



# Sodium titanium tris(glycolate) as a catalyst for the chemical recycling of poly(ethylene terephthalate) via glycolysis and repolycondensation



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## ABSTRACT

Poly(ethylene terephthalate) (PET) was chemically recycled through glycolysis with ethylene glycol (EG) and repolycondensation of its main depolymerized product bis(2-hydroxyethyl terephthalate) (BHET). In this process, synthesized sodium titanium tris(glycolate) was used as a new catalyst for both reactions. The catalytic efficiency and selectivity of sodium titanium tris(glycolate) in both reactions has been investigated and compared with conventional catalysts used in glycolysis or polycondensation. The results indicate that sodium titanium tris(glycolate) is a desirable catalyst for chemical recycling of PET because it can present high catalytic activity and selectivity not only in glycolysis but also in repolycondensation, which means high cost of the catalysts separation between two reactions during chemical recycling process could be avoided. Meanwhile, a mechanism of the glycolysis of PET catalyzed by sodium titanium tris(glycolate) was proposed based on the results of interactions among BHET, EG and catalysts revealed by infrared spectroscopy.

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## 1. Introduction

Poly(ethylene terephthalate) (PET), one of most cost-effective and indispensable commodity polymers, has been widely used as synthetic fibrous and packaging materials. The global production of PET is likely to exceed 24.39 million tons in 2015 [1]. Consequently, the recycling of PET has found its continuously growing popularity owing to economic and ecological considerations. Although PET wastes can be mechanically recycled by melt-reforming process, the regenerated products with inferior properties are limited in application and will terminate the recycling loop eventually. In contrast, chemical recycling is an ideal method which can achieve the closed-loop through depolymerizing PET into its starting monomer or intermediate and then repolymerizing them. With ester groups, PET can be depolymerized by solvolytic reactions including hydrolysis [2], methanolysis [3], glycolysis [4–6], aminolysis [7] and ammonolysis [8]. Among them, glycolysis with ethylene glycol (EG) is one of the most widely studied processes for chemical recycling of PET, because it requires mild conditions and

its product bis(2-hydroxyethyl terephthalate) (BHET) can be readily integrated into conventional production of PET [9].

Kinetic studies on the glycolysis of PET have shown that uncatalyzed process is sluggish and cannot be completed before many side reactions occur. Therefore, various catalysts for the glycolysis of PET have been investigated and can be classified into three categories: 1) Metal salts, such as acetates [4,10] (activity order as  $Zn^{2+} > Mn^{2+} > Co^{2+} > Pb^{2+}$ ), chlorides [11] (activity order as  $Zn^{2+} > Nd^{3+} > Li^+ > Fe^{3+} > Mg^{2+}$ ), titanium phosphate [12], carbonates and sulphates [13] (activity order as  $Zn^{2+} > Na^+ > K^+$ ); 2) Ionic liquids [14–16]; 3) Heterogeneous catalysts, such as metal oxides [17,18], zeolite [19], hydrotalcites [20] and solid acids [21]. Since the complexity of mass transfer, the efficiency of heterogeneous catalyst is relatively low. Although zinc salts and ionic liquids as homogeneous catalysts are effective, high content of residual  $Zn^{2+}$  and halide ions (contained in ionic liquids and metal chlorides) in the glycolysis products can seriously degrade the quality of regenerated PET, because the degradation will be highly boosted by them in the repolycondensation step of recycling [22,23]. Therefore, high cost of catalysts separation is required, which is unfavorable for chemical recycling widely practiced. Consequently, there is no denying that developing a homogeneous catalyst which can effectively and specifically boost both glycolysis and polycondensation to avoid the separation of glycolysis catalyst before repolymerization is an

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interesting idea and crucial to the implementation of continuous chemical recycling of PET in industrial scale.

Glycolysis and polycondensation of PET all proceed via the acyl-type ( $A_{AC}2$ ) mechanism, and both of them can be regarded as transesterification but with different reactants [23,24]. Therefore, catalyzing them by using the same catalyst is theoretically possible. Metallic compounds are the main catalysts for  $A_{AC}2$  type reactions. However, different metallic elements catalyze these reactions through different mechanisms, which lead to the difference of their catalytic activity in glycolysis and polycondensation. Otton [25–27], Weingart [23], Parshall [28], Silling [29] and Apicella [30] et al. have demonstrated catalytic mechanisms of different metallic compounds with model molecules, which has been generally accepted. The mechanisms can be classified into three categories: 1) alkali metals salts ( $Na^+$ ,  $K^+$ ) activate the nucleophile ( $R-OH$ ) to attack the carbonyl carbon of ester group by forming the metal alcoholates ( $R-O^-$ ) [25]; 2)  $Zn^{2+}$  and  $Mn^{2+}$ , as Lewis acids, activate the carbonyl oxygen of the ester group which favors nucleophilic attack to boost the transesterification [25,30]; 3) Sb(III) compounds and Ti(IV) alkoxides catalyze  $A_{AC}2$  reactions through ligand-exchange that these tri-, tetravalent metals coordinated to the alkoxide oxygen of ester and render oxygen of their ligands for the carbonyl carbon [28–30]. Active nucleophile ( $R-O^-$ ) can be formed only when  $-R$  is a small-molecular group, that's why  $Na^+$  and  $K^+$  only presents catalytic activity in glycolysis. The activity of divalent transition metal ions, such as  $Zn^{2+}$ , is strongly affected by the resonance of the molecule due to the catalytic mechanism of Lewis acid [30]. So, they are optimal for glycolysis and the transesterification between dimethyl terephthalate (DMT) and EG, but not highly efficient catalysts for polycondensation. Moreover,  $Zn^{2+}$  is a heavy metal ion and has the strongest catalytic activity for the thermal degradation of PET as well [22,31,32]. Therefore high residual content of  $Zn^{2+}$  in the glycolysis product has to be separated before repolymerization. Unlike the catalytic mechanism of Lewis acid, based on ligand-exchange, Sb(III) compounds and Ti(IV) alkoxides present highly efficient and stable activity for polycondensation due to the coordinated oxygen atom is from alkoxide of ester rather than carbonyl, however they are not optimal for glycolysis [25]. Additionally, because of the toxicity of antimony compounds, titanium catalysts have been regarded as the most favorable ones for polycondensation and may replace antimony in the near future.

Fortunately, based on the ligand-exchange mechanism, the activity of titanium catalyst for  $A_{AC}2$  reactions can be changed by modifying the coordination number and ligand structure of titanium [33,34]. Therefore, aiming for developing an environment-friendly, highly efficient homogeneous catalyst for both glycolysis and repolycondensation, we intended to combine different catalytic mechanisms into one catalyst by using sodium ion as the modifier and promoter for titanium coordination compound catalyst to achieve this purpose. In this study, sodium titanium tris(glycolate) was synthesized and has been successfully used as a catalyst for both glycolysis and repolycondensation. The catalytic efficiency and selectivity in both reactions has been fully investigated in order to get a comprehensive evaluation of this catalyst for chemical recycling of PET. Moreover, a reasonable mechanism of the glycolysis of PET catalyzed by sodium titanium tris(glycolate) was proposed.

## 2. Experimental

### 2.1. Materials and instruments

PET chips (super bright textile grade, intrinsic viscosity:  $0.650 \pm 0.015$  dL  $g^{-1}$ , antimony(Sb) content  $\leq 200$  ppm, size:

$3.0 \times 2.5 \times 2.0$  mm) and ethylene glycol antimony ( $Sb_2(OCH_2CH_2O)_3$ ) were supplied by Jiangyin Huahong Chemical Fiber Co., Ltd., Jiangsu Province, China. Other reagents were all of chemical pure grade and obtained from the Sinopharm Chemical Reagent Shanghai Co., Ltd., China. The materials were used without any further treatment.

The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by Nicolet 8700 FT-IR spectrometer in the range of  $4500$   $cm^{-1}$  to  $400$   $cm^{-1}$  (KBr pellet). Nuclear magnetic resonance (NMR) spectra were recorded by Bruker Avance-400 Spectrometer operating at 400 MHz. Differential scanning calorimetry (DSC) thermograms were recorded by TA-Q20 DSC. The scanning electron microscopy (SEM) image and energy dispersive X-ray spectroscopy (EDS) graph were recorded by JSM-5600LV SEM and IE-300X EDS.

### 2.2. Synthesis of sodium titanium tris(glycolate)

The sodium titanium tris(glycolate) were synthesized according to the alcohol interchange route reported by Gainsford, G. J. et al. [35] with modification, the synthesis scheme are shown in Scheme 1. Sodium hydroxide (NaOH, 2.41 g, 60.25 mmol) was dissolved in ethylene glycol (EG, 50 ml) at  $100$   $^{\circ}C$  with vigorous stirring. Meanwhile, the system was bubbled with dry nitrogen for 30 min to remove the water and oxygen. Then, tetrabutyl titanate ( $Ti(OC_4H_9)_4$ , 10 g, 29.4 mmol) was added into the system via syringe and heated to  $150$   $^{\circ}C$  with vigorous stirring, the n-butanol and water produced during the reaction was removed by distillation. After 1 h reaction at  $150$   $^{\circ}C$ , the system was heated to  $200$   $^{\circ}C$  with EG refluxed for another 3 h, then EG was removed by distillation to obtain the crude product. Colorless crystal sodium titanium tris(glycolate) was obtained by recrystallizing crude product from methanol/acetonitrile (20:80, v/v) at  $4$   $^{\circ}C$  for 24 h twice and dried at  $90$   $^{\circ}C$  under vacuo for 48 h.

### 2.3. Glycolysis of PET

30.0 g PET chips (equivalent to 0.156 mol of repeating unit), certain amount of EG and different catalysts was loaded into a 500 mL four-necked flask equipped with reflux condenser, mechanical agitator, thermometer, nitrogen inlet and heated in an oil bath. Glycolysis reactions were carried out at  $190$   $^{\circ}C$  for required time under atmospheric pressure with nitrogen atmosphere and EG refluxed. The glycolysis rate was tested previously and found no change between stirring rates of 800 rpm and 1000 rpm, therefore all stirring rates of glycolysis was settled at 800 rpm in order to exclude the influence of mass transfer on glycolysis rate. The experimental conditions of these runs carried out in this work are listed in Table 1. It is worth pointing out that the amount of catalysts refers to the molar content of metallic element in each catalyst, which can clearly demonstrate the activity of different catalysts.

When each glycolysis reaction finished, the flask was cooled down immediately by quenched in cool water. 2000 ml distilled water was used to dissolve the monomer products (BHET) with vigorous stirring at  $70$   $^{\circ}C$  for 30 min (the dissolve of dimer at this temperature is negligible) and then filtered. The filtrate was collected and concentrated to about 500 ml by distilled under reduced pressure and stored in refrigerator at  $0$   $^{\circ}C$  for 24 h. White crystalline BHET flakes was formed, then separated and dried. The yield of BHET was calculated based on the Eq. (1):

$$\text{Yield of BHET(\%)} = \frac{W_{\text{BHET},t} / M_{\text{BHET}}}{W_{\text{PET},0} / M_{\text{PETu}}} \times 100\% \quad (1)$$

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