Article

JOURNAL OF THE CHINESE
CHEMICAL SOCIETY

Catalysis Studies of Macroreticular Polystyrene Cation-exchange Resin with Terminal Perfluoroalkanesulfonic Acids

Zhenghuan Lin,[a,b] Chuanjin Guan,[c] Limei Huang,[a] Wen Wang,[a] Qidan Ling[a,d,]* and
Chengxue Zhao[b,]*
[a] *College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China*
[b] *Department of Chemistry, Shanghai Jiao Tong University, Shanghai 200240, China*
[c] *Department of Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China*
[d] *Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, Fujian, P. R. China*

(Received: Aug. 6, 2012; Accepted: Oct. 31, 2012; Published Online: Dec. 20, 2012; DOI: 10.1002/jccs.201200431)

Macroreticular *p*-(ω-sulfonic-perfluoroalkylated) polystyrene (FPS) resin with the advantages of both sulfonic polystyrene (such as macroreticular Amberlyst-15) and perfluoroalkanesulfonic resin (such as superacidic Nafion NR50) has exhibited excellent catalytic selectivity and activity in cyclization of pseudoionone and condensation of indole. In this paper, FPS was characterized by XPS, nitrogen sorption technique, FESEM and Hammett indicator method, and employed as the solid acid catalyst in the esterification, acylation and alkylation reactions. The FPS resin showed better activity than commercial solid acid catalysts (Amberlyst-15 and Nafion NR50) owing to its high surface area and strong acidity close to superacidity.

Keywords: Macroreticular; Solid acid; Cation-exchange resin; Perfluoroalkanesulfonic.

INTRODUCTION

Organic reactions catalyzed by acids have widely existed in every aspect of laboratorial research and industrial application. There are so many kinds of acids used in organic reactions: liquid and solid acids (different phase); inorganic and organic acids (different composition); weak, strong and super acids (different acidity); Brønsted and Lewis acids (different catalytic process).[1] Generally, catalytic activity of liquid acids is higher than that of solid acids for homogeneous reaction. However, its disadvantages of high toxicity, difficult separation and recovery, environmental pollution and equipment corrosion greatly limit its further applications in organic synthesis.[2-4] Therefore, it is desirable in the chemical transformation employing acids as catalysts to replace liquid acids with more environmentally friendly solid acids such as zeolites, metal salts, oxides, clays, heteropolyacids and sulfides, etc.[1] However, the properties and structure of solid acids still need to be improved, like stability, acidity, accessibility of acidic sites,[5] synthetic method, deactivation of catalysts, water-tolerance, etc.[2]

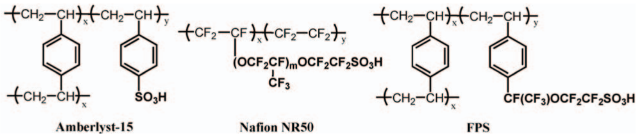
Since macroreticular polystyrene resins were synthesized in 1960s, cation-exchange resins as solid acid catalysts have received more and more interests[6-11] for their stable structure which enables them to be used in all kinks of media (aqueous, non-aqueous; polar and non-polar), and their high selectivity which enables them to be used in separation of the mixtures with close boiling temperatures[12] and in fixed bed reactor.[13,14] There are two kinds of commercial cation-exchange resins: non-fluorinated macroreticular sulfonic resins (such as Amberlyst-15) and perfluoroalkylsulfonic resins (such as Nafion NR50). They have own advantages and disadvantages. For example, Amberlyst-15 is of high surface area and exchange capacity (4.2 mmol/g) with low usage temperature up to 120 °C. Nafion NR50 is superacid ($H_0 = \sim -12$), and has extremely good chemical resistance and thermostability with low surface area of 0.02 m^2/g and exchange capacity of 0.9 mmol/g. Although the Nafion nanocomposite with silica (Nafion/SiO_2) has expanded the surface area, its exchange capacity turns less to 0.12 mmol/g.[15,16]

Recently, Zhao et al.[17] reported a kind of fluorinated sulfonic resin FPS (Scheme I) composed of macroreticular polystyrene skeleton and perfluoroalkanesulfonic side chain. Due to its unique structure, FPS exhibits some advantages of both Amberlyst and Nafion resins, such as high exchange capacity of 2.0 mmol/g, surface area of 107 m^2/g, thermostability (stable up to 190 °C) and strong acidity. FPS resins have shown higher activity than commercial solid acids in cyclization of pseudoionone into α-ionone

---

* Corresponding author. Tel: +86 591 22868666; Fax: +86 591 22868666; E-mail: lingqd@fjnu.edu.cn (Qidan Ling);
Tel: +86 21 54709629; Fax: +86 21 54741297; E-mail: cxzhao@sjtu.edu.cn (Chengxue Zhao)

Scheme I Structure of cation-exchange resins



and condensation of indole with aldehyde or imine.[18] In this work, Hammett indicators and XPS were employed to determine the acid strength and element composition on the surface of FPS. The porosity of FPS was analyzed by nitrogen sorption technique and FESEM. We tested further the catalytic activity of FPS in other organic reactions, like esterification, acylation and alkylation.

RESULTS AND DISCUSSION

Structure and property of FPS

FPS resin has been synthesized by following perfluoroalkylation of ω-fluorosulfonylperfluorodiacyl peroxides (SFAP) with polystyrene (PS), alkali hydrolysis and acidification. X-ray photoelectron spectroscopy (XPS) was employed to analyzing the element composition in the surface of macroreticular PS and FPS. As shown in Fig. 1, XPS spectra of FPS show one peak of F_{1s} at 688.1 eV, one peak of S_{2p} at 168.5 eV, two peaks of C_{1s} at 284.5 eV and 290.1 eV for two kinds of carbon atoms in FPS: the hydrogenated carbon (284.5 eV) in the main chain and the fluorinated carbon (290.1 eV) in the side chain. There is only one C_{1s} peak at 284.5 eV in the XPS spectra of polystyrene. The XPS results provided the evidence that the perfluoroalkylsulfonic groups were introduced successfully into the surface of polystyrene to produce FPS.

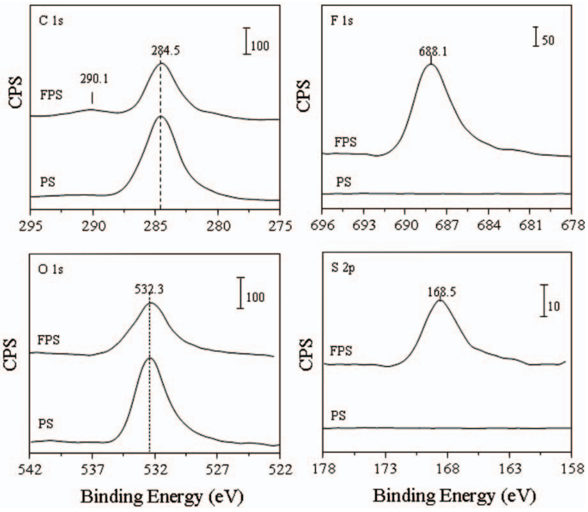


Fig. 1. XPS spectra of polystyrene (PS) and FPS.

Table 1. Acidic strength of FPS resin[a]

Resin	Anthraquinone (H_0, -8.2)	*p*-Nitrotoluene (-11.35)	*p*-Nitrochlorobenzene (-12.7)
Amberlyst-15	–	–	–
FPS	+	±	–
Nafion NR50	+	+	±

[a] (+) Color changed clearly; (–) Color unchanged; (±) Color changed unclearly.

The acidic strength of FPS was determined by observing the color change of the indicator adsorbed on the surface of the sample. The indicators used in this work are anthraquinone (H_0 = -8.20), *p*-nitrotoluene (H_0 = -11.35) and *p*-nitrochlorobenzene (H_0 = -12.70). The solvent used in the experiment is *n*-heptane. The results were listed in the Table 1. The H_0 value of FPS is approximately -11.4, which is close to the superacidity (H_0 = -12).

The porosity of FPS was characterized by nitrogen sorption technique. Fig. 2 gives the adsorption and desorption isotherm of FPS. The adsorption curve displays a type II isotherm with a similar H3 hysteresis typical of disorder slit pores caused by particles accumulation. At low pressures, the gradual adsorption curve shows first an adsorbate monolayer is formed on the pore surface, which is followed by the multilayer formation. At high pressures, the steep adsorption step indicates the relatively large pore size and narrow pore size distribution of FPS, which is matched with the pore size distribution shown in Fig. 3. Compared to PS, the pore size of FPS turns less for some pores occupied by perfluoroalkanesulfonic chain. Their pore parameters (shown in Table 2) were obtained by BET and BJH methods. High resolution field emission scanning electron microscopy (HR-FESEM) was used to observe the microstructure and morphology of FPS. The HR-FESEM photo

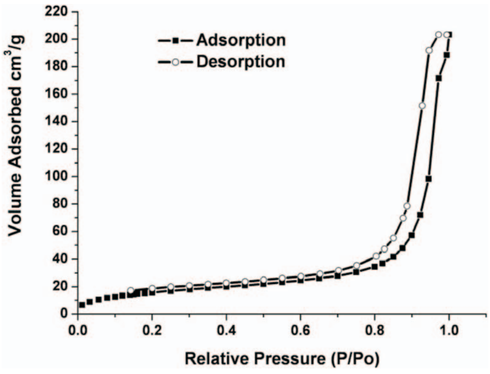


Fig. 2. Adsorption and desorption isotherm of FPS.

Table 2. Physical characteristics of various resins

Resin	BET surface area (m^2/g)	BJH pore volume (cm^3/g)	BJH pore diameter (nm)	Exchange capacity (mmol/g)	H_0
Amberlyst-15	42	0.36	34.3	4.8	-2.2
Amberlyst-36	35	0.28	32.9	5.3	-2.2
Nafion NR50	0.02	/	/	0.9	-12.7
Nafion/SiO_2	88	0.56	21.8	0.15	-12
FPS	107	0.44	14.6	1.3	-11.4
PS	361	0.83	15.1	/	/

(Fig. 4) at 40,000-fold magnification exhibits that the microstructure of FPS is irregular particulate in nature and that there are plenty of complex and disorder slit pores between particles. The result is consistent with adsorption isotherm.

Catalytic activity of FPS

The Physical characteristics of FPS and commercial cation-exchange resins were listed in Table 2. For the combination of advantages of both Amberlyst and Nafion resin, FPS has behaved excellent activity as the solid catalyst in the cyclization of pseudoionone into α-ionone and condensation of indole with aldehyde or imine.[18] The catalytic activity of FPS was evaluated further in the esterification, acylation and alkylation.

Esterification of acids with alcohols

Recently, the esterifications catalyzed by cation-exchange resins have attracted much attention for their high activity and stability.[10,19-24] In this work, the esterification of benzoic acid with *n*-butanol was investigated with FPS, Amberlyst-15, Amberlyst-36, Nafion NR50 and its nanocomposite Nafion/SiO_2. Table 3 gives the conversion rate of benzoic acid catalyzed by these solid acids. FPS (Entry 5) exhibits best catalytic activity in the reaction with 91% of conversion of benzoic acid for being of the advantages of both Amberlyst-15 and Nafion NR50 resins such as big surface area, easy accessibility of acidic sites and superacidity. Owing to forming big surface area through introducing Nafion resin into silica framework, benzoic acid's conversion is greatly improved from 49% under Nafion NR50 to 81% under Nafion/SiO_2. FPS was also used to catalyze benzoic acid with different alkyl alcohols with the results listed in Table 4. FPS also exhibits high activity with the conversion rate of aryl acid in the range of 89-95%, except for isoamyl alcohol with 74% of conversion rate of benzoic acid, because there is bigger steric hindrance of OH group in isoamyl alcohol than in primary alcohol.

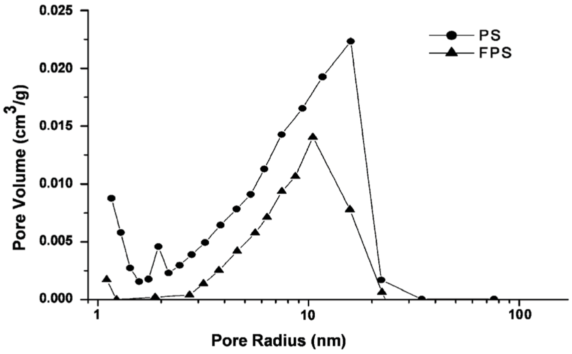


Fig. 3. Pore size distribution of PS and FPS.

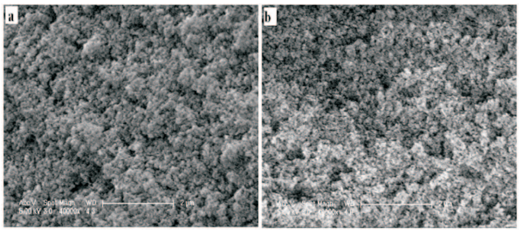


Fig. 4. HR-FESEM photo of PS (a) and FPS (b).

For benzyl alcohol being prone to dehydrate to produce benzyl ether, its esterification was employed to determine the selectivity and activity of solid acids at low temperature. Table 5 shows the result of esterification of benzyl alcohol with acetic acid catalyzed by 10 mol% of solid acids (Amberlyst-15, Nafion NR50 and FPS) at 78 °C. Like the esterification of benzoic acid, FPS presents the best ac-

Table 3. Esterification of benzoic acid with *n*-butanol catalyzed by solid acids

Entry	Catalyst	Conversion of benzoic acid (%)
1	Amberlyst-15	69
2	Amberlyst-36	30
3	Nafion NR50	49
4	Nafion/SiO_2	81
5	FPS	91

Table 4. Esterification of benzoic acid with different alcohols catalyzed by FPS

Entry	Alcohol	Conversion of acid (%)
1	n-C_4H_9OH	91
2	n-$C_5H_{11}OH$	90
3	i-$C_5H_{11}OH$	74
4	n-$C_6H_{13}OH$	89
5	n-$C_{12}H_{25}OH$	90
6	n-C_4H_9OH[a]	95

[a] Esterification of phenylacetic acid with *n*-butanol.

Table 5. Esterification of benzyl alcohol with acetic acid catalyzed by solid acids

Resin	Conversion of benzyl alcohol (%)	Yield of ester (%)[a]	Selectivity of ester (%)
Amberlyst-15	40	5	12
Nafion NR50	74	15	20
FPS	89	10	11

[a] Isolated yield.

Table 6. Acylation of different arenes catalyzed by solid acids

Entry	Substrate	Acylating agent	Yield (%)[a]
1	toluene	Ph-COCl	84
2	anisole	Ph-COCl	92
3	*m*-xylene	Ph-COCl	87
4	mesitylene	Ph-COCl	89
5	toluene	$(CH_3CO)_2O$	72
6	benzene	$(CH_3CO)_2O$	19

[a] Isolated yield.

Table 7. Alkylation of toluene with isopropanol catalyzed by solid acids

Entry	Resin	Yield of cymene[a]
1	Amberlyst-15	7
2	Amberlyst-36	8
3	Nafion NR50	6
4	FPS	10

[a] Isolated yield.

tivity in low temperature with 89% of conversion of benzyl alcohol and similar selectivity as Amberlyst-15. In these solid acids, Nafion NR50 exhibits best selectivity and good activity with 15% of yield of ester and 74% of conversion.

Acylation of arenes

Friedel-Crafts acylation, one of frequently used reaction in organic synthesis, is an important method of synthesizing arone which is a crucial intermediate in the industry of fine chemicals.[19,25] We used FPS to catalyze the acylation of different arenas with benzoyl chloride or acetic anhydride. From Table 6, it is found that the benzoyl chloride (Entry 1-4) gives higher yield (above 84%) than acetic anhydride for its strong electrophilicity, which is favorable for the acylation reaction according to electrophilic substitution mechanism. The substituent groups in the phenyl ring have big effect on the yield. The acylation of anisole gets high yield up to 92% for strong electron-donating ability of the methoxy group. Though the acylating ability of acetic anhydride is lower than that of benzoyl chloride, the acylating yield of toluene with acetic anhydride can reach 72%, which prove that FPS is a kind of high effective catalyst.

Alkylation of toluene

Alkylation of arene with alkylating reagents (like alkene, halohydrocarbon and alcohol) is one of the important reaction synthesizing aromatic derivatives. However, alkene or halohydrocarbon makes alkylation turn complex or contaminate the environment for polymerization or generating HX. Relatively, alkylating reaction with alcohols has attracted much attention for its safety and cleanliness.[26] The alkylation of toluene with isopropanol was investigated with non-fluorinated sulfonic resin (Amberlyst-15 and Amberlyst-36), perfluorosulfonic resin (Nafion NR50) and fluorinated sulfonic resin (FPS). From the results shown in Table 7, all of these resins give isopropyltoluene in low yield up to 10%, because most of isopropanol underwent a dehydrolysis process to yield propene which escapes from the reaction medium. The result is consistent with one reported in the literature.[26] The formation of propene was confirmed by bubbling the gas effluent into a solution of Br_2/CCl_4. However, FPS resin gives the highest yield of isopropyltoluene in the alkylation for its unique structure and strong acidity.

EXPERIMENTAL

Materials

Organic reagents used in catalysis studies were purchased from Sinopharm Chemical Reagent Co. without further purification before use. FPS was synthesized from polystyrene (PS, 36% of crosslink degree) by following the reported procedure.[18] Amberlyst-15, Amberlyst-36 and Nafion NR50 were purchased from Aldrich. The commercial catalysts and Nafion/SiO_2 nanocomposites (13% of Nafion resin) prepared according to the reported method[15] were dried at 60 °C under vacuum overnight before use.

Characterization

XPS spectra were obtained on an Omicron ESCA spectrometer. Acid strength was determined by Hammett indicator method in vacuo. Nuclear magnetic resonance was performed using Varian Mercury 400 spectrometer. Adsorption isotherm and pore size distribution were obtained by using a Micromeritics instrument (ASAP Micromeritics 2000). The morphological characteristics were observed with a high resolution field emission scanning electron microscope (Philips Sirion 200).

Catalysis studies

The esterification of aryl acid was carried out in a 25 mL round flask. To the flask was added aryl acid (2 mmol), alkanol (6 mmol) and 10 mol% of solid catalyst in turn. The mixture was stirred at 115 °C for 6 h, filtered and washed with ethyl acetate for three times, and then evaporated under vacuum. The residue was analyzed by column chromatography to give the conversion of aryl acid.

In the esterification of benzyl alcohol with acetic acid, to 10 mol% of solid catalyst was added acetic acid (0.12 g, 2.0 mmol), benzyl alcohol (0.22 g, 2.0 mmol). Then the mixture was stirred for 6 h at 78 °C. The catalyst was filtered and washed with ethyl acetate three times. The combined solution was evaporated under reduced pressure. The residue was purified via column chromatography (silica gel, petroleum ether: ethyl acetate = 5:1). ^{1}H NMR of benzyl acetate ($CDCl_3$, 400 MHz): δ 7.37 (m, 1H), 7.26 (d, 2H), 7.17 (m, 2H), 4.04 (s, 2H), 2.4 (s, 3H).

The acylation of arene with benzoyl chloride or acetic anhydride was investigated in a 25 mL round flask. Benzoyl chloride (0.4 g, 2.8 mmol) or acetic anhydride (0.29 g, 2.8 mmol), and 10 mol% of catalyst were added to 15 mL of arene under a nitrogen atmosphere. The mixture was stirred for 8 h under refluxing. The catalyst was filtered and washed with toluene three times. The combined solution was evaporated under reduced pressure. The residue was purified via column chromatography (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR of tolylphenylmethanone ($CDCl_3$, 400 MHz): δ 7.81~7.77 (m, 2H), 7.73~7.71 (d, 2H), 7.58~7.53 (m, 1H), 7.47~7.44 (m, 2H), 7.29~7.25 (d, 2H), 2.43 (s, 3H).

^{1}H NMR of methoxyphenyl phenylmethanone ($CDCl_3$, 400 MHz): δ 7.8 (m, 2H), 7.7 (d, 2H), 7.6 (m, 1H), 7.5 (m, 2H), 7.3 (d, 2H), 2.4 (s, 3H).

^{1}H NMR of (2,4-dimethylphenyl)phenylmethanone ($CDCl_3$, 400 MHz): δ 7.80~7.76 (m, 2H), 7.58~7.50 (m, 1H), 7.45~7.39 (m, 2H), 7.24~7.20 (m, 1H), 7.10~7.02 (d, 2H), 2.38 ~2.31 (m, 6H).

^{1}H NMR of mesitylphenylmethanone ($CDCl_3$, 400 MHz): δ 7.83~7.79 (m, 2H), 7.60~7.54 (m, 1H), 7.47~7.40 (m, 2H), 6.90 (s, 2H), 2.33 (s, 3H), 2.08 (s, 6H).

^{1}H NMR of acetyltoluene ($CDCl_3$, 400 MHz): δ 7.80 (m, 2H), 7.27 (m, 2H), 2.57 (s, 3H), 2.43 (m, 3H).

^{1}H NMR of acetylbenzene ($CDCl_3$, 400 MHz): δ 7.95 (m, 2H), 7.58 (m, 1H), 7.44 (m, 2H), 2.61 (s, 3H).

The alkylation of toluene with isopropanol was carried out in a 25 mL three-neck flask connected with a bubbler loaded with the solution of Br_2/CCl_4. To 3 mL of toluene was added isopropanol (0.12 g, 2 mmol) and 10 mol% of catalyst. The mixture was stirred at 80 °C for 5 h, filtered and washed with ethyl acetate for three times. The combined solution was evaporated under reduced pressure. The residue was purified via column chromatography. ^{1}H NMR of isopropyltoluene ($CDCl_3$, 400 MHz): δ 7.86 (m, 2H), 7.25 (m, 2H), 2.58 (s, 3H), 2.41 (m, 1H), 1.26 (m, 6H).

CONCLUSION

The surface composition and acidity of FPS resin bearing terminal perfluoroalkanesulfonic groups was analyzed by XPS and Hammett indicator method, respectively. The XPS spectra show that the perfluoroalkanesulfonic group was successfully introduced into the surface of FPS. By Hammett indicator method, the acidity of FPS, $H_0 = -11$, was determined. Owing to the nearly superacidity and easy accessibility of the acid sites, the FPS resin behaved superior activity over other commercial solid acid catalysts in some reactions, like esterification, acylation and alkylation. For example, the esterification of aromatic acids with primary alcohols can smoothly proceed by using FPS catalyst with high conversion of the acids over 89%. It is expected that FPS may be used as an efficient catalyst in various reactions.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (60976019), Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP 20093223110002), Program for Innovative Research Team in Science and Technology in Fujian Province University (IRTSTFJ), Key Programs of Fujian Educational Committee (JA12059).

REFERENCES

1. Busca, G. *Chem. Rev.* **2007**, *107*, 5366.
2. Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641.
3. Tanabe, K.; Hölderich, W. F. *Appl. Catal. A* **1999**, *181*, 399.
4. Cole-Hamilton, D.; Tooze, R. In *Catalyst Separation, Recovery and Recycling*; Cole-Hamilton, D. J.; Tooze, R. P., Eds; Springer Netherlands: Dordrecht, 2006; Vol. 30, p 1.

5. Chen, F.; Meng, X.; Xiao, F.-S. *Catal. Surv. Asia* **2011**, *15*, 37.
6. Heidekum, A.; Harmer, M. A.; Hoelderich, W. F. *J. Catal.* **1999**, *181*, 217.
7. Barbaro, P.; Liguori, F. *Chem. Rev.* **2008**, *109*, 515.
8. Alexandratos, S. D. *Ind. Eng. Chem. Res.* **2008**, *48*, 388.
9. Yadav, G. D.; Kulkarni, H. B. *React. Funct. Polym.* **2000**, *44*, 153.
10. Yadav, G. D.; Thathagar, M. B. *React. Funct. Polym.* **2002**, *52*, 99.
11. Harmer, M. A.; Sun, Q. *Appl. Catal., A* **2001**, *221*, 45.
12. Sharma, M. M. *React. Funct. Polym.* **1995**, *26*, 3.
13. Son, S. M.; Kimura, H.; Kusakabe, K. *Bioresour. Technol.* **2011**, *102*, 2130.
14. Cheng, Y.; Feng, Y.; Ren, Y.; Liu, X.; Gao, A.; He, B.; Yan, F.; Li, J. *Bioresour. Technol.* **2012**, *113*, 65.
15. Harmer, M. A.; Farneth, W. E.; Sun, Q. *J. Am. Chem. Soc.* **1996**, *118*, 7708.
16. Harmer, M. A.; Sun, Q.; Vega, A. J.; Farneth, W. E.; Heidekum, A.; Hoelderich, W. F. *Green Chem.* **2000**, *2*, 7.
17. Lin, Z. H.; Zhao, C. X. *Chem. Commun.* **2005**, 3556.
18. Lin, Z. H.; Guan, C. J.; Feng, X. L.; Zhao, C. X. *J. Mol. Catal. A* **2006**, *247*, 19.
19. Yadav, G. D.; Rahuman, M. S. *Org. Process Res. Dev.* **2002**, *6*, 706.
20. Iimura, S.; Manabe, K.; Kobayashi, S. *Chem. Commun.* **2002**, 94.
21. Blagov, S.; Parada, S.; Bailer, O.; Moritz, P.; Lam, D.; Weinand, R.; Hasse, H. *Chem. Eng. Sci.* **2006**, *61*, 753.
22. Delgado, P.; Sanz, M. T.; Beltrán, S. *Chem. Eng. J.* **2007**, *126*, 111.
23. Feng, Y.; He, B.; Cao, Y.; Li, J.; Liu, M.; Yan, F.; Liang, X. *Bioresour. Technol.* **2010**, *101*, 1518.
24. Zhang, Y.; Ma, L.; Yang, J. *React. Funct. Polym.* **2004**, *61*, 101.
25. Yadav, G. D.; Bhagat, R. D. *J. Mol. Catal. A* **2005**, *235*, 98.
26. Lachter, E. R.; da, S. S.; Tabak, D.; Costa, V. G.; Chaves, C. P.; Dos, S. J. *React. Funct. Polym.* **2000**, *44*, 1.