

Note

SINGLE LANTHANUM TRIS(*N*-PHENYLETHYL-3,5-DI-*t*-BUTYLSALICYLALDIMINATO)S INITIATOR FOR RING-OPENING POLYMERIZATION OF 1,4-DIOXAN-2-ONE IN BULK*

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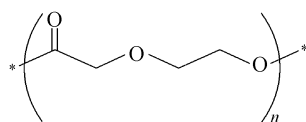
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Abstract A rare earth Schiff base complex: lanthanum tris(*N*-phenylethyl-3,5-di-*t*-butylsalicylaldiminato)s [La(OPEBS)₃] was successfully applied as single component initiator for the ring-opening polymerization of 1,4-dioxan-2-one (PDO) in bulk. The influence of reaction conditions, such as polymerization temperature, the molar ratio of the monomer to initiator (M/I) on the monomer conversion and molecular weight of the polymer has been investigated. Poly(1,4-dioxan-2-one) with a viscosity-average molecular weight (M_v) of 8.29×10^4 and yield of 91.5% was prepared.

Keyword: 1,4-Dioxan-2-one; Ring-opening polymerization; Lanthanum tris(*N*-phenylethyl-3,5-di-*t*-butylsalicylaldiminato)s.

INTRODUCTION

Aliphatic polyesters, as new functional polymer materials with outstanding biodegradability, bioabsorbability and biocompatibility, have attracted great interest from researchers in recent years^[1–6]. Poly(1,4-dioxan-2-one) (PPDO) (Scheme 1) as a well-known biodegradable aliphatic polyester has its own special characters^[7]. PPDO has attracted much attention as biomaterials for medical purposes such as surgical devices^[8]. PPDO can be obtained by the ring-opening polymerization of 1,4-dioxan-2-one (PDO) using lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) initiator^[9]. Schiff bases and their metal complexes have been synthesized and characterized because Schiff bases are able to stabilize different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Aluminum Schiff base complexes were reported to be efficient in initiating the polymerization of lactide^[10]. Rare earth Schiff base complexes are easy to be synthesized and handled with and have been used as a single component initiator for the ring-opening polymerization of ϵ -caprolactone^[11], and as a main initiator for the polymerization of styrene^[12]. In this paper, lanthanum Schiff base complex La(OPEBS)₃ (Scheme 2) is first reported for the polymerization of PDO.

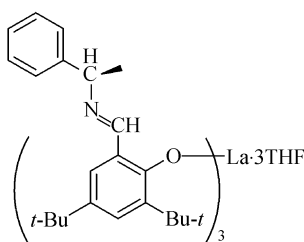


Scheme 1 Structure of PPDO

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Scheme 2 Structure of $\text{La}(\text{OPEBS})_3$

EXPERIMENTAL

1,4-Dioxan-2-one (PDO) was provided by Jinan Daigang Biotech. Co. Ltd. (Shandong, China). It was distilled twice under reduced pressure before use. $\text{La}(\text{OPEBS})_3$ was synthesized according to literature and dissolved in dry toluene^[11]. Other chemicals were used as received.

Polymerization was carried out in ampoules that were heated, evacuated and filled with argon several times before use. Monomer and initiator solution were introduced in order. The polymerization was stopped after a predetermined time. The polymer was dissolved in 1,1,2,2-tetrachloroethane and precipitated from diethyl ether/ligroin mixture (4:1 volume ratio), and dried to constant weight under vacuum at room temperature.

MEASUREMENTS

The intrinsic viscosity measurements were performed in a phenol/1,1,2,2-tetrachloroethane (2:3 W/W) solution at 25°C using an Ubbelohde viscosimeter. The viscosity average molecular weight of the polymer was calculated by the following equation^[13]: $[\eta] = 79 \times 10^{-3} M_v^{0.63}$.

¹H-NMR spectra of polymers were recorded on a Bruker AR-500 NMR spectrometer in CDCl_3 at room temperature.

RESULTS AND DISCUSSION

The influence of polymerization temperature on viscosity-average molecular weight of PPDO and the monomer conversion is listed in Table 1. The results show that the viscosity-average molecular weight of PPDO decreases while the monomer conversion varies a little with increasing temperature. The higher polymerization temperature probably results in transesterification and the back-biting reaction.

Table 1. Effect of polymerization temperature on PDO bulk polymerization

Entry	Temperature (°C)	Conversion (%)	$M_v \times 10^{-4}$
1	40	91.5	5.99
2	60	91.7	4.84
3	80	97.1	2.64
4	100	87.7	1.86

Conditions: $[\text{PDO}]/[\text{La}(\text{OPEBS})_3] = 200$; Polymerization time: 24 h

The effect of M/I molar ratio on viscosity-average molecular weight of PPDO and the monomer conversion is shown in Fig. 1. It is found that the viscosity-average molecular weight of PPDO increases at first with increasing the M/I molar ratio, then decreases, while the conversion of monomer decreases with the increase of M/I molar ratio. PPDO with a viscosity-average molecular weight of 8.29×10^4 can be obtained when M/I molar ratio is 600 with the reaction temperature of 40°C and the reaction time of 24 h. Both conversion and average-viscosity molecular weight of PPDO decreased while M/I molar ratio reached 800. The result showed that the higher the M/I molar ratio was, the less the number of active centers was. The trend also can be seen at 80°C (Fig. 2).

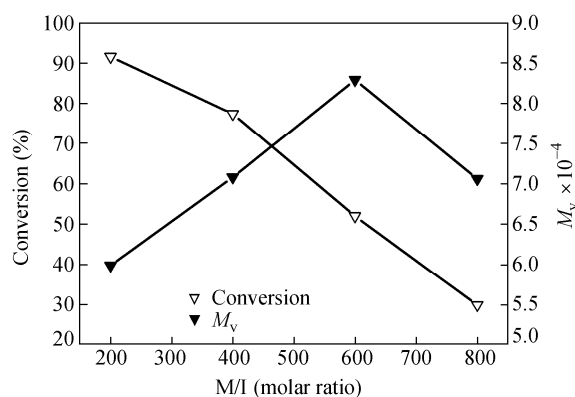


Fig. 1 The influence of $[\text{PDO}]/[\text{La}(\text{OPEBS})_3]$ molar ratio on PDO bulk polymerization 40°C; Polymerization time: 24 h

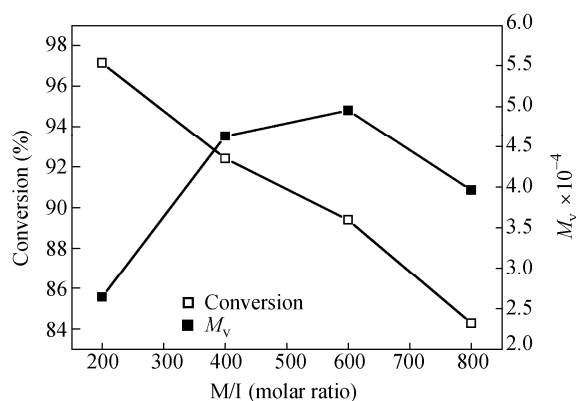


Fig. 2 The influence of $[\text{PDO}]/[\text{La}(\text{OPEBS})_3]$ molar ratio on PDO bulk polymerization 80°C; Polymerization time: 24 h

It was observed that signals of different kinds of hydrogen in PPDO appeared at $\delta = 4.0, 4.45, 4.62$, respectively, in the ^1H -NMR spectrum of PPDO which is in agreement with literature^[14].

CONCLUSIONS

Lanthanum tris(*N*-phenylethyl-3,5-di-*t*-butylsalicylaldiminato)s $[\text{La}(\text{OPEBS})_3]$ was used as a single component initiator for the ring-opening polymerization of 1,4-dioxan-2-one (PDO). PPDO with high monomer conversion and relatively high viscosity-average molecular weight can be prepared under mild reaction conditions.

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