

Effect of polycarbodiimide on the thermal stability and crystallization of poly(*p*-dioxanone)

Song-Dong Ding · Zhong-Ping Liu · Tang Yang ·
Guang-Can Zheng · Yu-Zhong Wang

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Abstract A kind of polycarbodiimide (PCD) as a thermal stabilizer was added into poly(*p*-dioxanone) (PPDO). The effect of PCD on the thermal stability and crystallization of PPDO was investigated by using non-isothermal thermal-gravimetry (TG), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray diffractometry (WAXD). It has been shown that the addition of PCD can enhance significantly the thermal stability of PPDO. The thermal decomposition temperature of PPDO increases with the increase of the amount of PCD added. The activation energies for non-isothermal thermal degradation estimated by Kissinger method are 160 and 106 kJ mol⁻¹ for PPDO added with 5 wt% PCD and neat PPDO respectively. The results obtained from DSC and POM indicate that PCD plays a role of nucleating agent in the process of crystallization of PPDO. WAXD analyses reveal that the addition of PCD has no effect on the crystal structure of PPDO.

Keywords Poly(*p*-dioxanone) · Polycarbodiimide · Thermal stability · Activation energy · Crystallization · Nucleation

Introduction

Poly(*p*-dioxanone) (PPDO) is a biodegradable poly(ether-ester) with good biocompatibility and mechanical properties [1]. It has been used in medical field such as sutures, bone repair devices and drug delivery systems [2–4]. With

the decrease of production cost of *p*-dioxanone (PDO) monomer and its polymer PPDO due to the great progress on the synthesis technology of PDO monomer from diethylene glycol in recent years [5], PPDO has also been viewed as a candidate for general applications such as film, molded products, laminates, foams, unwoven materials, adhesives, and coatings [6]. However, because of its poor thermal stability, the use of PPDO as bulk material is hampered greatly. Under air atmosphere, it was found that the thermal degradation of PPDO began at 140 °C [7]. Even under nitrogen atmosphere, the thermal degradation is also detectable above 150 °C [8]. Due to the melting point of about 110 °C for PPDO, there is a very narrow range of temperatures for thermal processing. This is very disadvantageous to its processing such as melt molding and spinning. Therefore, it is very important to enhance its thermal stability.

The thermal decomposition of PPDO is mainly unzipping depolymerization reaction caused by terminal hydroxyl groups, but some random reactions such as nucleophilic attacks on the carbonyl carbons in the main chain by the carboxyl groups proceed competitively, especially in the initial process [9, 10]. For the enhancement of thermal stability of PPDO, some efforts have been dedicated. Acid anhydride and monoisocyanate such as 4-methylcyclohexene-1,2-dicarboxylic anhydride (MNDA) [10], methylcyclohexene-1,2-dicarboxylic anhydride (MCDA) [10], and trichloroacetyl isocyanate (TCAI) [11] have been employed as end-capped reagents to react with terminal hydroxyl groups for suppressing the unzipping depolymerization. In a previous study [12], we reported another method to improve the thermal stability of PPDO by adding a chelator of 4-benzoyl-3-methyl-1-phenyl-5-one (PMBP) to deactivate the residual catalyst such as tin which can catalyze the unzipping decomposition. By the addition of the compounds mentioned above, the thermal stability of PPDO can be enhanced to some extent. However,

S.-D. Ding (✉) · Z.-P. Liu · T. Yang · G.-C. Zheng · Y.-Z. Wang
Center for Degradable and Flame-Retardant Polymeric Materials,
College of Chemistry, Key Laboratory of Green Chemistry
and Technology (Ministry of Education), Sichuan University,
Chengdu 610064, People's Republic of China
e-mail: dsd68@163.com

there are some defects in respect of these methods. For anhydride, the end-capping reaction does not go to completion because of the low reactivity of terminal hydroxyl groups toward anhydride. The unreacted anhydride may deteriorate the properties of PPDO such as mechanical and degradable properties. For monoisocyanate, it has high reactivity with terminal hydroxyl groups, but at the same time, it has high toxicity. For PMBP, there is a poor compatibility between PPDO and PMBP, which may lead to the dramatic loss of mechanical properties of PPDO. In addition, the above mentioned methods for enhancement of thermal stability of PPDO have focused on suppressing the unzipping depolymerization reaction initiated from terminal hydroxyl groups, without respect to the random degradation reactions initiated by terminal carboxyl groups. In fact, terminal carboxyl groups plays an important role in the process of thermal degradation of PPDO, especially in the initial process [9, 10]. In the present paper, the unzipping depolymerization reaction and the random degradation reactions are expected to be suppressed simultaneously. In order to attain this purpose, a kind of polycarbodiimide (PCD) was employed to stabilize PPDO in melt. Carbodiimide compounds can react not only with carboxylic acid easily but also with alcohol over a temperature of 100 °C [13, 14], and have been used to stabilize poly (butylene terephthalate) [15]. It may be possible to suppress simultaneously the thermal decomposition initiated by terminal hydroxyl groups and carboxyl groups. In this study, the effect of addition of PCD on thermal stability of PPDO was studied by using non-isothermal thermalgravimetry (TG). In addition, the crystallization is considered to be very important for polymer materials and will be certainly influenced by an additive of PCD. Therefore, the effect of PCD on the crystallization of PPDO was also investigated.

Experimental

Materials

Preparation of PPDO

PPDO was prepared through ring opening polymerization of PDO, which was provided by Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China) and dried before use. Reactors with magnetic stirring were purged with argon several times prior to the addition of PDO and stannous octoate catalyst solution with a syringe (the molar ratio of PDO and stannous octoate was 10,000:1). Then the reactors were immersed into a silicone oil bath kept at 80 °C for 72 h. The crude polymer obtained was milled into powder, which were then purified by removing the unreacted monomers in Soxhlet extractor with toluene and dried under vacuum at 50 °C to constant weight.

Sample preparation

A kind of polycarbodiimide with number average molecular weight of about 550 (PCD, see Fig. 1) was adopted because of its suitable melting point of 85 °C at which is near to that of PPDO of 110 °C, low toxicity and no volatility. PCD was provided by Jianxin Chemical Factory (Jiangsu, China) and used as received. The samples containing desired weight percentage of PCD (1wt%, 3wt% and 5wt%, remarked as PPDOCD1, PPDOCD3 and PPDOCD5, respectively.) were prepared through the following procedures. Firstly, PPDO was melted in a reactor equipped with a mechanical agitator under nitrogen atmosphere at 130 °C. Then PCD in anhydride tetrahydrofuran (THF) solution was added with a syringe. After stirring for 15 min at the above temperature, THF was removed under vacuum. The blend obtained was cut into small chips and stored in a desiccator over silica gel.

Measurements

Intrinsic viscosity measurement

PPDO with middle or high molecular weight can not be measured by gel permeation chromatography (GPC) due to its poor solubility in common solvents employed to perform GPC at room temperature. Therefore, Ubbelohde viscometer was employed to determine the viscosity-average molecular weight. The tests were performed at 25 °C with phenol/1,1,2,2-tetrachloroethane (2:3, w:w) as solvent.

Thermalgravimetry analysis

Thermogravimetry (TG) measurements were conducted with a Dupont 2100 system (USA) in platinum pans under a steady nitrogen flow of 50 mL min⁻¹ (sample weight of ca.5 mg). The weight losses of the specimens were measured non-isothermally with heating at a constant rate of 5, 10, 15, 20, 25 °C min⁻¹ in a range of ambient temperature to 400 °C.

Infrared analysis

The infrared absorption spectra were performed on a Nicolet FTIR 170SX (USA) infrared spectrometer using KBr wafer.

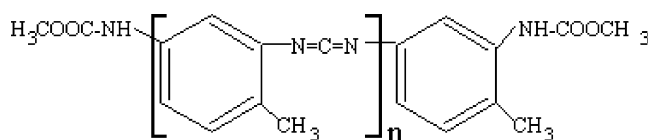


Fig. 1 Chemical structure of PCD

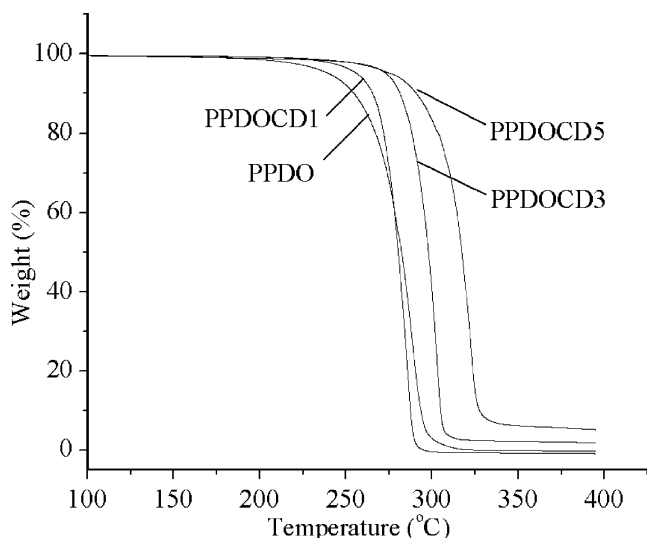


Fig. 2 TG curves of various PPDO in N_2 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$

Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analyses were performed on a TA Q-100 DSC (USA) thermal analyzer under nitrogen atmosphere. Sample with a weight of 7–10 mg was placed in an aluminum pan and heated to $140\text{ }^\circ\text{C}$. After erasing the previous thermal history by maintaining at this temperature for 5 min, the sample was cooled to $-40\text{ }^\circ\text{C}$ at a cooling rate of $10\text{ }^\circ\text{C min}^{-1}$, and then a subsequent heating was performed from $-40\text{ }^\circ\text{C}$ to $140\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Polarized optical microscopy analysis

The crystallization morphology was studied with an Nikon Eclipse LV100POL (Japan) polarized optical microscopy (POM). A small piece of sample was placed between two glass coverslips, melted on a hot stage at $140\text{ }^\circ\text{C}$ for 5 min and squeezed between the two slips, and then the film was quickly cooled to $60\text{ }^\circ\text{C}$. At this temperature, the spherulitic morphology was evaluated on completion of crystallization.

Wide angle X-ray diffraction analysis

Wide angle X-ray diffraction (WAXD) experiments were conducted with Cu $K\alpha$ radiation on a Philips X'Pert Pro X-ray apparatus (Holland). The equipment was operated at 40 Kv and 35 mA under room temperature, and the scan range was between 2° to 40° with a scan rate of 3°min^{-1} .

Results and discussion

Thermal degradation of PPDO and PPDO containing PCD

In order to avoid the effect of intrinsic viscosity (or molecular weight) on thermal degradation of PPDO [16], the samples with near intrinsic viscosities were employed for TG test. Sample PPDOCD5, PPDOCD3, PPDOCD1 and PPDO have an intrinsic viscosities of 1.43, 1.41, 1.44 and 1.45 dL g^{-1} , respectively. The remaining weight percentages of various PPDO samples as a function of temperature, which were obtained non-isothermally at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ with a steady flow of nitrogen, is shown in Fig. 2. The relevant characteristics are summarized in Table 1. It is found that the thermal degradation of PPDO is detectable above $150\text{ }^\circ\text{C}$ and the thermal degradation rate reaches a maximum rate at about $280\text{ }^\circ\text{C}$. This result is in agreement with that reported by Kricheldorf and Damrau [8]. Compared with neat PPDO, the thermal stability of PPDO added with PCD is enhanced significantly. The more the amount of PCD added is, the more obvious the efficiency is.

Activation energy of thermal degradation

TG has been used to evaluate the kinetic parameters of polymer degradation. Figures 3 and 4 show the TG curves of PPDO and PPDOCD5 under a steady nitrogen flow at five different heating rates as 5, 10, 15, 20 and $25\text{ }^\circ\text{C min}^{-1}$. The TG traces are shifted up the temperature scale by the increase of rate. Some methods [17–20] have been developed to analyze the TG data. In this investigation,

Table 1 TG data of various PPDO in N_2 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$

Sample	$T_{5\%}(\text{ }^\circ\text{C})$	$T_{20\%}(\text{ }^\circ\text{C})$	$T_{50\%}(\text{ }^\circ\text{C})$	$T_{\text{max}}(\text{ }^\circ\text{C})$	$T_{70\%}(\text{ }^\circ\text{C})$
PPDOCD5	276.5	303.7	317.3	322.6	321.8
PPDOCD3	273.6	288.3	297.9	303.4	301.7
PPDOCD1	256.6	272.0	280.3	273.7	284.1
PPDO	240.4	267.2	282.3	279.5	287.8

$T_{5\%}$, $T_{20\%}$, $T_{50\%}$ and $T_{70\%}$ are the temperature of 5%, 20%, 50% and 70% mass loss, respectively

T_{max} is the temperature at which the rate of mass loss reaches a maximum

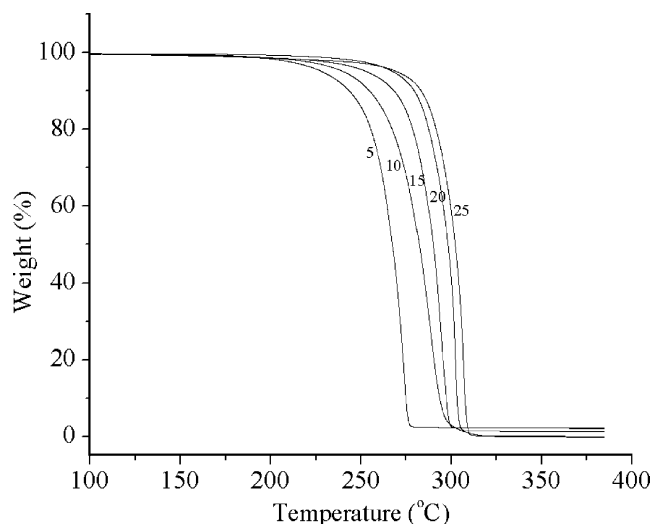


Fig. 3 TG curves of PPDO at different heating rates (5, 10, 15, 20, 25 °C min⁻¹) in nitrogen flow

Kissinger method [17] was employed because of its independence of any thermal degradation mechanism. This method is often used to determine the thermal decomposition activation energy [21–23] and is based on the Eq. (1).

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

where β 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, E is the thermal decomposition activation energy, n is the apparent kinetic order of the degradation reaction, α_{\max} is the fraction of conversion at the maximum rate of weight loss, and R is the

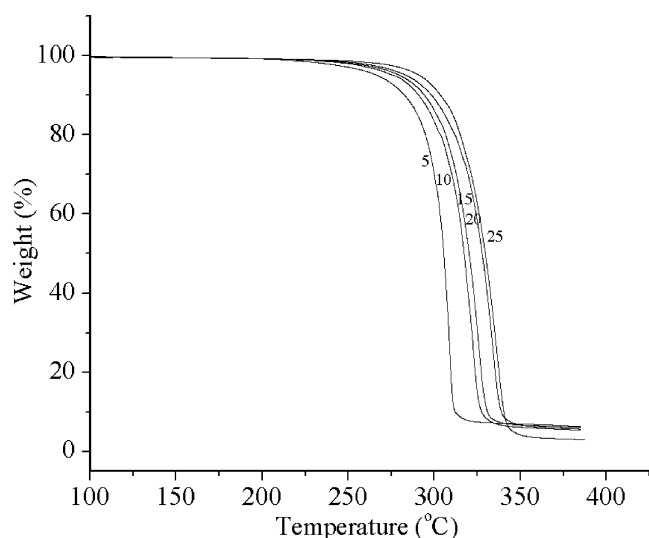


Fig. 4 TG curves of PPDOCD5 at different heating rates (5, 10, 15, 20, 25 °C min⁻¹) in nitrogen flow

universal gas constant. The value of E can be determined from the linear regression plot of $\ln(\beta/T_{\max}^2)$ versus $1,000/T_{\max}$ shown in Fig. 5. The thermal decomposition activation energies calculated from the slope values are 106 kJ mol⁻¹ and 160 kJ mol⁻¹ for PPDO and PPDOCD5, respectively. The activation energy increases by 54 kJ mol⁻¹. This increase may be ascribed to the reaction of PPDO with PCD. Generally speaking, PPDO prepared by ring-opening polymerization of PDO with SnOct₂ as a catalyst has terminal carboxyl and hydroxyl groups. These terminal groups can react with carbodiimide. The reaction scheme is shown in Fig. 6. Reaction I which occurs very easily represents the reaction of terminal carboxyl groups with carbodiimide, while reaction II expressing the reaction of terminal hydroxyl groups with carbodiimide occurs at a temperature of above 100 °C [13, 14]. Under the investigated experiment conditions, both reaction I and reaction II can occur simultaneously. The reaction for PPDO and PCD can be confirmed from the infrared spectra (see Fig. 7). A pyrolysis experiment was carried out at 250 °C under nitrogen atmosphere. It has been observed that the characteristic absorption peak of carbodiimide group at 2,130 cm⁻¹ disappears after pyrolysis for 20 min, which suggests that carbodiimide groups react with the terminal carboxyl and hydroxyl groups of PPDO. Therefore, due to the simultaneous suppression of carbodiimide for the thermal decomposition initiated by terminal hydroxyl groups and carboxyl groups during the pyrolysis process of PPDO, the thermal stability of PPDO can be enhanced by the addition of PCD.

Crystallization property of PPDO and PPDO containing PCD

As a kind of additive, PCD can not only enhance the thermal stability of PPDO, but also influence its crystallization simultaneously. Due to the importance of crystallization for

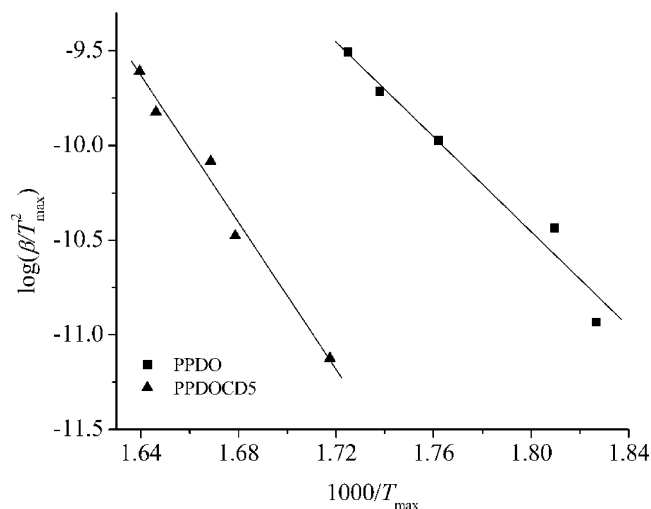
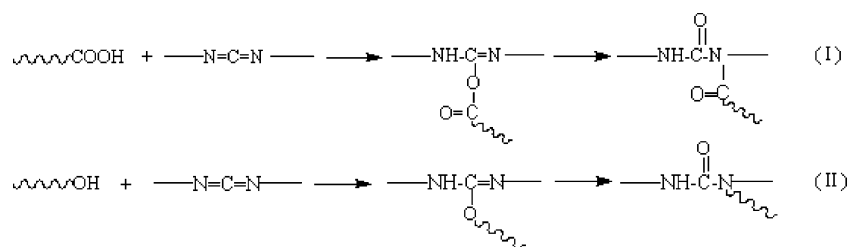


Fig. 5 Kissinger plots of PPDO and PPDOCD5

Fig. 6 Reactions of terminal carboxyl groups and hydroxyl groups with carbodiimide



polymer materials, the effect of PCD on the crystallization of PPDO was investigated. By using DSC measurement, the thermal and crystallization properties of various PPDO was studied. Figure 8 is the cooling scans after erasing previous thermal history at 140 °C for 5 min and Fig. 9 is the subsequent heating scans after the cooling runs. The relevant data obtained from the two scans are listed in Table 2. During the cooling scans, all samples exhibit a crystallisation exothermal peak. The peak of PPDOCD5 is the most strongest, while those of PPDOCD1 and PPDOCD3 are the most weakest. As shown in Table 2, the peak crystallization temperature (T_c) increases from 34.4 to 69.8 °C with the increase of the amount of PCD added. When 5 wt % PCD was added into PPDO, a clear nucleating effect was observed, which was reflected by the pronounced increase in the peak crystallization temperatures [24]. However, this nucleation of PCD was hardly observed for PPDOCD1 and PPDOCD3 samples during the cooling scan. For PPDOCD1 and PPDOCD3, the crystallization enthalpies are 11.3 and 12.7 Jg⁻¹, respectively. The values are significantly lower than that not only for PPDOCD5 50.1 Jg⁻¹, but also for neat PPDO 30.3 Jg⁻¹. This phenomenon may be interpreted by the reaction of PCD with PPDO in the process of sample preparation, as well as in

the process of DSC test. On the one hand, for PPDOCD1 and PPDOCD3 samples, PCD was exhausted through the reaction with PPDO due to the lower amount added and can not play a nucleating agent. On the other hand, due to the introduction of the rigid PCD fragment (containing phenyl group) into the molecular chain of PPDO, the molecular mobility is confined and the ability of crystallization is declined. Therefore, the crystallization enthalpies of PPDOCD1 and PPDOCD3 are lower than that of neat PPDO. However, for PPDOCD5, the higher amount of PCD added causes the existence of unreacted PCD. The free PCD can act as a nucleating agent and promote the crystallization of PPDO. Although the transport of polymeric segments toward the crystal nucleus and their build-up to the growing crystal surface is also hampered due to the similar effects of PCD on the the molecular mobility, the nucleation is dominate compared to the crystal growth for PPDOCD5. Therefore, PPDOCD5 has the highest crystallization enthalpy during the cooling scans. In the subsequent heating scans, PPDO shows two crystallization exothermal peaks, which is in agreement with that reported by others [25–27]. This indicates that PPDO does not crystallize fully during cooling from the melt at 10 °C min⁻¹, although there are flexible chemical structures in the macromolecular chains. PPDOCD1 and PPDOCD3 have

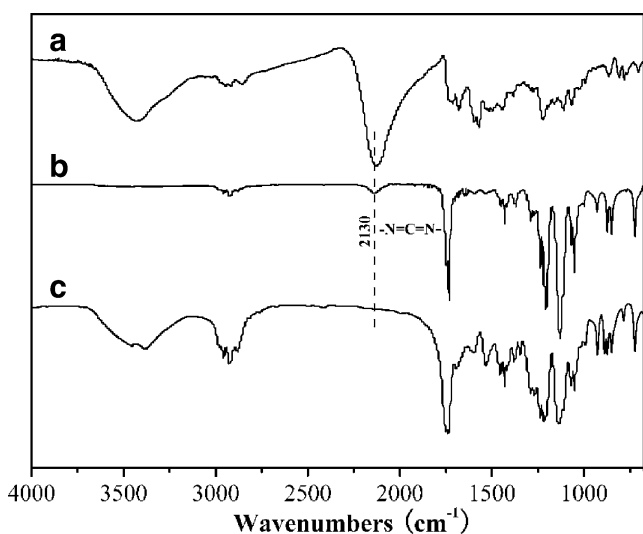


Fig. 7 FTIR spectra of a PCD, b PPDOCD5 before pyrolysis and c PPDOCD5 after pyrolysis

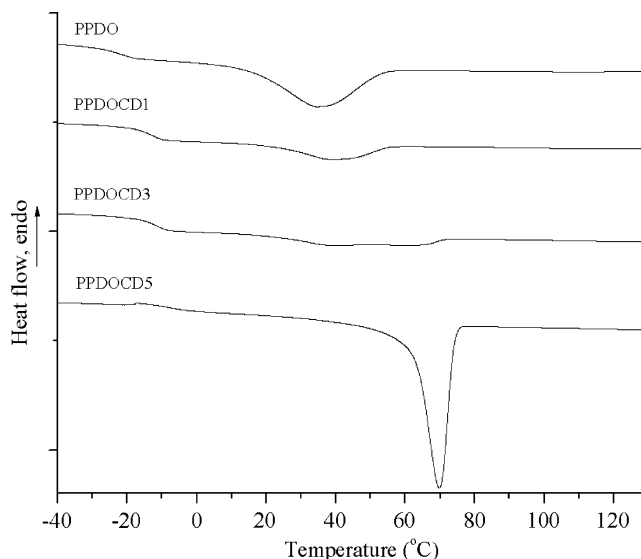


Fig. 8 DSC cooling scans of various PPDO after erasing the samples thermal history by heating at 140 °C for 5 min

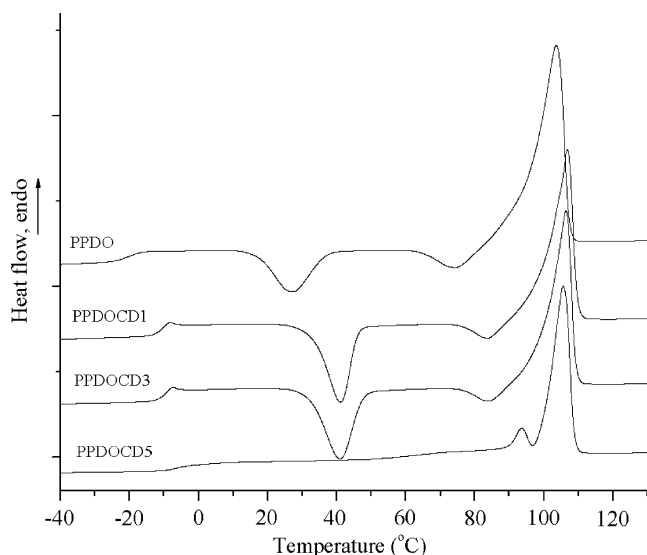


Fig. 9 DSC heating scans of various PPDO after the cooling runs

also two crystallization exothermal peaks. When the temperature is above the glass transition temperature, the crystals of three samples experience reorganization and become more perfect during the heating run [25–27]. As shown in Figs. 8 and 9, the cold crystallization peak is more evident by the subsequent heating scan than the previous cooling scan. The behavior indicated that the crystal reorganization for PPDOCD1 and PPDOCD3 is more obvious than that for neat PPDO. This may be ascribed to the improvement of the molecular mobility and crystallizability during the heating run. For PPDOCD5, the crystallization peak is not observed, which is shown that the crystallization of PPDOCD5 goes to completion during the cooling scan. As can be seen from Fig. 9, there is a small melting endothermic peak at 95 °C for PPDOCD5. It may be owing to the melt of the unreacted

PCD as a nucleating agent. In addition, the addition of PCD has an effect on the glass transition temperature (T_g) and fusion enthalpy (ΔH_m) of PPDO. An increase for T_g and a decrease for ΔH_m are observed from the heating scans with the increase of PCD content.

When PPDO is crystallized from the melt, it forms spherulites that can exhibit well defined Maltese crosses [25]. Figure 10 displays a series of polarized optical micrographs of neat PPDO, PPDOCD1 and PPDOCD5 spherulites isothermally crystallized at 60 °C. As can be seen from this figure, PPDOCD5 has many small spherulites after crystallization for 3 min, extensive nucleation and crystal growth progress until they impinge one another. PPDO and PPDOCD1 have fewer and bigger spherulites than PPDOCD5. This difference can be attributed to the unreacted PCD which acts as a nucleating agent. Spherulitic growth rates can be determined by measuring spherulitic radius from sequential polarized optical micrographs as a function of time. Figure 11 shows the spherulitic growth rates of various PPDO. In all cases, the growth rates are found to be linear. Neat PPDO has the biggest slope and PPDOCD5 has the smallest slope, which means that the former has the fastest radius growth rate and the latter has the slowest radius growth rate. With the increase of PCD content, the molecular mobility declines, which leads to the decrease of spherulitic growth rate. In the meantime, the total crystalline rate is also controlled by nucleation [25]. When more nuclei are present, more spherulites are formed and at the end of the process the typical spherulite will be smaller [28].

WAXD is a convincing tool to investigate the crystal structure. The WAXRD patterns in the range of 2θ 10°~35° for neat PPDO and PPDOCD5 samples are shown in Fig. 12. PPDO has the diffraction peaks at 2θ of 22.2°,

Table 2 Thermal characteristics of various PPDO obtained from DSC curves

Sample	Scan (10°C min ⁻¹)	T_g (°C)	T_c^a (°C)	ΔH_c^b (J/g)	T_{c1}^c (°C)	ΔH_{c1}^d (J/g)	T_m^e (°C)	ΔH_m^f (J/g)
PPDO	Cooling		34.4	30.3				
	Heating	-18.5			27.3	21.9	103.5	100.2
PPDOCD1	Cooling		38.9	11.3				
	Heating	-11.3			41.0	32.1	106.5	77.6
PPDOCD3	Cooling		50.8	12.7				
	Heating	-9.5			40.9	35.0	106.2	78.8
PPDOCD5	Cooling		69.8	50.1				
	Heating	-5.5			—	—	106.0	49.7

^a Peak crystallization temperature determined from the cooling scan

^b Crystallization enthalpy at T_c

^c First peak crystallization temperature determined from the heating scan

^d Crystallization enthalpy at T_{c1}

^e Melting temperature determined from the heating scan

^f Fusion enthalpy at T_m

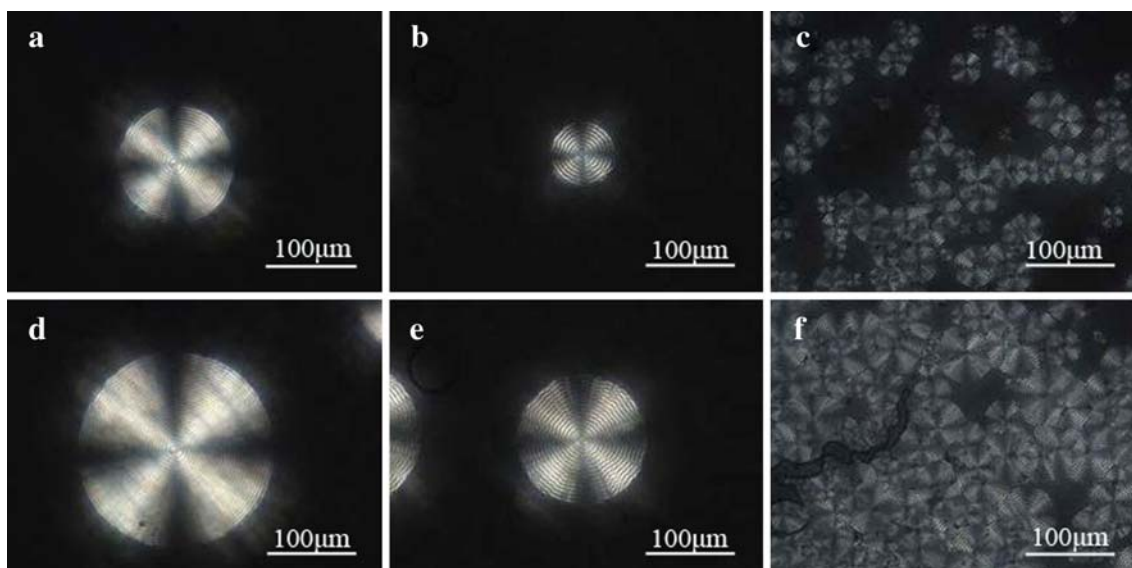


Fig. 10 The spherulitic growing process of various PPDO at 60 °C. **a, b** and **c** are pictures of PPDO, PPDOCD1 and PPDOCD5 of crystallization for 3 min, respectively; **d, e** and **f** are pictures of PPDO, PPDOCD1 and PPDOCD5 of crystallization for 6 min, respectively

24.0° and 29.2° with the intensity of 5569, 1609 and 392 counts, respectively. The corresponding d spacings calculated from the Bragg equation are 4.00 (d_{210}), 3.71 (d_{020}) and 3.06 (d_{310}) Å, respectively. In respect of PPDOCD5, there are also three diffraction peaks at 2θ of 22.0°, 23.9° and 29.2° with the intensity of 5272, 2222 and 612 counts, respectively. The corresponding d spacings are 4.04 (d_{210}), 3.73 (d_{020}) and 3.05 (d_{310}) Å, respectively. These measured values are in good agreement with those reported by Furuhashi and Ooi [29, 30] and do not change with the addition of PCD (within experimental error). Both of PPDO and PPDOCD5 give near identical diffraction peaks. This result reveals that the addition of PCD has no effect on the crystal structure of PPDO.

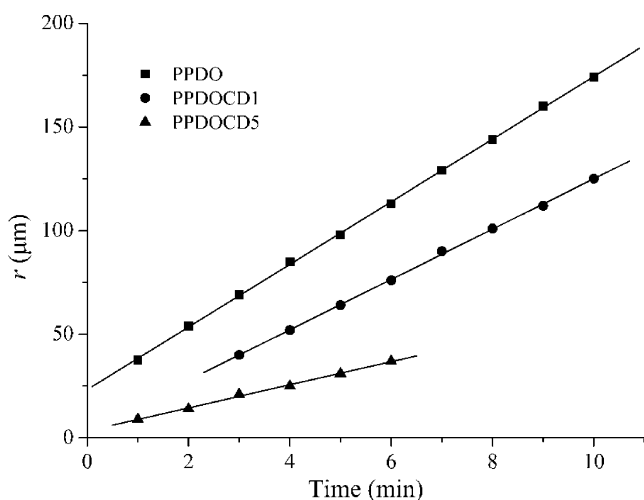


Fig. 11 The linear relationship between spherulitic radius and crystallization time of various PPDO at 60 °C

Conclusions

TG analyses indicate that the addition of PCD can enhance significantly the thermal stability of PPDO. The thermal decomposition temperature of PPDO increases with the increase of the amount of PCD added. The thermal decomposition activation energies for non-isothermal thermal degradation estimated by Kissinger method are 160 and 106 kJ mol^{-1} for PPDO added with 5 wt% PCD and neat PPDO, respectively. The results obtained by DSC and POM reveal that the addition of PCD decreases the molecular mobility and crystallinity of PPDO and the unreacted PCD

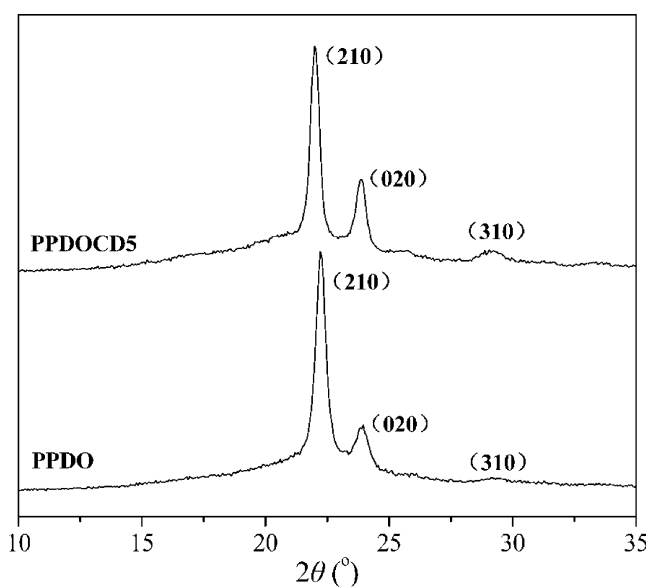


Fig. 12 WAXD curves of PPDO and PPDOCD5

acts as a nucleating agent in the process of crystallization. WAXD analyses show that the addition of PCD has no effect on the crystal structure of PPDO.

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