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Microwave-assisted Polycondensation of L-2-Hydroxy-3-phenylpropanoic Acid

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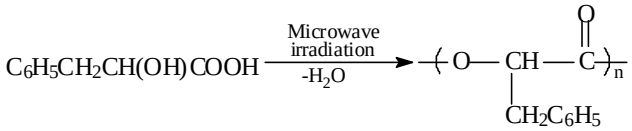
Abstract: Amorphous poly (L-2-hydroxy-3-phenylpropanoic acid) (PLHPPA) was synthesized by the microwave-assisted polycondensation of L-2-hydroxy-3-phenylpropanoic acid (LHPPA). The weight average molar mass (Mw) of PLHPPA ranged from 3600 to 5300 and polydispersity index (Mw/Mn) from 1.0 to 1.4 when the reaction mixture was irradiated by microwave at 255, 340 and 510 w for 1 to 10 h, respectively.

Keywords: Poly (L-2-hydroxy-3-phenylpropanoic acid), microwave-assisted polycondensation.

The attempts to prepare novel biodegradable polymer carriers for drug controlled release systems have been tried in our group[1,2]. Poly (L-2-hydroxy-3-phenylpropanoic acid) (PLHPPA) can be considered as derivative of poly (lactic acid) (PLA) which has been applied as biomaterials in drug delivery systems, surgical repair and tissue engineering materials[3] for its excellent biodegradability and biocompatibility. PLHPPA contains phenyl groups in its structure. It is designed as a hydrophobic carrier of drug controlled release systems. Microwave-assisted polycondensation of LHPPA was tried for synthesis of PLHPPA and compared with the conventional methods. The reaction is shown as follows.



Experimental

0.1g of LHPPA was placed in a glass tube and polycondensized in a domestic microwave oven (2450 MHz, 850 w) at pointed power level for appropriate time. After cooling to room temperature, the reaction mixture was dissolved in CH_2Cl_2 and precipitated by ethanol. PLHPPA was collected by centrifugation and dried under reduced pressure.

Results and Discussion

LHPPA was synthesized according to literature[4]. The structure of PLHPPA was characterized by ^{1}HNMR, Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Specific Rotation. ^{1}HNMR ($CDCl_3$, δ ppm): 3.00 (m,

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2H, CH_2), 5.60 (m, 1H, CH), 7.25 (m, 5H, C_6H_5). $[\alpha]_D^{25} = -19.5$ (c=1, CH_2Cl_2). The reaction conditions and data are listed in **Table 1**.

Table 1 Results by polycondensation of L-2-hydroxy-3-phenylpropanoic acid

Method	Power (w)	Time (h)	Yield (%)	Mw	Mw/Mn	Tm (°C)
Microwave-assisted polycondensation	255	6	10	3900	1.2	Nd*
	255	10	13	3700	1.3	Nd
	340	1	10	3800	1.3	Nd
	340	2	20	3600	1.4	Nd
	510	0.5	9	1800	1.8	Nd
	510	1.5	22	3900	1.0	Nd
	510	2.5	20	5300	1.4	Nd
Solution polycondensation		96	36	5409	1.6	Nd
Melting polycondensation		30	38	8308	1.4	49.3

*: Not determined.

The microwave-assisted polycondensation of LHPPA was carried out at 255, 340, 510, 595 and 680 w for 0.5, 1, 1.5, 2, 2.5, 6 and 10 h, respectively. The polymerization of LHPPA was found to take place in all the cases. The Mw of PLHPPA ranged from 3600 to 5300 and Mw/Mn from 1.0 to 1.4 when the time of microwave irradiation was from 1 to 10 h. The low molecular weight (Mw 1800) PLHPPA was formed at 510 w for 0.5 h. When the microwave power was higher than 595 w, an obvious decomposition of reaction mixture occurred. In the following conditions: 340 w, 2 h; 510 w, 1.5 h and 510 w, 2.5 h, PLHPPA was obtained in a yield of twenty percent, but at lower microwave power (255 w), the yield of PLHPPA was only around ten percent. The Mw of PLHPPA from the polycondensation at 510 w for 2.5 h was 5300, which is about 30% higher than that for 1.5 h and two times higher than that for 0.5 h.

The solution polycondensation of LHPPA was carried out with DCC/DMAP mixture as catalyst[5] and the conditions of melting polycondensation was at 0.35 KPa and 190°C. Both methods took much longer time (96 h and 30 h, respectively) than the microwave-assisted polycondensation (2.5 h at 510 w).

No melting peak was found in the DSC thermogram of PLHPPA prepared by microwave-assisted polycondensation, which means the product was amorphous. The degradation product of PLHPPA is LHPPA, which is one of the metabolites of phenylalanine in human body[6]. So, the amorphous PLHPPA can be as potential material for drug controlled release.

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