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, ,
(, 200237)

: 、 ,
L- (PLLA) *D*- (PDLA), (M_w)
。 (NMR)、 (GPC)、
(DSC) X (XRD) 、 、 。
, 。
, 。 PLLA PDLA $M_w\approx5\times10^4$, , 1.83×10^5。 , $M_w\approx5\times10^4$
。

: ; ; ;
:TQ316 :A

Effect of Prepolymer Molecular Weight on Structure and Properties of Products Prepared by Solid State Polycondensation of Stereocomplex Polylactide

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Abstract: Prepolymer *L*-polylactide and *D*-polylactide with reactivity for condensation polymerization and different molecular weights were prepared by using lactide as monomer, lactic acid and stannous octoate as initiator and catalyst respectively. A series of stereoblock polylactides were synthesized via solid state polycondensation using precursors obtained by melting blend of *L*-polylactide (PLLA) and *D*-polylactide (PDLA) with similar weight-average molecular weights. The chain structure, molecular weight, thermal properties and crystal structure of products acquired were characterized by H-NMR, GPC, DSC and XRD, respectively. The results show that the products have stereoblock structure. The molecular weight of the prepolymers will affect the relative content of homochiral crystal and stereocomplex crystal in the precursor, and thus affect the structure of the solid-phase polycondensation product. When the average molecular weight of PLLA and PDLA are both about 5×10^4, the molecular weight of the product increases rapidly and reaches 1.83×10^5, and which is beneficial to the improvement of crystallinity of the stereocomplex crystal in the final product.

Key words: solid state polycodensation; molecular weight of prepolymer; stereoblock poly(lactic acid); stereocomplex poly(lactic acid)

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L- (PLLA) *D*- (PDLA)
(SC-PLA),SC-PLA
,
50 ℃[1-2], ,SC-PLA
、
。SC-PLA (SC)
PLLA、PDLA (
10^5)[3], ,SC
。
($M_w>10^5$)
。
(SSP)
[4], PLLA PDLA
[5-6]。
[7-10] PLLA PDLA
、 ,
、
。 ,
。Tomonari [11]
,
。 PLLA
PDLA ,
, 、 、
。

1

1.1

L-、*D*- : 90%,
99.8%, ;*L*- 、
D- : 99.8 %,
; 、 、 (TSA):
, 。

1.2

1.2.1 *L*- *D*-
- ,
8 000∶1,
L-、*D*- 。 450
Pa, 2 h, 。 170
℃ 4.5 h, PLLA
PDLA。
1.2.2 PLLA
PDLA 3 ,
,
1∶1。 450
Pa,60 ℃ 2 h,110 ℃ 2 h
, 190 ℃, 30 min。
, , PLLA
PDLA。 PLLA、PDLA
, PLLA、PDLA
8∶2 ,
MBPLA*x* (*x* 1、2、3,
M_w 2×10^4、5×10^4、7×10^4)。
1.2.3 MBPLA,
(
), , , 450
Pa,105 ℃ 2 h, , ,
, 150 ℃
, ,
(SBPLA),
SBPLA*x*-*t*(*x* 1、2、3,
M_w 2×10^4、5×10^4、7×10^4;*t*
, h)。

1.3

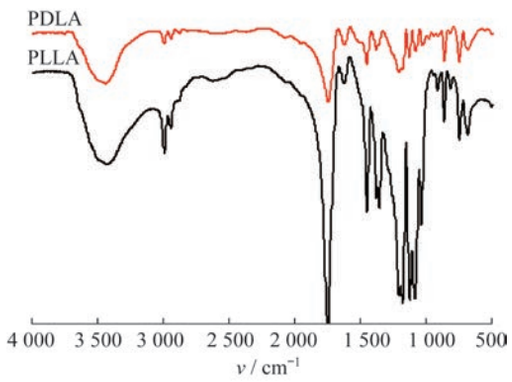
1.3.1
, , 25 ℃
。
1.3.2 Waters 1515
,
, , 1.0 mL/min。
1.3.3 Bruker
Advance III ,
(
10%) 。
1.3.4 :
DSC200 F3 ,
20 mL/min , 10 ℃/min
。 Rigaku SA-HF3 X
, 5°～40°,
4°/min。

2

2.1 (FT-IR)

,
, ,
, 1 。

1 756 cm^{-1} C═O □3 440 cm^{-1} □2 996 cm^{-1} 2 945 cm^{-1} C—H □ 1 180 cm^{-1} C—O—C □ PLLA PDLA□



1 PLLA PDLA

Fig. 1 FT-IR spectra of prepolymer PLLA and PDLA

2.2 PLLA PDLA

□2□ □ □M_w□ 3 PLLA 3 PDLA □ PLLA PDLA 1□ 1 □ □ □ □PDI□ □□η□□ □

1 PLLA PDLA

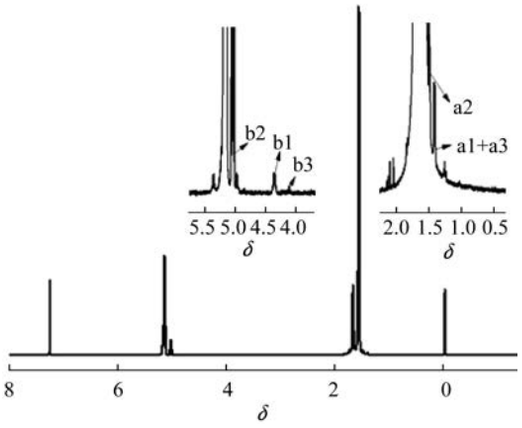
Table 1 Molecular weight and intrinsic viscosity of prepolymer PLLA and PDLA

Prepolymer	w□Lactic acid□□%	M_n	M_w	PDI	□η□
PDLA	0.28	1.75×10^4	1.90×10^4	1.09	0.42
PLLA	0.28	2.16×10^4	2.63×10^4	1.22	0.54
PDLA	0.10	4.22×10^4	5.35×10^4	1.28	0.75
PLLA	0.10	3.50×10^4	4.99×10^4	1.42	0.64
PDLA	0.07	4.94×10^4	6.84×10^4	1.38	0.83
PLLA	0.07	4.59×10^4	7.52×10^4	1.64	0.86

2.3 (¹H-NMR)

2 *L*- *L*- PLLA ^{1}H-NMR □ PDLA PLLA ^{1}H-NMR □ PLLA □□ δ=1.57 □a2 □ δ=5.13 □b2 □ □δ=1.49 □a1 □ δ=4.37 □b1 □ □δ=1.49 □a3 □ δ=4.12 □b3 □ □

□ □



2 PLLA

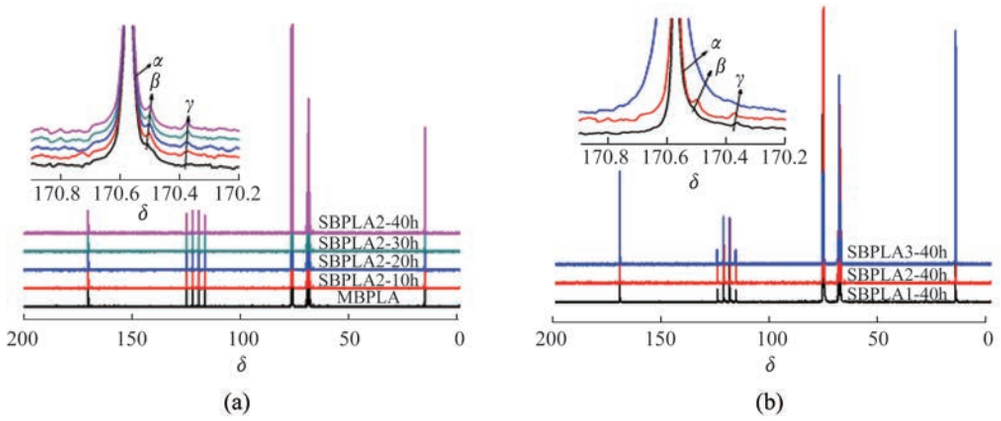
Fig. 2 ^{1}H-NMR spectrum of prepolymer PLLA

2.4 (¹³C-NMR)

3 □ α PLLA PDLA □ MBPLA□SBPLA ^{13}C-NMR β γ □ □□□ 3□a□ MBPLA β □ □ 3□b□ □M_w≈5×10^4□ 40 h□ □SBPLA2-40h□ β γ □ □ SBPLA1-40h SBPLA2-40h□ □M_w≈7×10^4□ □SBPLA3-40h□ □α □ □ β γ □ □ □

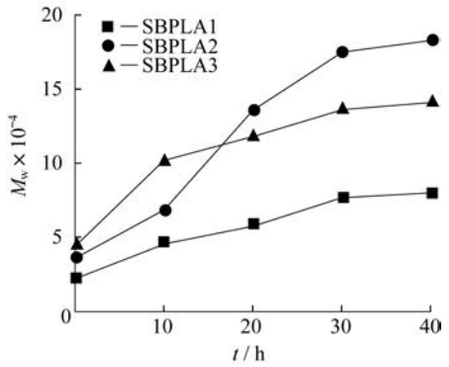
2.5

4 □ □3 □ 30 h □ □ □ M_w≈5×10^4 SBPLA2 □ 10 h □□ □ M_w □ 1.83×10^5□



3

Fig. 3 ^{13}C-NMR spectra of the carbonyl region of SSP products



4

Fig. 4 Molecular weight-time curves of SSP products

PLLA PDLA

MBPLA

,

,

。 MBPLA1

,

, ,

SBPLA1-40h ;MBPLA3

,

SBPLA3-40h SBPLA1-40h

;MBPLA2

,

SBPLA2-40h 。

2.6

5 DSC ,

,

2 。 5(a) $M_w \approx 5\times10^4$

DSC , 160 ～ 180 ℃ (PLLA

PDLA) ,

。

210～225 ℃

(PLLA PDLA

) , ,

。

6 XRD ,

2θ 11.9°、20.7° 23.9°

(110)、(300)/(030) (220)

, ,

PLLA PDLA

。 2θ 14.8°、16.6°、19.0°

22.2° (010)、

(110)/(200)、(111)/(201) (102)/(210)

, α ,

PLLA PDLA [13]。

5 DSC (1)

(X_{s_1}), MDI

Jade 6 XRD ,

(2) (X_{s_2}), 2

。

$$X_{s_1} = \frac{\Delta H_{m_s}}{\Delta H_{m_0}} \times 100\% \quad (1)$$

$$X_{s_2} = \frac{A_s}{A_s + A_h + A_a} \times 100\% \quad (2)$$

(1) :ΔH_{m_s} ,

J/g;ΔH_{m_0} , 142

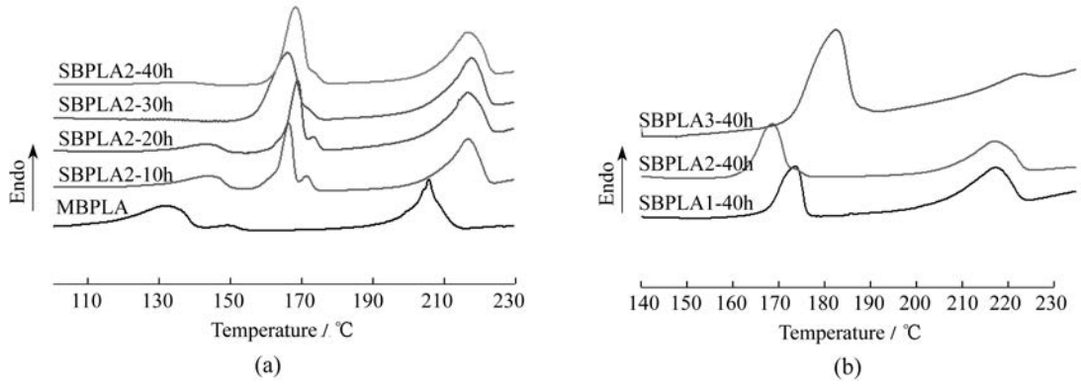
J/g[14]。 (2) :A_s

;A_h ;A_a

。

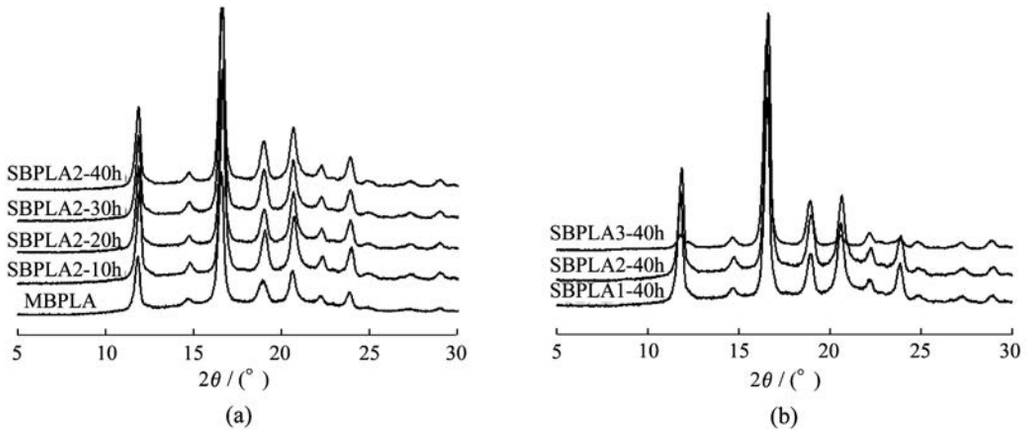
5(b) 6(b) 2 ,

SBPLA1-40h SBPLA2-40h



5 DSC

Fig. 5 DSC curves of SSP products



6 XRD

Fig. 6 XRD spectra of SSP products

2

Table 2 Melting point and enthalpy of different SSP products

Samples	T_{m_h} a) /℃	ΔH_{m_h} a) /(J·g^{-1})	T_{m_s} b) /℃	ΔH_{m_s} b) /(J·g^{-1})	X_{s_1} c) / %	X_{s_2} d) / %
MBPLA1	151.77	19.87	215.35	28.11	19.85	29.90
MBPLA2	135.85	13.34	206.92	18.17	12.80	22.49
MBPLA3	173.76	46.21	226.01	3.97	2.80	9.63
SBPLA1-40h	173.58	29.58	217.47	39.45	27.78	33.70
SBPLA2-40h	169.06	29.31	219.69	38.27	26.95	37.30
SBPLA3-40h	182.43	77.31	222.49	6.94	4.89	12.73

a) Melt point and enthalpy of homochiral crystal; b) Melt point and enthalpy of stereocomplex crystal; c) Crystallinity of stereocomplex crystal obtained from DSC curves; d) Crystallinity of stereocomplex crystal obtained from XRD spectrum

, (2) SBPLA3-40 h
SBPLA2-40h ,
SBPLA1-40h, 37.30%。 、 。
, $M_w \approx 5\times10^4$ PLLA PDLA
,
, 110.55% 65.85%。

,
, ,
;
,
, ,
PLLA PDLA
, 。

3

,
。
。 ,
PLLA PDLA $M_w \approx 5\times10^4$
,
,
, 1.83×10^5;
26.95% (XRD 37.30%);
, 110.55% (XRD 65.85%)。 ,
$M_w \approx 5\times10^4$
。

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[1] , , . [J]. ,2015,31(5):185-189.

[2] HIDETO T. Poly (lactide) stereocomplexes: Formation, structure, properties, degradation, and applications [J]. Macromolecular Bioscience,2005,5(7):569-597.

[3] PAN P J, HAN L L, BAO J N, *et al*. Competitive stereocomplexation, homocrystallization, and polymorphic crystalline transition in poly(*L*-lactic acid)/poly(*D*-lactic acid) racemic blends: molecular weight effects[J]. Physical Chemistry,2015,119(21):6462-6470.

[4] VOUYIOUKA S N,KARAKATSANI E K,PAPASPYRIDESC D. Solid state polymerization [J]. Progress in Polymer Science,2005,30(1):10-37.

[5] FUKUSHIMA K,KIMURA Y. A novel synthetic approach to stereo-block poly (lactic acid) [J]. Macromolecular Symposium,2005,224(3):140-142.

[6] FUKUSHIMA K, CHANG Y H, KIMURA Y. Enhanced stereocomplex formation of poly(*L*-lactic acid) and poly(*D*-lactic acid) in the presence of stereoblock poly(lactic acid) [J]. Macromolecular Bioscience,2007,7(6):829-835.

[7] FUKUSHIMA K, KIMURA Y. An efficient solid-state polycondensation method for synthesizing stereocomplexed poly (lactic acid)s with high molecular weight[J]. Journal of Polymer Science: Part A. Polymer Chemistry,2008,46(11): 3714-3722.

[8] FUKUSHIMA K, KIMURA Y. Stereoblock poly (lactic acid): Synthesis via solid-state polycondensation of a stereocomplexed mixture of poly(*L*-lactic acid) and poly(*D*-lactic acid) [J]. Macromolecular Bioscience, 2005, 5 (1): 21-29.

[9] RAHAMAN M H,TSUJI H. Synthesis and characterization of stereo multi-block poly (lactic acid)s with different block lengths by melt polycondensation of poly(*L*-lactic acid)/poly (*D*-lactic acid) blends [J]. Macromolecular Reaction Engineering,2012,6(11):446-457.

[10] NOBUHIKO Y, PIETER J D, JAN F. Stereo block copolymers of *L*-and *D*-lactides [J]. Macromolecular Chemistry,1990,191(3):481-488.

[11] TOMONARI K, HIDEKO T, OYAMA S U. Effects of molecular weight and catalyst on stereoblock formation via solid state polycondensation of poly (lactic acid) [J]. European Polymer Journal,2014,54:62-70.

[12] HIDETO T,TAKESHI W,YUZURU S,*et al*. Stereocomplex crystallization and spherulite growth behavior of poly(*L*-lactide)-b-poly (*D*-lactide) stereodiblock copolymers [J]. Polymer,2010,51(21):4937-4947.

[13] SHAO J, SHENG X, BIAN X C. Remarkable melting behavior of PLA stereocomplex in linear PLLA/PDLA blends [J]. Industrial and Engineering Chemistry Research, 2015, 54:2246-2253.

[14] FUKUSHIMA K,HIRATA M,KIMURA Y. Synthesis and characterization of stereoblock poly (lactic acid)s with nonequivalent *D*/*L* sequence ratios [J]. Macromolecules, 2007,40(9):3049-3055.