TPA-ZrO$_2$-SiO$_2$-Catalyzed Polyesterification of TMP Polyester

Li Fang*[a,b], Xiang-Dong Geng [a], Diansheng Liu [a], Jian Gao [a], Li-Juan He [a], Ya-Juan Hao [a] and Surin Saipanya**[c]
[a] School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, P R China.
[c] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200 Thailand.
Author for correspondence; e-mail*: fangli@sxu.edu.cn , e-mail**: saipanya@chiangmai.ac.th
Received: 22 April 2009
Accepted: 23 October 2009

ABSTRACT

A series of tungstophosphoric acid (TPA)-ZrO$_2$-SiO$_2$ particles (30 wt% TPA) with various ZrO$_2$ contents were prepared by sol-gel method. Using heptanoic acid (HA) as an end-capping agent, trimethylolpropane (TMP) polyester plasticizers were prepared by the TPA-ZrO$_2$-SiO$_2$-catalyzed polyesterification of TMP and adipic acid (AA). The particles were characterized by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), fourier transform infrared (FT-IR), ultraviolet-visible diffuse reflectance (UV-VIS DR) and transmission electron microscopy (TEM). TPA with 200 nm microspheric particles were mostly embedded into the network of ZrO$_2$-SiO$_2$ mixed oxide. Mole ratio of ZrO$_2$: SiO$_2$ was 3:7 resulted in the most suitable composition for the catalyzed polyesterification. Excess ZrO$_2$ induced destruction of the ZrO$_2$-SiO$_2$ framework whilst some TPA only adsorbed on the support surfaces. TPA-3Z-7S exhibited high catalytic activity and better controllable of the weight average molecular weight (MW) distribution of the TMP polyesters. Under the optimal reaction condition the TMP polyester with MW between ca. 600- 3800 was achievable prepared with excellent yield (up to 93%).

Keywords: TPA-ZrO$_2$-SiO$_2$, sol-gel method, TMP polyester, polyesterification.

1. INTRODUCTION

Polyester plasticizers have attracted a lot of polymer researchers due to their superior plasticizing properties such as low volatility and excellent resistance to extraction and migration, good biodegradabilities and non-toxicities [1-3].

Aliphatic dicarboxylic acid esters, linear ester structures, tend to be incompatible with polymers. With molecular weight around 400, they are too volatile in general use [1]. Therefore, the synthesis of the higher molecular weight polyesters having good compatibilities with polymers is still one of the most challenging research topics.

Trimethylolpropane (TMP), a well-known branched polyol, has been used as a
core moiety in the preparation of hyperbranched polyester polymers [4-11]. In the present work, TMP was chosen as a core of the branched polyester plasticizer to improve compatibility and thermal stability of the polymers. Most esterifications are reversible acid-catalyzed reactions employing inorganic acid catalysts such as sulfuric acid and phosphoric acid and the difficulty of catalyst separation from the products and acidic waste produced from the preparation step are obstacle.

As an environmental catalyst, tungstophosphoric acid (H₃PW₁₂O₄₀, TPA), a very strong acid with a well-characterized microstructure, has been widely used as homogeneous and heterogeneous catalysts in alkene hydrolysis, esterification, acylation, trans-esterification, acetalization [12-19], etc. The TPA possesses low specific surface and high solubility in polar solvent while the supported TPA catalyst becomes to be greater catalytic activity, insolubility and easy for separation. The preparation of TPA supported on silica [20-28], zirconia [29-32], active carbon [33, 34] and MCM-14 [35, 36] was studied by either immersion or sol-gel method. A limitation of this catalyst for applications is dissolubility of the TPA in the reaction medium [21].

ZrO₂-SiO₂ mixed oxides have been used as catalyst [37-41] and catalyst support [42-49] due to their strong surface acidity, high catalytic activity and thermal stability. For instance, ZrO₂-SiO₂ supported phosphomolybdic acid in methanol oxidation resulted in the introduction of ZrO₂ into the supports led to a change in the catalytic character [46]. This mixed oxide would be a promising support to develop the TPA for applications.

In this work, the sol-gel preparation of TPA-ZrO₂-SiO₂ and its application as catalyst for the polyesterification are stated. A series of TPA-ZrO₂-SiO₂ particles (30 wt% TPA) with various ZrO₂ contents have been successfully prepared by sol-gel method and then characterized by means of ICP-AES, XRD, FTIR, UV-VIS DR and TEM. The TPA-ZrO₂-SiO₂-catalyzed polyesterification of AA with TMP using HA as an end capping agent was prepared and the factors affecting yield and Mw of the TMP polyesters were discussed.

2. MATERIALS AND METHODS

2.1 Synthesis of TPA-ZrO₂-SiO₂ by sol-gel Method

For TPA-1Z-9Si, zirconium nitrate (1.12 g ZrO(NO₃)₂·2H₂O) dissolved in distilled water (20.3 ml) and tetraethyl orthosilicate (8.5 ml TEOS) dissolved in ethanol (13 ml) were mixed together and kept stirring at 313 K for 1 h. TPA (1.2 g) was then added to the mixture and heated to 353 K. The prepared gel was aged at room temperature for 24 h and then dried in a vacuum drier for 5 h at 353 K. The color of the sample changed from white to light yellow during drying step. Finally, the dried gel was charged to white again after calcination at 723 K [15, 16, 23] for 4 h in a muffle furnace.

According to the mole ratio of the two oxides, the samples are labeled as TPA-S, TPA-1Z-9S, TPA-3Z-7S and TPA-5Z-5S designated to mole ratio of ZrO₂ and SiO₂ as 0: 100, 10:90, 30:70, 50:50, respectively.

2.2 Characterization of Catalysts

The chemical compositions of the catalyst samples were determined by ICP-AES using a PE Optima-5300 V ICP-OES instrument. XRD patterns were recorded on a Japanese Rigaku D/MAX-250 diffractometer with a Cu Kα irradiation operating at 40 V, 100 mA. Each XRD pattern was recorded in a 2θ range (scattering angle) between 10 and 60°. IR spectra were obtained by a Bruker FT-IR instrument with the number of scans...
16 per second and resolution 4 cm\(^{-1}\). UV-VIS DR spectra were recorded on a Cary 300 UV-VIS spectrophotometer at ambient conditions using MgO as a reference in reflectance mode. TEM images were obtained by JEOL-TEM 200CX transmission electron spectroscopy operated at 100 kV. The molecular weight (weight average molecular weight, MW) of the TMP polyester was measured by gel permeation chromatography (GPC, PL GPC-50, UK) with the mobile phase of tetrahydrofuran (THF), using PLgel 5 \(\mu\)m 10\(^{2}/10\(^{3}/500\) Å/100 Å 50x7.5mm column combinations and a differential refractive index detector for measurements. The flow rate was 1 ml/min and the column oven temperature was 313 K. 100µml TMP polyester solution (3~5mg/ml) was injected into the chromatograph and the eluted solution was collected between 6 min and 14.5 min.

2.3 Catalytic Polyesterification for TMP Polyester

The polyesterification reaction of TMP and AA catalyzed by TPA-ZrO\(_2\)-SiO\(_2\) is illustrated in scheme 1. A four-necked (500 ml) round bottom flask was equipped with a condenser, a water separator, a thermometer and a stirrer. 27.0 g TMP, 29.2 g AA, 0.5 g TPA-ZrO\(_2\)-SiO\(_2\) and 170 ml xylene were added into the flask at room tempera-

![Scheme 1. Reaction scheme for synthesis of TMP polyester.](image-url)
ture. After the mixture was maintained at 413 K for about 10-140 h, the end capping agent 44.0 ml HA was then added to the flask through a dropping funnel over a period of 30 min while stirring. The mixture was then refluxed for another 2 h to complete the reaction. The refluxed mixture was cooled to 340-350 K, filtered to separate the reaction liquid from the solid catalysts. The solvent and excess reactant were removed via a rotary evaporator. The crude was diluted with cyclohexane, washed with 10 wt% sodium carbonate solution and 3 times with distilled water to remove the residual acid in the mixture. 48.6 g TMP polyester as colourless viscous liquid was obtained after vacuum distillation.

3. RESULTS AND DISCUSSION

3.1 Characterization of Catalysts

3.1.1 Composition and Surface Area of Various Catalysts

The compositions of the TPA catalysts with various ZrO$_2$/SiO$_2$ mole ratios and the surface areas measured by BET method are listed in Table 1. It can be seen that the acquired TPA contents increase corresponding to an addition of ZrO$_2$ contents indicating that TPA was efficiently incorporated into the SiO$_2$-ZrO$_2$ matrix. The results also prove that the surface areas of the TPA catalysts increase steadily with an increase of zirconium amounts, implying the dispersion of the TPA catalysts also increases with an addition of zirconia.

3.1.2 XRD Patterns Analysis

XRD patterns of the TPA catalyst samples with different zirconium contents are shown in Figure 1.

The pure TPA shows the fine crystalline X-ray patterns of TPA Keggin structure, all the sol-gel prepared samples show broad and flat peaks indicating that the prepared catalysts were amorphous. It was therefore assumed that TPA molecules were exceedingly well incorporated into the ZrO$_2$-SiO$_2$ framework. The 2 theta angle shifts slightly to a higher degree as the zirconia contents increase, which is in agreement with the results obtained by Zhan et al.[48] and Wu et al.[49] previously reported that the wave number of Si-O-Si asymmetric stretch vibration $\nu_{as}$ (Si-O-Si) is at 1100 cm$^{-1}$ in pure SiO$_2$ but it shifts to lower wave number for the SiO$_2$-ZrO$_2$ matrix. Moreover, the band at 800 cm$^{-1}$ corresponding to symmetric stretching vibrations $\nu_{s}$ (Si-O-Si) of Si-O-Si decrease to become negligible with the increase of ZrO$_2$ contents. Our acquired

Table 1. Composition and surface area of various catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Amount of ZrO$_2$ (wt% Zr)</th>
<th>Amount of SiO$_2$ (wt% Si)</th>
<th>TPA loaded (wt% W)</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TPA</td>
<td>0.0</td>
<td>0.0</td>
<td>74.8</td>
<td>6.00</td>
</tr>
<tr>
<td>TPA-S</td>
<td>0.0</td>
<td>30.5</td>
<td>20.9</td>
<td>66.62</td>
</tr>
<tr>
<td>3Z-7S</td>
<td>36.7</td>
<td>26.9</td>
<td>0.0</td>
<td>112.58</td>
</tr>
<tr>
<td>TPA-1Z-9S</td>
<td>9.4</td>
<td>26.8</td>
<td>21.3</td>
<td>118.65</td>
</tr>
<tr>
<td>TPA-3Z-7S</td>
<td>23.5</td>
<td>17.8</td>
<td>22.0</td>
<td>135.12</td>
</tr>
<tr>
<td>TPA-5Z-5S</td>
<td>35.9</td>
<td>12.6</td>
<td>22.5</td>
<td>140.79</td>
</tr>
</tbody>
</table>

3.1.3 IR Spectra of Catalysts

It is obtained from Figure 2 that the four characteristic peaks at 1080, 983, 889 and 798 cm$^{-1}$ can be attributed to pure TPA (a). The peak intensities of the supported catalysts decrease gradually with the zirconia addition. Zhan et al.[48] and Wu et al.[49] previously reported that the wave number of Si-O-Si asymmetric stretch vibration $\nu_{as}$ (Si-O-Si) is at 1100 cm$^{-1}$ in pure SiO$_2$ but it shifts to lower wave number for the SiO$_2$-ZrO$_2$ matrix. Moreover, the band at 800 cm$^{-1}$ corresponding to symmetric stretching vibrations $\nu_{s}$ (Si-O-Si) of Si-O-Si decrease to become negligible with the increase of ZrO$_2$ contents. Our acquired
IR spectra with bands at 1,082 and 802 cm$^{-1}$ are corresponding to the previous work. It can also be seen that an increase of ZrO$_2$ contents result in strong TPA –S signal observed (1,080 cm$^{-1}$), indicating that the ZrO$_2$ increases the dispersion extent of the support. Reasons can be addressed for these strong signals: the addition of ZrO$_2$ may decrease the Si-O-Si bonds; the TPA peaks were strengthened by ZrO$_2$ addition indicating the destruction of the ZrO$_2$-SiO$_2$ framework and some TPA only adsorbed on the surfaces of the framework. This is consistent with the conclusion drawn from the above surface area measurements. It can be concluded that the Keggin structure of TPA is still maintained after sol-gel process [23, 27]. The excess ZrO$_2$ amounts induced the destruction of the ZrO$_2$-SiO$_2$ framework and only some TPA adsorbed on the surfaces of the framework, which can be further confirmed by TEM micrographs.

### 3.1.4 UV-VIS Spectra of Catalysts

Figure 3 shows the UV-VIS spectra of the catalysts with different ZrO$_2$ contents. UV-VIS characteristic bands of pure TPA are obtained at 254 and 347 nm [27] while 3Z-7S exhibits no such peaks. The evolution of the reflectance wavelength of the supported samples clearly shows that TPA was well incorporated into SiO$_2$-ZrO$_2$ framework without weight loss after being calcined. The peaks red shifted with increasing zirconia.
content, indicating that the interaction between TPA and the support was strengthened. This is consistent with the IR results.

3.1.5 TEM Results

The TEM images of the supported catalyst samples are illustrated in Figure 4.

Figure 3. UV-VIS spectra of the catalysts (calcined at 723K) with different ZrO$_2$ contents; (a) Pure TPA, (b) TPA-5Z-5S, (c) TPA-3Z-7S, (d) TPA-1Z-9S, (e) 3Z-7S and (f) SiO$_2$.

Figure 4. TEM images of the catalysts (calcined at 723 K) with different ZrO$_2$ contents; (a) TPA-S, (b) TPA-1Z-9S (c) TPA-3Z-7S and (d) TPA-5Z-5S.
The zirconia to silica ratio affected the shape of the supported catalysts depicted in Figure 4. Fine TPA-S particles have been obtained in Figure 4 (a). 1 to 9 mole ratio of Zr : Si resulted in the transformation of catalysts particles to be short sticks with length of ca. 20 nm in Figure 4(b). In Figure 4(c) microspheric particles with ca. 200 nm in diameter were obtained at Zr : Si of 3 : 7 indicating that the introduction of zirconia enhanced the interaction between TPA and those supports. Excess ZrO₂ induced the destruction of the ZrO₂-SiO₂ framework as shown in Figure 4 (d) whilst some TPA only adsorbed on the surfaces of the particles. Therefore, our method could be able to prepare TPA incorporated in ZrO₂-SiO₂ framework with high ZrO₂ amount. The results of our catalyst is more promising as the previous work reported that spherical ZrO₂-SiO₂ could be prepared by sol-gel method with less amount of ZrO₂ content (< 18 wt%) [50].

3.2 Catalyzed Polyesterification of TMP and AA

3.2.1 Effect of Zirconium Contents on the Catalytic Activity

TPA-S, TPA-1Z-9S, TPA-3Z-7S, TPA-5Z-5S were employed to catalyze the polyesterification reaction to determine the influence of the zirconia contents on the catalytic activity. As the water is the product of esterification, the polyesterification reaction was monitored by measuring amount of water produced during the reaction.

![Figure 5](image.png)

**Figure 5.** Amount of water produced during the polyesterifications before adding HA in the presence of catalysts containing various ZrO₂ contents: (a) TPA-5Z-5S, (b) TPA-3Z-7S, (c) TPA-1Z-9S and TPA-S.
From the result in Figure 5, the zirconium contents provide no obvious influence on the rate of polyesterification. It can be assumed that the fine TPA was embedded into the oxide supports.

Before adding end capping agent HA, the effect of zirconia contents on the MW distribution of the TMP polyester was investigated by maintaining the polyesterification time for 30 min. In Figure 6, three main MW distribution ranges were obtained for each catalyst, named high MW range, a middle MW range and a low MW range. The results show that the ZrO$_2$-SiO$_2$ mole ratios affected the MW of TMP polyesters.

From the results, ZrO$_2$-SiO$_2$ with mole ratio 3:7 provided the high MW polyester however giving more ZrO$_2$ amounts resulted in low MW polyester. 3:7 mole ratio of ZrO$_2$-SiO$_2$ was chosen for further study of the catalytic polyesterification.

3.2.2 Effect of reaction time

Using TPA-3Z-7S as the catalyst, the influence of the polyesterification time (before addition of the end-capping agent HA) on yield of polyester and its MW distribution were also investigated. In Figure 7, the longer times for the esterification reaction (0.5 – 2.5h) employed the higher the MW of the polyester (2,990 - 6,271) could be achieved, revealing that the MW of the end product can be well regulated by the polyesterification time. As the MW range of commercial polyester plasticizers was reported from 600 to 3500 [1], our method to prepare TMP polyester is one of the promising way for future use.

3.2.3 Reused catalysts for polyesterification

After first use of TPA-3Z-7S, the light yellow catalyst powders were filtered from
Figure 7. Effect of the reaction time on yield and MW distribution of the TMP polyester using TPA-3Z-7S catalyst.

It is obtained that the yield of the poly-

Figure 8. Yield of the TMP polyesters from reused TPA-3Z-7S catalysts.
ester in the highest Mw range decreased from 69% to 61% while that in the middle Mw ranges increase a little after the catalyst was reused for three times. The overall yield of the polyester, however, decreased by only 1% (from 93% to 92%), indicating that the TPA-3Z-7S catalyst is very stable and reusable for the catalytic processes. Therefore, TPA-3Z-7S is a promising catalyst for polyesterification applications.

4. CONCLUSIONS
The TPA-ZrO$_2$-SiO$_2$ catalysts were firstly prepared by a one-step sol-gel method, with TPA being fully incorporated into the ZrO$_2$-SiO$_2$. The addition of zirconium amount into the ZrO$_2$-SiO$_2$ supports improved the catalytic activity and the stability of the nanocatalysts. The optimal ZrO$_2$-SiO$_2$ mole ratio is 3:7 for the polyesterification reaction. The TPA-ZrO$_2$-SiO$_2$ catalysts show high catalytic activity and well MW control in the polyesterification reaction for TMP polyester. Under the optimal reaction conditions, more than 90% yield of the TMP polyester was obtained with MW around 600-3,800. Moreover, the catalysts are readily reusable without loss of catalytic activity.

ACKNOWLEDGEMENT
The authors acknowledge the financial support from the government of Shanxi Province, P R China (Project No. 051140).

REFERENCES


