

AlEt₃-H₂O-H₃PO₄ catalyzed polymerizations of 1, 4-dioxan-2-one

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Summary

A new catalytic system, AlEt₃-H₂O-H₃PO₄(C), was successfully used as a catalyst for synthesizing poly (1,4-dioxan-2-one) (PPDO) in bulk via the ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDO). The effects of the molar ratio of monomer to catalyst (M/C), the polymerization temperature (T), the reaction time (t) and the water content of monomer PDO (W) were studied systematically. AlEt₃-H₂O-H₃PO₄ has been proved to be a very effective catalyst for ROP of PDO. High molecular weights of PPDO can be obtained under following conditions: T = 80°C, M/C = 1311-1573, t = 8-10 hours and W < 80ppm.

Introduction

Aliphatic polyesters, with outstanding biodegradability, bioabsorbability and biocompatibility, have attracted great interest of researchers in recent decades. The related papers and patents increase sharply in a very short period, and remarkable progress have been achieved in this field [1-3]. As a result, a series of polyesters and copolyesters have been synthesized successfully from the lactone monomers such as glycolide (GA)[4], lactide (LA)[5-7], and E-caprolactone (CL) [8, 9], and dioxanone monomers such as 1,4-dioxan-2-one (PDO) [10-12], 1,5-dioxan-2-one (DXO) [13], and 1,3-dioxan-2-one (TMC) [14], *etc.*

Compared with other aliphatic polyesters, poly (1,4-dioxan-2-one) (PPDO) has its own special character, except for its ultimate biodegradability due to the existence of ester bonds in polymer chains. The unique ether bonds endue it with good flexibility, therefore, PPDO is a good candidate not only for medical use, but also for general uses, such as films, molded products laminates, foams, nonwoven materials, adhesive and coatings [15]. Because of the growing significance of PPDO in practice, various catalysts or initiators for ROP of PDO have been developed in the recent decades [16-19]. However, most of them are centered on heavy metals such as Ti, Zr, Sn, Pd, La, Yb, and Hg, which are not acceptable as “by products” when a pharmaceutical or medical application of PPDO is taking into account. Thereafter, the catalysts including Tin octoate [16], Aluminum isopropoxide [16], Zinc (II) L-lactate [17], enzymes [18] have been used most frequently in ROP of PDO, even though the long reaction time and the quite low conversion of monomer make them be less effective catalysts.

However, Cherdron *et al.* [20-22] have found that $\text{AlEt}_3/\text{H}_2\text{O}$ system is a very efficient catalyst for the ROP of lactones. Deng *et al.* [23,24] successfully synthesized PLA and a series of copolymers by using a complex catalyst of triisobutyl aluminum together with phosphoric acid and water, and found that it exhibited high activity. In this paper, the $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ catalyst system has been used to catalyze ROP of PDO for the first time, and proved to be a highly efficient catalyst containing no heavy metal for the synthesis of PPDO.

Experimental section

Materials

1,4-Dioxan-2-one was provided by the Pilot Plant of Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), and it was twice distilled in vacuum immediately before use. The water content in PDO was measured using 831 KF Coulometer (Metrohm Ltd., Switzerland).

Triethyl-aluminum (AlEt_3) was provided by Nanjing Tonglian Chemical Corporation, and it was dissolved in anhydrous toluene in a concentration of 6.4%. Phosphoric acid, Calcium hydride, Sodium (Na), Benzophenone, 1,1,2,2-tetrachloroethane, Phenol, Toluence, and 1,4-dioxane (DOX), which all were of A. R. grade, were purchased from Chengdu Kelong Reagent Corporation.

Preparation of catalyst and polymerization

All procedures were carried out in an atmosphere of highly purified nitrogen. Water and H_3PO_4 at a certain molar ratio of $\text{Al}/\text{H}_2\text{O}/\text{H}_3\text{PO}_4/\text{DOX}$ were added dropwise to a solution of AlEt_3 in toluence at -70°C . After the evolution of alkane gas had ceased, the solution was heated at 60°C for 2h, and the resulting reaction mixture was a colorless and transparent solution.

ROP of PDO was performed in bulk with magnetic stirring in oven-dried and silanized 10ml vials. PDO (3.6g, 35mmol) was charged into each vial, which was sealed with a butyl rubber stopper, and $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ was injected into the vial through the butyl rubber stopper with a syringe at a certain molar ratio. The vials were then transferred to a temperature-adjusted silicone oil bath and immersed up to their caps. The precision of oil bath temperatures was controlled to $\pm 1^\circ\text{C}$, and the vials were taken away from the reaction bath at the predetermined reaction time.

The resulting polymer products were purified by extraction in boiling toluene for 48h, and were dried in vacuum to a constant weight at 50°C . The monomer conversion was determined by weighing the dried PPDO. Reproducibility of the polymerization reaction and polymer recovery method has been checked by repetitive experiments, which give monomer conversion values with relative error estimated to maximum $\pm 4\%$.

Measurements

As the conventional solvents such as chloroform, tetrahydrofuran, and toluene used in GPC measurements cannot resolve the resulting polymers with higher molecular weights, only the viscosity-average molecular weights of the resulting polymers were measured in phenol/1,1,2,2-tetrachloroethane (2:3 w/w) solution using an Ubbelohde

viscosimeter thermostated at 25°C. The molecular weights of PPDO can be calculated from the intrinsic viscosity $[\eta]$ according to Mark-Houwink equation $[\eta] = K\overline{M}_v^\alpha$, where $\alpha=0.63$ and $K=79\times 10^{-3}\text{cm}^3\text{g}^{-1}$ [10].

$^1\text{H-NMR}$ spectra were recorded in CDCl_3 on a Varian Gemini 400 MHz NMR spectrometer using TMS as internal standard.

Results and Discussion

For comparisons, the results of ROP of PDO with different catalyst systems were shown in Table 1. It was found that with addition of a small amount of water to AlEt_3 , the percent conversion of PDO and the viscosity-average molecular weights of PPDO increased largely, and that with addition of a small amount of phosphoric acid to $\text{AlEt}_3\text{-H}_2\text{O}$, the conversion and the viscosity-average molecular weights further increased. $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ was the best catalyst system of AlEt_3 , $\text{AlEt}_3\text{-H}_2\text{O}$ and $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ catalyst systems. So the present study was focused on the $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$.

Table 1. Effect of various catalyst system on the polymerization of PDO

Catalyst system	M/C (mol/mol)	Temp. (°C)	Time. (h)	Conv. (%)	$[\eta]$ (dL/g)	$M_v\times 10^{-4}$
AlEt_3	1500:1	80	10	87.2	1.20	11.2
$\text{AlEt}_3\text{-H}_2\text{O}$	1500:1	80	10	90.5	1.85	22.0
$\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$	1500:1	80	10	92.5	2.15	28.3

Polymerization conditions: $\text{AlEt}_3/\text{H}_2\text{O}=2:1$, $\text{AlEt}_3/\text{H}_2\text{O}/\text{H}_3\text{PO}_4=8/4/1$, $W<80\text{ppm}$.

In order to investigate the efficiency of the catalyst and the effect of reaction conditions on the conversion of PDO and molecular weights of resulting PPDO, a series of polymerization experiments were carried out.

The first series of polymerizations were conducted in such a way: the molar ratio of monomer/ $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ (8:4:1) (M/C) varied in a range from 983/1 to 1966/1; Furthermore the reaction temperature was fixed at 80°C, the reaction time 10h, and the water content in PDO 43ppm. It has been found that the M/C ratio is one of the most important factors influencing the polymerization of PDO. Figure 1 shows the effects of the M/C ratio on the viscosity-average molecular weights M_v and the monomer conversion of PDO. It can be seen that viscosity-average molecular weights of PPDO increase at first as the M/C ratio increases, and reach a maximum of 2.8×10^5 when the M/C ratio increases to 1573. However, the further increase of M/C ratio will induce the gradual decrease of the viscosity-average molecular weights of PPDO. When the M/C ratio increases to 1966, the viscosity-average molecular weight of PPDO is only 1.2×10^5 . On the other hand, the percent conversion of monomer gradually decreases with the increase of the M/C ratio. Generally, the less the M/C ratio, the more the active centers. As a result, the viscosity-average molecular weight of PPDO is low even though the percent of the monomeric conversion is high. However, when the M/C ratio is too high, the number of active centers is very small. In that case, the number of monomers participating in the polymerization becomes relatively small, resulting in the obvious decrease of the percent of monomeric conversion and the viscosity-average molecular weight of PPDO. An optimal M/C ratio of the ring-opening polymerization of PDO can be found to fall into the range from 1311 to 1573.

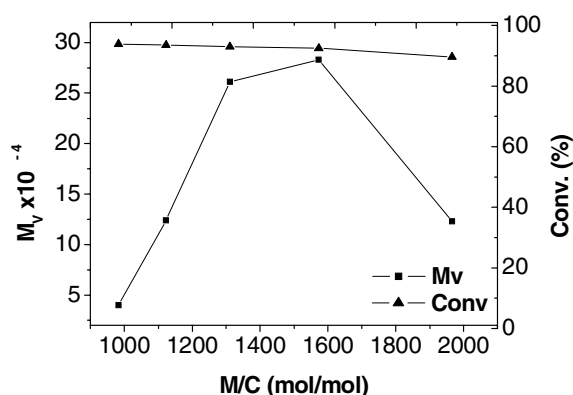


Figure 1. Effect of the M/C ratio on the polymerization of PDO

In the second series of polymerizations, the temperatures varied in a range from 40°C to 120°C, whereas the molar ratio of monomer/ $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ (8:4:1) (M/C) was fixed at 1573, the reaction time 10 hours, and the water content in PDO 43ppm. Figure 2 shows the effect of temperature on the viscosity-average molecular weights of PPDO and the percent conversion of monomer.

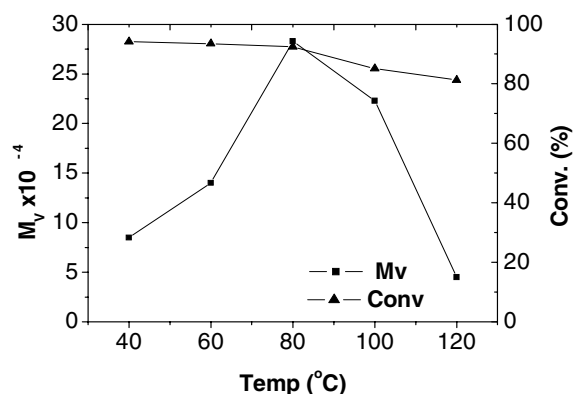


Figure 2. Effect of temperature on the polymerization of PDO

The results drawn in Figure 2 allow the following conclusion: the viscosity-average molecular weights of PPDO and the percent conversion of monomer vary obviously with the reaction temperature. When the reaction temperature is 40°C, the viscosity-average molecular weight of PPDO is only 8.5×10^4 ; when the reaction temperature rises to 80°C, the viscosity-average molecular weight of PPDO increases to 2.8×10^5 . However, with the further increase of reaction temperature, the viscosity-average molecular weights of PPDO decrease. For example, the viscosity-average molecular weight of PPDO decreases to 4.5×10^4 at 120°C. On the other hand, the percent conversion of monomer decreases with the increase of the reaction temperature. The possible reason is that at lower temperatures, the viscosity of the reaction system is higher, and the diffusion of monomers is more difficult, leading to the decrease of percent conversion and molecular weights. On the contrary, at high temperature, some side reactions, such as chain cleavage and degradation occur, which cause the

molecular weight of PPDO to decrease. Therefore, a temperature of around 80°C seems to be the optimum for ROP of PDO.

In the third series of polymerizations, the reaction time varied between 1h and 24h; the reaction temperature was fixed at 80°C, the molar ratio of monomer/ $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ (8:4:1) (M/C) 1573, and the water content in PDO 43ppm. As we know, ROP of PDO initiated by tin octoate generally take a long time at normal reaction temperatures (80-120°C) in order to obtain higher molecular weights of PPDO (say a number-average molecular weight of 8.0×10^4 for more than 20 hours) [16]. However, $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ behaves a high catalytic activity for ROP of PDO, and PPDO with a high viscosity-average molecular weight ($M_v = 2.8 \times 10^5$) of PPDO can be obtained when the polymerization is conducted for only 10 hours (Figure 3).

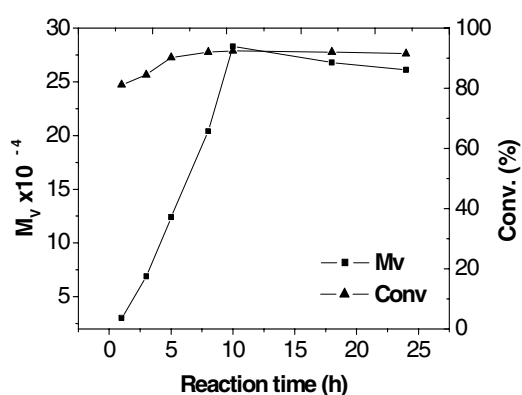


Figure 3. Effect of reaction time on the polymerization of PDO

In the initial stages of polymerization, the viscosity-average molecular weights of PPDO and the percent conversions of monomer increase sharply with the increases of the reaction time. The viscosity-average molecular weight of PPDO can reach 3.0×10^4 , and the percent conversion of PDO 81.2% when the reaction of polymerization is conducted for 1 hour. However, 10 hours later when the viscosity-average molecular weight of PPDO reaches a maximum of 2.8×10^5 , and the percent conversion of monomer 92.5%, the viscosity-average molecular weights of PPDO and the percent conversions of monomer almost remain unchanged, even decreased, indicating that chain cleavage and degradation occur due to long reaction time. Therefore an optimum reaction time of ROP of PDO should be 8~10 hours.

In the fourth series of polymerizations, the water content in PDO varied between 43ppm and 180ppm; the molar ratio of monomer/ $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ (8:4:1) (M/C) was fixed at 1573, the reaction temperature 80°C, and the reaction time 10 hours. Figure 4 shows the effect of the water content in PDO on the viscosity-average molecular weights of PPDO and the percent conversions of monomer.

It can be seen that the viscosity-average molecular weight of PPDO and the percent conversion of monomer decrease with the rise of the water content in PDO. When the water content in PDO is 43ppm, the viscosity-average molecular weight of PPDO is 2.8×10^5 , and the percent conversion of monomer 92.5%; when the water content in PDO increases to 180ppm, the viscosity-average molecular weight of PPDO decreases to 1.5×10^4 , and the percent conversion of monomer to 63.5%. Therefore, the water content in PDO is a very sensitive factor influencing the molecular weights of PPDO

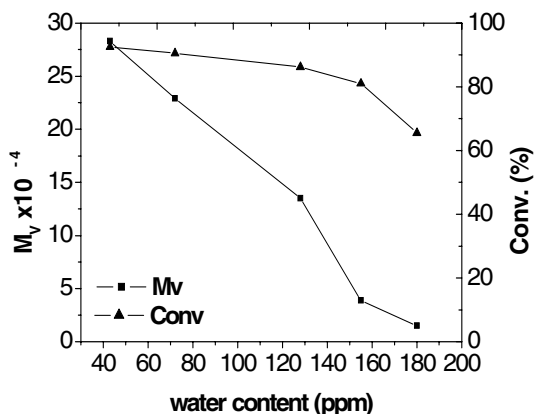


Figure 4. Effect of the water content on the polymerization of PDO

and the percent conversions of PDO during the polymerization of PDO. In order to obtain higher weights of PPDO and high monomeric percent conversions, the water content in PDO should be controlled to a very small amount, and generally lower than 80ppm.

The solubility of PPDO in common solvents strongly depends on its molecular weights. Only low molecular weight of PPDO samples can be re-solved in common solvents such as chloroform, while PPDO samples with high molecular weights can only be resolved in a few solvents such as phenol/1, 1, 2, 2-tetrachloroethane (2:3 w/w). In order to characterize the structure of the products, the purified sample with very low molecular weight (say a viscosity-average molecular weight of 7000), was analyzed using $^1\text{H-NMR}$. Different kinds of hydrogen in PPDO gave the corresponding signals at $\Delta 4.33\text{ppm}$, $\Delta 4.16\text{ppm}$, and $\Delta 3.78\text{ppm}$, respectively. The above characterizations of structures show that the resulting PPDO in this study has the same structures as PPDO reported by other researchers [16].

Conclusions

A catalyst system consisting of triethyl-aluminum, phosphoric acid and water is effective for ROP of PDO. The molecular weights of the resulting PPDO from the polymerization and the percent conversion of monomer PDO are seriously affected by the reaction conditions. The viscosity-average molecular weights of PPDO increase monotonously with the decrease of water content in PDO, but increase at first and then decrease with the increases of monomer/catalyst molar ratio or reaction temperature, i.e. there exist a maximum viscosity-average molecular weight. On the other hand, in the initial stages of polymerization, the viscosity-average molecular weights of PPDO and the percent conversions of monomer increase sharply with the increases of the reaction time, but do not increase after a maximum of 2.8×10^5 is reached 10 hours later. High viscosity-average molecular weights of PPDO can be obtained under following conditions: temperature 80°C , monomer/catalyst molar ratio 1311-1573, reaction time 8-10 hours and water content $<80\text{ppm}$. The mechanisms of $\text{AlEt}_3\text{-H}_2\text{O-H}_3\text{PO}_4$ catalyzed polymerizations of 1, 4-dioxan-2-one will be a subject of further investigation.

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