

The influence of coexisted monomer on thermal, mechanical, and hydrolytic properties of poly(*p*-dioxanone)

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ABSTRACT: Poly(*p*-dioxanone) (PPDO), a typical aliphatic poly(ether-ester), is generally synthesized via ring-opening polymerization of 1,4-dioxan-2-one (*p*-dioxanone, PDO) monomer. However, a quite amount of PDO monomer should coexist with PPDO product due to the characteristics of the equilibrium polymerization. To clarify the effects of PDO on the properties of PPDO, a series of PPDO/PDO mixtures with different PDO content were prepared by adding PDO to pure PPDO. The thermal, mechanical, and hydrolytic properties of PPDO and PPDO/PDO mixtures were investigated systematically. It reveals that the existence of PDO in the polymer can act as plasticizer to facilitate the crystallization of PPDO, but the increasing of PDO content deteriorates the mechanical properties of the polymers, especially when the PDO loading is more than 3 php. The PDO does not distinctly affect PPDO thermal decomposition, but obviously accelerates the PPDO hydrolytic degradation. This work may provide an important reference for the industrialization and application of PPDO. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43483.

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INTRODUCTION

As an aliphatic poly(ether-ester), poly(*p*-dioxanone) (PPDO) exhibits excellent biodegradability and biocompatibility as well as good mechanical performance,^{1–3} moreover, it is worth to mention that PPDO can be called as ecofriendly polymer with excellent feedstock recyclability.^{4,5} These unique characters make it a good candidate for biomaterials as well as general uses such as films, molded products, laminates, foams, nonwoven materials, adhesives, and coatings.^{6–8} Recently, the cost of its monomer, 1,4-dioxan-2-one (*p*-dioxanone, PDO), decreased significantly as the catalytic synthesis technology of PDO from diethylene glycol had made breakthrough,⁹ which further reduced the cost of PPDO. Therefore, PPDO is a kind of promising and competitive biodegradable material.

Generally it is easy to polymerize PDO using initiators to produce a high molecular weight polymer. However, whichever initiator is used for the polymerization of PDO, the conversion of polymerization converges to a thermodynamic equilibrium. For example, it was found the polymerization of PDO at 100 °C with Zn(Lac)₂ never exceed 80% yield.¹⁰ With SnOct₂ or AlEt₃, the equilibrium conversions of PDO decrease in a similar manner with increasing polymerization temperature: the conversion decreases from 85% at 80 °C to 80% at 100 °C and 74% at 120 °C.¹¹ These equilibrium conversions are lower than that of L-lactide reported as 98.68%

(130 °C) and 97.85% (160 °C).¹² In our previous reports,^{13–16} we researched the polymerizations of PDO catalyzed by AlEt₃-H₂O-H₃PO₄, La(OiPr)₃, Novozym 435, and Sn(Oct)₂ with conventional polymerization method or microwave irradiation polymerization. But the highest conversion obtained is only 96.0% under microwave irradiation with AlEt₃ at 80 °C. The dissolution/precipitation and extraction methods were usually employed to remove the unreacted PDO.^{11,17–20} However, it is difficult to ensure all the unreacted monomer to be removed completely, especially for industrial application. Furthermore, the large amount of solvent used for purification is also unrealistic due to high cost.

Actually, the remained monomer should influence the properties of the results polymer material more or less. Recently, researchers have found that the monomer of PLLA affects its thermal and mechanical properties.^{21,22} Pretreatment of PLLA in nitrogen atmosphere at 150 °C for 60 min before processing is useful to remove the lactic acid and lactide.

To our best knowledge, there is no report concerned about the influence of PDO monomer on the properties of PPDO. Hence, to make clear this feature is highly expected. In this article, a series of PPDO/PDO samples with various PDO content were prepared via melt blending under nitrogen atmosphere. The influence of PDO on the thermal, mechanical, and hydrolytic properties of PPDO has

been investigated; the hydrolytic degradation mechanisms of pure PPDO and PPDO/PDO mixtures have also been explored.

EXPERIMENTAL

Materials

p-Dioxanone was obtained from the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China). It was dried over CaH₂ for 48 h, then distilled twice in vacuum immediately before use. Stannous Octoate (AR grade) was purchased from Sigma (USA). Phenol/1,1,2,2-tetrachloroethane, acetone and other chemicals with AR grade were purchased from KeLong Reagent Corporation (Chengdu, China) and used without further purification.

Synthesis of PPDO and Purification

PPDO was synthesized in our laboratory via ring-opening polymerization (ROP) of PDO performed in the bulk with magnetic stirring in flame-dried glass reactors. The reactors had been previously flame-dried, evacuated and purged with nitrogen several times prior before adding PDO and SnOct₂ solution (mole ratio: [catalyst]/[PDO] = 1/10,000) with a syringe. The reaction was performed at 80 °C for 72 h. The obtained crude polymer was crushed into powder and purified by acetone to remove the unreacted monomer in Soxhlet extractor for 48 h. Then the obtained PPDO was dried to constant weight under vacuum at 50 °C.

Preparation of PPDO/PDO Mixtures

The purified PPDO was mixed with desired amount of PDO (0 php, 3 php, 6 php, 9 php, and 12 php), which were coded as PPDO, PPDO/3PDO, PPDO/6PDO, PPDO/9PDO, and PPDO/12PDO, respectively. The blending were performed in reactors with mechanical agitator under nitrogen atmosphere at 140 °C for 10 min, then the reactors were rapidly cooled down to room temperature and the obtained PPDO/PDO mixtures were milled into small chips. The intrinsic viscosities [η] and PDO amounts of the obtained PPDO/PDO samples were listed in Table I. The [η] of PPDO in PPDO/PDO mixtures was maintained at 1.1 to 1.2 dL g⁻¹ and the actual PDO amount were 0, 4.1, 5.9, 8.8, and 11.7 php, respectively.

Characterization

Intrinsic Viscosity Measurement. Intrinsic viscosities ([η]) of PPDO/PDO mixtures were measured at 30 °C with concentration of $c = 0.1$ g/dL in phenol/1,1,2,2-tetrachloroethane (1:1 v/v) solution using an Ubbelohde viscometer.

PDO Content Measurement. Each sample was weighed on an analytical balance before being placed in the Soxhlet extractor. The unreacted monomer was removed by acetone in Soxhlet extractor for 48 h, then the samples were dried to constant weight under vacuum at 50 °C. After drying, the samples were weighed based on the changes of weight. The PDO content of samples was calculated as follows:

$$\text{PDO content (php)} = (W_a - W_b) \times 100 / W_b$$

where W_a and W_b represent the initial and remaining weights of the dried samples, respectively.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis was performed with a TA Instrument (DSC Q200, TA Co., Delaware). Tests were

Table I. The PDO Content^a and Intrinsic Viscosities of PPDO/PDO Mixtures

Sample	PPDO (php)	PDO (php)	[η] ^b (dL g ⁻¹)	PDO ^c (php)
PPDO	100	0	1.21	0
PPDO/3PDO	100	3	1.13	4.1
PPDO/6PDO	100	6	1.18	5.9
PPDO/9PDO	100	9	1.15	8.8
PPDO/12PDO	100	12	1.12	11.7

^a php: parts per hundred of PPDO by weight.

^b The [η] of PPDO in the PPDO/PDO mixtures were determined in phenol/1,1,2,2-tetrachloroethane (1:1 v/v) at 30 °C using an Ubbelohde viscometer.

^c Determined from PDO content measurement.

carried out under nitrogen atmosphere and all samples (3–5 mg) were placed in aluminum pans. For the virgin samples of PPDO and PPDO/PDO, it was first heated to 140 °C and kept for few minutes to erase all previous thermal history, then conducted the cooling and heating cycle at a rate of 10 °C/min. For the hydrolysis degradation samples of PPDO and PPDO/PDO, a direct scan from 40 to 140 °C at a heating rate of 10 °C/min was conducted without erasing previous thermal history. The absolute degree of crystallinity (χ_c) was calculated by the ratio of the melting enthalpy (ΔH_m) of samples to that of 100% crystalline PPDO (141.2 J/g),²³ and the relative degree of crystallinity (χ_t) was calculated by the ratio of the crystallization enthalpy (ΔH_c) in the cooling scan of samples to the sum of crystallization enthalpy both in cooling scan and in heating scan.²⁴

X-ray Diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) measurement was carried out using an X-ray diffractometer (Bruker D8 Advance, Bruker AXS Handheld Inc., GER). The radiation used was Cu-K α radiation at room temperature and the scan range was between 5° and 40° with a scan rate of 2°/min. Both the virgin samples and the hydrolysis degradation samples are from the same source with the samples conducted in DSC test without any treatment. The crystallinity (D_c) values of samples were estimated from the WAXD measurements using the following equation:

$$D_c(\%) = 100S_c / (S_c + S_a)$$

where S_c and S_a are crystalline and amorphous diffraction peak areas, respectively.

Thermogravimetric Analysis (TGA)

TGA measurements were conducted with a Dupont 2100 system in platinum pans under a steady N₂ flow of 50 mL min⁻¹. Sample weights were 3 to 5 mg. The weight losses of the specimens were measured with a heating rate of 10 °C/min up to 400 °C. Another TGA temperature profile has also been used that the samples first stayed isothermally at 150 °C for 30 min, then were heated to 400 °C at a heating rate of 10 K min⁻¹.

Measurement of Mechanical Properties

The mechanical properties of PPDO samples were measured with a tensile tester (Sans Testing Machine Co. Ltd., China) at a drawing speed of 50 mm/min at 25 °C. Each test was conducted based on the results from five samples.

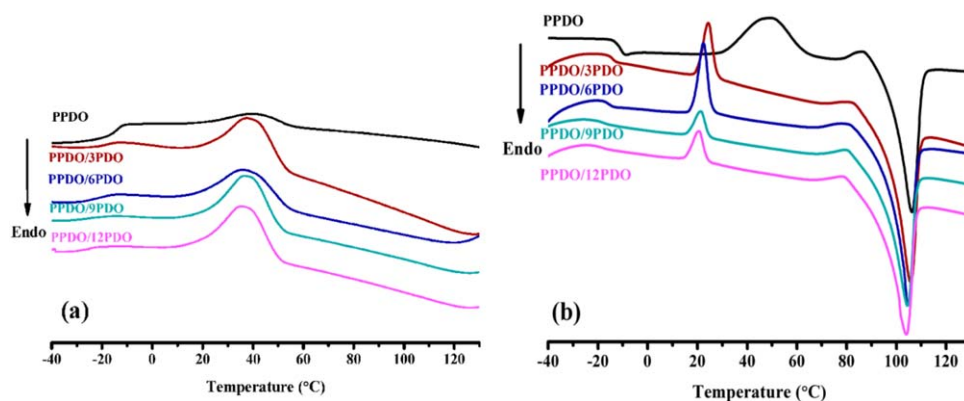


Figure 1. DSC traces of samples in cooling scan (a) and the followed heating scan (b) with a rate of 10 °C/min after erasing thermal history. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. DSC Cooling Data after Erasing All Previous Thermal History and Second Heating Data after the Cooling Runs for PPDO/PDO Mixtures

Samples	The cooling scan		The second heating scan						
	T_{c1} (°C)	ΔH_{c1} (J/g)	T_{g2} (°C)	T_{c2} (°C)	ΔH_{c2} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c^a (%)	χ_t^b (%)
PPDO	40.4	9.6	-10.8	50.0	41.9	106.1	74.8	53.0	18.6
PPDO/3PDO	41.3	30.9	-13.8	24.5	13.9	105.6	82.6	60.4	68.9
PPDO/6PDO	37.0	30.8	-15.8	22.4	17.7	104.5	82.4	62.2	63.6
PPDO/9PDO	39.2	36.0	-17.4	21.7	6.8	104.2	77.2	60.2	84.2
PPDO/12PDO	37.9	36.7	-18.0	20.9	8.4	103.8	80.5	64.8	81.4

^a Absolute degree of crystallinity, χ_c (%) = $100 \times \Delta H_m / (141.2 \times (1 - \phi))$, ϕ is the weight fraction of PDO.

^b Relative degree of crystallinity, χ_t (%) = $100 \times \Delta H_{c1} / (\Delta H_{c1} + \Delta H_{c2})$.

In Vitro Degradation Test

PPDO and PPDO/PDO bars with the dimension of 15 mm × 4 mm × 0.5 mm were prepared by compression molding using vulcanizing press at a pressure of 10 MPa at 140 °C for 5 min. The hydrolysis experiments of PPDO/PDO mixtures were conducted in phosphate buffer solution (based on Na₂HPO₄ and NaH₂PO₄)

with a pH value of 7.40 at 37 °C. The solution was periodically replaced with fresh solution to ensure a constant pH. Every week, the degraded samples were taken out from the hydrolysis medium and dried to a constant weight for measurement.

Scanning Electron Microscopy (SEM)

Surface morphology was observed with scanning electron microscope (SEM) (JSM-5900LV, Jeol Co., JP). The sample surface was coated with a thin layer of gold by vacuum deposition.

Electrospray Ionization-Mass Spectroscopy (ESI-MS)

ESI-MS was carried out using a Waters Quattro Premier XE mass spectrometer equipped with an electrospray ionization source. The samples were diluted in distilled water, and directly introduced into the ESI source using a syringe pump (flow rate of 10 mL/min). Mass spectra were acquired by scanning from $m/z = 50$ to 1000.

RESULTS AND DISCUSSION

Thermal Properties

Melting and Crystallization Behavior. Figure 1 and Table II show the cooling scan and the second heating scan of PPDO/PDO mixtures. PPDO chains are unable to completely crystallize during cooling from the melt at 10 °C/min, and in the subsequent heating curve, the polymer shows cold crystallization. Hence, the endotherm of the final melting peak includes the fusion of both crystals formed during cooling and those formed or recrystallized during the heating run, this phenomena obtained is in agreement with previous literatures about PPDO.^{1,25–28} The glass transition temperature (T_{g2}), as well as

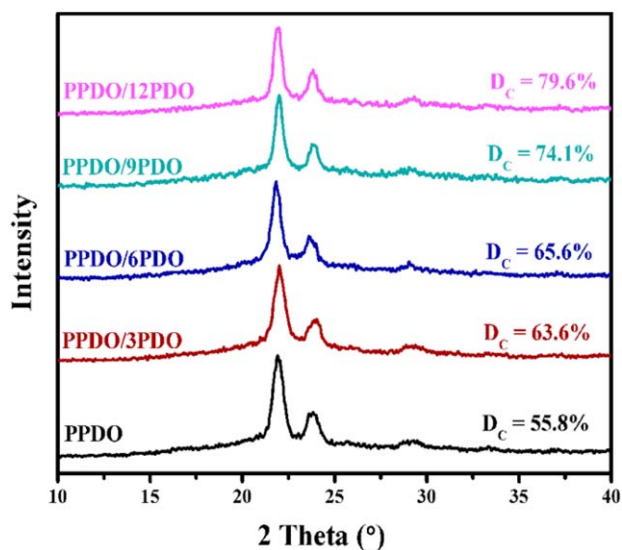


Figure 2. WXR patterns of PPDO/PDO samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

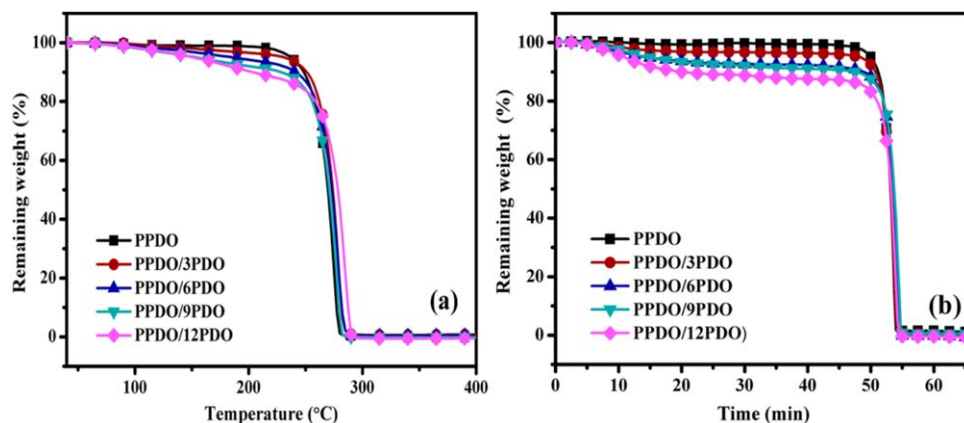


Figure 3. TGA curves of PPDO/PDO samples: (a) a heating rate of 10 K min^{-1} under N_2 flow of 50 mL min^{-1} , (b) isotherm at 150°C for 30 min, then were heated to 400°C at a heating rate of 10 K min^{-1} under N_2 flow of 50 mL min^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Effects of PDO on PPDO Decomposition Temperature

Samples	T_{dec1} ($^\circ\text{C}$) of PPDO with nonisothermal treatment	T_{dec2} ($^\circ\text{C}$) of PPDO with previous isothermal treatment
PPDO	274.7	275.4
PPDO/3PDO	278.3	275.1
PPDO/6PDO	279.5	277.8
PPDO/9PDO	277.0	280.5
PPDO/12PDO	284.4	275.8

Table IV. Mechanical Properties of PPDO/PDO Samples

Samples	Tensile strength (MPa)	Elongation at break (%)
PPDO	53.2 ± 2.5	713 ± 48
PPDO/3PDO	53.5 ± 2.7	724 ± 65
PPDO/6PDO	48.0 ± 3.2	580 ± 49
PPDO/9PDO	43.0 ± 2.4	573 ± 29
PPDO/12PDO	34.9 ± 1.4	489 ± 30

cold crystallization temperature (T_{c2}), and melting temperature (T_m) of samples at the second heating scan gradually decrease with increasing PDO content. T_{c2} decreases as well as relative degree of crystallinity (χ_t) and absolute degree of crystallinity (χ_c) increase, suggesting that PDO as a plasticizer facilitates the crystallization of PPDO in the mixtures. Meanwhile, the existence of PDO also results in less perfect crystallites, consequently, T_m decreases from 106.1°C for neat PPDO to 103.8°C for PPDO/12PDO. Actually, the incorporation of PDO in polymer chains decreases the intermolecular interactions and increase the free volume, and further lead to better flexibility, which is similar to the plasticization of poly-L-lactide with L-lactide,

D-lactide, and D,L-lactide monomers.²² When 3 php of PDO is mixed, the χ_c and χ_t increase sharply; then the crystallinity of the mixture has no obvious change with further increase of the PDO content.

WAXD is a convincing tool to investigate the crystal structure.²⁹ The diffraction profiles for PPDO/PDO samples are shown in Figure 2. Apparently, the diffraction peaks appear at 2θ of around 22.2° , 23.9° , 29.2° for all PPDO/PDO samples. The corresponding d spacings calculated from the Bragg equation are about 4.00 (d_{210}), 3.71 (d_{020}), and 3.06 (d_{310}) \AA , respectively. These values are in agreement with those reported about PPDO by Furuhashi *et al.*³⁰ and Ooi and Cameron,³¹ and have no

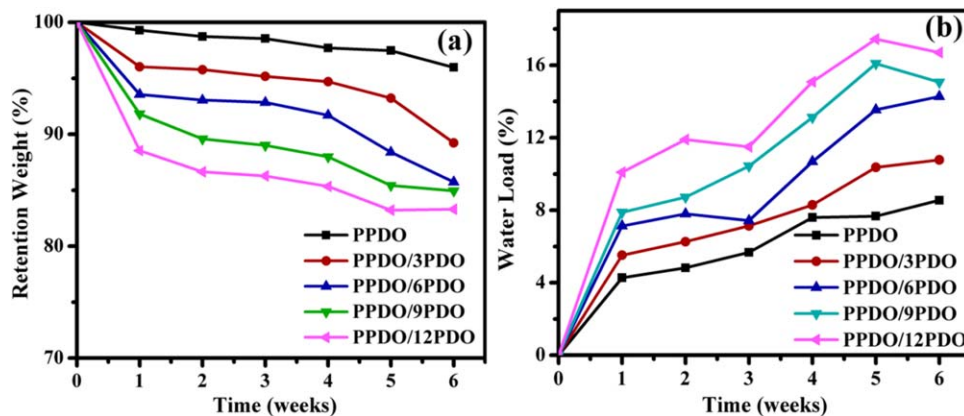


Figure 4. Changes of (a) the weight retention and (b) water absorption of PPDO/PDO mixtures during degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

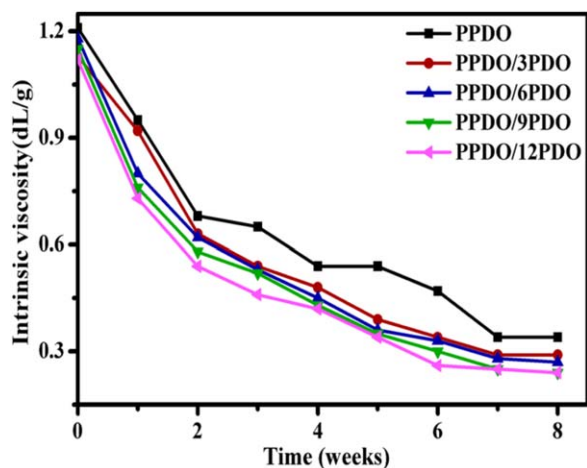


Figure 5. Changes of the intrinsic viscosity of PPDO/PDO samples during degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change with the addition of PDO. This result reveals that the coexisted PDO has no effect on the crystal structure of PPDO. The crystallinity of PPDO/PDO samples can also be determined by WAXD, and the results were showed at each profile in Figure 2. Overall, the values of WAXD increase significant with the increase of PDO content, which also shows the existence of PDO can obviously promote the crystallization of PPDO chain segment.

Thermal Stability. Figure 3(a) illustrates the decomposition curves of PPDO/PDO mixtures performed with non-isothermal treatment, the remaining weight shows a slight decrease with the increasing PDO content in the initial stages of decomposition (40–250 °C), caused by the evaporation of PDO, and the maximum decomposition temperature keep a similar level according to the T_{dec1} values (Table III). However, the overdose PDO slight increases PPDO maximum decomposition temperature. Especially, PPDO/12PDO whose maximum decomposition temperature is 10 °C higher than PPDO, which may due to the equilibrium polymerization behavior of PDO reported by Nishida *et al.*¹¹

The PPDO/PDO mixtures had also undergone an isothermal at 150 °C for 30 min, followed heat up to 400 °C at a heating rate of 10 K min⁻¹ under nitrogen atmosphere. The samples lose their mass almost 0.5, 3.5, 7.5, 8.6, and 11.9 wt % corresponding to the PDO content of the PPDO/PDO mixtures during isotherming at 150 °C for 30 min from Figure 3(b), which has no influence on its follow thermal stability. The pure PPDO and PPDO/PDO mixtures have similar maximum decomposition temperature (T_{dec2} in Table III) indicates that the previous isothermal treatment of PPDO succeed in removing PDO without affecting its thermal stability.

Mechanical Properties

The mechanical properties of PPDO and PPDO/PDO mixtures are listed in Table IV. A small amount of PDO monomer (3 php) does not affect the tensile strength and elongation at

Table V. Changes of the Crystallinity (χ_c) of PPDO/PDO Mixtures during Degradation

Time (weeks)	PPDO		PPDO/3PDO		PPDO/6PDO		PPDO/9PDO		PPDO/12PDO	
	ΔH_m (J/g)	χ_c (%)	ΔH_m (J/g)	χ_c (%)	ΔH_m (J/g)	χ_c (%)	ΔH_m (J/g)	χ_c (%)	ΔH_m (J/g)	χ_c (%)
0	73.6	52.2	89.8	63.7	88.0	62.4	79.5	56.4	80.8	57.3
2	99.6	70.6	103.2	73.2	100.4	71.2	100.6	71.4	90.9	64.5
4	102.9	73.0	98.3	69.7	95.8	68.0	94.5	70.0	95.0	67.4
6	111.3	78.9	97.6	69.2	95.7	67.9	96.8	68.9	93.0	65.6
8	117.6	83.4	100.9	71.6	94.6	67.0	82.7	58.6	89.1	63.2

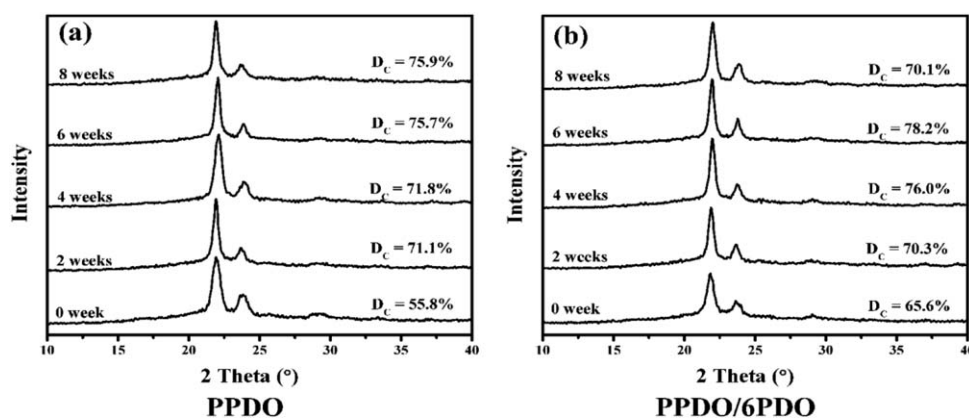


Figure 6. WAXD patterns and relative degree of crystallinity (D_c) for PPDO (a) and PPDO/6PDO (b) with varying degradation time.

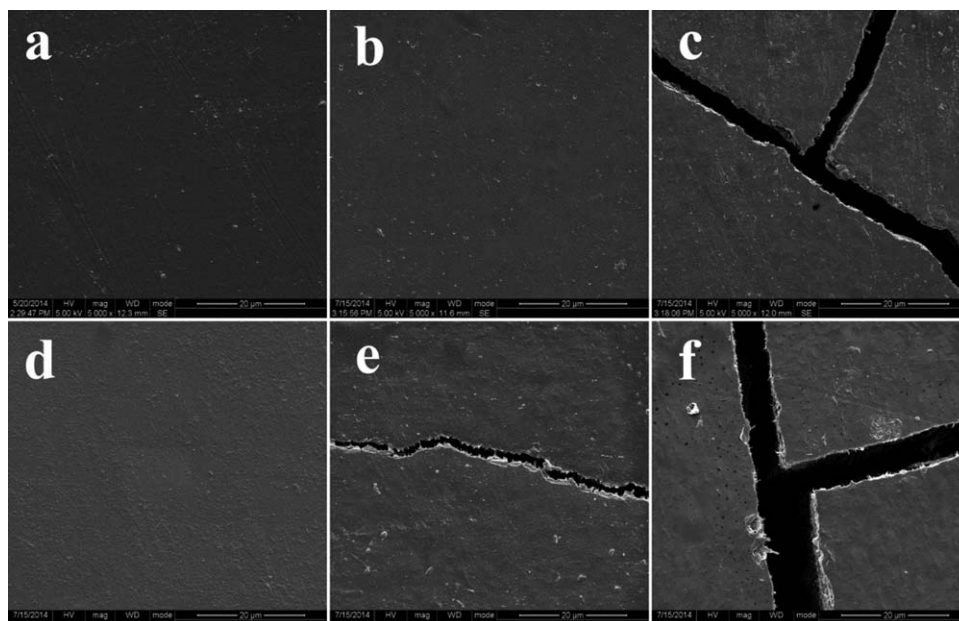


Figure 7. Surface morphology of PPDO and PPDO/6PDO during degradation, (a) PPDO 0 week, (b) PPDO 2 weeks, (c) PPDO 4 weeks, (d) PPDO/6PDO 0 week, (e) PPDO/6PDO 2 weeks, (f) PPDO/6PDO 4 weeks.

break of the PPDO polymer, which is due to the fact that small amount of PDO can obviously facilitate the crystallization of PPDO. As we known, the incorporation of the small amount of PDO into PPDO will weaken the interaction between polymer chains to some extent, which increase the flexibility of polymer chains and therefore allow the polymer matrix to sustain large deformations before fracture. When quite amount of PDO small molecules are embedded in, however, the deterioration of mechanical properties for PPDO becomes non-negligible. For example, the elongation at break and tensile strength of PPDO/12PDO decrease 31.4% and 34.4% compared with pure PPDO, respectively. Although a large amount of PDO located in the regions of amorphous phase of the PPDO polymer improves the deformation, its accumulating within the interspherulitic

boundaries will worsen the union between adjacent lamellae within the same spherulite and adjacent spherulites, which finally results in the deterioration of mechanical properties. This phenomenon has also been reported in some similar aliphatic polyester contained with relative monomer.^{21,32}

Hydrolytic Degradation Properties

Weight Retention and Water Absorption. The samples were evaluated every week during the hydrolysis process of PPDO/PDO mixtures, the variation tendency of weight retention percentage and water absorption percentage are shown in Figure 4(a,b). The weight retention decreases and the water absorption increases significantly with the increase of PDO in the PPDO, especially in the first week, is mainly caused by PDO migrate from the interior to the surface and diffuse away from the samples, thus forming micro caverns, gaps, and leading the water absorption to increase. Moreover, polymer degradation generates some chain fragments that are low enough to dissolve into the medium, which also contributes to the decreasing weight retention and increasing water absorption at this stage.

Molecular Weight Change. The changes of molecular weight were measured by Ubbelohde viscosimeter and the results are shown in Figure 5. The intrinsic viscosity decreases with the degradation time increases. Moreover, the viscosity of the PPDO/PDO mixtures decrease much faster than pure PPDO: the $[\eta]$ of pure PPDO decreases from 1.20 dL g^{-1} to about 0.35 dL g^{-1} within 8 weeks, while PPDO/12PDO mixtures decreases to about 0.34 dL g^{-1} within only 5 weeks. This is consistent with the trends from the weight retention and water absorption of the samples. Apparently, the hydrolytic degradation rate could be controllable by altering the PDO content, which has similar effect with the controllable hydrolytic degradation rate by altering the block lengths or branching architecture of PLA.^{33–36}

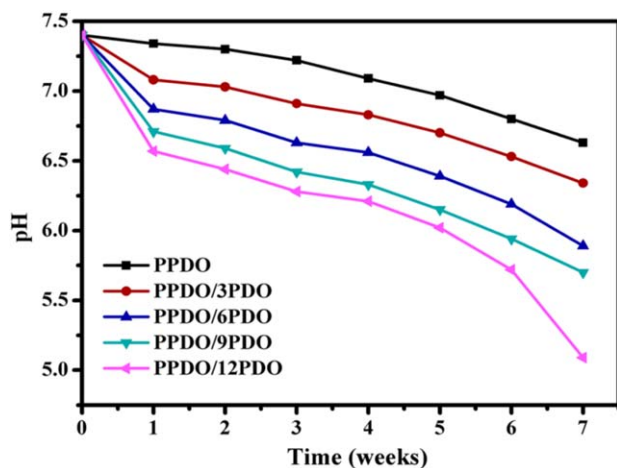


Figure 8. pH changes of PPDO/PDO samples in PBS at 37°C as a function of different degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

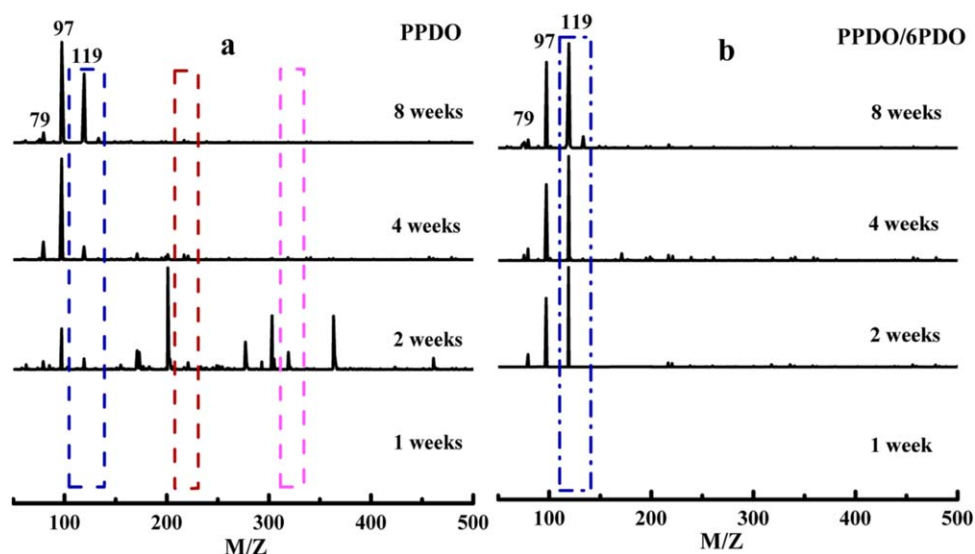


Figure 9. ESI-MS (negative-ion mode) of the degradation liquid of PPDO (a) and PPDO/6PDO (b) after degradation 1, 2, 4, and 8 weeks at 37°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Crystallinity Change by DSC and XRD. The crystallinity of samples determined by DSC measurement as a function of hydrolysis time are listed in Table V. In 8 weeks of hydrolysis, the crystallinity of pure PPDO gradually increases with increasing time, it reveals that the degradation mainly occurs in the amorphous region in this period. Comparatively, the crystallinity of PPDO/PDO mixtures first increases and then decreases, suggesting the degradation in crystalline domains already happens. Apparently, PPDO/PDO mixtures display a higher degradation rate. It has been reported that the temperature and relative humidity influence the hydrolytic degradation of PPDO.³⁷ The increasing in crystallinity of PPDO is a consequence of the hydrolytic chain scission of unstable ester bonds

and can be explained by the “cleavage-induced crystallization” mechanism.³⁸ The degradation of PPDO first begins in the amorphous region and could be attacked easily by water, leading to a decrease in molecular entanglement; further these short segments could organize themselves to crystals at 37°C above the T_g of PPDO, therefore the crystallinity of PPDO first increases. As the degradation process continues, degradation also occurs in the crystalline region, thus decreasing the crystallinity of PPDO.

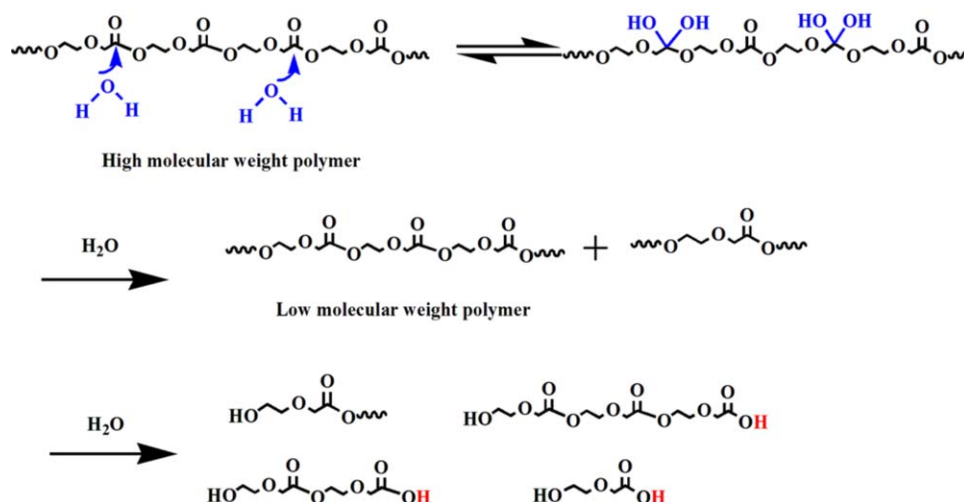
WAXD measurement was also carried out for further investigation of the changes of crystallinity, in view of the samples have the same thermal history as the samples conducted in first heating run during DSC analysis. The WAXD patterns for PPDO and PPDO/6PDO during degradation are shown in Figure 6. Both the virgin and degradation samples of PPDO and PPDO/6PDO have similar identical diffraction peak positions during the degradation, suggesting the crystalline structure does not change during degradation. The crystallinity of PPDO increases with the increase of degradation time, while that of PPDO/6PDO increases at first and then decreases. Similarly, the WAXD results agree well with those trend obtained for DSC results.

Morphology. SEM is a very effective technique to monitor the degree of the polymer degradation by observing the change of morphology in surface section. As an aliphatic polyester, PPDO exhibits fast degradation rate. While the hydrolysis proceeds, water molecules can easily access and attack these ester bonds, the fragments of chains involved in this hydrolysis can diffuse away from the polymer or incorporate into the crystal, leaving empty spaces in the sample, in result, the cracks could be observed by SEM. The morphological features of surface on samples in the degradation process are revealed by scanning electron microscopy (Figure 7). In Figure 7, it clearly shows that both PPDO (a) and PPDO/6PDO (d) before hydrolysis have a relative smooth and clear surface. After 2 weeks of

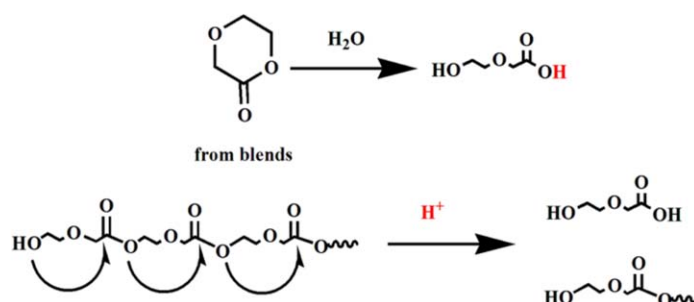
Table VI. The Structures of Peaks from ESI-MS after 2 Weeks of PPDO Degradation

M/Z	Structure
119	
177	
203	
221	
279	
305	
323	
365	

PPDO hydrolysis: Random ester cleavage



PPDO/PDO hydrolysis: Chain end cleavage



Scheme 1. Hydrolytic degradation mechanisms of PPDO and PPDO/PDO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation, however, some small cracks exhibit on the surface of PPDO/6PDO while no cracks are observed on the surface of PPDO. After 4 weeks, the cracks of PPDO/6PDO become much wider although it just appears on the surface of PPDO. The cracks appear on the surface of PPDO degradation samples have also been reported previously.^{37,39–41} As we known, PDO in PPDO/PDO mixture can leach out of the mixtures and dissolve in the solution, and it can convert to monomer acid which can catalyze the hydrolysis during the degradation process further. Now, it is easy to understand that the PPDO/PDO mixtures preserve more cracks and rough surface than PPDO during the degradation. In brief, PPDO preserves more physical integrity than PPDO/PDO mixtures during the degradation, suggesting a faster hydrolytic degradation of PPDO/PDO than that of pure PPDO.

Hydrolysis Mechanism. In order to investigate the hydrolysis mechanisms of the PPDO and the PPDO/PDO mixtures, 0.2 g sample of each type was placed in test tube containing 10 mL buffer solution at 37 °C. The pH values of the solutions were

monitored every week (Figure 8), and the water-soluble degradation products were analyzed using ESI-MS after 1, 2, 4, and 8 weeks of degradation (Figure 9). For PPDO, oligomers such as dimeric acid and trimeric acid appear after 2 weeks of degradation. It is worthy to note that some other peaks ($m/z = 177, 203, 279, 305, 365$ from Table VI) are probably formed by fragmentation of the oligomers, which occur during the ionization process in the ESI-MS spectrometer and do not correspond directly to real hydrolytic degradation products of PPDO, and these product can be formed by the cleavage of an $-\text{CH}_2-\text{O}-\text{CH}_2-$ ether bond with transfer of a hydrogen atom and formation of the product ions: one bearing a carboxyl and an unsaturated end group and the other terminated with carboxyl and hydroxyl end groups, which has previously been reported in the case of fragmentation of PEG oligomers⁴² and poly(1,5-dioxepan-2-one oligomers);⁴³ after 4 weeks, most of the oligomers disappear and the main degradation product is the monomer hydroxyl acid. These results suggest that during hydrolysis the PPDO, ester bond is mainly randomly attacked along the chain that produces low molecular weight polymers with carboxylic

acid end groups. The formed carboxylic acid end groups in the polymer matrix catalyze further hydrolysis into their oligomer and monomer hydroxyl acid. Finally, the oligomers degrade into their monomeric hydroxyl acid. This is accordance with the bulk erosion process of aliphatic polyesters.^{44,45}

For PPDO/PDO mixtures, however, oligomers are hardly detected during the hydrolysis process, and the main product is the monomer hydroxyl acid (Figure 9), indicating a dominant chain-end cleavage mechanism. Figure 8 shows that during the hydrolysis process, the solution of the PPDO/PDO mixtures possess lower pH values than that of PPDO, and the higher PDO amount in the mixtures leads to lower pH of the solution. PDO can leach out of the mixtures and dissolve in the solution, then ring-opening of PDO can form the monomeric acid, which lowers the pH of the solution, and thus catalyzes the hydrolysis at the beginning of the degradation process. The lower pH of PPDO/PDO as well as the short distance between the functional groups (carbonyl and the alkoxy group) in PPDO, accounts for faster chain-end cleavage (“unzipping”) than the random (“internal”) ester cleavage during hydrolysis. Similar results have been observed for PLA hydrolysis.^{46,47} A presumable hydrolysis mechanism of PPDO and PPDO/PDO has been described in Scheme 1.

CONCLUSIONS

Residual PDO monomer in PPDO after polymerization affects the properties of the product markedly. In present work, PPDO/PDO mixtures with different PDO content were prepared by adding PDO to pure PPDO. The DSC and XRD analysis show that PDO can act as a plasticizer to facilitate the crystallization of PPDO, therefore, the crystallinity of the PPDO/PDO mixtures increases with the increase of the PDO content. PDO monomer is considered as a suitable candidate to plasticize the PPDO, primarily to obtain a homogeneous mixture that will be biodegradable and biocompatible. The tensile test discloses that a small amount of PDO monomer (3 php) does not affect mechanical properties of the PPDO polymer, however, further increase of the PDO content decreases the mechanical properties of the mixtures. The results of hydrolysis experiments reveal that the existence of PDO greatly reduces the hydrolytic stability of PPDO: The weight retention percentage and the viscosity decreases, the water absorption percentage increases significantly with the increase of PDO in the PPDO, because PDO can leach out of the mixtures and dissolve in the solution, then ring-opening of PDO can form the monomer acid, which lowers the pH of the solution, and thus catalyzes the hydrolysis of the degradation process, and the hydrolytic degradation rate could also be controllable by altering the PDO content. A presumable hydrolysis mechanism has been proposed that with the addition of PDO, a random ester cleavage hydrolysis mechanism for PPDO shifts to a dominant chain-end cleavage mechanism (“unzipping”) for PPDO/PDO mixtures.

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