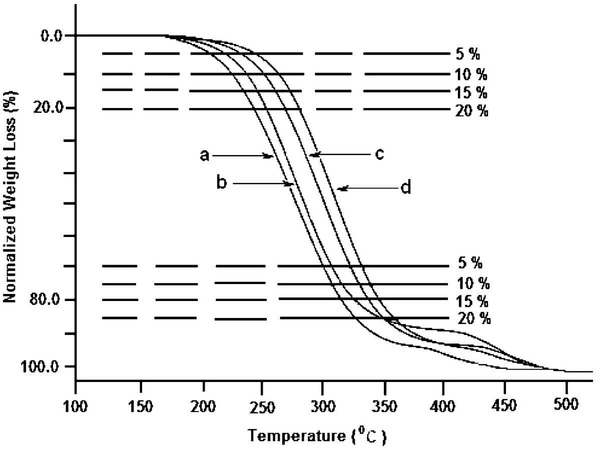

Figure 1. The TG curves of PIBORNMA (a = 5 °C/min; b = 10 °C/min; c = 15 °C/min and d = 20 °C/min).

Flynn–Wall–Ozawa, Kissenger–Akahira–Sunose, Tang and Coats–Redfern method. The methods of Coats–Redfern method is based on a single heating rate, while the other methods are based on multiple heating rates. Isoconversional methods have been firstly employed to analysis the TG data of PIBORNMA, because it is independent of any thermal degradation mechanisms. Equation (6) has been used to obtained the apparent activation energies of thermal decomposition which can be calculated from the plot of ln $(\beta/T^{1.894661})$ versus $1000/T$ and fitting to a straight line. The mean value of apparent activation energies of thermal decomposition of PIBORNMA in N_2 is 80.30 kJ/mol. The calculated results have been summarized in table 2.

Another isoconversion method used in this paper is that of Kissenger–Akahira–Sunose. Equation (7) has been utilized to determine the values of apparent activation energies of thermal decomposition from plots of $\ln(\beta/T^2)$ against $1000/T$ over a wide range of conversation. In this case $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 have been chosen to evaluate E values of PIBORNMA. The determined apparent activation energies of thermal decomposition are listed in table 2 and the average value is 79.81 kJ/mol over the range of α given. This result agrees better with the mean value of apparent activation energies of thermal decomposition obtained by Tang method.

Flynn–Wall–Ozawa method is an integral method also being independent of the degradation mechanism. Equation (4) has been used and the apparent activation energy of thermal decomposition of PIBORNMA can therefore be obtained from a plot of log β against $1000/T$ for a fixed degree of conversion since the slope of such a line is given by $-0.456\ E/RT$. Figure 2 illustrated the plots of ln β versus $1000/T$ at varying conversion. The apparent activation energies of thermal decomposition calculated from the slopes and the values are given in table 2. The mean value of apparent activation energy of thermal decomposition was found to be 84.69 kJ/mol. The comparatively, the E value of PIBORNMA is very close to ones obtained by the two methods. The E values of PIBORNMA obtained by Tang, KAS and FWO methods are 80.30, 79.81, 84.69 kJ/mol, respectively.

Table 2
The apparent activation energies of thermal decomposition and correlation coefficient of PIBORNMA obtained by KAS, FWO and Tang methods

Conversion	KAS method		Tang method		FWO method	
	Activation energy, E (kJ/mol)	Correlation coefficient, r	Activation energy, E (kJ/mol)	Correlation coefficient, r	Activation energy, E (kJ/mol)	Correlation coefficient, r
0.1	90.15	0.99352	90.53	0.99357	92.68	0.99448
0.2	75.24	0.99519	75.71	0.99583	79.93	0.99538
0.3	76.14	0.98010	76.62	0.99035	81.04	0.99684
0.4	70.96	0.99628	71.45	0.99669	76.37	0.99759
0.5	80.72	0.98086	81.22	0.99112	85.79	0.99508
0.6	79.52	0.99428	80.02	0.99433	84.77	0.99543
0.7	82.68	0.98569	83.19	0.98590	87.91	0.98858
0.8	79.87	0.99789	83.53	0.99889	88.32	0.99904
0.9	83.00	0.99799	80.39	0.99789	85.43	0.99829
mean	79.81		80.30		84.69	

Constant mass loss lines are determined by measuring the temperature at a given mass percent for each rate. In figure 3 the Arrhenius type plots of dynamic TG runs are shown for mass ranging from $\alpha = 0.1$ to 0.9 in N_2. Table 2 summaries the apparent activation energy of thermal decomposition and correlation coefficient on the overall mass loss from 10 to 90 mass% in N_2. The results indicate an acceptable correlation coefficient always superior to 0.98010.

The thermal decomposition of PIBORNMA in N_2 presents a same behavior for Tang, KAS and FWO methods. The initial apparent activation energy of thermal decomposition required to initial decomposition was about 83 kJ/mol. When 60% mass of PIBORNMA is loss, the apparent activation energy of thermal decomposition decreases to a maximum value such as 72 kJ/mol. This is followed by an increase from about 72 kJ/mol to about 91 kJ/mol in the region $0.6 < \alpha < 0.95$. This increase corresponds to the transition region the second step in the mass loss.

In order to find out the mechanism of the thermal decomposition of PIBORNMA, Coats-Redfern method has been chosen as it involves the mechanisms of solid-state process. According to equation (5), apparent activation energies of thermal decomposition for every $g(\alpha)$ function listed in table 1 can be calculated at constant heating rates from fitting of $\ln(g(\alpha)/T^2)$ versus $1000/T$ plots. The apparent activation energies of thermal decomposition and the correlations at constant heating rates 5, 10, 15 and 20 °C min^{-1}, have been tabulated in table 3 for thermal degradation of PIBORNMA. In order to determine the mechanism the degradation of PIBORNMA agrees better with, we have compared the apparent activation energies of thermal decomposition obtained by methods above. According to table 3, it could be found that the E values of PIBORNMA in N_2 corresponding to mechanism $P_{3/2}$ have best agreement with the values obtained by Tang (80.30 kJ/mol), KAS (79.81 kJ/mol) and FWO methods (84.69 kJ/mol).

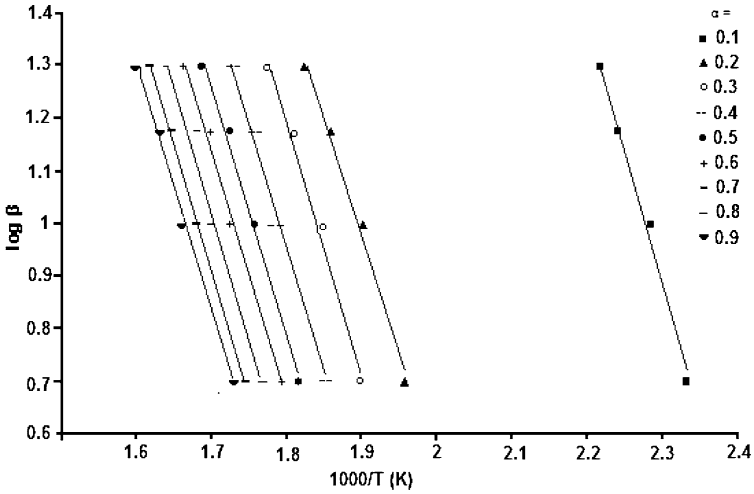

Figure 2. FWO plots of PIBORNMA at varying conversation in N_2 atmosphere.

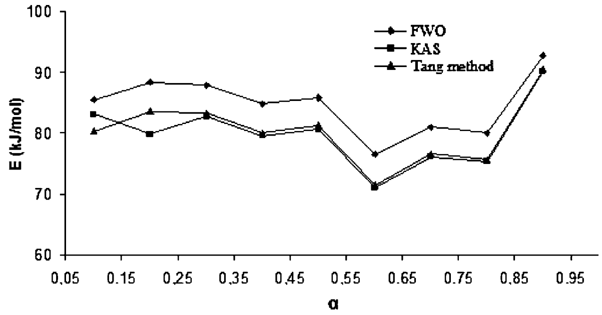

Figure 3. The apparent activation energy of thermal decomposition (E) as a function of degree of conversion for the decomposition process of PIBORNMA calculated by Tang, KAS and FWO methods.

Table 3
The apparent activation energies of thermal decomposition of PIBORNMA in N_2 atmosphere obtained by Coats-Redfern method

	5 °C min^{-1}		10 °C min^{-1}		15 °C min^{-1}		20 °C min^{-1}	
	E (kJ/mol)	r	E (kJ/mol)	r	E (kJ/mol)	r	E (kJ/mol)	r
A_1	69.501	0.97485	67.242	0.98111	67.101	0.98739	69.492	0.97457
$A_{1.5}$	43.752	0.98612	42.001	0.97128	41.822	0.97249	43.453	0.97187
A_2	30.764	0.98567	29.374	0.97788	29.174	0.98660	30.424	0.98893
A_3	17.766	0.97446	16.755	0.98866	16.536	0.98060	17.405	0.98989
A_4	11.268	0.98835	10.446	0.98412	10.217	0.97548	10.884	0.97625
D_1	120.18	0.99687	115.38	0.99808	116.67	0.99492	119.11	0.99803
D_2	127.09	0.99393	122.27	0.99715	123.28	0.99073	126.22	0.99706
D_3	130.17	0.99161	125.36	0.99458	126.22	0.98786	129.41	0.99570
D_4	136.68	0.98481	131.89	0.99072	132.42	0.97996	136.15	0.99080
D_5	113.77	0.99794	109.05	0.99769	110.50	0.99687	112.60	0.99782
R_2	61.851	0.98898	59.319	0.99411	59.576	0.98434	61.297	0.99412
R_3	64.223	0.98331	61.698	0.98983	61.834	0.97776	63.756	0.98995
P_1	55.985	0.99659	53.449	0.99780	53.964	0.99441	55.235	0.99775
P_2	23.877	0.99581	22.471	0.99690	22.605	0.99296	23.298	0.99691
P_3	13.175	0.99452	12.156	0.99520	12.152	0.99049	12.644	0.99534
P_4	7.8261	0.99215	6.9954	0.99150	6.9843	0.98565	7.3224	0.99200
$P_{3/2}$	88.087	0.99679	84.413	0.99800	85.312	0.99476	87.171	0.99794
$P_{2/3}$	34.576	0.99624	32.966	0.99742	33.054	0.99377	33.924	0.99739
$P_{3/4}$	39.921	0.99637	37.965	0.99755	38.285	0.99400	39.266	0.99752

Especially at the heating rate in 10 °C min^{-1}, the apparent activation energy of thermal decomposition corresponding to mechanism $P_{3/2}$ is 84.413 kJ/mol, which is very close to the value of 84.69 kJ/mol obtained by FWO method. The correlation coefficient is also much higher than other.

In order to confirm the conclusions, the experimental master plots $P(u)/P(u_{0.5})$ against α constructed from experimental data of the thermal decomposition of PIBORNMA under different heating rates and the theoretical master plots of various kinetic functions are all shown in figure 4. The comparisons of the experimental master plots with theoretical ones indicate that the kinetic process of the thermal decomposition of PIBORNMA agree with the $P_{3/2}$ master curve very well.

By assuming P_n law, experimental data, the expression of the P_n model, and the average reaction energy predetermined were introduced into equ. (2), the following expression was obtained.

$$\ln[\beta R/E] - \ln[P(u)] = \ln A - 1.5\ln[\alpha^{1.5}] \qquad (10)$$

A group of lines were obtained by plotting $\ln[/E] - \ln[P(u)]$ against $-\ln[\alpha^{1.5}]$. As shown in figure 5 and table 4, the pre-exponential factor was calculated from the intercepts of the lines corresponding to various heating rates.

The apparent activation energies of thermal decomposition of PIBORNMA were obtained by Tang, KAS, FWO and Coats-Redfern methods in N_2 atmosphere. The results are similar to the values for other methacrylate polymers given in the literature [9, 21].

4. Conclusions

The apparent activation energy values of thermal decomposition of PIBORNMA were calculated by Tang, KAS, FWO and Coats-Redfern methods and this values were 80.30, 79.81, 84.69, 84.413 kJ/mol, respectively. The resulting logarithmic value of the pre-exponential factor ln A (s^{-1}) is 14.79. The analysis of the results obtained by Coats-Redfern method and master

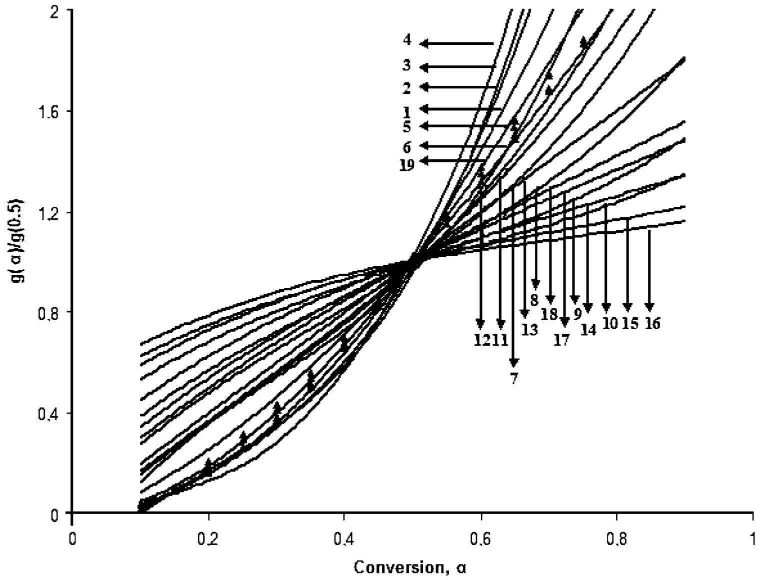

Figure 4. Master plots of theoretical $g(\alpha)/\,g(0.5)$ against α for various reaction models (solid curves represent 19 kinds of reaction models given in table 1) and experimental data (▲) of PIBORNMA at the heating rates 5, 10, 15 and 20 °C min^{-1}.

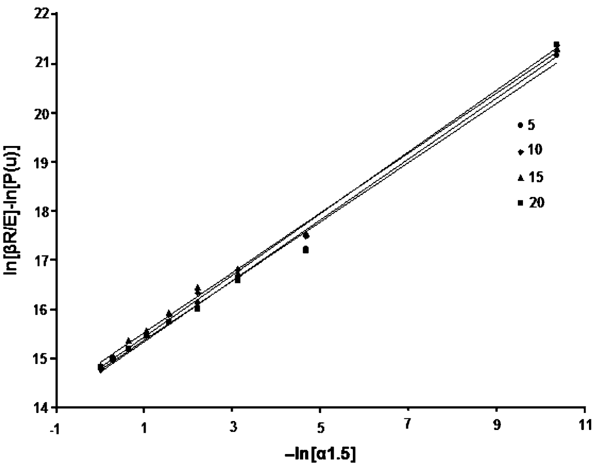

Figure 5. Plotting $\ln[\beta R/E] - \ln[P(u)]$ against $-\ln[\alpha^{1.5}]$ for PIBORNMA at heating rates.

Table 4

The correlation coefficients obtained by plotting $\ln[\beta R/E] - \ln[P(u)]$ against $-\ln[\alpha^{1.5}]$

β (K mol^{-1})	$\ln A(\text{s}^{-1})$	r
5	14.76	0.99729
10	14.80	0.99844
15	14.90	0.99845
20	14.72	0.99569
mean	14.79	

plots method shows that the degradation mechanism of PIBORNMA in N_2 goes to $P_{3/2}$ mechanism. Thermal analysis methods have proved useful not only in defining suitable processing conditions for polymers as well as useful service guidelines for their application, but also in gaining information on relationships of thermal properties of polymer chain structure. By the way, the decomposition mechanism of PIBORNMA also can be determined by the Py-GC-MS method.

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