

## ENHANCED THERMAL STABILITY OF POLY(*p*-DIOXANONE) IN MELT BY ADDING AN END-CAPPING REAGENT

S.-D. Ding<sup>1</sup>, C.-Y. Bai<sup>1</sup>, Z.-P. Liu<sup>1</sup> and Y.-Z. Wang<sup>1,2\*</sup>

<sup>1</sup>Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry; Key Laboratory of Green Chemistry and Technology of Ministry of Education, Sichuan University, Chengdu 610064, P.R.China

<sup>2</sup>State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, P.R.China

For the enhancement of thermal stability of poly(*p*-dioxanone) (PPDO), the isocyanate end-capping reagent was prepared by treatment of toluene-2,4-diisocyanate with an equivalent of 1-hexyl alcohol. The end-capping reagent and the end-capping PPDO with an inherent viscosity of 0.26 dL g<sup>-1</sup> were characterized by FTIR and <sup>1</sup>H-NMR. Thermal stability of the end-capping PPDO with an inherent viscosity of 0.92 dL g<sup>-1</sup> was investigated isothermally and non-isothermally under air atmosphere using thermogravimetry. It has been shown that the addition of the prepared isocyanate can enhance significantly the thermal stability of PPDO. The activation energies for non-isothermal degradation estimated by Kissinger method and Friedman method are 91, 81 kJ mol<sup>-1</sup> for as-prepared PPDO, and 160, 149 kJ mol<sup>-1</sup> for the end-capping PPDO, respectively. The activation energy increases by about 70 kJ mol<sup>-1</sup> through the end-capping.

**Keywords:** activation energy, end-capping reagent, isocyanate, poly(*p*-dioxanone), thermal stability

### Introduction

Poly(*p*-dioxanone) {poly(1,4-dioxan-2-one), PPDO} prepared via the ring-opening polymerization of *p*-dioxanone (PDO) is a linear thermoplastic aliphatic polyester. It has good biocompatibility, biodegradability as well as mechanical properties [1] and has been used in medical field such as sutures, bone repair devices and drug delivery systems. In recent years, owing to the great progress on the catalytic synthesis technology of PDO monomer from diethylene glycol [2], the production cost of PDO as well as its polymer PPDO decreased significantly. At present, PPDO has been viewed as a candidate not only for medical use but also for general applications such as films, molded products, laminates, foams, unwoven materials, adhesives and coatings [3–5]. However, due to its poor thermal stability (the ceiling temperature of PPDO is only 265°C [6–8]), the thermal processing such as melt molding and spinning is very difficult. This hampers greatly its applications. Therefore, it is very important to enhance its thermal stability.

In respect of the thermal stability of PPDO, some studies have been reported. Ishikiriyama and Pyda [9] determined the heat capacities of PPDO both in solid-state and liquid-state. Yang *et al.* [10] studied the kinetics of thermal degradation of PPDO and gave the activation energy value of 89 kJ mol<sup>-1</sup> for thermal oxidative degradation. Kricheldorf and Damrau [11]

investigated the thermal stability of PPDO by thermogravimetric (TG) analysis. The results indicate that the thermal degradation is detectable above 150°C and reaches a loss of mass of 3–4% at 200°C, and the thermal degradation rate reaches its maximum around 300°C. Nishida *et al.* [12, 13] studied the thermal decomposition behaviors of PPDO. It has been shown that unzipping depolymerization is a primary reaction accounting for the decomposition of PPDO and that the active species responsible of the initiation of the decomposition reaction are terminal hydroxyl groups. Although the thermal degradation of PPDO has been thoroughly studied, there are only a few reports on the enhancement of the melt stability for PPDO. Ding and Wang [14] used a chelator of 4-benzoyl-3-methyl-1-phenyl-5-one (PMBP) to improve the thermal stability of PPDO in melt under air atmosphere. The significant improvement was achieved, but there is a poor compatibility between PPDO and PMBP, which may lead to the dramatic loss of mechanical properties of PPDO. Raquez *et al.* [15] found that the copolymerization of PDO with a few amounts of lactones, such as ε-caprolactone (CL) and δ-valerolactone (VL), was an effective way to enhance the thermal stability of PPDO. However, the resulting copolymers obtained by solution or bulk polymerization have low molecular masses. It is still needed to solve some technical problems for further increasing the molecular mass. Forscher *et al.* [16]

\* Author for correspondence: yzwang@mail.sc.cninfo.net

used the end-capping reaction of terminal hydroxyl groups with anhydride such as pyromellitic anhydride to suppress the thermal degradation of PPDO. In addition, 4-methylcyclohexene-1,2-dicarboxylic anhydride (MNDA) and methylcyclohexene-1,2-dicarboxylic anhydride (MCDA) [13] were also employed as end-capping reagents to enhance the thermal stability of PPDO. However, the end-capping reaction does not go to completion because of the low reactivity of end groups toward anhydride. The un-reacted anhydride may deteriorate the properties of PPDO such as mechanical and biodegradable properties. Besides anhydride, carbonyl halide is also usually used as an end-capping reagent to react with terminal hydroxyl groups, but this reaction will produce small molecules such as hydrochloric acid, which may cause the thermal degradation of PPDO. Therefore, the better end-capping reagent for PPDO should be the reagent with high reaction activity, and at the same time, the end-capping reaction should not bring on small molecules. As an end-capping reagent, isocyanate is able to meet the above requirements. The most commonly used isocyanate is toluene-2,4-diisocyanate (TDI), but the reaction of TDI with PPDO is not easy to be controlled and the cross-linking products are liable to be generated for its bi-functional groups. In order to avoid the above problems, the mono-functional group isocyanate will be used. As a common mono-functional group isocyanate, phenyl isocyanate can be directly purchased (the other mono-functional group isocyanates are scarce in chemical market), but it has a low boiling point of 162–163°C and is easy to volatilize at high temperatures. This is not good for the end-capping of PPDO. Therefore, it is necessary to find a more thermally stable isocyanate as an end-capping reagent. In the present paper, the preparation of a new isocyanate by treatment of TDI with an equivalent of 1-hexyl alcohol have been reported. 1-hexyl alcohol was chosen because of the easier control for the above reaction than the use of methanol or ethanol. Through the reaction of the self-prepared isocyanate with PPDO, the end-capping polymer was obtained. The thermal stability of the end-capping PPDO was investigated isothermally and non-isothermally under air atmosphere using thermogravimetry.

## Experimental

### Materials

*p*-Dioxanone (PDO), which was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials, was dried over CaH<sub>2</sub> for 48 h, distilled under reduced pressure, and stored under nitrogen. Stannous octoate (Sn(Oct)<sub>2</sub>) (≥95%) was purchased

from Sigma Chemical and used as received. After dilution with dry toluene, Sn(Oct)<sub>2</sub> solution was stored in a glass ampule under nitrogen. Toluene-2,4-diisocyanate, 1-hexyl alcohol and other chemicals were purchased from Kelong Chemical Factory (Chengdu, China) and used without further purification.

### Preparation of PPDO

PPDO was prepared through bulk polymerization of PDO in our laboratory [10, 17]. Ring-opening polymerization of PDO was performed with magnetic stirring in a flame-dried glass reactor. The reactor was evacuated and purged with nitrogen several times prior to addition of PDO and Sn(Oct)<sub>2</sub> solution with a syringe. Then, the reactor was immersed into a temperature-adjusted oil bath for predetermined intervals. After the desired reaction time, the reactor was rapidly cooled to room temperature. The polymer obtained was milled into small chips and stored in a desiccator over silica gel.

### Preparation of the end-capping reagent

The reaction of toluene-2,4-diisocyanate with equimolar 1-hexyl alcohol was carried out with magnetic stirring in a flame-dried glass reactor. The reactor was evacuated and purged with nitrogen several times prior to addition of toluene, toluene-2,4-diisocyanate and 1-hexyl alcohol with a syringe. The reaction proceeded at room temperature for 2 h. Then, the temperature was raised to 80°C and the reaction was continued for 4 h. Finally, toluene was removed by rotatory evaporator under vacuum, and the obtained product was stored in a glass ampule under nitrogen.

### Preparation of end-capping PPDO

A desired amount of the self-prepared end-capping reagent was added into as-prepared PPDO in a reactor equipped with a mechanical agitator under nitrogen atmosphere at 160°C for 30 min. The end-capping PPDO was milled into small chips and stored in a desiccator over silica gel.

### Characterization

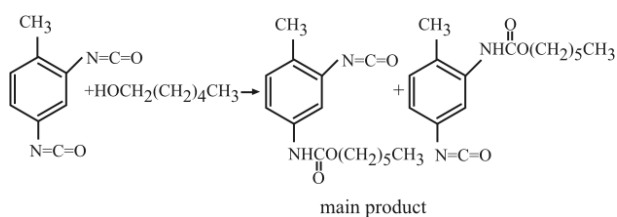
Inherent viscosities of PPDO were measured at 25°C with the concentration of 0.1 g dL<sup>-1</sup> in phenol/1,1,2,2-tetrachloroethane (2:3 w/w) solution using an Ubbelohde viscosimeter. The infrared absorption spectra were performed on a Nicolet FTIR 170SX infrared spectrometer using KBr wafer. The 200 MHz <sup>1</sup>H-NMR spectra were recorded with a Varian Inova 400 spectrometer and performed at 30°C with 5% (w/v) polymer solution in CDCl<sub>3</sub>. Due to the poor solubility of PPDO

with middle or high molecular masses in the common solvents, the samples with low molecular masses were employed for FTIR and HNMR tests. Thermogravimetry measurements were conducted with a Q100 system in platinum pans under a steady air flow of  $60 \text{ mL min}^{-1}$  (sample mass of ca. 5 mg). The mass losses of the specimens were measured isothermally under the constant holding temperatures (180–220°C) for 60 min or non-isothermally with heating at a constant rate of 5, 10, 15, 20°C  $\text{min}^{-1}$  up to 400°C, respectively.

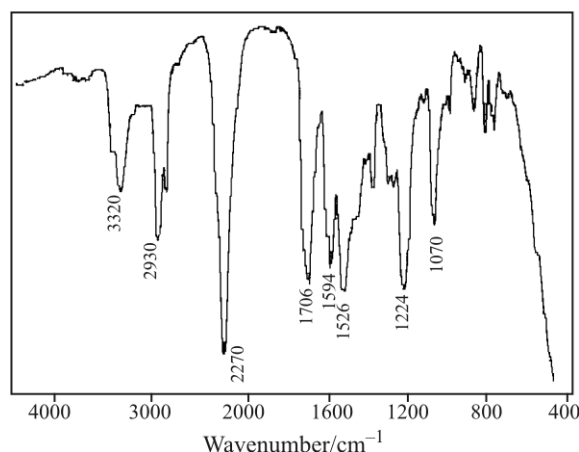
## Results and discussion

### Preparation of the end-capping reagent

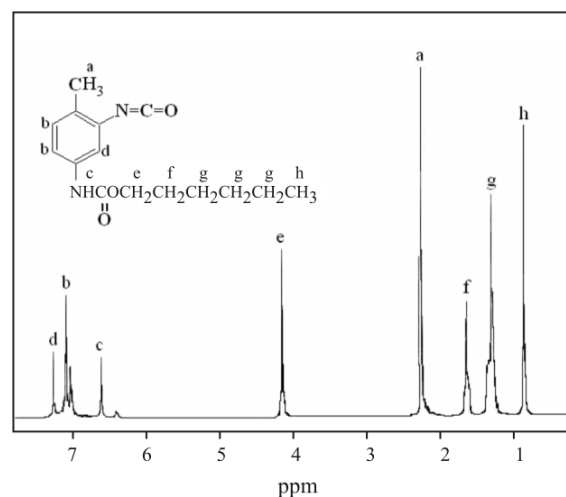
The end-capping reagent was prepared by treatment of TDI with an equivalent of 1-hexyl alcohol. In the molecule of TDI, there are two isocyanato groups with different reaction activity due to steric hindrance. The reaction activity of para-isocyanato group is usually several times higher than that of ortho-isocyanato group. The lower the reaction temperature is, the more significant the difference of reaction activity is. At room temperature, the main product obtained from the reaction of TDI with an equivalent of 1-hexyl alcohol is the addition product at para-isocyanato group. The synthetic route of end-capping reagent is shown in Scheme 1. The FTIR spectrum of the prepared end-capping reagent is shown in Fig. 1. The absorption bands at 3320, 2270 and  $1706 \text{ cm}^{-1}$  are attributed to the vibrations of N–H, –NCO and C=O groups, respectively. The peaks at 1594 and  $1526 \text{ cm}^{-1}$  are the characteristic absorption of phenyl group. The absorption bands of C–O–C group are located at 1224 and  $1070 \text{ cm}^{-1}$ . The FTIR analysis shows the formation of mono-functional group isocyanate by treatment of TDI with an equivalent of 1-hexyl alcohol.  $^1\text{H-NMR}$  (Fig. 2) analysis also illustrates the existence of mono-functional group isocyanate (–NH, 6.62 ppm; –C(O)–O–CH<sub>2</sub>–, 4.17 ppm). In addition, titration analysis by the method of hydrochloric acid and dibutylamine was employed to determinate the content of isocyanato group before and after the reaction of TDI with an equivalent of 1-hexyl alcohol. It has been shown that the content of isocyanato group in



**Scheme 1** Synthetic route of the end-capping reagent



**Fig. 1** FTIR spectrum of the end-capping reagent



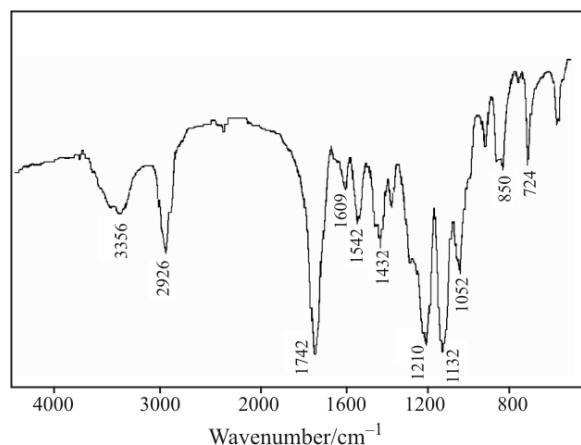
**Fig. 2**  $^1\text{H}$  NMR spectrum of the end-capping reagent

the resulting product is just right a half of that in the initial TDI. This result is also in accordance with the expectancy.

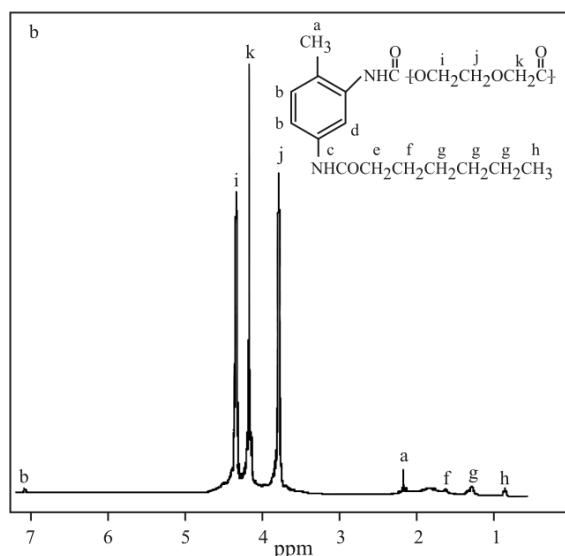
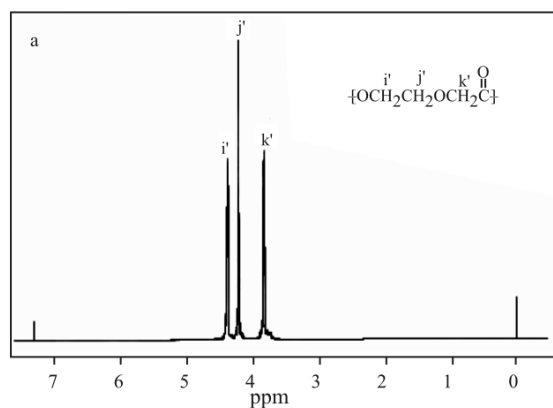
### End-capping of PPDO

PPDO prepared by ring-opening polymerization of PDO with  $\text{SnOct}_2$  as a catalyst has terminal hydroxyl groups, which can react with isocyanate. The results from the reaction of the prepared end-capping reagent with PPDO having different molecular masses are as follows. For PPDO with initial inherent viscosity of  $0.25 \text{ dL g}^{-1}$ , the resulting product has an inherent viscosity of  $0.26 \text{ dL g}^{-1}$ . The inherent viscosity is almost unchanged. For PPDO with initial inherent viscosity of  $1.08 \text{ dL g}^{-1}$ , the resulting product has an inherent viscosity of  $0.92 \text{ dL g}^{-1}$ . The slight decrease of inherent viscosity may be ascribed to the thermal degradation during the end-capping process. A little changes of inherent viscosity suggest that the prepared isocyanate is a mono-functional group compound which plays an end-capping role (not a chain-ex-

tended role like TDI). In order to explain intensively the above point of view, the end-capping PPDO with an inherent viscosity of  $0.26 \text{ dL g}^{-1}$  was characterized by IR and  $^1\text{H-NMR}$ . FTIR spectrum of the end-capping PPDO is shown in Fig. 3. Compared with the



**Fig. 3** FTIR spectrum of the end-capping PPDO

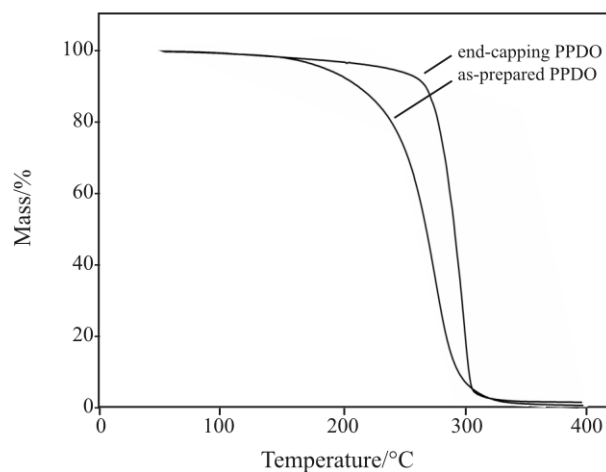


**Fig. 4** a –  $^1\text{H-NMR}$  spectrum of as-prepared PPDO,  
b –  $^1\text{H-NMR}$  spectrum of the end-capping PPDO

FTIR spectrum of PPDO, there are new absorption bands at  $1609$  and  $1542 \text{ cm}^{-1}$  in that of the end-capping PPDO, which are attributed to the characteristic absorption of phenyl group. This result indicates that the prepared isocyanate has reacted with the terminal hydroxyl groups of PPDO. Figure 4 shows the  $^1\text{H-NMR}$  spectra of PPDO and the end-capping PPDO. In the  $^1\text{H-NMR}$  spectrum of the latter, there are not only the signals of methyl group of PPDO at  $4.33 \text{ ppm}$  (i),  $4.16 \text{ ppm}$  (k) and  $3.78 \text{ ppm}$  (j), but also several new weak signals. The peaks at  $7.08 \text{ ppm}$  (b) and  $2.20 \text{ ppm}$  (a) are ascribed to phenyl group and methyl group, respectively. The signals of other methylene radicals introduced from the end-capping reagent occur at the chemical shifts of  $1.65$ ,  $1.31$  and  $0.90 \text{ ppm}$ . FTIR and  $^1\text{H-NMR}$  analyses confirm that the resulting product from the reaction of PPDO with the prepared isocyanate is the end-capping PPDO.

#### Non-isothermal degradation

The TG data of as-prepared PPDO with an inherent viscosity of  $1.08 \text{ dL g}^{-1}$  and the end-capping PPDO with an inherent viscosity of  $0.92 \text{ dL g}^{-1}$  for non-isothermal degradation have been taken under a steady flow of air at four different heating rates as  $5$ ,  $10$ ,  $15$ ,  $20^\circ\text{C min}^{-1}$ . The percentage remaining mass of as-prepared PPDO and the end-capping PPDO at a heating rate of  $10^\circ\text{C min}^{-1}$  as a function of temperature is shown in Fig. 5. The relevant characteristics were summarized in Table 1. The result shows that the thermal stability of end-capping PPDO is significantly higher than that of the as-prepared PPDO. From the TG curves of as-prepared PPDO and the end-capping PPDO at varying heating rates under air atmosphere (Figs 6 and 7), the activation energy

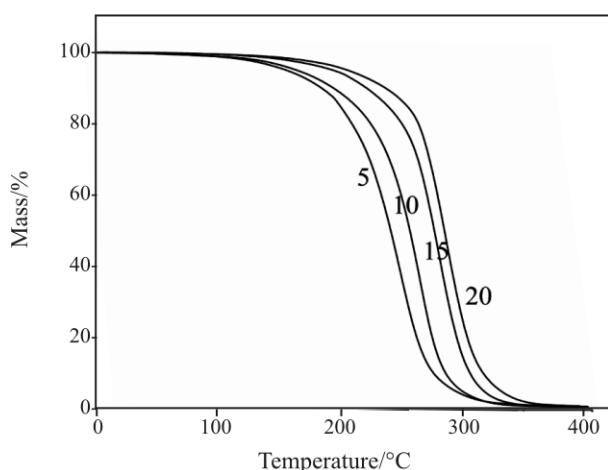


**Fig. 5** Mass of as-prepared PPDO and the end-capping PPDO measured non-isothermally at the constant heating rate of  $10^\circ\text{C min}^{-1}$  as a function of temperature

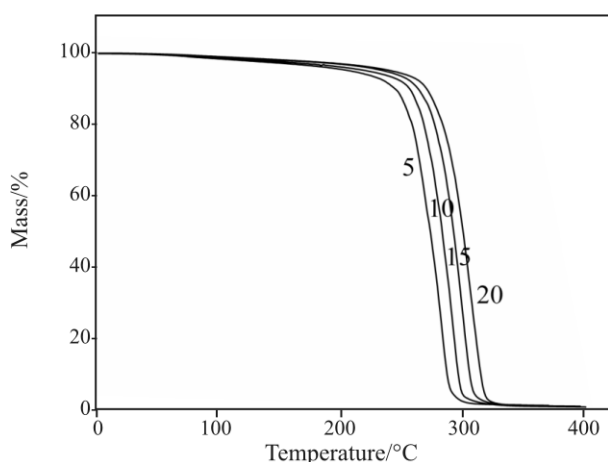
**Table 1** Non-isothermal degradation data of as-prepared and the end-capping PPDO

Code	$T_{d,20\%}^a/$ °C	$T_{d,50\%}^a/$ °C	$T_{d,max}^c/$ °C	$T_{d,70\%}^d/$ °C
As-prepared PPDO	239	267	275	278
End-capping PPDO	277	291	298	297

<sup>a</sup>Temperature at mass loss value of 20%;  
<sup>b</sup>Temperature at mass loss value of 50%;  
<sup>c</sup>Temperature at which a maximum decomposition rate is reached;  
<sup>d</sup>Temperature at mass loss value of 70%



**Fig. 6** Non-isothermal degradation curves of as-prepared PPDO at different heating rates in air



**Fig. 7** Non-isothermal degradation curves of the end-capping PPDO at different heating rates in air

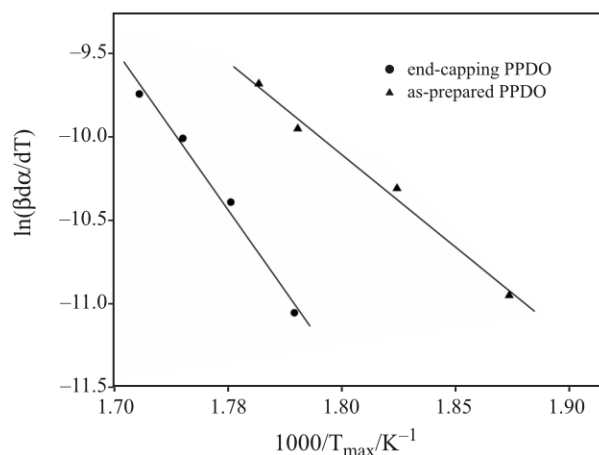
( $\Delta E_{td}$ ) for non-isothermal degradation can be obtained by employing Kissinger method [18–20] and Friedman method [21–23].

Kissinger method is a differential method for studying the kinetics of thermal degradation.

The Kissinger expression is as Eq. (1).

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

where  $\beta$  is the heating rate in TG measurement,  $T_{max}$  is the temperature at which a maximum decomposition rate is reached,  $A$  is the pre-exponential factor,  $\Delta E_{td}$  is the thermal decomposition activation energy,  $n$  is the apparent kinetic order of the degradation reaction,  $\alpha_{max}$  is the fraction of conversion at the maximum rate of mass loss, and  $R$  is the universal gas constant. The value of  $\Delta E_{td}$  can be determined from the linear regression plot of  $\ln(\beta/T_{max}^2)$  vs.  $1/T_{max}$  shown in Fig. 8. The values calculated from these plots were  $160 \text{ kJ mol}^{-1}$  for the end-capping PPDO and  $91 \text{ kJ mol}^{-1}$  for the as-prepared PPDO.  $\Delta E_{td}$  increases by about  $70 \text{ kJ mol}^{-1}$  through the end-capping.



**Fig. 8** Activation energy plots for as-prepared PPDO and the end-capping PPDO according to the Kissinger relationship

The other differential method used in this paper is Friedman method. This method is based on the intercomparison of the rates of mass loss  $d\alpha/dt$  with different linear heating rates  $\beta$  for a given fractional mass loss. The Friedman expression is as Eq. (2).

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\frac{\beta d\alpha}{dT}\right) = \ln A + n \ln(1-\alpha) - \frac{\Delta E_{td}}{RT} \quad (2)$$

where  $\beta$ ,  $A$ ,  $n$ ,  $\Delta E_{td}$  and  $R$  are the same as Eq. (1).  $\alpha$  is the fraction of conversion,  $t$  and  $T$  represent time and temperature, respectively. Equation (2) is also used to estimate the value of  $\Delta E_{td}$  from the plot of  $\ln(d\alpha/dt)$  vs.  $1/T$  over a wide range of conversion fractions. In order to calculate the value of  $\Delta E_{td}$ ,  $\alpha$  was given as 0.05, 0.08, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9. The calculated results were summarized in Tables 2 and 3. Although the mean values of as-prepared PPDO and end-capping PPDO,  $81$  and  $149 \text{ kJ mol}^{-1}$ , respectively, were found lower than the values obtained by Kissinger method, the difference is still about  $70 \text{ kJ mol}^{-1}$ . This re-

**Table 2** Activation energies ( $\Delta E_{td}$ ) of as-prepared PPDO in air obtained by Friedman method

Conversion, $\alpha$	Activation energy, $\Delta E_{td}/\text{kJ mol}^{-1}$	Correlation coefficient, $r$
0.05	48	0.9353
0.08	52	0.9465
0.10	54	0.9546
0.15	52	0.9959
0.20	75	0.9888
0.30	94	0.9947
0.40	99	0.9964
0.50	100	0.9905
0.60	98	0.9815
0.70	97	0.9659
0.80	100	0.9523
0.90	107	0.9152
Mean	81	

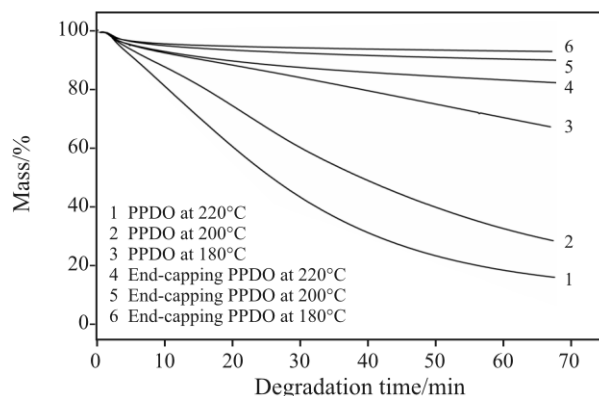
**Table 3** Activation energies ( $\Delta E_{td}$ ) of the end-capping PPDO in air obtained by Friedman method

Conversion, $\alpha$	Activation energy, $\Delta E_{td}/\text{kJ mol}^{-1}$	Correlation coefficient, $r$
0.05	116	0.9990
0.08	164	0.9949
0.10	184	0.9876
0.15	150	0.9840
0.20	135	0.9693
0.30	132	0.9878
0.40	150	0.9843
0.50	162	0.9807
0.60	158	0.9798
0.70	147	0.9794
0.80	154	0.9704
0.90	136	0.9534
Mean	149	

sult is in good agreement with that from Kissinger method. TG analyses for non-isothermal degradation show that the thermal stability of PPDO in melt is enhanced significantly by means of the end-capping.

#### *Isothermal degradation*

In order to investigate in detail the thermal degradation behaviors and stability of PPDO in air, the isothermal measurements were performed at constant holding temperatures of 180, 200 and 220°C. Figure 9 illustrates the percentage remaining mass of the as-prepared PPDO and the end-capping PPDO at dif-

**Fig. 9** Isothermal degradation curves of PPDO and the end-capping PPDO at various temperatures in air

ferent holding temperatures as a function of degradation time. At the given temperatures, the remaining masses of end-capping PPDO are much higher than those of as-prepared PPDO. For example, at 60 min, the remaining masses of the as-prepared PPDO decrease to 71.3% at 180°C, and to 18.5% at 220°C, whilst those of the end-capping PPDO decrease only to 93.4 and to 83.8%, respectively. Even at 220°C, the remaining masses of the end-capping PPDO are higher than those of as-prepared PPDO at 180°C. The results from isothermal degradation also reveal that the thermal stability of PPDO in melt is enhanced obviously through the end-capping.

## Conclusions

The isocyanate end-capping reagent can be prepared by treatment of TDI with an equivalent of 1-hexyl alcohol, and reacts with the terminal hydroxyl groups of PPDO to form the end-capping product. TG analyses for non-isothermal degradation and isothermal degradation show that the thermal stability of the end-capping PPDO is significantly higher than that of as-prepared PPDO. The activation energies for non-isothermal degradation estimated by Kissinger method and Friedman method were 91, 81  $\text{kJ mol}^{-1}$  for as-prepared PPDO, and 160, 149  $\text{kJ mol}^{-1}$  for the end-capping PPDO, respectively. The activation energy of thermal degradation of PPDO increases by about 70  $\text{kJ mol}^{-1}$  through the end-capping. It is possible to enhance the thermal stability of PPDO in melt by adding the isocyanate end-capping reagent.

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