Hydrolysis of Poly(ethylene terephthalate) Waste Bottles in the Presence of Dual Functional Phase Transfer Catalysts

Lirong Zhang, Jie Gao, Jianzhong Zou, Fengping Yi

School of Perfume and Aroma Technology, Shanghai Institute of Technology, Shanghai 201418, People's Republic of China
Correspondence to: F. Yi (E-mail: zlir77@hotmail.com)

ABSTRACT: The hydrolysis of poly(ethylene terephthalate) (PET) obtained from waste bottles was studied. The dual functional phase transfer catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$ exhibited outstanding catalytic activity to the hydrolysis of PET. Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy were used to confirm the main product terephthalic acid (TPA) of hydrolysis. The effects of temperature, time, particle size of PET and dosage of catalyst on hydrolysis reaction were examined. Under the optimum conditions of reaction temperature 145°C, time 2 h, particle size of PET at 0.5–1 mm and dosage of catalyst at 7 wt %, the conversion of PET and the yield of TPA were almost 100% and 93%, respectively. After easily separated from the product, the catalyst could be reused more than three times without obvious decrease in the conversion of PET and yield of TPA. An economical and convenient process was developed for hydrolysis of PET. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2790–2795, 2013

INTRODUCTION

Poly(ethylene terephthalate) (PET) resin, a common form of plastics, has excellent characteristic features, that is widely used for producing fibers, textiles, video and audiotapes, food packing and containers.[1] With the rapid increase in the production and consumption of PET, the amount of waste PET is growing rapidly. This kind of polyester does not decompose readily in nature, thus, the effective recycling of PET wastes for the preservation of resources and protection of the environment has received considerable attention. Chemical recycling is one of the most important processes leading to total depolymerization of PET to terephthlic acid, ethylene glycol and other chemical substances. Several chemical processes for depolymerization of PET can be summarized by the following technologies: hydrolysis, alcoholysis, aminolysis, and ammonolysis.[2–15] However, most of these reactions require severe conditions, such as long reaction time, high temperature and pressure, or even take place under supercritical conditions and in the presence of a large amount of concentrated acids or bases. Several reports have documented the introduction of different types of solvent systems and catalysts.[16–23] As might be expected, the most environmentally friendly reagent in PET degradation is water and the chemical recycling process of hydrolysis. The traditional acidic hydrolysis process needs concentrated acid. Large quantities of acid cannot be reused and might result in other disadvantages such as equipment corrosion, tedious workup procedure, and

environmental problem. Ionic liquid have attracted increasing interest and much attention in recent years. The hydrolysis of PET using ionic liquid as solvent and acid functionalized ionic liquid as catalyst were also been documented.[18] However, the high cost and complex synthesis route might hinder its wide use. Therefore, it is necessary to explore a new approach for hydrolysis of PET.

Phase-transfer catalysis and micellar catalysis as the conventional reaction media often result in dramatic increases in reaction rates through introducing the surfactant to the reaction systems. Recently, Li's group reported a surfactant-type catalyst that can be synthesized by using a suitable combination of hydrophilic heteropolyanions and lipophilic quaternary ammonium cations, which showed high activity toward selective oxidation of alcohol and sulfur-containing molecules.[24,25] Heteropoly acid is one kind of important solid super acids. Also, phase transfer catalyst agents were studied to depolymerize PET in an alkaline solution medium.[26–29] Therefore, this surfactant-type of catalyst was expected to show activity to the degradation of PET.

In order to develop a more economical and convenient hydrolytic method for PET, we examined the deolymerization of PET in the presence of dual functional phase transfer catalysts. The cheap and wide starting materials sources made the process more economical. Several dual functional phase transfer catalysts were obtained by combination of heteropoly acid and quaternary ammonium salt and used them to facilitate the

hydrolysis of PET. Furthermore, the influences of the reaction conditions on the conversion of PET and yield of terephthalic acid (TPA), and recycling of catalyst were investigated.

MATERIALS AND METHODS

Post-consumer soft drink PET bottles were used as starting materials. These bottles were cleared, dried and cut into small pieces of approximate size after separating from the non-PET components such as labels and caps. Their average molecular weight was measured in a 50:50 (w/w) phenol/1,1,2,2-tetra-chloroethane solution at 25°C, and found to be 1.8×10^4 g/mol. Analytical grade chemical and solvents were obtained from China National Medicines Corp. and used without further treatment. Fourier transform infrared spectroscopy (FT-IR) was carried out on a VERTEX70 FT-IR spectrometer in the range of 4500–400 cm^{-1}. The NMR spectra were recorded on a BRUKER Avance III (500MHz for ^{1}H) in deuteron dimethyl sulfoxide $(CD_3)_2SO$ at room temperature.

Synthesis of Catalysts
A solution of quaternary ammonium cation (6 mmol) in 30 mL of alcohol (95%) was added dropwise into 20 mL aqueous solution of $H_3PW_{12}O_{40}$ (5.76 g, 2.0 mmol) under stirring at room temperature. A white precipitate was immediately formed. After continuously stirring for 2 h, the resulting mixture was filtered and dried at 50°C in vacuum for 24 h to give catalyst.

Hydrolysis of PET Waste Material
In a typical experiment, 3.0 g of PET (w_1), 30 mL water and appropriate quantity of catalyst were added in an autoclave with a stirrer and a thermometer. The mixture was heated up to the given temperature for certain time. The mixture was filtered and centrifuged. The lower layer solid was the recycled catalyst, which was washed with ethanol and water and dried. The upper layer residue was diluted with an equal volume of cold water and a precipitate was obtained and filtered. The filter cake which is mainly TPA and unreacted PET was treated with sodium hydroxide solution to dissolve TPA and then unreacted PET solid was removed by filtration. The undepolymerized PET was collected, dried, and weighed (w_2). The obtained solution is then acidified to pH = 2–3 with concentrated HCl to precipitate TPA. The precipitate was washed with water, dried to afford

Table I. Hydrolysis of PET Using Different Quaternary Ammonium Polytungstophosphate as Catalysts^a

Catalyst	PET conversion (%)	TPA yield (%)
H_2SO_4	83	75
$H_3PW_{12}O_{40}$	82	73
$[(CH_3)_3N(C_{12}H_{25})]_3PW_{12}O_{40}$	93	85
$[(CH_3)_3N(C_{16}H_{33})]_3PW_{12}O_{40}$	100	93
$[(CH_3)_3N(C_{18}H_{37})]_3PW_{12}O_{40}$	98	91
$[(C_4H_9)_4N]_3PW_{12}O_{40}$	89	81
$[(CH_3)_2N(C_{18}H_{37})_2]_3PW_{12}O_{40}$	83	76

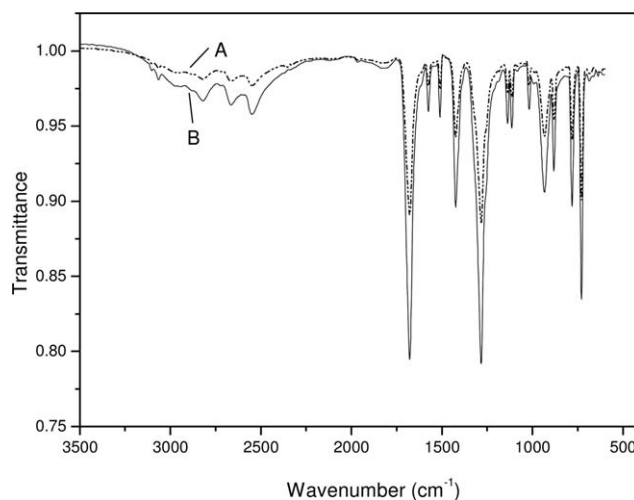^{a} Reaction conditions: 10 wt % catalyst, t = 3 h, T = 160°C.

Figure 1. FT-IR spectra of standard TPA (A) and TPA obtained from hydrolysis reaction (B).

TPA product (w_3). Conversion of PET and yield of TPA were calculated by following formula: Conversion of PET = $[(w_1-w_2)/w_1] \times 100\%$. Yield of TPA = $(w_3/w) \times 100\%$, where w is the weight of TPA which should obtained theoretically.

RESULTS AND DISCUSSION

Effect of Catalyst on Hydrolysis Results of PET
The hydrolysis of PET was tested with the different quaternary ammonium polytungstophosphate catalysts and the results were summarized in Table I. When compared with the catalyst sulfuric acid and $H_3PW_{12}O_{40}$, the quaternary ammonium polytungstophosphate catalyst exhibited better catalytic performance. This is because the dual functional catalysts acted as not only a catalyst to activate the hydrolysis, but also a phase transfer catalyst. From Table I, it can be seen that the size of quaternary ammonium cations play a vital role in the hydrolysis reaction. The catalyst $[(CH_3)_2N(C_{18}H_{37})_2]_3PW_{12}O_{40}$ with two long alkyl chains and $[(C_4H_9)_4N]_3PW_{12}O_{40}$ with four long alkyl chains showed poor activity comparing with the other catalyst, and it might due to the steric hindrance. Instead, the catalysts with only one long alkyl chain exhibited relatively high catalytic activity for the hydrolysis of PET. The results suggested that the catalyst $[(CH_3)_3N(C_{16}H_{33})]_3PW_{12}O_{40}$ exhibited an outstanding performance and was an excellent catalyst for hydrolysis of PET.

The purity of TPA formed was confirmed by the FT-IR and HNMR as shown in Figures 1 and 2, respectively. The FT-IR spectrum of the TPA product showed the same characteristic bands when compared with reference FT-IR spectrum of TPA. The characteristic bands at 2500–3250 cm^{-1}, 1685 cm^{-1}, and 1574–1425 cm^{-1} are related to carboxylic group, carbonyl group, and aromatic ring, respectively. These results show good agreement with the reference data, indicating that the purity of the product in the mentioned method is acceptable. In HNMR spectrum, the signal at δ 8.05 ppm indicated the presence of the four aromatic protons of the benzene ring. Signals at δ13.31 ppm are characteristic of the protons of the carboxy group. The HNMR spectrum also accords very well with the standard
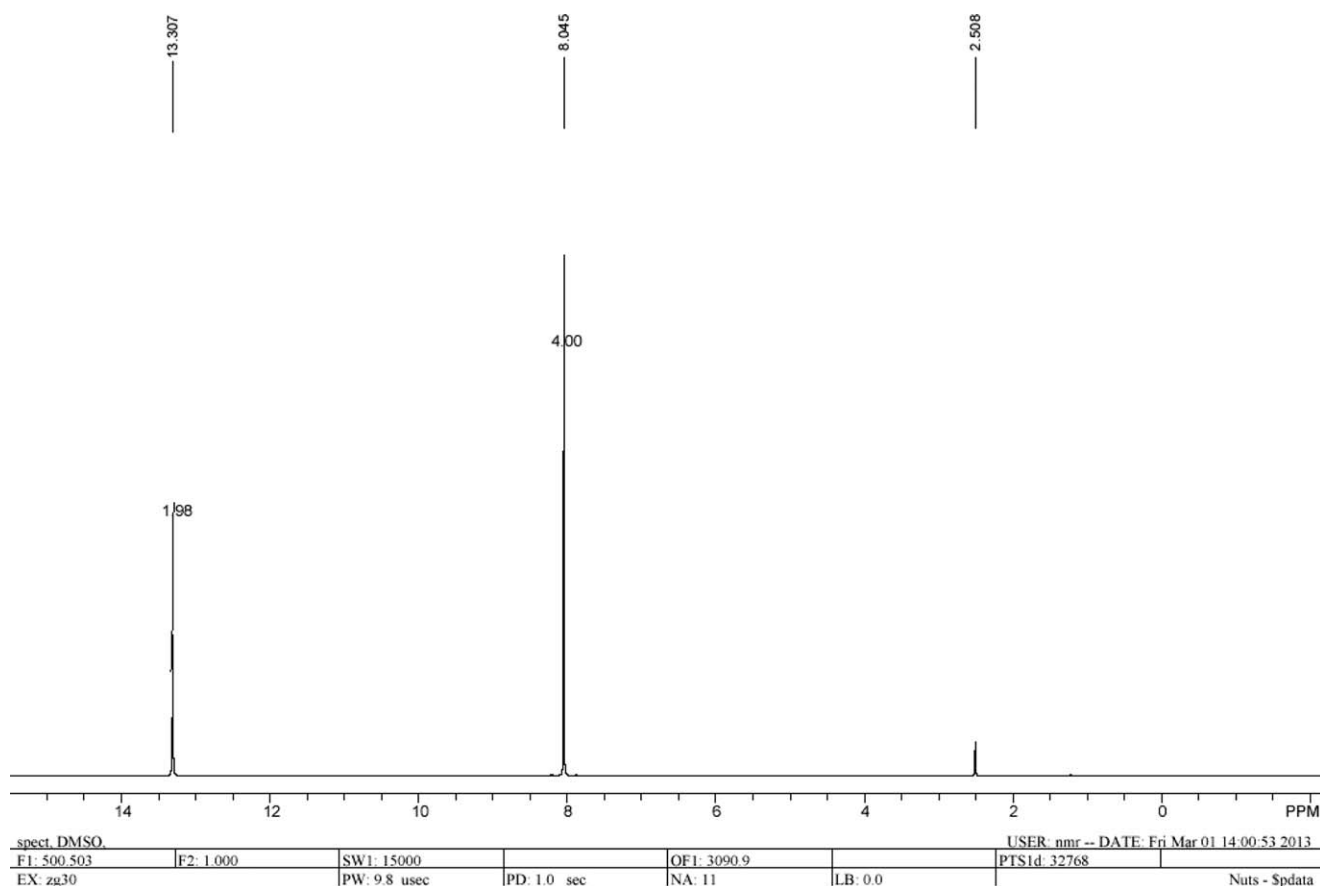
Figure 2. HNMR spectra of TPA obtained from hydrolysis reaction.

sample. These results indicated that the purity of the product obtained from the process described here was acceptable.

Effect of Reaction Conditions on Hydrolysis Results of PET

The effect of reaction temperature on the conversion of PET and the yield of TPA was investigated and the results were shown in Figure 3. A great increase in the PET conversion and TPA yield with increasing reaction temperature was observed.

The conversion of PET increased apparently and rapidly reached 100% when the temperature was higher than145°C. Furthermore, the yield of TPA dramatically increased from 23 to 93% when the hydrolysis temperature rose from 130 to 145°C. Thus, the high temperature was beneficial to the formation of TPA from the hydrolysis of PET. The best hydrolysis temperature that we choose for the optimum condition was 145°C.
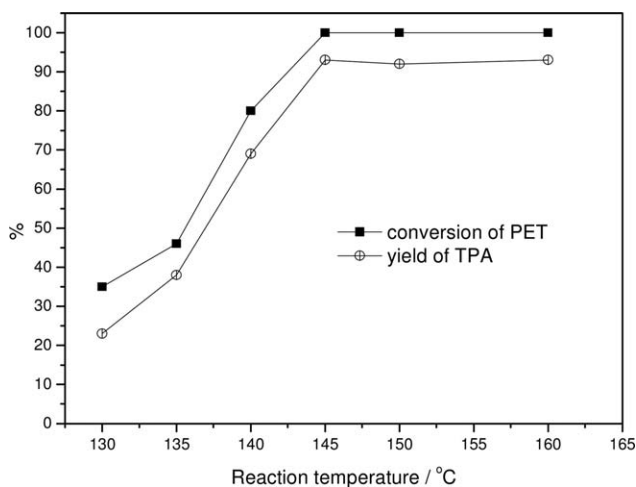

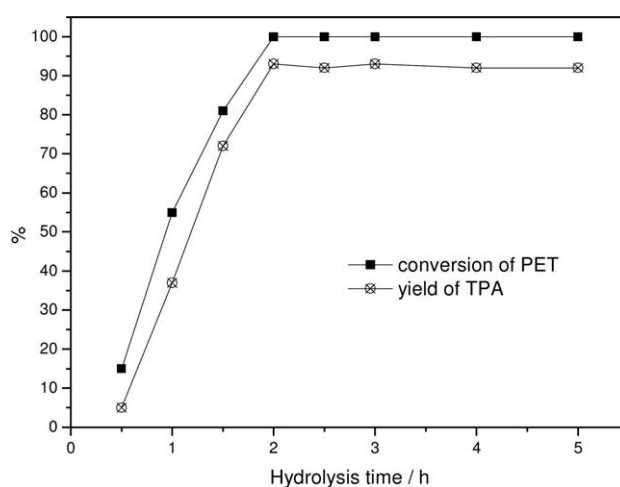**Figure 3.** Effect of reaction temperature on the hydrolysis of PET (time: 3 h, catalyst[$(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}$]: 10%wt).

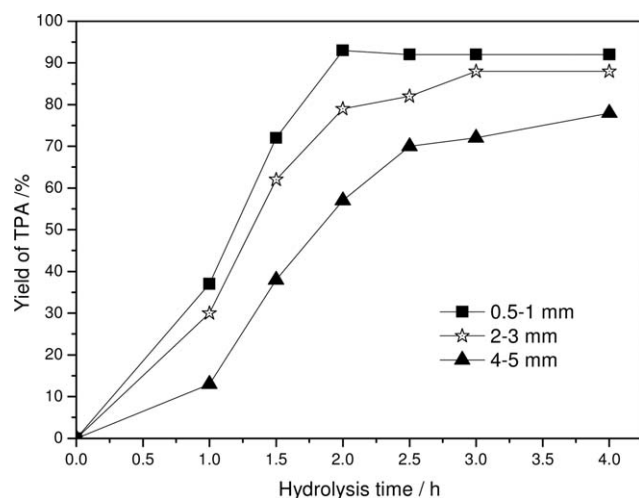**Figure 4.** Effect of reaction time on the hydrolysis of PET (temperature: 145°C, catalyst [$(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}$]: 10% wt).

Figure 5. Effect of particle size of PET on the hydrolysis (temperature: 145°C, time: 2 h, catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$: 10% wt).

Figure 7. FT-IR spectra of the fresh catalyst (A) and the catalyst after three cycles (B).

The effects of reaction time on the conversion of PET and the yield of TPA were examined. Form Figure 4, it was indicated that the conversion of PET increased distinctly with increasing time. When the reaction time was extended to 2 h, the hydrolysis conversion was achieved 100%. And when the reaction time was more than 2 h, the conversion and yield did not show obvious change.

The particle size has a key influence on heat and mass transfer phenomena and the effect of particle size on the TPA recycle yield were investigated. As shown in Figure 5, the particle size of PET was varied from 0.5 to 5 mm with the particle size increasing, the yield of TPA decreased. Moreover, the reaction time depended on the particle size. It was found that as the particle size of ground PET decreased, the rate of depolymerization increased. With a particle size of <1mm, the rate is faster compared to that with a larger particle size. Since the solubility of PET is the hydrolysis reaction rate determining step, the smaller the particle size, the faster the dissolving and hydrolysis occur. Furthermore, a smaller particle size provides a larger contact
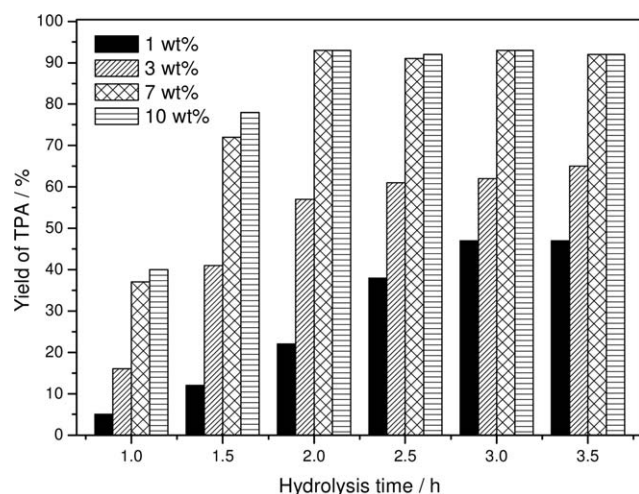
surface area, which promotes heat transfer inside the reaction mixture that would accelerate the entire hydrolytic reaction.

The concentration of catalyst is also a very important parameter for the hydrolysis. The effect of the dosage of catalyst on the hydrolysis of reaction was summarized in Figure 6. The yield of TPA improved with the dosage increase of the catalyst and reached 93% when the amount of catalyst was more than 7 wt % after 2 h. It was also found that the reaction time depended on the catalyst concentration, demonstrating that the higher concentration of catalyst, the faster reaction.

As a result, the optimum reaction conditions were afforded, while Parikh et al. have found that the highest yield of TPA in the catalysis by the combination of base and phase transfer catalyst is about 90% at reaction temperature higher than 150°C under 5 bar.[27] Thus, the catalytic activity from the dual functional phase transfer catalyst at 145°C is comparable to that from the catalysis by traditional phase transfer catalyst at higher reaction temperature and pressure.

Figure 6. Effect of catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$ concentration on the hydrolysis of PET (temperature: 145°C).
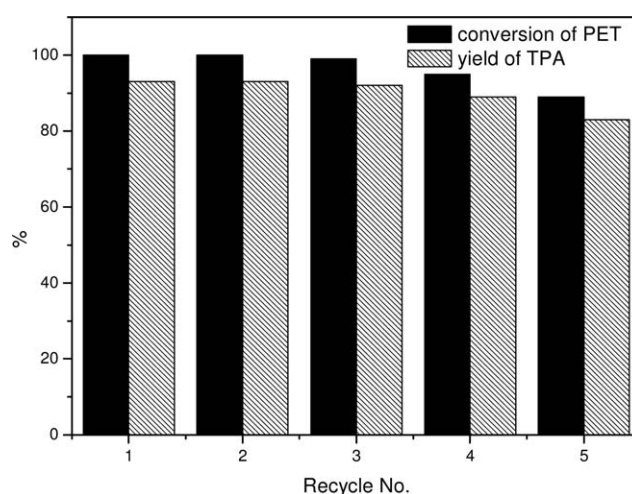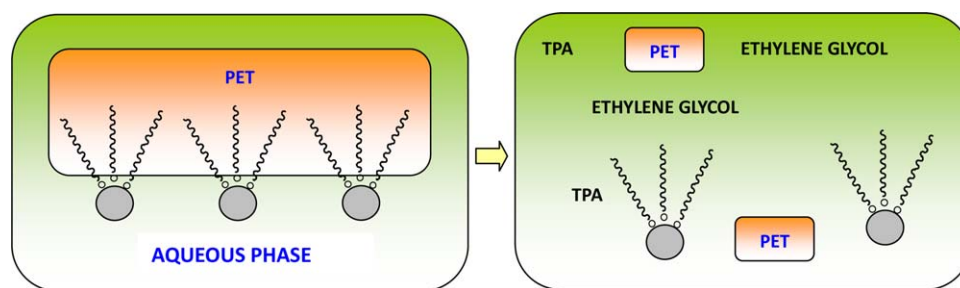

Figure 8. Reusability of catalyst (temperature: 145°C, time: 2 h, catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$: 10% wt).

Catalyst Stability and Reusability

The reusability of the catalyst was investigated and the catalyst was recycled for five times. Figure 7 shows the FT-IR spectra of the fresh catalyst and the recovered catalyst (three cycles). The two catalysts have almost the same IR spectra, suggesting that the structure of the catalyst had no significant change during the reaction. The catalyst was relatively stable under the reaction conditions. As shown in Figure 8, the catalytic activity of the recycled catalysts kept the same as that of the fresh catalyst after three cycles. The minor decrease of activity after four cycles might due to the loss of the catalyst during recycling. Due to the high activity and good reusability, the $[(CH_3)_3N(C_{16}H_{33})]_3$ $[PW_{12}O_{40}]$ catalyst can be considered to be a promising catalyst for the hydrolysis of PET.

Role of the Dual Functional Phase Transfer Catalyst

A schematic presentation of the role of the dual functional phase transfer catalyst was shown in Scheme 1. The catalyst molecule could be uniformly distributed in the aqueous-organic interface and form a film. Consequently, the lipophilic quaternary ammonium cations would lie on the organic side and the hydrophilic heteropolyanions would lie on the aqueous side. The reaction mixture consists of the solid organic phase of the PET and the aqueous phase, so the dual functional phase transfer catalyst works with interfacial mechanism.[27] In this way, the PET macromolecules on the surface of the flakes can be more easily depolymerized than catalyzed by traditional catalyst without phase transfer catalyst. The reaction proceeds to complete depolymerization of PET, while the catalyst remains in the aqueous phase.

CONCLUSIONS

In summary, the dual functional phase transfer catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$ could behave as the efficient catalyst for the hydrolysis of PET. When compared with traditional catalyst sulfuric acid, the dual functional phase transfer catalysts exhibited better catalytic activity. Under the optimum conditions of reaction temperature 145°C, time 2 h, particle size of PET at 0.5–1 mm and dosage of catalyst at 7 wt %, the conversion of PET and the yield of TPA were almost 100% and 93%, respectively. Investigation into recycling of the catalyst showed that the catalyst could be reused without significant decrease of activity at least three cycles. Due to the mass loss of recycling catalyst, a minor decrease of activity was observed

after four cycles. The process provided in this article could be as an economically and convenient approach for the hydrolysis of PET waste bottles.

REFERENCES

1. Yoshioka, T.; Ota, M.; Okuwaki, A. *Ind. Eng. Chem. Res.* **2003**, *42*, 675.

2. Sato, O.; Arai, K.; Shirai, M. *Catal. Today* **2006**, *111*, 297.

3. de Carvalho, G. M.; Muniz, E. C.; Rubira, A. F. *Polym. Degrad. Stabil.* **2006**, *91*, 1326.

4. Guclu, G.; Yaicinyuva, T.; Ozgumus, S.; Orbay, M. *Thermochem. Acta.* **2003**, *404*, 193.

5. Grause, G.; Kaminsky, W.; Fahrbach, G. *Polym. Degrad. Stabil.* **2004**, *85*, 571.

6. Firas, A.; Dumitru, P. *Eur. Polym. J.* **2005**, *41*, 1453.

7. Sato, O.; Arai, K.; Shiria, M. *Catal. Today* **2006**, *111*, 297.

8. Karayannidis, G. P.; Achilias, D. S.; Sideridou, I. D.; Bikiaris, D. N. *Eur. Polym. J.* **2005**, *41*, 201.

9. López-Fonseca, R.; Duque-Ingunza, I.; de Rivas, B.; Arnaiz, S.; Gutiérrez-Ortiz, J. I. *Polym. Degrad. Stabil.* **2010**, *95*, 1022.

10. Abdelaal, M. Y.; Sobahi, T. R.; Makki, M. S. I. *Constr. Build. Mater.* **2011**, *25*, 3267.

11. Viana, M. E.; Riul, A.; Carvalho, G. M.; Rubira, A. F.; Muniz, E. C. *Chem. Eng. J.* **2011**, *173*, 210.

12. Shukla, S. R.; Harad, A. M. *Polym. Degrad. Stabil.* **2006**, *91*, 1850.

13. Pingale, N. D.; Palekar, V. S.; Shukla, S. R. *J. Appl. Polym. Sci.* **2010**, *115*, 249.

14. Sinha, V.; Patel, M. R.; Patel, J. V. *J. Polym. Environ.* **2010**, *18*, 8.

15. Mittal, A.; Soni, R. K.; Dutt, K.; Singh, S. *J. Hazard Mater.* **2010**, *178*, 390.

16. Wang, H.; Yan, R. Y.; Li, Z. X.; Zhang, X. P.; Zhang, S. J. *Catal. Commun.* **2010**, *11*, 763.

17. Wang, H.; Li, Z. X.; Liu, Y. Q.; Zhang, X. P.; Zhang, S. J. *Green Chem.* **2009**, *11*, 1568.

18. Liu, F. S.; Cui, X.; Yu, S. T.; Li, Z.; Ge, X. P. *J. Appl. Polym. Sci.* **2009**, *114*, 3561.

19. Shah, R. V.; Borude, V. S.; Shukla, S. R. *J. Appl. Polym. Sci.* **2013**, *127*, 323.

20. Thom, V.; Yoshida, M.; Araujo, M. H.; Lago, R. M. *J. Appl. Polym. Sci.* **2006**, *102*, 5284.

21. Magdy, Y. A.; Tariq, R. S.; Mohamed, S. I. *Int. J. Polym. Mater.* **2008**, *57*, 73.

22. Kurakawa, H.; Ohshima, M.; Sugiyama, K.; Hiura, H. *Polym. Degrad. Stabil.* **2003**, *79*, 529.

23. Zhu, M. L.; Li, S.; Li, Z. X.; Lu, X. M.; Zhang, S. J. *Chem. Eng. J.* **2012**, 185,186, 168.

24. Li, C.; Jiang, Z.; Gao, J.; Yang, Y.; Wang, S.; Tian, F.; Sun, F.; Sun, X.; Ying, P.; Han, C. *Chem. Eur. J.* **2004**, *10*, 2277.

25. Li, C.; Gao, J. B.; Jiang, Z. X.; Wang, S. G.; Lu, H. Y.; Yang, Y. X.; Jing, F. *Top Catal.* **2005**, *35*, 169.

26. Kosmidis, V.; Achilias, D. S.; Karayanndis, G. *Macromol. Mater. Eng.* **2001**, *286*, 640.

27. Das, J.; Halgeri, A. B.; Sahu, V.; Parikh, P. A. *Indian J. Chem. Technol.* **2007**, *14*, 173.

28. Lpez-Fonseca, R.; Gonzalez-Marcos, M. P.; Gonzalez-Velasco, J. R.; Gutitrrez-Ortiz, J. I. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 92.

29. Khalaf, H. I.; Hasan, O. A. *Chem. Eng. J.* **2012**, *192*, 45.