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Synthesis of poly(lactic acid-*b*-*p*-dioxanone) block copolymers from ring opening polymerization of *p*-dioxanone by poly(L-lactic acid) macroinitiators

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Summary

Poly(lactic acid-*b*-*p*-dioxanone) block copolymers (P(LA-*b*-PDO)) were synthesized by ring-opening polymerization of *p*-dioxanone using poly(lactic acid) (PLA) with different molecular weights as macroinitiators in N_2 atmosphere. The copolymers were characterized by ^{1}H-NMR spectra. The thermal and crystalline behaviors and thermal stability of these copolymers were investigated by DSC, TGA and WAXD. The results indicated that the contents of each segment and the intrinsic viscosities affected the properties of copolymers obviously.

Keywords

poly(lactic acid), poly(*p*-dioxanone), block copolymer, biodegradable

Introduction

Poly(p-dioxanone) (PPDO), one of the biodegradable and biocompatible aliphatic polyesters, has high flexibility and good tensile strength [1]. Due to its good biocompatibility and physical properties, PPDO has been considered as a candidate not only for medical uses but also for universal uses such as films, molded products, laminates, foams, non-woven materials, adhesives and coatings [2-4]. Although high cost and rigorous synthetic condition of PPDO are the main barriers for the application of PPDO now, it cannot obstruct the development of PPDO as a promising biodegradable material in the future. Copolymerization and blending, two effective ways to modify the properties of polymer materials and to widen their applications, have already been introduced into PPDO systems and some valuable results have been achieved recently [5-13]. Polylactide (PLA), another linear aliphatic polyester, has been considered as one of the most promising materials because it can be made from agriculture products and is readily biodegradable. However, PLA has poor flexibility which limited its application. Copolymerizing or blending PPDO with PLA has been found as a conceivable way to combine the merits of these two polymers. A. P. T. Pezzin et al [14,15] prepared blends of PPDO with PLLA, and explored its properties. A tri-block copolymers derived from *p*-dioxanone (PDO), L-lactide and poly (ethylene glycol) has been investigated by Narayan Bhattarai et al [16-18]. To our best knowledge, all of the existing copolymers were synthesized by ring opening polymerization (ROP) of lactide and PDO. However, manufacture materials from lactic acid has been accepted as more economical route. In this paper, not lactide but L-lactic acid has been chosen to prepare the block copolymers of PPDO and PLA (P(LA-*b*-PDO)). Firstly, PLA prepolymer was synthesized by condensation polymerization, then P(LA-*b*-PDO) was produced by ROP of PDO monomer initiated by PLA prepolymers. Characterization and properties investigation of the resulting copolymers have also been made.

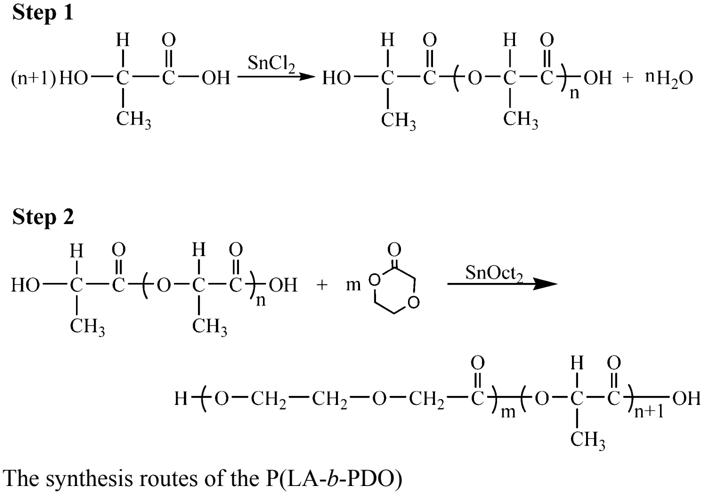
Experimental

Materials

L-lactic acid was purchased from Guangshui National Chemical Co., Ltd. (Hubei, China). *p*-Dioxanone (PDO) was provided by the pilot plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), which was dried over CaH_2 for 48 h, distilled under reduced pressure. Stannous octoate ($SnOct_2$) from Sigma (USA) was used after dissolving in pure and dry toluene. Acetone and other solvents with AP grade were purchased from Kelong Chemical Factory (Chengdu, China) and used without further purification.

Synthesis of P(LA-b-PDO)

The synthesis routes of P(LA-*b*-PDO) was shown in Scheme 1. PLA prepolymers with different molecular weight were synthesized by condensation polymerization following literature procedures [19].



Scheme 1. The synthesis routes of the P(LA-*b*-PDO)

The copolymerization reaction was carried out in a glass reactor under a nitrogen atmosphere. PLA prepolymers were added into the reactor, which was evacuated and purged with nitrogen three times. Then the reactor was immersed in a silicone oil bath (T=160°C). After the PLA prepolymers were completely molten, $SnOct_2$ and PDO monomer were charged with a syringe successively. Copolymerization was carried out with programmed decreasing temperature (keeping temperature at 160°C, 140°C, 120°C, 100°C, 80°C for 1h before cooling promptly to next stage, respectively), then the reactor was rapidly cooled to 0°C. The P(LA-*b*-PDO) copolymers were washed by acetone to eliminate residual PDO monomers as well as PLA homopolymers, and then the resulting products were dried in vacuum.

Characterization

The intrinsic viscosities [η] of the resulting copolymers were measured in phenol/1,1,2,2-tetrachloroethane (1/1, v/v) solution using an Ubbelohde viscometer maintained at 30°C. ^{1}H-NMR spectra were recorded in $CDCl_3$ with 400 MHz spectrometer (INOVA Varian). Wide angle X-ray diffraction (WAXD) patterns were recorded with an X-ray diffractometer (Philips X'Pert) with Cu Kα radiation. Differential Scanning Calorimetry (DSC) was performed with a SEIKO EXSTAR6000 DSC (SEIKO, Japan) under an ultrahigh-purity nitrogen atmosphere. The equipment was calibrated with indium and tin standards. Samples were heated to 180°C for 5 minutes to erase all previous thermal history and then were cooled to -50°C at a nominal rate of 10°C/min. The samples were again heated at the same rate up to 180°C. The thermogravimetric analysis (TGA) measurements were conducted with a Dupont 2100 system in platinum pans at prescribed heating rates of 10°C/min in a range of ambient temperature to 450°C under a steady flow of nitrogen (5mL/min).

Results and discussion

Synthesis of P(LA-b-PDO)

In this work, L-lactic acid and PDO were chosen to produce the P(LA-b-PDO) copolymers. Considering the two monomers have different structure and characters, two steps were conducted with different polymerization method. Firstly, PLA was synthesized from L-lactic acid by condensation polymerization. In this work, three types of PLA prepolymers were synthesized, with molecular weight of 2.14×10^4 g/mol, 6.93×10^4 g/mol, and 8.41×10^4 g/mol, respectively. The resulting PLA were then used as macroinitiators in the ring opening polymerization of PDO catalyzed by $SnOct_2$. The reaction condition and the relevant data of P(LA-b-PDO) copolymers prepared by this approach were listed in Table 1. Unfortunately, we were not able to obtain GPC traces of the copolymers in view of their poor solubility in the solvents such as THF which commonly employed to perform GPC at ambient temperatures. Only the intrinsic viscosities [η] of the resulting copolymers were measured for a relative comparation.

As a block copolymer, not only the molecular weight but also the content of each segment plays very important roles in determining the properties of material. Taking this into account, two series of copolymers were designed, one is the copolymers with same PLA segment length but different block content, the other is the copolymers

Table 1. Results of the copolymerization

Sample	$^a M_{\eta(PLA)} \times 10^{-4}$ (g/mol)	$f_{PLA}{}^b$ (%)	$F_{PLA}{}^c$ (%)	$[\eta]^d$ (dL/g)
S1	2.14	13.60	12.93	0.74
S2	2.14	26.15	23.24	0.61
S3	2.14	37.78	34.54	0.45
S4	2.14	48.57	41.23	0.39
S5	6.93	13.60	12.64	0.82
S6	6.93	26.15	/	0.69
S7	6.93	37.78	/	0.60
S8	6.93	48.57	/	0.56
S9	8.41	13.60	12.18	0.97
S10	8.41	26.15	/	0.79
S11	8.41	37.78	/	0.69
S12	8.41	48.57	/	0.61

[a] Viscosity-average molecular weight of PLA prepolymers obtained at 37°C (tetrahydrofuran THF) using $[\eta]=KM^{\alpha}$ ($K=1.04\times10^{-4}$ cm^3g^{-1},$\alpha=0.75$) as Mark-Houwink parameters.
[b] Molar fraction of PLA in feed
[c] Molar fraction of PLA in copolymers calculated from ^{1}H-NMR
[d] Intrinsic viscosities of the resulting copolymers which were measured in phenol/1,1,2,2-tetrachloroethane (1/1 v/v) at 25°C.

with the same block content but different molecular weight. In the first series, the PLA prepolymers with the same molecular weight and different PLA/PDO feed ratio were tested. From Table 1, we found that the contents of each segment correspond with the feed ratio quite well while the PLA fraction was relatively low. In the case of S1, the fraction of PLA in feed is 13.60%. Exhilaratingly, the fraction of PLA segment in the resulting copolymer was calculated as 12.93%, which was very close to theoretical value. With the increasing of PLA fraction in feed, the reaction system became more viscous, and the initiating efficiency of PLA reduced. As a result, the fraction of PLA in copolymers has been found a little lower than what was in the feed. When PLA fraction exceeded 60%, it was difficult to induce the ring-opening polymerization of p-dioxanone, and no copolymer was obtained. Beacuse PLA acted as macroinitiator in the copolymerization, the monomer/initiator (mol/mol) ratio decreased with the increasing of the PLA/PDO feed ratio while the PLA prepolymers with same molecular weight were employed. Undoubtedly, the molecular weight of copolymers should decrease. In the scond series, the copolymerization with the same PLA/PDO feed ratio but different molecular weight PLA prepolymers were performed. The PLA/PDO feed ratio of S1, S5 and S9 all were keeped at 13.60%, but the molecular weight of PLA macroinitiators were 2.14×10^4 g/mol, 6.93×10^4 g/mol, and 8.41×10^4 g/mol, respectively. While the same content of PLA were added, the monomer/initiator (mol/mol) ratio increased with the increasing of its molecular weight, therefore, the molecular weight of resulting copolymer also increased. As a result, S9 has the highest molecular weight in this series. In conclusion, the copolymerization of PPDO and PLA has good controllability when feed fraction of PLA was lower than 50%, and the molecular designing of copolymers can be easily accomplished by this approach.

In order to identify P(LA-b-PDO) copolymer, the ^{1}H-NMR spectra of purified samples were recorded. Figure 1 illustrated a typical ^{1}H-NMR spectra of S4. The

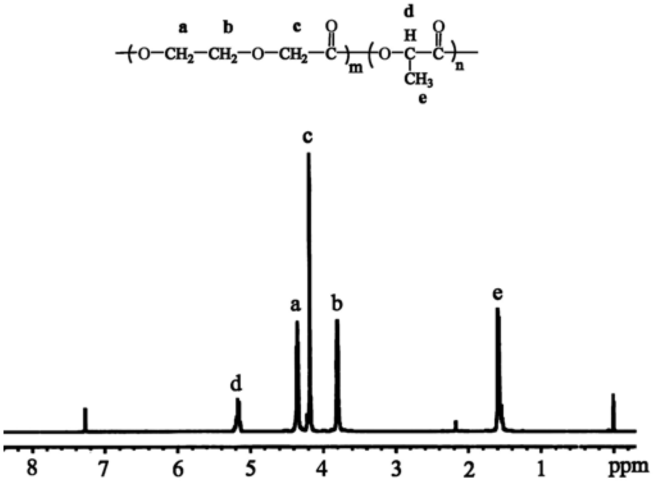


Fig 1. The ^{1}H-NMR spectra of S4

existence of PLA segments can be identified by the chemical shifts at 1.53-1.59 (δH^e) and 5.14-5.19 (δH^d) ppm, which were attributed to the resonances of $-CH_3$ and $-CH$ of PLA, respectively. The partly overlapped peaks observed at 3.79-3.81 (δH^b), 4.18-4.22 (δH^c), 4.34-4.38 (δH^a) ppm are attributed to $-CH_2-$ of PPDO chains. It demonstrated that the copolymers really are composed by PLA and PPDO segments.

The thermal properties and crystalline behavior of copolymers

A series of P(LA-b-PDO) copolymers with the same PLA segment length were analyzed by DSC. All curves are shown in Figure 2, and the relevant detailed data were listed in Table 2. Since the copolymerization disturbs the regularity of the polymer chains, the crystalline behavior somehow has been changed. The content of each segment has also been considered as a key factor which dominate the properties of material. In the case of S1, the content of PLA segments is about 12.93% with PLA chains still forming crystal domains although the heat of fusion is very small. Otherwise, the remainder PPDO chains in the copolymers exhibited crystalline

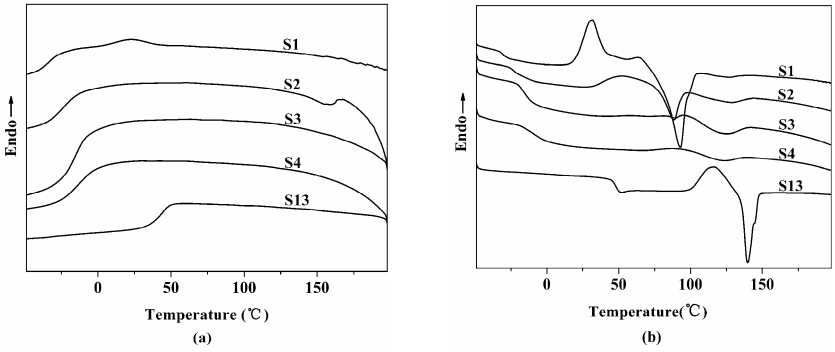


Fig 2. DSC cooling scans (a) and subsequent heating scans (b) of copolymers

behavior similar to that of PPDO homopolymers. When the content of PLA segments in copolymers increased, the PLA chains can fold easier, but the crystallinity of PPDO chains drop down dramatically due to the regularity of chains reduced. For S4, the content of PLA segments rise to 41.23%, no crystal domain of PPDO chains could be found, and the sample is almost transparent.

Table 2. Results from DSC heating scans of copolymers and PLA homopolymer

Sample	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_m' (°C)	$\Delta H_m'$ (J/g)
S1	-30.31	31.04	25.27	92.97	51.81	125.31	1.451
S2	-23.14	50.93	8.082	88.05	10.69	125.37	5.007
S3	-16.39	/	/	89.78	0.2729	119.25	6.032
S4	-8.81	/	/	/	/	119.08	4.858
S13[a]	48.23	116.77	23.56	/	/	139.84	22.19

[a] PLA homopolymer with viscosity-average molecular weight of 2.14×10^4 g/mol

As showed in the Table 2, the glass transition temperature (T_g) of copolymers ranged from -30.31°C to -8.81°C between the T_g of each homopolymer and increased with the content of PLA segments. This information shown that no obvious phase-separation occurred for all copolymer samples.

The WAXD patterns of copolymers and PLA homopolymer are shown in Fig 3. All the copolymers exhibit 2θ peaks of about 22°, 24° and 29° characteristic of PPDO homopolymer. This suggests the PPDO segments retain their crystal structures, only the crystallinity decreased while the content of PLA segments rose. Since the crystallinity of PLA segments was very low, and that only the main diffraction peak (at about 16.6°) of PLA segments was detected in the copolymers, and the other weak peaks (at 14.8°, 19.1°, 22.4°), which were observed for PLA homopolymers, were not found.

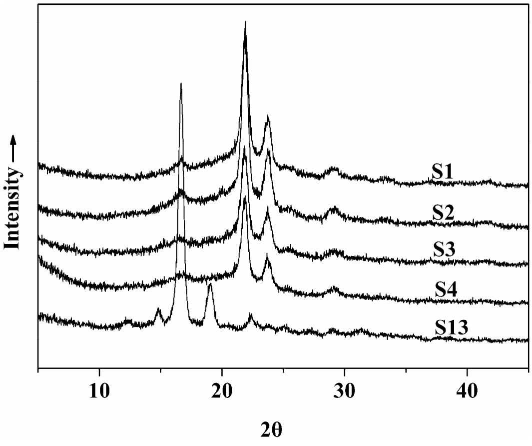


Fig 3. The WAXD curves of copolymers and PLA prepolymer

Thermal stability of copolymers

The TGA curves of the copolymers with similar composition but distinct intrinsic viscosities are shown in Fig 4, and the relevant data were enumerated in Table 3. The test results revealed that the increase of molecular weight is helpful to enhance the thermal stability of the copolymers with the same composition. The values of $T_{5\%}$, T_{max} and $T_{95\%}$ all increased to some extent with the increase of molecular weight.

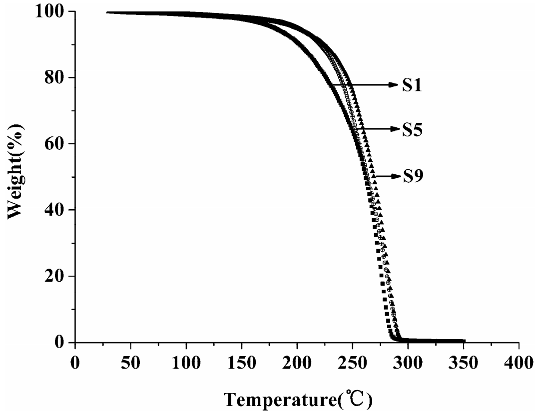


Fig 4. TG curves of copolymers with similar composition

Table 3. Relevant data of copolymers with similar compose from TG curves

Sample	$T_{5\%}{}^{a}$(°C)	$T_{max}{}^{b}$ (°C)	$T_{95\%}{}^{c}$ (°C)
S1	180	275	283
S5	199	281	289
S9	201	282	290

[a] Weight loss was 5%

[b] Temperature corresponding to the maximum rate of weight loss

[c] Weight loss was 95%

Conclusions

A series of P(LA-b-PDO) diblock copolymers with different segment content or different PLA chain length were synthesized via the ring opening polymerization of PDO initiated by PLA macroinitiators in the presence of $SnOct_2$. ^{1}H-NMR showed that the content of each block was correspond to the feed ratio quite well, and the molecular weight, as well as the molecular structure, of copolymers can be modulated by varying the original molecular weight of PLA prepolymers or the PLA/PDO feed ratio. The crystalline behaviors of P(LA-b-PDO) copolymers have been described by DSC and WAXD. Obviously, copolymerization disturbs the regularity of the polymer chains to some extent, and it influences the crystallization rate and crystallinity of each block especially the PPDO segment. The content of PLA segment was also an important factor, effecting the properties of copolymers. TGA curves showed that the thermal stability can be improved by increasing the molecular weight of P(LA-b-PDO) copolymers.

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