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Stannous oxalate: An efficient catalyst for poly(trimethylene terephthalate) synthesis

JIA ShuYong[1,3,4], REN YuRong[1,2,4], ZHANG Dan[1,4], HU Jing[1], ZENG Yi[1] & WANG GongYing[1,3†]

[1] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China;
[2] College of Chemistry, Jilin Normal University, Siping 136000, China;
[3] Changzhou Institute of Chemistry, Changzhou 213164, China;
[4] Graduate University of Chinese Academy of Sciences, Beijing 100039, China

A complete study on the catalytic activity of stannous oxalate for poly(trimethylene terephthalate) (PTT) synthesis via esterification method is carried out by comparison to the well known catalysts (tetrabutyl titanate (TBT), dibutyltin oxide (Bu_2SnO), and stannous octoate (SOC)). Their catalytic activity in the esterification process is monitored by measuring the amount of water generated, while intrinsic viscosity (IV) and content of terminal carboxyl groups (CTCG) are used as the index in the polycondensation process. Stannous oxalate shows higher activity than the other catalysts. Decrease in reaction time and improvements in PTT property are observed. The higher catalytic activity of stannous oxalate is attributed to its chelate molecular structure.

stannous oxalate, poly(trimethylene terephthalate), 1,3-propanediol, esterification method

Poly(trimethylene terephthalate) (PTT) is newly commercialized thermoplastic polyesters, and unifies the main characteristics of nylon and other polyester[1] for the most disparate applications, such as carpet fiber and engineering plastics[2]. Furthermore, PTT can also be used in blends with other elastic fibers, e.g., polyurethane-, polyester-, or polyether-based fiber[3−6]. PTT fiber has been considered to be one of the most important fibers of the after-polyester period.

Although PTT was reported as early as in the 1950s, it had not been commercialized until 1,3-propanediol (1,3-PDO) was manufacturable by catalytic hydrogenation of the intermediate 3-hydroxypropionaldehyde and hydroformylation of ethylene oxide[7]. Recently, economic fermentive production of 1,3-PDO[8,9] was discovered and interest in poly(trimethylene terephthalate) (PTT) has developed. Currently, the industrial production of PTT is carried out via esterification method in the presence of catalyst[10−12]. In our work, it was carried out in two steps: esterification process and polycondensation process (Scheme 1).

In the last years, much attention was paid to the studies of structure and property, kinetics and morphology, blend and synergistic behavior with other polymers, and depolymerisation of PTT polyester instead of catalysts. However, the effect of catalyst on the reaction rate and PTT property is ubiquitous and cannot be neglected. Although titanium (Ti)[10,11], Tin (Sn)[11,12], and antimony (Sb)[13,14] compounds were described for PTT synthesis, they present a few limitations. Ti-based catalysts are active, but the corresponding PTT polyesters are discolored. Sb-based catalysts are toxic and only active in polycondensation. Tin-based catalysts exhibit favorable effect on PTT property but lower catalytic activity than Ti-based catalysts. Karayannidis[13] reported stannous octoate as catalyst for PTT synthesis, but its catalytic activity is poor and results in a relatively low molecular weight of PTT.

Previous work has shown that stannous oxalate is

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†Corresponding author (email: gywang@cioc.ac.cn)

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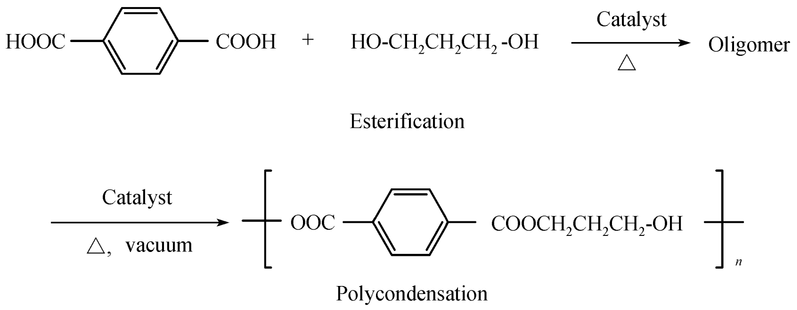


Scheme 1 PTT synthesis via esterification method.

active for PET[14] and PBT[15] synthesis and can also be used as additive to improve polymer property[16]. For all the reasons presented above, stannous oxalate was used as a catalyst in order to evaluate if it could lead to any improvements in the industrial process and in the property of the final PTT polyester. Part of the results of this study have already been published in our recent patent[17]. Here, we report a complete study of the catalytic activity of stannous oxalate.

1 Experimental

1.1 Materials

Pure terephthalatic acid (purity⩾99.0%) and 1,3-propanediol (purity⩾98.0%) were commercial products from Acros. Tetrabutyl titanate, dibutyltin oxide, stannous octoate, oxalic acid, and stannous chloride were analytical reagents. All reagents were used as received without any further purification.

1.2 Catalyst preparation

Stannous oxalate was prepared according to the literature[18] and authenticated by XRD (JCPDS 51-0614) and FT-IR (Sadtler Y 980 K).

1.3 PTT preparation

Esterification process: 0.20 mol of PTA, 0.30 mol of 1,3-PDO, and a quantitative catalyst were charged into 100 mL reactor of the polyesterification apparatus, then heated up to 260℃ under dried nitrogen atmosphere, and stirred at 100 r/min. This process was considered to be complete until there was no water distilled off.

Polycondensation process: When the reaction temperature descended to 200℃, a vacuum (60 Pa) was applied slowly over a period of 30 min. The reaction temperature was increased to 260℃ and remained for 2 h. The polymer was stirred at 200 r/min.

1.4 Measurements

Powder X-ray Diffraction (XRD) was undertaken in a X′ Pert Pro MPD diffractometer, using Cu Kα radiation ($\lambda = 1.54056$ Å). Infrared spectroscopy (FT-IR) was recorded in a Nicolet MX-1E infrared spectrophotometer with KBr pellets. ^{1}H-NMR spectrum was performed in a Brucker Avance 300 MHz instrument using deuterated trifluoroacetic acid (d-TFA) as solvent and tetramethylsilane (TMS) as reference.

Gel permeation chromatography (GPC) was carried out on a Waters GPCV 2000 connected to a refractometer coupled to a viscosimeter. Three columns made by Waters in series with model numbers of Styragel HT 5, Styragel HT 4, and Styragel HT 3 were used and controlled at 130℃. Monodisperse polystyrene standards with molecular weights of 1 300, 2 960, 6 870, 13 800, 30 500, 54 100, 202 000, 575 000, 1 040 000, 2 170 000, and 3 650 000 were used to calibrate the columns. 2-Methylphenol was used as eluent at a flow rate of 0.92 mL per minute.

Intrinsic viscosity (IV) measurement was performed using an Ubbelohde viscometer at 25℃, and 0.005 g/mL PTT solution of 1, 1, 2, 2-tetrachloroethane/phenol (50/50, *w*/*w*) was used. Content of terminal carboxyl group (CTCG) was determined by titrating. 25 mL of chloroform and three drops of phenolphthalein indicator were added to the solution of 1.000 g of PTT and 25 mL of benzyl alcohol, and a titer (V_1, mL) was obtained in a solution of 0.561 g of potassium hydroxide in 1 L of benzyl alcohol. On the other hand, by a control titration without PTT sample, a titer (V_0, mL) was obtained. The CTCG of per ton PTT sample was calculated by the following equation: CTCG (mol/t) = $(V_1 - V_0)\times 10^3$.

2 Results and discussion

2.1 Catalytic activity

TBT, Bu_2SnO, and SOC were the well-known catalysts for polyester synthesis and used for comparison. Their catalytic activity in esterification process was monitored by measuring the amount of water generated and characterized by degree of esterification (DE) of PTA, which was expressed as the following equation: $DE = V/7.2 \times 100\%$ (V: water generated, mL). The value 7.2 in the denominator was used to express the total volume of water that should be produced when all PTA reacted. While in polycondensation process, intrinsic viscosity (IV) and content of terminal carboxyl groups (CTCG) were used as the index.

As shown in Figure 1, as the esterification proceeds and the reaction temperature rises, DE of PTA increases due to the gradual dissolution of solid PTA into 1,3-PDO that participates in the reaction as well as the continuous removal of water[13]. Because the esterification is taking place in the liquid phase and the solubility of PTA in 1,3-PDO is extremely low, the DE value increased slightly at the initial stage of esterification, whatever the catalysts are. However, the DE value increases dramatically when more and more PTA dissolves in 1,3-PDO. Stannous oxalate (SnC_2O_4) exhibited higher catalytic activity for esterification than Bu_2SnO, TBT, and SOC. When the reaction time is 1.6 h, the DE value is as high as 97.2% and is sufficient for the operation of the next process.

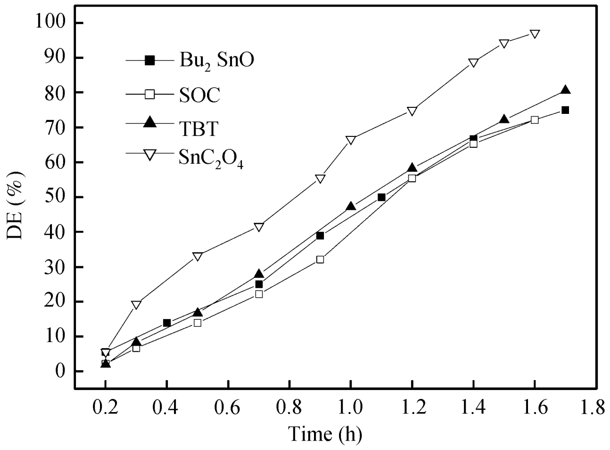


Figure 1 Effect of different catalysts on esterification. Reaction condition: catalyst amount: 5×10^{-4} mol/mol PTA.

Meanwhile, their catalytic activities for polycondensation reaction are shown in Table 1. The catalyst with higher catalytic activity in esterification process also has better effect on PTT property. When stannous oxalate is used, PTT polyester with higher IV and lower CTCG was produced. Furthermore, the polyester also has lower color intensity, which is favorable to its industrial applicability. These results indicate that SnC_2O_4 is a more promising catalyst for PTT synthesis.

Table 1 Effect of catalysts on PTT property

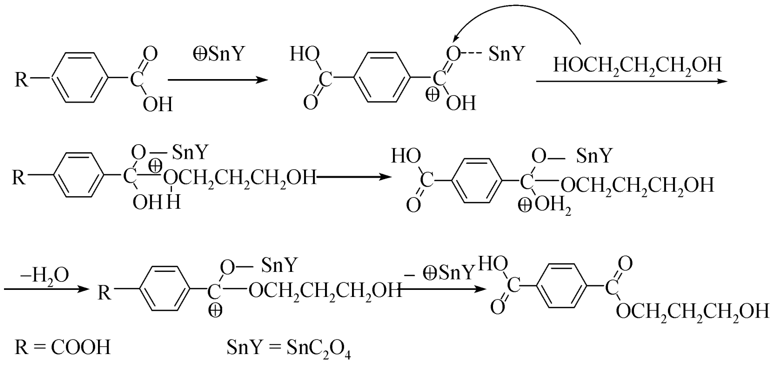
Catalyst	PTT	
	IV (dL/g)	CTCG (mol/t)
SnC_2O_4	0.8950	15
SOC	0.6155	34
Bu_2SnO	0.8192	21
TBT	0.8491	20

Reaction conditions: catalyst amount: 5×10^{-4} mol/mol PTA, esterification time: 1.6 h.

2.2 Reaction mechanism

The high catalytic activity of stannous oxalate can be ascribed to its unique chelate molecular structure[19]. First, stannous oxalate has appropriate Lewis acidity. Each tin atom in stannous oxalate molecule becomes highly electrophilic because of the stronger electron-attracting inductive effect of the conjoint O atoms, and thereby improves the Lewis acidity of the active center (Sn atom). Thus, the O atom in carbonyl group of PTA is easier to coordinate on the tin center and then accelerate the reaction. There is also M (Ti, Sn)—O bond and electron-attracting effect in TBT, Bu_2SnO, and SOC molecules, but it is not so strong because of the weaker inductive effect of ligand (butyl and octyl) that results in the lower Lewis acidity of active center (Ti, Sn). Second, stannous oxalate has planar molecular structure and thus lowers the steric hindrance. TBT, Bu_2SnO, and SOC have stronger steric hindrance because of the larger ligands and their more changeful conformation. Thus, the Sn atom in stannous oxalate is easier to attack and coordinates on the O atom in carbonyl group of PTA. Furthermore, stannous oxalate is so stable because of its chelate structure that it does not decompose until around 350℃[20]. All of these advantages contribute to its higher catalytic activity.

The possible reaction mechanism is expressed as Scheme 2. When both of the carboxyl groups in every PTA molecule react with 1,3-PDO, a long-chain PTT molecule is obtained.



Scheme 2 Reaction mechanism.

2.3 Effect of stannous oxalate amount on PTT preparation

The amount of stannous oxalate has evident effect not only on esterification rate, but also on polycondensation reaction and property of PTT. As shown in Figure 2, DE value increases rapidly with the increase of stannous oxalate amount even if it is very low. When stannous oxalate amount is 5×10^{-4} mol/mol PTA, the DE value is as high as 97.2%, which is sufficient for polycondensation reaction. Although it is beneficial to accelerate the reaction by increasing the catalyst amount, a superabundant amount did not improve the DE value and the esterification rate remarkably.

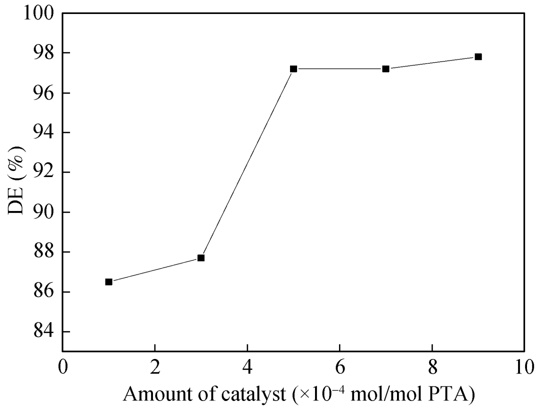


Figure 2 Effect of stannous oxalate amount on DE. Reaction condition: esterification time: 1.6 h.

Table 2 shows the effect of stannous oxalate amount on polycondensation. When it steps up to 5×10^{-4} mol/mol PTA, the IV of PTT rises to the maximum (0.8950 dL/g), while the CTCG decreases to the minimum (15 mol/t). The more amount of stannous oxalate did not give more improvement to PTT property any more.

Combined with the results of Figure 2 and Table 2, the optimum amount of stannous oxalate is 5×10^{-4} mol/mol PTA. All of the above results demonstrate that stannous oxalate is a promising and economical catalyst for PTT synthesis.

Table 2 Effect of stannous oxalate amount on PTT property

Catalyst amount ($\times10^{-4}$ mol/mol PTA)	PTT	
	IV (dL/g)	CTCG (mol/t)
1	0.7728	23
3	0.8144	18
5	0.8950	15
7	0.8890	15
9	0.8878	15

Reaction condition: esterification time: 1.6 h.

2.4 GPC analysis

Figure 3 presents the High Temperature GPC trace of the original PTT in 2-methylphenol catalyzed by stannous oxalate.

The number average molecular weight and polydispersity is 27 300 and 3.00, respectively. Therefore, when stannous oxalate is used as a catalyst, a polyester with relatively narrow molecular weight distribution was obtained.

2.5 Characterization of PTT

The FT-IR spectrum of PTT polyester catalyzed by stannous oxalate is shown in Figure 4. The peak at 2971 and 2905 cm^{-1} corresponds to the asymmetric and symmetric stretching vibration of methylene group, respectively. The peak at 1466 cm^{-1} is attributed to the special vibration of the methylene group. The peak at 1718 cm^{-1} represents the stretching vibration of C=O group, while the peak at 729 cm^{-1} is due to the interfacial swinging vibration of the three methylene groups. The peaks at 1270 cm^{-1} and 1504 cm^{-1} are assigned to the stretching

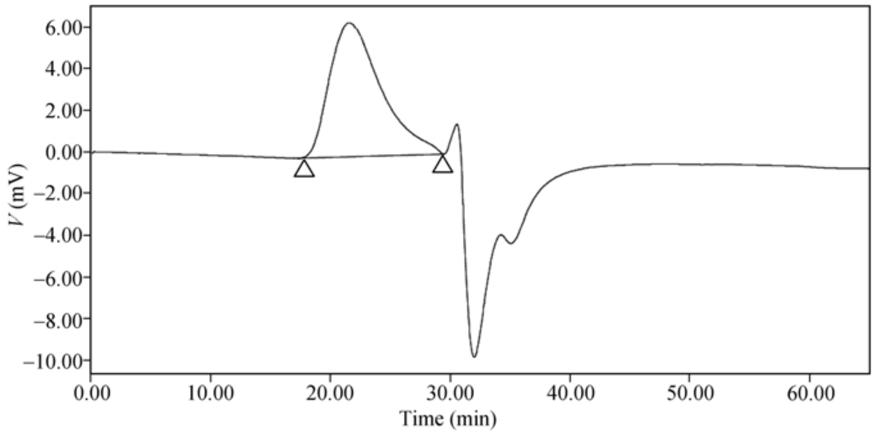


Figure 3 GPC elution trace of PTT catalyzed by stannous oxalate.

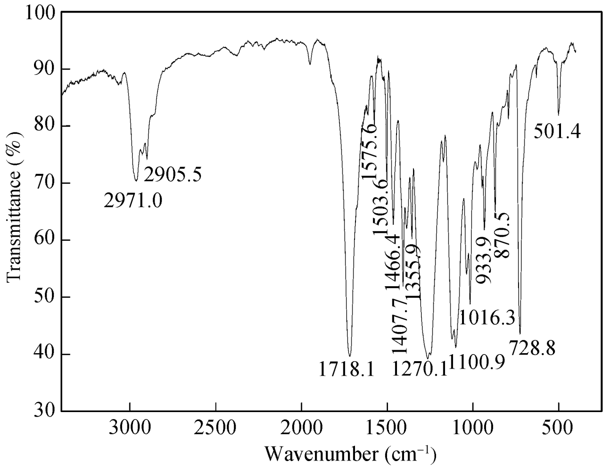


Figure 4 FT-IR spectrum of PTT.

vibration of C-O in carboxyl group and the characteristic adsorption of phenyl group[21].

The ^{1}H-NMR spectrum of PTT product shows four peaks, which represent four kinds of proton. The peak at 11.43 ppm corresponds to the proton of d-TFA. While the peak located at 2.33 ppm and 4.59 ppm corresponds to the protons of the middle and end methylene group of 1,3-PDO in PTT molecule, respectively. The peak at 8.05 ppm corresponds to the proton of the phenyl group in PTT molecule. Furthermore, the ratio of the last three peak areas is 2∶2∶1. Since the area of each peak is proportional to the number of proton of the related group, the product can be determined as PTT[22].

3 Conclusions

Stannous oxalate shows higher catalytic activity than tetrabutyl titanate, dibutyltin oxide, and stannous octoate, both in reaction rate and PTT property. The excellent catalytic behavior is due to its unique chelate molecular structure. Enhanced reaction rate and improved PTT property are the features of this catalytic system. Stannous oxalate is more promising for the synthesis of PTT polyester.

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