

Novel Catalysts Based on Titanium Dioxide/Silicon Dioxide for Poly(ethylene terephthalate)

Ming Yin,^{1,2} Chuncheng Li,¹ Guohu Guan,¹ Dong Zhang,¹ Yaonan Xiao¹

¹Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

²Graduate University, Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Received 20 March 2009; accepted 17 June 2009

DOI 10.1002/app.30949

Published online 15 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of titanium dioxide/silicon dioxide based poly(ethylene terephthalate) (PET) polycondensation catalysts were synthesized with different Si/Ti molar ratios and various amounts of polyvinylpyrrolidone (PVP). The composition, structure, and catalytic activities of the catalysts and the properties of the PET samples catalyzed by these catalysts were characterized with thermogravimetric analysis, electron probe microanalysis, X-ray diffraction, X-ray photoelectron spectroscopy, and so forth. The results indicated that the Si/Ti molar ratios of the catalysts could

be well controlled by the synthesis processes used in this study, whereas the content of PVP was influenced by the amount of titanium dioxide. The activities of the catalysts greatly depended on the Si/Ti molar ratios and coordinative effects between titanium and PVP. Some of the catalysts possessed ultrahigh activities, and the corresponding PET material had excellent properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2470–2478, 2010

Key words: catalysts; polycondensation

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important thermoplastics because of its balance of excellent mechanical properties, good thermal properties, and low cost.^{1–4} The global demand for PET was 37 million tons in 2004, and the output of PET will grow 8–10% annually in the next 10 years.^{5,6}

The synthesis of PET involves two steps: (1) the synthesis of bis(2-hydroxyethylene terephthalate) (BHET) and (2) the polycondensation of BHET to produce PET. For the first step, a catalyst is not necessary because pure terephthalic acid and ethylene glycol (EG) can undergo direct esterification under a certain pressure to form BHET while water is distilled out of the reaction system. This process is widely applied in industry.^{5,6} However, the polycondensation of BHET must be catalyzed if a technically useful polymer is to be obtained because the reaction without a catalyst is too slow and many side reactions will occur when the melt is heated at high temperatures for a long time. The polycondensation of BHET and its oligomers is generally catalyzed by antimony compounds in the form of an oxide or acetate. Antimony compounds are the predominant catalysts for PET because they can offer high catalytic

activity and good properties and color for the final products and the cost remains quite low.^{7,8}

However, there has been more and more concern about human health and the protection of the environment nowadays, so the extensive use of antimony, a kind of heavy metal, is suffering more and more serious restrictions. It has been proved that antimony poses some risks to human health because antimony can leach from the beverage bottles made of PET.^{6,7,9,10} Moreover, the treatment of hazardous waste derived from PET synthesis, which contains antimony, increases the cost of PET. Besides, antimony can cause gray discoloration of PET materials.^{8,11} Germanium compounds may be a possible alternatives for antimony when only the whiteness, molecular weight, and hydrolytic stability of the obtained PET are taken into consideration. Unfortunately, the prohibitive price of germanium limits its use in global industries. In fact, only a small percentage of the total worldwide production of PET is catalyzed by germanium compounds.^{7,12}

As a result, the most promising substitutes for antimony catalysts are titanium compounds. Titanium-based catalysts have been known for many years and actually are used for PET, poly(butylene terephthalate), and poly(trimethylene terephthalate) production.^{13,14} Otton and coworkers^{15,16} investigated the kinetics and mechanism of formation of PET catalyzed by titanium compounds using monofunctional reactants as model molecules. The polycondensation catalytic activity of titanium-based

Correspondence to: C. Li (lichch@iccas.ac.cn).

catalysts was found to be higher than that of antimony. Siling and Laricheva¹⁷ stated that the activity of titanium can be influenced by the reaction medium because titanium derivatives can undergo ligand exchange with esters and alcohols. However, the drawbacks of titanium-based catalysts, usually in the form of titanium alkoxides, are also prominent. Titanium alkoxides are prone to hydrolysis, and this leads to reduced activity and haze in the polymer. If titanium alkoxides are directly used as polycondensation catalysts for PET, because of its poor selectivity, not only polymerization but also some side reactions are greatly accelerated, producing higher carboxylic end group (CEG) contents, so the obtained PET material will be discolored and have poor mechanical, thermal, and hydrolytic properties.^{7,12,18,19}

A number of articles and patents have been issued about overcoming the defects of titanium-based catalysts.^{13,20–24} There are two main approaches that have been developed: first, the use of another kind of metal or silicon with titanium; second, the use of a cocatalyst, usually containing phosphorus, in addition to the effective titanium component. These catalysts preserve the high activity of the traditional titanium-based catalysts; moreover, PET produced with these kinds of titanium-based catalysts has better properties. For example, Banach and coworkers^{25–27} developed a new kind of catalyst for poly(butylene terephthalate) using Ti/La and Ti/Hf systems with phosphate as cocatalysts. The activities of the catalysts and the properties of the products were better than those when only titanium compounds were used as catalysts. However, within all these novel PET catalysts, the titanium content is quite high (some of them have a Ti/Si molar ratio of 9), and the diethylene glycol (DEG) and terminal carboxyl group contents of the PET products are not satisfying; this results in yellow discoloration and a higher chroma *b* value. Therefore, some kind of stabilizer is required to be used together with the catalysts to improve the appearance and stability of the PET products, increasing the cost of PET.

Therefore, it is of theoretical and practical importance to explore novel titanium-based catalysts for polyesters. In our recent work, a novel kind of catalyst based on a titanium dioxide (TiO₂)/silicon dioxide (SiO₂) sol was prepared with an ultrahigh activity: only 5 mg of the catalyst could successfully catalyze the synthesis of 100 g of PET, and the properties of the products were excellent. The influence of the Si/Ti molar ratios and the amount of the organic component polyvinylpyrrolidone (PVP) on the activities of the catalysts was studied. The titanium content of this kind of catalyst was quite low, and the organic component PVP played an important role in the catalysts.

EXPERIMENTAL

Materials

Bis(2-hydroxyethylene terephthalate) (BHET) without any transesterification catalyst was kindly supplied by Sanfangxiang Group, Co., Ltd. (Jiangsu, China). PVP (analytical reagent, >98%, number-average molecular weight \approx 30,000), tetrabutyl titanate [TBT or Ti(OC₄H₉)₄; analytical reagent, >98%], antimony trioxide (Sb₂O₃; analytical reagent, >99%), and tetraethoxide orthosilicate [TEOS or Si(OC₂H₅)₄; analytical reagent, >99%] were purchased from Beijing Chemical Reagents Co. (Beijing, China). The chemicals were used as received.

Synthesis of the catalysts without PVP (TS series)

Because the synthesis methods of this series of catalysts were similar, only one example is given here. First, a TiO₂/SiO₂ sol was prepared according to the procedures reported by Yamanaka et al.²⁸ The silicon hydrate sol solution was prepared through the mixing of TEOS, 2 mol/L HCl, and ethanol in a ratio of 4.2 g to 2.5 mL to 3 mL at room temperature. The titanium hydrate sol was obtained through the hydrolysis of 1.7 g of TBT in a 1 mol/L HCl solution, and the molar ratio of HCl to TBT was about 4. The resulting slurry was peptized into a clear sol solution by continuous stirring for 3 h at room temperature. The two sol solutions were then mixed and stirred for 30 min at 20°C (solution A); Si/Ti was equal to 4 (molar ratio). Second, 30 g of a distilled water and ethanol mixture (H₂O/ethanol = 1/9 w/w) was added dropwise to the obtained mixed sol, and the white precipitate was isolated with a centrifuge and washed with deionized water until no Cl⁻ could be detected out of the liquid phase by one drop of a AgNO₃ solution. The wet cake was then dried at 80°C to a constant weight. This catalyst was named TS-4.

Synthesis of the catalysts with PVP (TSP series)

Only one typical example is given here. First, the mixed TiO₂ and SiO₂ sol mentioned previously was obtained (Si/Ti = 4) and stirred for 30 min (solution A). PVP (2.22 g), which had been dried at 80°C *in vacuo* for 8 h to remove any absorbed water before being weighed, was dissolved into 150 mL of distilled water (solution B). Solution A was added dropwise to solution B (the molar ratio of the nitrogen atoms in PVP/Ti equaled 4). The obtained precipitate was isolated with a centrifuge and washed with deionized water until no Cl⁻ could be detected out of the liquid phase by one drop of a AgNO₃ solution. The wet cake was then dried at 80°C to a constant weight. This catalyst was named TSP-44.

TABLE I
Compositions of the Catalysts and Specifications of the PET Samples

Sample	Si/Ti molar ratio		N/Ti molar ratio		Corresponding PET sample ^c
	Theoretical	Practical ^a	Theoretical	Practical ^b	
TS-1	1	1.1	—	—	—
TS-2	2	1.8	—	—	—
TS-4	4	3.3	—	—	—
TS-9	9	8.5	—	—	—
TSP-22	2	1.8	2	0.6	P-TSP22
TSP-24	2	2.2	4	0.9	P-TSP24
TSP-28	2	2.2	8	1.1	P-TSP28
TSP-42	4	3.8	2	1.8	P-TSP42
TSP-44	4	4.1	4	3.5	P-TSP44
TSP-48	4	4.2	8	3.9	P-TSP48
TSP-92	9	7.9	2	1.9	P-TSP92
TSP-94	9	8.6	4	3.4	P-TSP94
TSP-98	9	8.4	8	4.0	P-TSP98

^a Obtained from EPMA results.

^b Obtained from TGA results.

^c The catalyst loading was 5 mg of catalyst/100 g of PET.

The theoretical and practical contents of every component of the catalysts are shown in Table I.

Preparation of PET

BHET (131.5 g; corresponding to 100 g of PET) and a given amount of a catalyst were added to a homemade 500-mL, four-necked flask with a mechanical stirrer. The temperature of the reaction system was raised to about 280°C, a vacuum (<50 Pa) was applied, and EG was continuously removed by distillation. The polycondensation step was finished until the mechanical stirring reached a certain torque (the corresponding intrinsic viscosity was ca. 0.7 dL/g for PET catalyzed by TSP series catalysts). The specifications of the PET samples are also listed in Table I.

Characterization

Thermogravimetric analysis (TGA) was performed on a PerkinElmer (Waltham, MA) TGA7. Samples were heated at a rate of 20°C/min from 50 to 700°C in a nitrogen atmosphere. The standard uncertainty of the reported decomposition temperature was $\pm 1^\circ\text{C}$.

The intrinsic viscosity of all the samples was measured at $25 \pm 0.1^\circ\text{C}$ in an Ubbelohde viscometer with a 50/50 w/w mixture of phenol and 1,1,2,2-tetrachloroethane as the solvent. The molecular weights of the PET samples were calculated according to the formula mentioned in the literature.²⁹

The chemical compositions of the catalysts synthesized in this study were determined with electron probe microanalysis (EPMA; JXA-8800R, JEOL, Tokyo, Japan). Before EPMA measurements, all the samples were dried at 80°C *in vacuo* to remove absorbed water, and then the catalysts were molded into a disk shape. The acceleration voltage was 20

kV, the beam current was 20 nA, and the beam diameter was 5 μm . The peak counting time was 10 s, and the time for the background was 10 s.

X-ray diffraction (XRD) was performed at room temperature with a Rigaku (Tokyo, Japan) model D/Max-2B diffractometer using Cu K α radiation (wavelength = 0.154 nm) with a generator voltage of 20 kV and a generator current of 200 mA. Testing data were collected from 1.5 to 80° at a scanning rate of 2°/min.

X-ray photoelectron spectra were recorded with a VG Scientific (East Grinstead, UK) Escalab 220i-XL X-ray photoelectron spectroscopy (XPS) instrument with an Al K $\alpha_{1,2}$ excitation source (300 W). Calibration of the spectra was done at the C_{1s} peak of surface contamination taken at 284.8 eV.

The terminal carboxyl group content ([COOH]) was measured by titration according to the methods reported in the literature.^{30,31} In a nitrogen atmosphere, about 0.3 g of the PET material was dissolved in 10 mL of benzyl alcohol under heating and titrated with a 0.01 mol/L KOH/EG solution with phenol red as an indicator. The titrations were carried out at a temperature higher than 100°C to avoid the precipitation of the polymer, and blank runs were carried out for correction. The test was repeated three times to get an average value.

A PerkinElmer DSC-7 differential scanning calorimetry (DSC) thermal analyzer was used for DSC analysis. Each sample (ca. 3 mg) was accurately weighed before the DSC tests. All DSC measurements were performed under a dry nitrogen atmosphere. The samples were first heated at 20°C/min to 290°C, held at 290°C for 5 min to remove any thermal history, then cooled at 20°C/min to 50°C, and finally heated again to 290°C at 20°C/min.

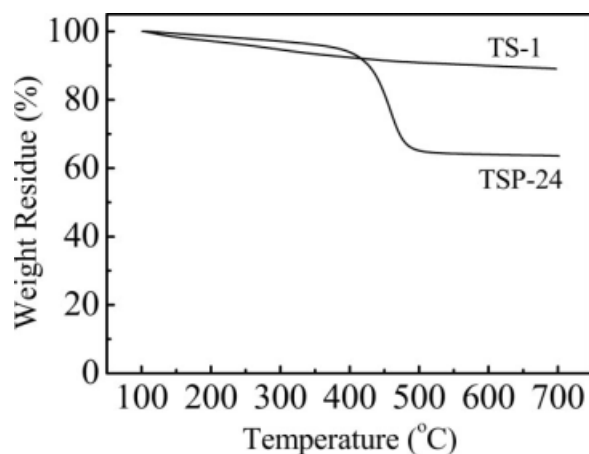


Figure 1 TGA curves of TS-1 and TSP-24.

DEG contents of the samples were examined on an Agilent (Berkshire, UK) 6890N gas chromatograph, and the chroma *L* and *b* values were obtained with a Hunter Lab (Reston, VA) Scan XE spectrophotometer.

RESULTS AND DISCUSSION

Characterization of the catalysts

TGA study

Both TS and TSP series catalysts had very good thermal stability. Because there was no organic content in the TS series, their thermal stability had to be very good, and only the TGA curve of TS-1 is shown in Figure 1. No distinctive peak could be discerned from the differential curve. At 700°C, TS-1 lost 8% of its initial weight, and this could be ascribed to the loss of the physically absorbed water and dehydration of hydroxyl groups. For TSP series catalysts (only the TGA curve of TSP-24 is shown in Fig. 1 for clarity; the TGA data for all the TSP series catalysts are summarized in Table II), the initial thermal decomposition temperatures were around 425°C, and this meant that the catalysts had excellent thermal stability and would not decompose during the synthesis of PET.

It is well known that PVP can have chemical interactions with TiO_2 sol,^{32–34} so the PVP contents of the catalysts had to be related to the amounts of PVP and titanium added during the synthesis processes (Fig. 2). As the theoretical N/Ti molar ratio increased from 2 to 8, the residue weight of the catalysts at 700°C decreased, and this indicated a higher PVP content of the catalyst. However, the increase in the quantity of PVP in the catalysts was not proportional to the amount of PVP added during the synthesis of the catalysts. For example, the practical N/Ti molar ratios for TSP-42 and TSP-44 were close to the theoretical values (Table I), but a further increase

TABLE II
TGA Results of the Catalysts

Sample	Initial decomposition temperature (°C)	Weight residue at 700°C (%)
TSP-22	422	69
TSP-24	426	64
TSP-28	424	59
TSP-42	431	57
TSP-44	427	42
TSP-48	422	40
TSP-92	436	66
TSP-94	436	57
TSP-98	428	53

in the addition of PVP did not result in a much higher content of PVP in TSP-48. The N/Ti ratio in TSP-48 was 3.9, not far from that of TSP-44. The same trend could be found in the catalysts of TSP-92, TSP-94, and TSP-98, and this indicated that titanium in the catalysts could react only with a certain amount of PVP. Moreover, the quantities of PVP in the catalysts were also affected by the contents of TiO_2 . For example, when the theoretical N/Ti molar ratio was 4 (TSP-24, TSP-44, and TSP-94), clearly TSP-44 had the highest practical organic content; it was followed by TSP-94, and TSP-24 had the lowest content of PVP (Fig. 2). Compared with TSP-44, TSP-94 had less titanium because PVP was chemically absorbed by titanium, and TSP-94 surely had less PVP. As for TSP-24, although it had the highest content of titanium among these three catalysts, the amount of PVP was the lowest. This phenomenon seems to contradict the previous discussion. However, according to Yamanaka et al.,²⁸ titanium was loaded outside the SiO_2 particles. When the TiO_2 content was low, the titanium derivatives could form a single layer outside the SiO_2 particles, so all the TiO_2 particles had opportunities to react with PVP. As the titanium content increased (e.g., TSP-24), TiO_2 might have existed in the form of multilayers³⁵ (as proved by the XRD results discussed

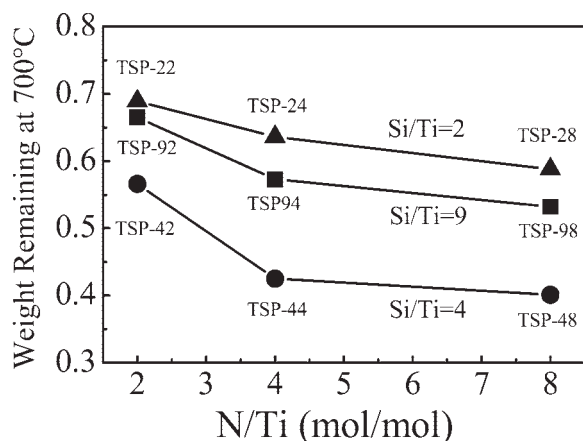


Figure 2 Weight residue of the catalysts at 700°C.

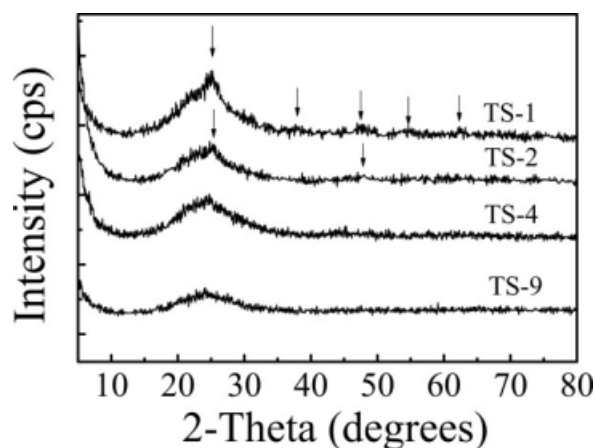


Figure 3 XRD curves of the catalysts.

later); as a result, the inner part of the titanium could hardly come into contact with PVP in the solution, so only some of the titanium could really react with PVP, and thus the PVP content of TSP-24 was low. As for the other samples, the same trend could be found; the catalysts with the Si/Ti molar ratio of 2 had the lowest weight percentage of PVP, which was far less than the theoretical values (Table I).

EPMA study

The Si/Ti molar ratios in the catalysts were determined by EPMA testing. The results are listed in Table I. Clearly, in the range of this study, the contents of titanium and silicon were controllable. The practical Si/Ti molar ratios in the TS series catalysts matched the theoretical values well. Furthermore, for the TSP series catalysts, the incorporation of PVP did not affect the Si/Ti molar ratios. For example, the value of Si/Ti (mol/mol) was 1.8 in TS-2, and the values of Si/Ti (mol/mol) for TSP-22, TSP-24, and TSP-28 were close to one another and around 2.0, matching the theoretical value well.

The aforementioned results indicated that the Si/Ti molar ratios could be well controlled, whereas the content of PVP was influenced by the amount of TiO₂.

XRD study

Figure 3 presents XRD curves of the catalysts. Clearly, when the TiO₂ content was low (e.g., TS-9 and TS-4), no typical TiO₂ crystal diffraction peaks could be found, and the whole substance seemed to be totally amorphous in agreement with Wang et al.³⁵ As the TiO₂ content increased, the diffraction peaks of TiO₂ started to emerge. For the XRD curves of TS-2, the peaks of TiO₂ crystals could be discerned. When the Si/Ti ratio reached 1, these peaks

became distinct, indicating that the TiO₂ crystals became more evident. On the basis of the XRD curves of TS-1, the TiO₂ crystals should be in the form of anatase.^{35,36} According to these results, it could be concluded that TiO₂ did form multilayer structures in TSP-22, TSP-24, and TSP-28 because the TSP series catalysts were obtained by the addition of a specific amount of PVP to the corresponding TS series catalysts, and these results confirmed our expectations based on the TGA results.

XPS study

PVP has been considered to be able to form some kind of complex with transition metals. Zhang et al.³⁷ synthesized PVP-supported metal complexes to act as polycondensation catalysts for polyesters. Also, PVP has been considered as a template for the synthesis of TiO₂ particles with a desired structure.^{33,34} Therefore, there must be some chemical interactions between titanium and PVP. XPS spectra confirmed our expectations, as shown in Table III. The introduction of PVP did change the chemical environment of titanium. For example, the binding energy of Ti_{2p} in TS-9 was 459.7 eV, and this was in good accordance with Pabon et al.³⁸ The binding energy of Ti_{2p} varied after treatment with different amounts of PVP. For TSP-92, the N/Ti molar ratio was low, about 2. As a result, the binding energy of Ti_{2p} in TSP-92 was quite close to that of TS-9, which was shown to be around 459.1 eV, 0.6 eV lower than that of TS-9. However, when N/Ti increased to 3.4 (practical ratio for TSP-94), the binding energy of Ti_{2p} drastically decreased to about 458.5 eV, 1.2 eV lower than that of TS-9. Clearly, titanium was not sufficiently coordinated by PVP in TSP-92, so the binding energy of Ti_{2p} changed little. As for TSP-98, the binding energy of Ti_{2p} (458.2 eV) hardly changed in comparison with that of TSP-94 because coordinative saturation for titanium would occur when the

TABLE III
Bonding Energy of Ti_{2p} in the Catalysts

Sample	Si/Ti (mol/mol)	N/Ti (mol/mol)	Bonding energy of Ti _{2p} (eV)
TS-2	1.8	—	458.8
TSP-22	1.8	0.7	458.4
TSP-24	2.2	0.8	458.1
TSP-28	2.2	1.0	458.3
TS-4	3.3	—	459.4
TSP-42	3.8	1.8	458.9
TSP-44	4.1	3.5	458.0
TSP-48	3.7	3.9	457.8
TS-9	7.5	—	459.7
TSP-92	7.9	2.1	459.1
TSP-94	8.3	3.4	458.5
TSP-98	7.8	4.0	458.2

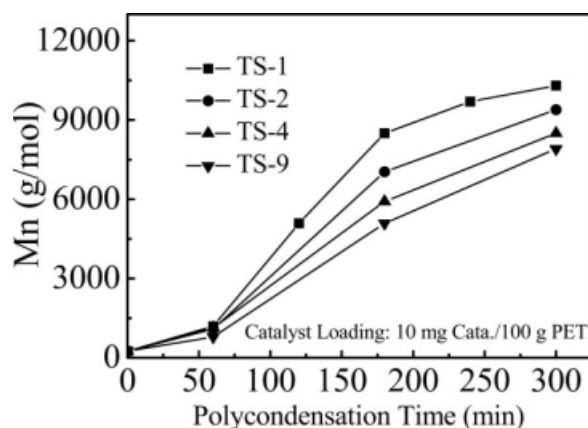


Figure 4 Plots of the number-average molecular weight (M_n) versus the polycondensation time of PET catalyzed by the TS series catalysts.

N/Ti ratio got close to 4.^{33,37} The same trend could be found for TSP-42, TSP-44, and TSP-48. The situation became a little more complicated when TSP-22, TSP-24, and TSP-28 were taken into consideration. As discussed previously, TiO_2 might form a multi-layer structure on the surface of SiO_2 in the case of TSP-22, TSP-24, and TSP-28; as a result, only some of the titanium in these catalysts could come into contact with PVP. Therefore, the binding energy of Ti_{2p} in TSP-22 would be close to that of TSP-24 and TSP-28. In short, PVP could chemically interact with titanium, changing its binding energy. When the practical N/Ti molar ratio reached about 3.5, the titanium atoms might be almost coordinatively saturated; further increasing the content of PVP would result in coordinative saturation of titanium. Because titanium was the key element that could catalyze the synthesis of PET, the differences in the binding energy of Ti_{2p} in the catalysts must have had some effects on their catalytic activities. Ahmadnian et al.³⁹ found that compared with nonchelated titanium derivatives, chelated titanium compounds were less active but more selective. In this study, PVP was expected to coordinate with titanium when titanium was in the form of TiO_2 (not organic titanium compounds), so it would be interesting to study the activities of these novel catalysts.

Catalyst activities in polycondensation

Figure 4 illustrates plots of the molecular weight versus the polycondensation time of PET catalyzed by the TS series samples. Clearly, the differences in the activities of the catalysts could be assigned to the TiO_2 contents. When the TiO_2 content was low (e.g., TS-9), the polymerization process took a very long time, and the molecular weight of the final product was only about 8000 g/mol. As the percentage of TiO_2 increased, the rate of polycondensation

increased gradually. In the case of TS-1, the obtained material had a molecular weight around 10,000 g/mol. However, over 300 min was needed. Therefore, the TS series catalysts were of no practical use because of the low catalytic activities.

The addition of PVP greatly elevated the activities of the catalysts. The times for the intrinsic viscosities of the polymers catalyzed by TSP series catalysts to reach about 0.70 dL/g (the corresponding molecular weight was ca. 20,000 g/mol) are shown in Table IV. Apparently, according to Table IV, the amount of PVP was the critical factor that influenced the catalytic activities of the catalysts. On the basis of the XPS results, PVP could affect the chemical environment of titanium; the mechanism of PET chain growth involves coordination of the metal ion to the ester carbonyl bond,⁸ so the amount of PVP had to have a great effect on the activities of the catalysts. Obviously, if the Si/Ti ratio remained constant, the catalysts with an N/Ti ratio of about 3.5 (practical ratio for TSP-24, TSP-44, and TSP-94) had the strongest ability to catalyze the synthesis of PET. Increasing the quantity of PVP would have resulted in the coordinative saturation of titanium (N/Ti ratio ~ 4), lowering the activities of the catalysts to some extent.^{37,40} Also, excessive PVP led to a decreased content of the effective part in the catalyst. When the N/Ti molar ratio was 2, the PVP contents were too low, so the activities of these catalysts were close to those of the corresponding TS series catalysts.

The Si/Ti ratio was another factor that could affect the activities of the catalysts. When the N/Ti ratio was held constant, the catalysts with a 9 : 1 Si/Ti ratio had the lowest activities. Clearly, in TSP-92, TSP-94, and TSP-98, the titanium contents were low, and this resulted in a longer polymerization time. For TSP-42, TSP-44, and TSP-48, the TiO_2 content increased. Usually, within a certain range, a more effective component would lead to higher activities

TABLE IV
Times for the Polymerization Systems Catalyzed by TSP Series Catalysts Reaching an Intrinsic Viscosity of About 0.7 dL/g

Catalyst	Polycondensation Time (min)
TSP-22	215
TSP-24	135
TSP-28	170
TSP-42	230
TSP-44	100
TSP-44	125 ^a
TSP-48	155
TSP-92	350
TSP-94	195
TSP-98	230

^a The intrinsic viscosity that was reached was 0.85 dL/g (molecular weight $\sim 25,000$ g/mol).

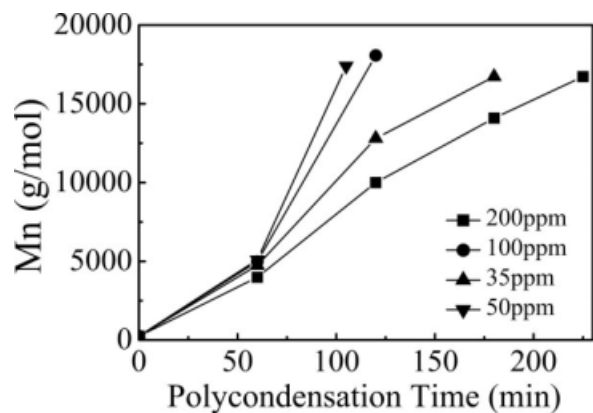


Figure 5 Plots of the number-average molecular weight (M_n) versus the polycondensation time with different catalyst (TSP-44) loadings.

for catalysts. As for the catalysts with a 2 : 1 Si/Ti ratio, although the TiO_2 content was further elevated, TiO_2 might have existed in the form of crystals, so only some could interact with PVP and react with the growing polymer chain. Therefore, the catalytic activities were not improved.

In short, the PVP contents of the catalysts were the most important factor that determined the activities of the catalysts. The coordination between PVP and titanium greatly increased the catalytic efficiency of the catalysts. However, once titanium was coordinatively saturated, the activity of the corresponding catalyst was lowered, as mentioned in the literature.³⁷ Unlike the results reported by Ahmadnian et al.,³⁹ the activity of titanium derivatives was improved after chelation; this might have been caused by the differences in the basic properties of TiO_2 and organic titanium compounds. However, the details of the mechanism by which PVP affected

the activities of the catalysts still need to be further investigated.

On the basis of this discussion, TSP-44 had the highest activity of the catalysts synthesized in this study. As shown in Table IV, PET catalyzed by 50 ppm TSP-44 needed only 125 min to reach the molecular weight of about 25,000 g/mol. To determine the best quantity of the catalyst (TSP-44) added to the polymerization system, a series of PET polycondensation experiments with various TSP-44 contents were conducted. Figure 5 illustrate plots of the molecular weight versus the polycondensation time with different catalyst loadings. Increasing the amount of TSP-44 did not shorten the polymerization time but slightly prolonged it. It is well known that PET polycondensation catalysts, especially titanium compounds, not only accelerate the polymerization process but also aggravate side reactions, such as thermal degradation. Therefore, the addition of more catalyst might bring on a longer polymerization time and undesired color in the final products because of side reactions. In the range of this study, the optimal concentration of TSP-44 was 5 mg of catalyst/100 g of PET, only 10–20 wt % of the amount of Sb_2O_3 needed to finish the polycondensation of PET within a similar time. Thus, the catalyst TSP-44 synthesized in this study possessed great catalytic activity.

Properties of PET catalyzed by the catalysts synthesized in this study

The properties of PET catalyzed by TSP series catalysts were compared with the properties of those synthesized with Sb_2O_3 (called P-Sb), TBT,⁴¹ and TiO_2 -based catalysts (P-Ti/Si; Ti/Si molar ratio = 9). The molecular weights of PET samples synthesized

TABLE V
Properties of the PET Samples

Sample	T_m (°C) ^a	T_c (°C) ^b	[COOH] (mmol/kg)	DEG content (wt %)	T_{on} (°C) ^c	L	b
P-TSP22	255	182	17.7	0.99	419	88.9	5.8
P-TSP24	253	170	24.2	0.79	424	79.0	5.6
P-TSP28	254	176	16.9	0.92	410	82.3	8.1
P-TSP42	254	174	22.2	0.83	422	84.5	5.2
P-TSP44	258	202	10.7	0.71	432	88.8	3.1
P-TSP48	254	174	19.6	0.87	421	86.5	5.3
P-TSP92	252	168	32.5	1.10	412	82.0	7.3
P-TSP94	250	173	21.8	0.80	426	90.0	5.4
P-TSP98	253	172	28.6	1.02	412	87.3	6.8
P-Ti/Si ^d	254	190	16.7	1.79	419	70.2	10.1
P-Sb ^e	253	194	17.7	1.12	423	60.6	3.4

^a Melting temperature from the second DSC heating scan.

^b Crystallization temperature from the cooling DSC scan.

^c Initial weight loss temperature based on the TGA study.

^d Catalyst loading = 5 mg of catalyst/100 g of PET; polycondensation time = 120 min.

^e Catalyst loading = 30 mg of catalyst/100 g of PET; polycondensation time = 135 min.

by TS series catalysts were too low, so the properties of these samples were not characterized.

CEG and DEG are the two main byproducts that can negatively influence the properties of PET. CEG can impair the hydrolytic stability of the product and cause discoloration, whereas the labile ether links in DEG are sites of potential weakness in PET. The contents of CEG and DEG depend on the polymerization routes and the kinds of catalysts. Because the synthesis processes of PET were almost the same for every sample, the polycondensation catalysts had to be the primary factors that influenced the qualities of the products. The contents of CEG and DEG of the PET samples are listed in Table V. Moreover, the chroma L and b values of the samples are also shown in Table V to describe the color of the products.

TBT exhibited very high activity: the polymerization process could be finished within 60 min, whereas the addition of TBT was only 25 ppm. However, because of the poor selectivity and stability of TBT, the product had to be discolored, for the chroma b value was up to 8.8 even when phosphorus compounds were used as stabilizers.⁴¹ Among the PET samples catalyzed by TSP series catalysts, the contents of CEG and DEG were lowest for the samples in which the corresponding catalyst had a practical N/Ti molar ratio equal to about 3.5. This trend seemed to coincide with the activities of the catalysts; PET products synthesized with catalysts with higher activities had lower CEG and DEG contents. This might be due to the fact that the temperature of the PET polycondensation step is very high, usually up to 280°C, and a long time in this severe environment must have some negative effects on the macromolecules, bringing on thermal degradation or other side reactions. Another possibility is that the coordination between titanium and PVP improved the selectivity of the catalysts, reducing the production of the byproducts.³⁹ However, this possibility needed further investigation. The PET products synthesized by TSP-44 (P-TSP44) had the best quality of the PET prepared in this study; the contents of CEG and DEG were 10.7 mmol/kg and 0.71 wt %, respectively, lower than those of P-Sb and P-Ti/Si. Simultaneously, P-TSP44 had a better appearance because the chroma b value was lower than 4 and the L value was around 90; this meant that the discoloration could be negligible. Although titanium-based catalysts for polyesters have been reported to negatively influence the properties and color of the final products because of their poor selectivity and stability,^{7,12} PET products with excellent properties were obtained in this study without any stabilizer, such as phosphorus compounds.

The thermal properties of the products are also presented in Table V. Because DEG was considered

a potential weakness in PET and CEG could trigger the thermal degradation of the polymer, the thermal stability of the PET samples was dependent on the contents of the two substances. Also, DEG broke the homostructure of the PET macromolecular chains, leading to decreased melting and cooling crystallization temperatures.

According to the data listed in Table V, the initial weight loss temperatures based on the TGA study of the PET samples greatly depended on the CEG and DEG contents. For example, the initial weight loss temperature of P-TSP92 was around 412°C, almost 20° lower than that of P-TSP44, because the DEG contents of P-TSP92 were 50% higher than those of P-TSP44 and the CEG content of P-TSP92 was almost 3 times as much as that of P-TSP44.

The melting and crystallization temperatures of the PET samples were greatly influenced by the contents of DEG. With the DEG contents reduced from 1.1 to 0.71 wt %, the crystallization temperatures of the corresponding PET samples increased from 168 (P-TSP92) to 202°C (P-TSP44). Also, a significant elevation of the melting temperatures was observed. The melting and crystallization temperatures of P-TSP44 were a bit higher than those of P-Ti/Si.

In short, the PET samples catalyzed by the catalysts synthesized in this study, especially TSP-44, exhibited superior properties, much better than those of the samples prepared with the traditional antimony-based catalysts and the novel TiO₂-based catalyst with a high titanium content.

CONCLUSIONS

A series of PET polycondensation catalysts based on a TiO₂/SiO₂ sol were prepared in this study. The catalysts varied in their PVP content and Si/Ti molar ratio. TGA and EPMA studies revealed that the catalysts were thermally stable and that the Si/Ti molar ratios of the catalysts could be well controlled, whereas the content of PVP was influenced by the amount of TiO₂. XPS results indicated that PVP had some interactions with the titanium atoms and modified the chemical environment of titanium.

The coordinative effects between titanium and PVP were the key factors that determined the activities of the catalysts. When the N/Ti molar ratio was 3.5, the activities of the corresponding catalysts reached the peak. Increasing the PVP content resulted in coordinative saturation of titanium, leading to decreased activity of the catalyst. On the other hand, less PVP might impair the coordination effects of PVP and drastically diminish the catalytic activities. In the range of this study, TSP-44 possessed the highest activities, much better than those of the traditional antimony-based polycondensation catalysts.

The properties of the PET samples catalyzed by the catalysts synthesized in this study were characterized. The compositions of the catalysts played a great role in the properties of the final products. PET samples prepared by the catalysts with higher activities, such as P-TSP44, had lower DEG and CEG contents and better color and thermal properties. For P-TSP44, the DEG content was 0.71 wt %, and the chroma *b* value was about 3; this was better than the PET samples synthesized with Sb_2O_3 and the novel TiO_2 -based catalyst with a high titanium content.

References

- Chang, J. H.; Kim, S. J.; Joo, Y. L.; Im, S. *Polymer* 2004, 45, 919.
- Li, Y.; Ma, J. H.; Wang, Y. M.; Liang, B. R. *J Appl Polym Sci* 2005, 98, 1150.
- Ke, Y. C.; Long, C. F.; Qi, Z. N. *J Appl Polym Sci* 1999, 71, 1139.
- Ou, C. F.; Ho, M. T.; Lin, J. R. *J Polym Res* 2003, 10, 127.
- Toufaily, F. A.; Feix, G.; Reichert, K. H. *J Polym Sci Part A: Polym Chem* 2006, 44, 1049.
- Toufaily, F. A.; Feix, G.; Reichert, K. H. *Macromol Mater Eng* 2006, 291, 1144.
- MacDonald, W. A. *Polym Int* 2002, 51, 923.
- Biros, S. M.; Bridgewater, B. M.; Villeges-Estrada, A.; Tanski, J. M.; Parkin, G. *Inorg Chem* 2002, 41, 4051.
- Shotyk, W.; Krachler, M. *Environ Sci Technol* 2007, 41, 1560.
- Ahmadnian, F.; Reichert, K. H. *Macromol Symp* 2007, 259, 188.
- Aharoni, S. M. *Polym Eng Sci* 1998, 38, 1039.
- Fineli, L.; Lorenzetti, C.; Messori, M.; Sisti, L.; Vannini, M. *J Appl Polym Sci* 2004, 92, 1887.
- Massa, A.; Scettri, A.; Contessa, S.; Valeria, B.; Concilio, S.; Iannelli, P. *J Appl Polym Sci* 2007, 104, 3071.
- Karayannidis, G. P.; Roupakias, C. P.; Bikiaris, D. N.; Achilias, D. S. *Polymer* 2003, 44, 931.
- Otton, J.; Rattom, S. *J Polym Sci Part A: Polym Chem* 1988, 26, 2183.
- Otton, J.; Rattom, S.; Vasnev, V. A.; Markova, G. D.; Nametov, K. M.; Bakhmutov, V. I.; Komarova, L. I.; Vinogradova, S. V.; Korshak, V. V. *J Polym Sci Part A: Polym Chem* 1988, 26, 2199.
- Siling, M. I.; Laricheva, T. N. *Russ Chem Rev* 1996, 65, 279.
- Pilati, F.; Munari, A.; Manaresi, P.; Bonora, V. *Polymer* 1985, 26, 1745.
- Ravens, D. A. S.; Ward, I. M. *Trans Faraday Soc* 1967, 21, 557.
- Martl, M.; Mezger, T.; Oberlein, G.; Haferland, K.; Boehringer, B.; Berger, U. U.S. Pat. 5,789,528 (1997).
- Lustig, S. R.; Burch, R. R.; McCarron, E. M. U.S. Pat. 6,034,203 (2000).
- Schmidt, W.; Thiele, U.; Griebler, W.; Hirthe, B.; Hirschberg, E. U.S. Pat. 5,656,716 (1997).
- Yamamoto, T. Eur. Pat. 1,110,988 (2001).
- Bell, A.; Strickland, H.; Tenn, K. U.S. Pat. 3,463,742 (1969).
- Banach, T. E.; Berti, C.; Colonna, M.; Fiorini, M.; Marianucci, E.; Messori, M.; Pilati, F.; Toselli, M. *Polymer* 2001, 42, 7511.
- Banach, T. E.; Colonna, M. *Polymer* 2001, 42, 7517.
- Banach, T. E.; Berti, C.; Colonna, M.; Fiorini, M.; Marianucci, E.; Messori, M.; Pilati, F.; Toselli, M. *Polymer* 2003, 44, 4773.
- Yamanaka, S.; Inoue, Y.; Hattori, M.; Okumura, F.; Yoshikawa, M. *Bull Chem Soc Jpn* 1992, 65, 2494.
- Conix, A. *Makromol Chem* 1958, 26, 226.
- Berti, C.; Bonora, V.; Colonna, M.; Lotti, N.; Sisti, L. *Eur Polym J* 2003, 39, 1595.
- Pilati, F.; Toselli, M.; Messori, M.; Manzoni, C.; Turturro, A.; Gattiglia, E. G. *Polymer* 1997, 38, 4469.
- Wang, W. J.; Gu, M. Y.; Jin, Y. P. *Mater Lett* 2003, 57, 3276.
- Wang, P.; Wang, D. J.; Li, H. Y.; Xie, T. F.; Wang, H. Z.; Du, Z. L. *J Colloid Interface Sci* 2007, 314, 337.
- Ou, Y.; Lin, J. D.; Fang, S. M.; Liao, D. W. *Catal Commun* 2007, 8, 936.
- Wang, S. P.; Ma, X. B.; Guo, H. L.; Gong, J. L.; Yang, X.; Xu, G. H. *J Mol Catal A* 2004, 214, 273.
- Bogdanichikova, N.; Pestryakov, A.; Farias, M. H.; Diaz, J. A.; Avalos, M.; Navarrete, J. *Solid State Sci* 2008, 10, 908.
- Zhang, Y.; Yang, G. H.; Li, X. X.; Luo, W.; Huang, M. Y.; Jiang, Y. Y. *Polym Adv Technol* 1999, 10, 108.
- Pabon, E.; Retuert, J.; Quijada, R.; Zarate, A. *Micropor Mesopor Mater* 2004, 67, 195.
- Ahmadnian, F.; Velasquez, F.; Reichert, K. H. *Macromol React Eng* 2008, 2, 513.
- Hirai, H.; Toshima, N. In *Tailored Metal Catalysis*; Iwasawa, Y., Ed.; Reidel: Dordrecht, 1986; p 87.
- Putzig, E. D.; McBride, E.; Do, H. Q.; Trainham, J. A.; Jaeger, H. L.; Schulte, H. Chin. Pat. 99,805,130.6 (1999).