

NOTE

Effect of Salts on the Formation of THF in Preparation of PBT by TPA Process

INTRODUCTION

Poly(butylene terephthalate) (PBT) can be prepared by reacting 1,4-butanediol with ether dimethyl terephthalate (DMT process) or terephthalic acid (TPA process). The TPA process involves two stages of reaction. At the first stage, terephthalic acid and stoichiometrically excess 1,4-butanediol are reacted in the presence of a catalyst system at a temperature below the boiling point of 1,4-butanediol. Water (removed by distillation) and oligomers are formed at this stage. At the second stage, the reaction temperature is raised and vacuum is applied; the excess 1,4-butanediol is distilled out and PBT is formed. A severe problem has been encountered at the first stage. The problem is that considerable amounts of THF (tetrahydrofuran) were found to be formed as a side product.¹⁻⁴

The formation of THF is caused mainly by acid-catalyzed cyclization of 1,4-butanediol and hydroxybutyl end of reaction intermediates.²⁻⁴ There have been many efforts made to reduce the formation of THF, such as by catalysts,⁴⁻⁶ improvements of process,⁷⁻¹⁰ and addition of organic salts.¹¹ The use of organic salts, such as potassium terephthalate, has been claimed to depress the rate of the cyclization reaction, and thus the THF content could be reduced.¹¹ The presence of potassium terephthalate might act as a buffer to regulate the pH value, which might influence the cyclization rate. It is possible that inorganic salts with strong buffer capacity will have similar effect. In our laboratory, we found that some inorganic salts such as sodium phosphate could be also used to depress the formation of THF. In this article, various salts, including both organic and inorganic salts, were used to depress the formation of THF. The influence of the salts on the THF formation at the first stage is discussed and the molecular weight of PBT formed after the second stage is investigated.

EXPERIMENTAL

TPA was supplied by the Chinese American Chemical Co. (Taiwan). 1,4-Butanediol, tetrabutyl orthotitanate, and other salts were Merck reagent grade.

A typical preparation procedure of PBT is as follows: At the first stage, 166.0 g (1.0 mol) of TPA, 153.0 g (1.7 mol) of 1,4-butanediol, and 0.33 g of tetrabutyl orthotitanate were charged into a 1 L stainless reactor, equipped

with a nitrogen gas inlet, a mechanical stirrer, a condenser, and a vacuum line. Under purge of nitrogen gas, the reactant mixture was heated to 220°C at a stirring speed of 50 rpm. The reaction time was set to zero when the temperature reached 220°C. Something was distilled out after a few minutes. Approximately every 5 mL of distillate was collected for analysis. After about 100 min, most water was distilled out. At the second stage, the reaction temperature was raised to 260°C and low vacuum (about 10 mm Hg) was applied. Most excess 1,4-butanediol was distilled out after 100 min. Afterwards, high vacuum (0.5 mm Hg) was applied for 100 min.

The procedure of the other batch was the same except 0.017 g of salt was charged in addition. In the presence of about 0.017 g of salt, better results were obtained.

The collected distillate obtained at the first stage was weighed and the wt % of THF in the distillate was determined by Hewlett-Packard Model 5890A GC, equipped with a TC detector and a Chromosorb 101 column (2.3 m), at 150°C. The hydrogen gas was used as the carrier gas and the flow rate was 28 mL/min. The intrinsic viscosity of PBT obtained after the second stage was determined by a Ubbelohde viscometer at 30°C with phenol/syn-tetrachloroethane (60/40 wt/wt) as the solvent.

RESULTS AND DISCUSSION

The result of GC measurement showed that the distillate at the first stage was comprised of water and THF only. The conversion of esterification can be determined from GC data. The maximum number of moles of water that could be formed is equal to double of that of the TPA charged. The conversion of esterification is calculated as the accumulated moles of water of the distillate, divided by the maximum moles of water (2.0 mol). The conversion of esterification vs. reaction time curves for the different batches are shown in Figure 1. The added amount of the salt for these batches was 0.017 g; no salt was added for the blank reaction. An induction time for the esterification was found for all the batches. The initial slope of the conversion vs. time curve could indicate the esterification rate (for a reaction time of less than 40 min). The initial slopes for the different batches are listed in Table I. In the presence of a salt, the esterification rate was higher than that of the blank reaction. Differing types of salt did not affect the esterification rate significantly.

The accumulated amount of THF vs. reaction time curves for the different baths are shown in Figure 2. The

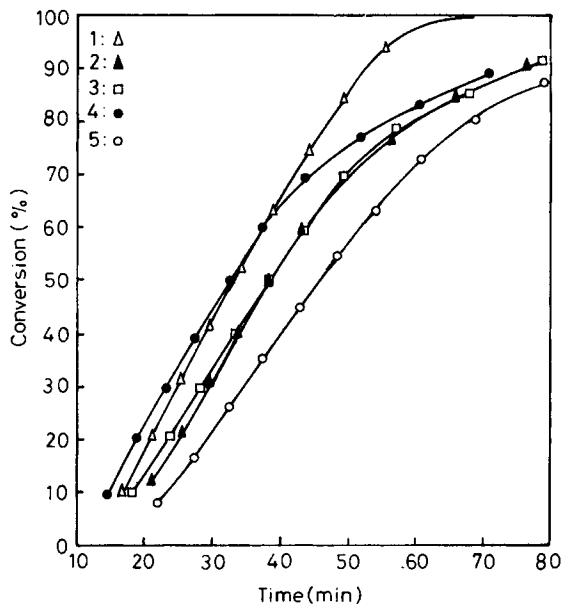


Figure 1 Conversion of esterification vs. reaction time curves in the presence of various salts. (1) Sodium phosphate, (2) Sodium citrate, (3) Potassium terephthalate, (4) Sodium carbonate, and (5) Blank.

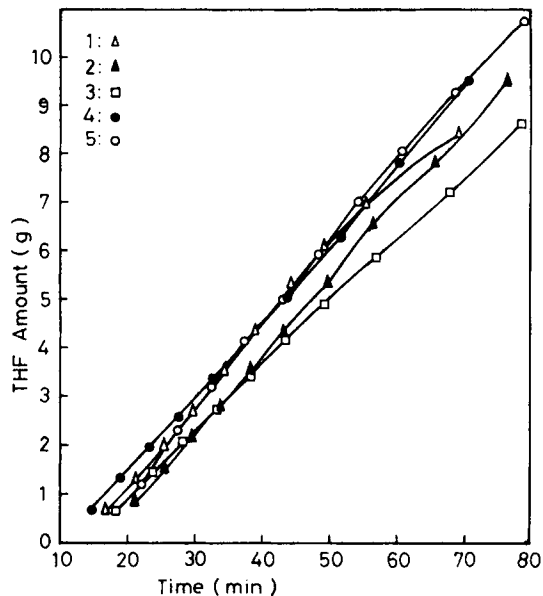


Figure 2 Accumulative THF amount vs. reaction time curves in the presence of various salts. (1) Sodium phosphate, (2) Sodium citrate, (3) Potassium terephthalate, (4) Sodium carbonate, (5) Blank.

initial slope (Table I) of the curve would indicate the formation rate of THF (for the reaction time less than 40 min). The THF formation rate in the presence of salt was slightly lower than the blank reaction. The THF content of each distillate vs. conversion curves for the different batches are shown in Figure 3. In the absence of any salt, the THF content of each distillate was higher than it was in the presence of salt, as the conversion was below 70%. When the conversion was above 70%, the THF content of each distillate increased significantly for the three batches in the presence of sodium citrate, potassium terephthalate, and sodium carbonate, respectively. In the presence of sodium phosphate, the THF content of each distillate was well below the blank reaction. The accumulated THF content at 60% and 85% conversion, in the presence of various salts, is shown in Table II. The ac-

cumulated THF content at 60% conversion in the presence of salt was significantly lower than it was for the blank reaction. Using 85% conversion as another reference point, the accumulated THF content decreased in the following order: blank > sodium citrate, potassium terephthalate, sodium carbonate > sodium phosphate.

Table I Initial Slopes of Conversion vs. Time and THF Amount vs. Time Curves in the Presence of Various Salts

Salt	Slope (l/min) (Conversion vs. Time)	Slope (g/min) (THF Amount vs. Time)
No (Blank)	0.017	0.17
Sodium Citrate	0.022	0.16
Potassium Terephthalate	0.022	0.16
Sodium Carbonate	0.020	0.13
Sodium Phosphate	0.023	0.15

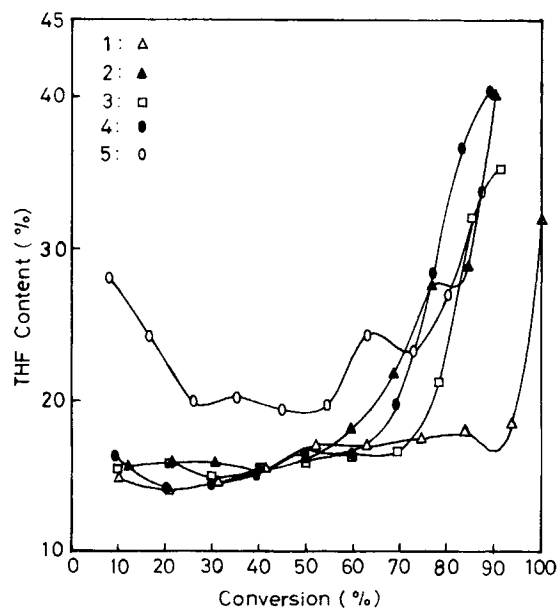


Figure 3 THF content of each distillate vs. conversion of esterification curves in the presence of various salts. (1) Sodium phosphate, (2) Sodium citrate, (3) Potassium terephthalate, (4) Sodium carbonate, (5) Blank.

The formation of THF is an acid-catalyzed cyclization reaction. The THF formation rate was expected to be regulated by the pH value. Our motivation was to use the salt to act as a buffer to reduce the formation of THF. However, the presence of a small amount of salt (i.e., 0.017 g) gave better results (lower THF content). Using sodium phosphate as an example, in the presence of 1.0 g of sodium phosphate, the accumulated THF content was about 25% (at about 85–90% conversion of esterification), and was not significantly better than the blank reaction. In the presence of 0.017 g of sodium phosphate, the final accumulated THF content was about 17%. Thus, 0.017 g of salt was used to compare the effect of the different salts. The presence of a small amount of salt did reduce the THF content. However, the phenomena were more complex than expected. Two factors should be considered: the formation rate of THF and the esterification rate. Initially, the presence of salt reduced the formation rate of THF to some extent, as shown in Table II. The esterification rate in the presence of salt was higher than that of the blank reaction, as shown in Table II. The net effect was that the formation of the THF content was reduced since the conversion was below 60%. Thus, the accumulated THF content at 60% conversion in the presence of salt was significantly lower than it was in the blank reaction.

It was our experience that the esterification conversion at the first stage should be above approximately 85 to 90% in order to obtain high molecular weight PBT. Thus, the last period of higher conversion of esterification was also very important. For the blank reaction, the THF content of each distillate increased significantly when the conversion was above 70%. This increase would be attributed to the slower esterification rate at higher conversion. When the conversion was higher, the reactant concentration of esterification decreased, thus the esterification rate decreased accordingly. But the reactant concentration of cyclization reaction was not considerably reduced at higher esterification conversion due largely to the excess of 1,4-butanediol. In the presence of sodium citrate, potassium terephthalate, or sodium carbonate, the esterification rate at higher conversion also decreased significantly, and the THF content of each distillate increased considerably when the conversion was above 70%, as shown in Figure 3. In the presence of sodium phosphate, the situation was

Table II Accumulated THF Content at 60% and 85% Conversion in the Presence of Various Salts

Salt	Accumulated THF Content (%)	
	At 60% Conversion	At 85% Conversion
No (Blank)	23.5	25.3
Sodium Citrate	17.0	20.8
Potassium Terephthalate	16.4	19.0
Sodium Carbonate	16.3	21.5
Sodium Phosphate	16.1	16.8

Table III Intrinsic Viscosity of PBT Prepared in the Presence of Various Salts

Salt	Intrinsic Viscosity (dL/g)
Blank	0.71
Sodium Citrate	0.70
Potassium Terephthalate	0.77
Sodium Carbonate	0.84
Sodium Phosphate	1.01

much different. As shown in Figure 1, the esterification rate was not reduced significantly up to about 90% conversion. Thus, the THF content of each distillate was not increased significantly at higher conversion (below 90%). This was why the accumulated THF content at 85% conversion, in the presence of sodium phosphate, was significantly lower than those of the reactions in the presence of other salts. The sodium phosphate system will be discussed in future works.

The intrinsic viscosity of PBT, prepared in the presence of various salts, is shown in Table III. Clearly, the addition of salt did not reduce the molecular weight. In conclusion, the use of these salts could reduce the formation of THF, and sometimes increase the molecular weight.

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