

# High-Resolution Thermogravimetry of Poly(4-methyl-1-pentene)

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**ABSTRACT:** Thermal degradation and kinetics of poly(4-methyl-1-pentene) were investigated by nonisothermal high-resolution thermogravimetry at a variable heating rate. Thermal degradation temperatures are higher, but the maximum degradation rates are lower in nitrogen than in air. The degradation process in nitrogen is quite different from that in air. The average activation energy and frequency factor of the first stage of thermal degradation for the poly(4-methyl-1-pentene) are 2.4 and 2.8 times greater in air than those in nitrogen, respectively. Poly(4-methyl-1-pentene) exhibits almost the same decomposition order of 2.0 and char yield of 14.3–14.5 wt % above 500°C in nitrogen and air. The isothermal lifetime was estimated based on the kinetic parameters of nonisothermal degradation and compared with the isothermal lifetime observed experimentally. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 2201–2207, 1999

**Key words:** poly(4-methyl-1-pentene); high-resolution thermogravimetry; nonisothermal thermogravimetry; thermal degradation; degradation kinetics; thermostability; isothermal lifetime

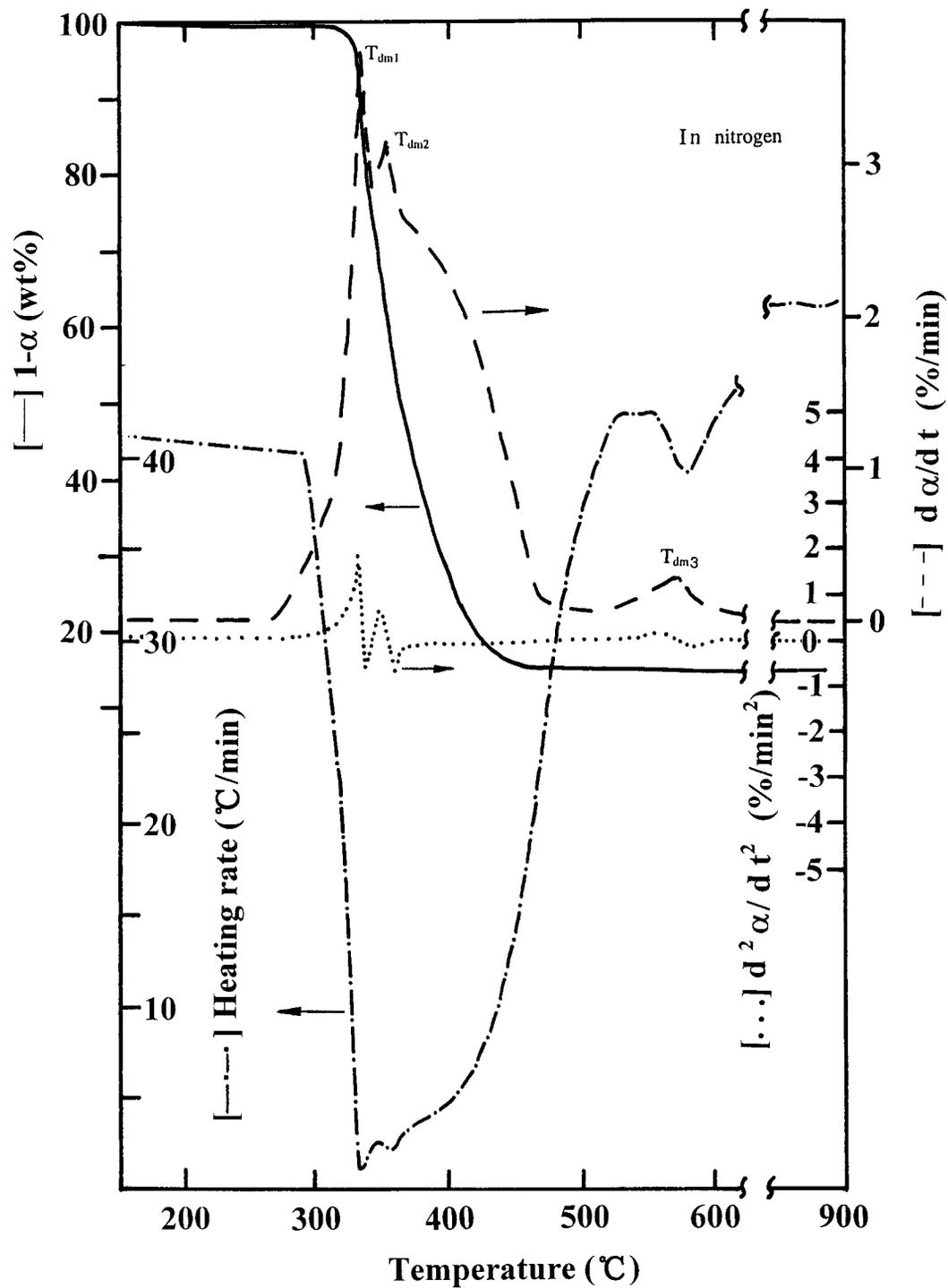
## INTRODUCTION

Thermal degradation of polymers is an important subject because it covers a wide field, ranging from the development of thermoresistant polymers and stabilization of thermolabile polymers to the recycling of polymer scrap.<sup>1</sup> In view of the expected shortage of raw materials,<sup>1</sup> the thermal degradation of polymers is sometimes considered an appropriate method to produce certain urgently needed chemicals, and might become more attractive in the future as raw material costs for chemicals increase.

Organic polymers consisting essentially of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms are distinguished from many inorganic materials that resist thermal decomposition to 2000°C. Polymers are thermally stable only below a certain limiting temperature range, usually from 250° to 350°C (for flexible aliphatic poly-

mers) or from 350° to 500°C (for rigid aromatic polymer). If the temperature is increased to 1000°C, the polymers decompose into many small fragments, such as free radicals, free ions, hydrogen, carbon oxide or dioxide, water, or sulfur dioxide. High thermosensitivity of the polymers is derived from the covalent bonds in the polymer chains with a certain limiting bond strength. Dissociation energies of single bonds are in the range of 147–736 kJ mol<sup>-1</sup>. Generally, the absorption of sufficient energy quanta that exceed the dissociation energy can only occur at temperatures higher than 400° to 600°C, at which the thermal cracking of the polymer chains takes place. In other words, the scissions of chemical bonds under the influence of heat are the result of overcoming bond dissociation energies.

There are only a few studies on the isothermal degradation of poly(4-methyl-1-pentene) (PMP).<sup>2–4</sup> Thermal degradation products and decomposition mechanisms have been revealed. However, there seems to be no systematic reports on nonisothermal

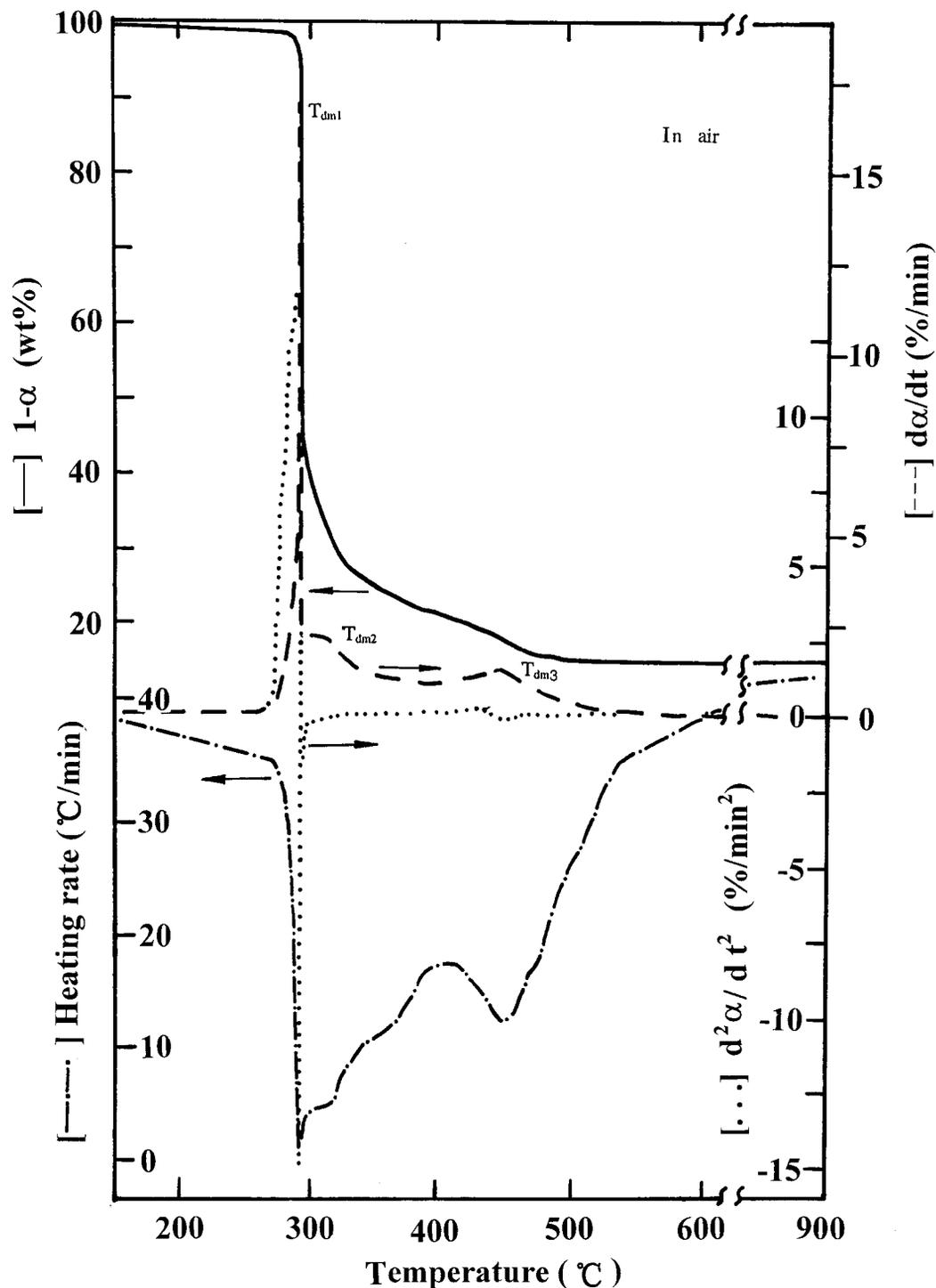


**Figure 1** High-Res TG (—), DTG (---), 2DTG (···), and heating rate (-·-·) curves of PMP in nitrogen flow at an initial heating rate  $50^{\circ}\text{C min}^{-1}$  and resolution 4.

degradation temperatures and kinetics of PMP. The various aspects of thermal degradation of the PMP will be discussed by high-resolution thermogravimetry (High-Res TG).

## EXPERIMENTAL

PMP pellets, designated as TPX MX-004 made by the Mitsui Petrochemical Co., Japan, was kindly



**Figure 2** High-Res TG (—), DTG (---), 2DTG (···), and heating rate (-·-·) curves of PMP in air flow at an initial heating rate  $50^{\circ}\text{C min}^{-1}$  and resolution 4.

supplied by Professor Guan-Wen Chen of the Chemistry Institute of Academia Sinica.

Thermogravimetry (TG) analyses were performed under both nitrogen and air flow of 30

$\text{mL min}^{-1}$  on a model high-resolution TGA 2950 thermal analyzer (Hi-Res™ TGA) produced by TA Instruments Inc. (New Castle, DE), using the high-resolution mode interfaced to TA In-

**Table I** Characteristics of Thermal Degradation of PMP by a High-Res TG

Sample Code	Atmosphere	Heating Rate (°C min <sup>-1</sup> )	$T_d/T_{dm1}/T_{dm2}/T_{dm3}$ (°C)	$(d\alpha/dt)_{m1}/(d\alpha/dt)_{m2}/(d\alpha/dt)_{m3}$ (%/min)	$(d\alpha/dT)_{m1}/(d\alpha/dT)_{m2}/(d\alpha/dT)_{m3}$ (%/°C)	Char Yield at 600°C (wt %)
MX-004	Nitrogen	Variable	331/337/353/571	3.7/3.1/0.3	3.0/1.4/0.1	14.5
MX-002 <sup>a</sup>	Nitrogen	20	343/371/—/—	44/—/—	2.2/—/—	0
MX-004	Air	Variable	292/292/318/444	17/2.7/1.5	50/0.6/0.1	14.3

<sup>a</sup> From ref. 4.

struments 2000 controller with a General V.4.1C microprocessor. Sample size was 1.0 mg (in nitrogen) and 0.72 mg (in air). The initial heating rate and resolution were fixed at 50°C min<sup>-1</sup> and 4.0, respectively. Sensitivity was fixed at its default value of 1 in the temperature range of 25°–900°C. Thermal degradation temperatures and kinetic parameters were determined using the techniques described previously.<sup>6–11</sup>

The *Freeman–Carroll method* uses the equation:

$$\frac{[\Delta \text{Ln}(d\alpha/dt)]/\Delta \text{Ln}(1 - \alpha)}{\Delta(1/T)/\Delta \text{Ln}(1 - \alpha)} = n - (E'/R) \cdot \Delta(1/T)/\Delta \text{Ln}(1 - \alpha) \quad (1)$$

From a plot of  $[\Delta \text{Ln}(d\alpha/dt)]/\Delta \text{Ln}(1 - \alpha)$  against  $\Delta(1/T)/\Delta \text{Ln}(1 - \alpha)$ ,  $-E'/R$  and  $n$  may be determined from the slope and intercept of the plot when a regular  $\Delta(1/T)$  value was taken.<sup>12</sup>

The *Friedman method* uses the following natural logarithmic equation:

$$\text{Ln}(d\alpha/dt) = \text{Ln} Z + n \cdot \text{Ln}(1 - \alpha) - E'/RT \quad (2)$$

By plotting  $\text{Ln}(d\alpha/dt)$  or  $\text{Ln}(1 - \alpha)$  against  $1/T$ , a straight line can be obtained with a slope of  $-E'/R$  or  $E'/n \cdot R$ .<sup>13</sup>

The *Chang method* uses the following equation:

$$\text{Ln}[(d\alpha/dt)/(1 - \alpha)^n] = \text{Ln} Z - E'/RT \quad (3)$$

A plot of  $\text{Ln}[(d\alpha/dt)/(1 - \alpha)^n]$  against  $1/T$  will yield a straight line only if the decomposition reaction order  $n$  was correctly selected.<sup>14</sup> The slope of the line will provide the  $E'$  and the intercept provides  $\text{Ln} Z$ .

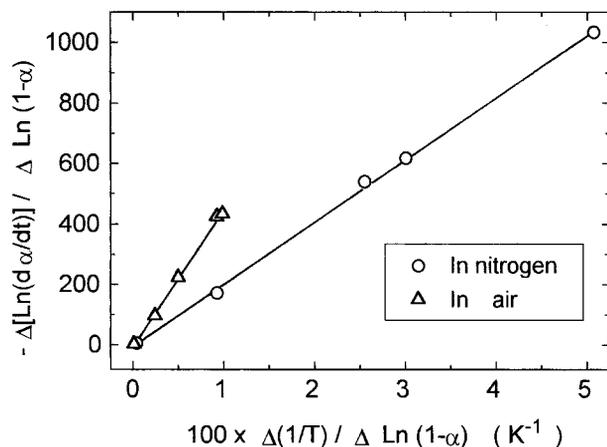
The degradation temperature,  $T_d$ , was obtained by an extrapolation of the initial degradation portion of the TG curve.  $T_{dm1}$ ,  $T_{dm2}$ , and

$T_{dm3}$  correspond to the peak temperatures at the first, second, and third maxima on the derivative TG (DTG) curves, respectively.  $(d\alpha/dt)_{m1}$ ,  $(d\alpha/dt)_{m2}$ , and  $(d\alpha/dt)_{m3}$  [or  $(d\alpha/dT)_{m1}$ ,  $(d\alpha/dT)_{m2}$ , and  $(d\alpha/dT)_{m3}$ ] represent the maximal weight-loss rates at the first, second, and third maxima on the DTG curves, respectively. These data were compared with existing literature values.

## RESULTS AND DISCUSSION

High-Res TG, DTG, second DTG (2DTG), and heating rate curves for the PMP in nitrogen and air are shown in Figures 1 and 2. Thermal degradation of the PMP in nitrogen occurs through two major fast degradation steps and a subsequent slow degradation step, whereas the thermal degradation of PMP MX-002 in nitrogen observed at a constant heating 20°C min<sup>-1</sup> appears to occur through only one quite fast degradation step.<sup>4</sup> This suggests that the High-Res TG indeed exhibits higher resolution than conventional TG at a constant heating rate. Thermal degradation behavior in air is different. Degradation in air seems to take place through one major very fast degradation step and then two slower degradation steps.

Characteristic degradation temperature ( $T_d$ ), the temperature at the maximal weight-loss rate ( $T_{dm}$ ), the maximal weight-loss rate  $(d\alpha/dt)_m$ , and  $(d\alpha/dT)_m$ , and char yield at 600°C are given in Table I. A series of decomposition data of PMP obtained at a constant heating rate of 20°C min<sup>-1</sup> is also listed in Table I.<sup>4</sup> It is found that the  $T_d$ ,  $T_{dm1}$ ,  $T_{dm2}$ ,  $(d\alpha/dt)_{m2}$ , and  $(d\alpha/dT)_{m2}$  are higher, but the  $(d\alpha/dt)_{m1}$  and  $(d\alpha/dT)_{m1}$  are lower in nitrogen than in air because the PMP is susceptible to oxygen in air. However, the char yield at 600°C in nitrogen is the same as that in air. The char yields at 600°C of 14.5% in nitrogen

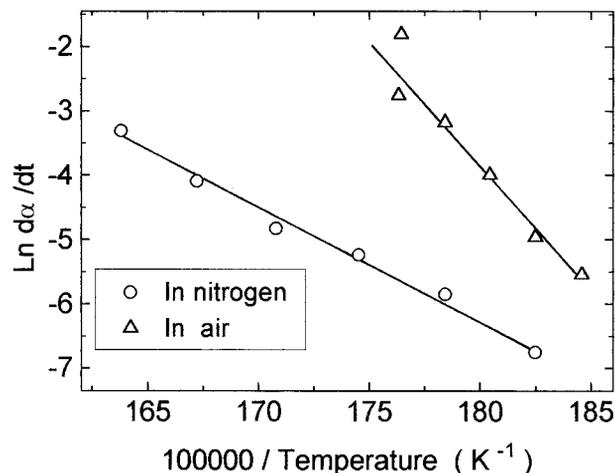


**Figure 3** Application of the Freeman–Carroll method to High-Res TG data obtained in nitrogen (○) and air (△) for PMP.

and 14.3% in air suggest that only one carbon per structural unit has char-forming ability, because the theoretical char residue is  $1 \times 12 \times 100 \div 84 = 14.3$  wt %.<sup>5</sup> It is appreciated that the  $T_d$ ,  $T_{dm1}$ , and  $(d\alpha/dt)_{m1}$  are higher by conventional TG than by High-Res TG, but  $(d\alpha/dT)_{m1}$  and char yield at 600°C by conventional TG are lower. Obviously, the thermostability and char yield of aliphatic PMP is lower than those of aromatic polymers, such as aromatic polyester,<sup>6,7</sup> aromatic polyamide,<sup>8</sup> bisphenol A polysulfone,<sup>9</sup> and polycarbonate.<sup>10</sup>

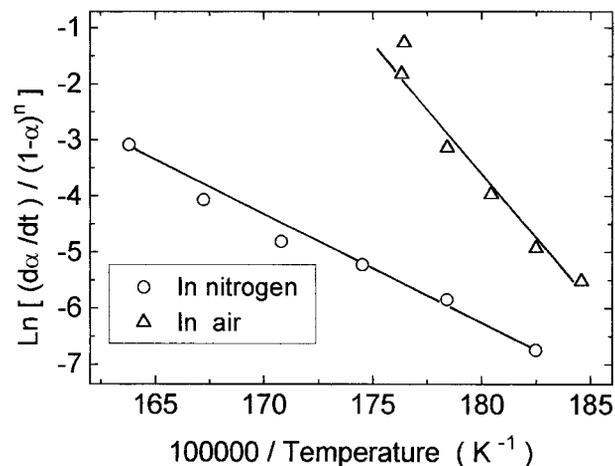
As can be seen in Table I, the weight loss of the first stage of the thermal degradation of PMP in nitrogen is 23.1%, which corresponds to the exclusion of the 44% pendant group in the form of propane. However, weight loss of first-step degradation in air is 55.5%, corresponding to the losses of 20% isobutene and 80% propane from all pendant isobutyl groups. It is reported that propane and isobutene are the main components of the volatile products during degradation in the temperature range from 290° to 360°C.<sup>3</sup>

Three plots for the calculation of kinetic parameters of the first step of thermal degradation of the PMP are shown in Figures 3–5. Kinetic data obtained are presented in Table II. There are a few variations in the three kinetic data with the mathematical methods used in the calculations. The  $E$  value in nitrogen calculated by the Freeman–Carroll method is the largest, whereas the  $E$  value in air by the Chang method is the largest among the three methods used. It is noted that the average  $E$  value of 375 kJ mol<sup>-1</sup> in air is at least two times as large as that in nitrogen (157



**Figure 4** Application of the Friedman method to High-Res TG data obtained in nitrogen (○) and air (△) for PMP.

kJ mol<sup>-1</sup>). The  $E$  value of 157 kJ mol<sup>-1</sup> in nitrogen is greater than the reported  $E$  value of 122 kJ mol<sup>-1</sup> (see ref. 15), but lower than the  $E$  value of 224 kJ mol<sup>-1</sup> obtained by isothermal TG in a vacuum.<sup>3</sup> It is known that, below 150°C, tertiary hydrogen on the tertiary carbons on the main chain is the major decomposition site. Above 150°C, the tertiary carbons on the pendant groups become reactive.<sup>16</sup> If tertiary hydrogen is abstracted from the pendant groups, the carbon–carbon bond situated in the side groups will break down. This will lead to the formation of propane and isobutene. The dissociation energies of C–H and C–C bonds are close to the average activa-



**Figure 5** Application of the Chang method to High-Res TG data obtained in nitrogen at  $n = 2.0$  (○) and in air at  $n = 1.5$  (△) for PMP.

**Table II Kinetic Parameters of Thermal Degradation of PMP by a High-Res TG Measurement in Nitrogen and Air**

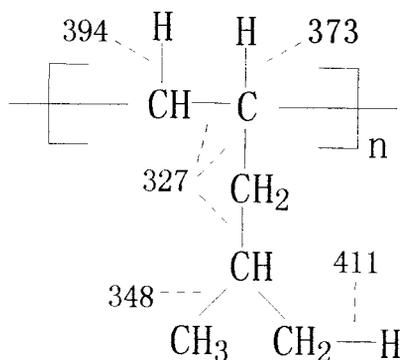
Calculating Method	Testing Atmosphere	$E$ (kJ mol <sup>-1</sup> )	$n$	Ln $Z$ (min <sup>-1</sup> )	Correlation Coefficient
Freeman–Carroll	Nitrogen	171	1.9	30	0.9995
Freeman–Carroll	Air	377	2.3	78	0.9991
Friedman	Nitrogen	146	2.0	25	0.9952
Friedman	Air	338	2.3	69	0.9718
Chang	Nitrogen	153	2.0	27	0.9918
Chang	Air	410	1.5	85	0.9794
Average	Nitrogen	157	2.0	28	
Average	Air	375	2.0	77	

tion energy in air, as shown in Figure 6. These thoroughly show that the first step of thermal degradation of the PMP is hydrogen abstraction and dealkylation on the pendant groups.

Figure 7 compares the calculated isothermal lifetimes at the weight loss of 0.3%, based on the nonisothermal degradation kinetic parameters obtained under nitrogen in this article with the practically observed isothermal lifetime range.<sup>17</sup> Calculated lifetime is situated in the range of the observed lifetime at 130°–200°C. This might indicate that the nonisothermal degradation follows the same degradation mechanism as the isothermal degradation, and the kinetic parameters of nonisothermal degradation calculated in this article are correct.

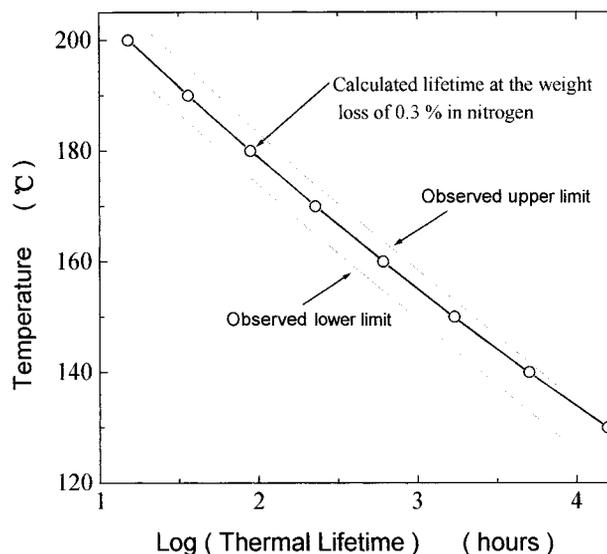
## CONCLUSIONS

Nonisothermal high-resolution thermogravimetric analyses suggest that thermal degradation of PMP is a multiple stage process in which the first stage of thermal degradation is major. PMP ex-

**Figure 6** Bond strength values (kJ mol<sup>-1</sup>) in PMP.

hibits higher thermostability in nitrogen than in air because the degradation temperature is higher and the maximal weight-loss rate is lower in nitrogen despite lower activation energy of the thermal degradation in nitrogen. But, PMP shows the same decomposition order (2.0) and char yield (14.3–14.5 wt %) at > 500°C on thermal decomposition in nitrogen and air. The isothermal lifetime of the PMP could be correctly predicted on the basis of the kinetic parameters of nonisothermal degradation obtained by High-Res TG.

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**Figure 7** A comparison of isothermal lifetimes observed experimentally with those calculated at a weight loss of 0.3%, according to the kinetic parameters obtained nonisothermally in nitrogen for PMP by the equation: Isothermal lifetime =  $\{[1 - (1 - \alpha)^{1-n}] / (1 - n)\} \exp(E/RT)$

ence Technology Development Foundation of Tongji University of China.

## REFERENCES

1. Schnabel, W. *Polymer Degradation*; Hanser International: Munich, 1981; Chapter 1.
2. Stivala, S. S.; Gabbay, S. M. *Polymer* 1977, 18, 807.
3. Reginato, L. *Macromol Chem* 1970, 115, 89; 1970, 132, 125.
4. Lee, J.-F.; Wang, Y.-C. *Sep Sci Technol* 1998, 33, 187.
5. Van Krevelen, D. W. *Polymer* 1975, 16, 615.
6. Li, X.-G.; Huang, M.-R.; Bai, H. *Angew Makromol Chem* 1998, 256, 9.
7. Li, X.-G.; Huang, M.-R. *Polym Int* 1998, 46, 289.
8. Li, X.-G. *J Appl Polym Sci* 1998, 70, to appear.
9. Li, X.-G.; Huang, M.-R. *React Funct Polym* 1998, to appear.
10. Li, X.-G.; Huang, M.-R. submitted.
11. Huang, M.-R.; Li, X.-G. *J Appl Polym Sci* 1998, 68, 293.
12. Freeman, E. S.; Carroll, B. *J Phys Chem* 1958, 62, 394.
13. Friedman, H. L. *J Polym Sci, C* 1964, 6, 183.
14. Chang, W. L. *J Appl Polym Sci* 1994, 53, 1759.
15. Emanuel, N. M.; Buchachenko, A. L. *Chemical Physics of Polymer Degradation and Stabilization*; VNU Science Press: Utrecht, 1987, p 139.
16. Gabbay, S. M.; Stivala, S. S. *Polymer* 1976, 17, 137.
17. Xin, H. D. *Practical Handbook of Plastics* (Suliao Shiyong Shouce); Institute of Scientific Technical Information of Dalian City: Liaoning Province, China, 1985; p. 150.