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# Journal of Dispersion Science and Technology

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/ldis20</u>

## Baeyer-Villiger Oxidation of Ketones with Hydrogen Peroxide Catalyzed by Chitosan-Supported Dendritic Sn Complexes

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 Accepted author version posted online: 28 Sep 2011. Version of record first published: 06 Jul 2012.

To cite this article: Cuilin Li, Ziqiang Lei, Hengchang Ma, Shang Wu & Qiangsheng Sun (2012): Baeyer-Villiger Oxidation of Ketones with Hydrogen Peroxide Catalyzed by Chitosan-Supported Dendritic Sn Complexes, Journal of Dispersion Science and Technology, 33:7, 983-989

To link to this article: <u>http://dx.doi.org/10.1080/01932691.2011.590434</u>

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## Baeyer–Villiger Oxidation of Ketones with Hydrogen Peroxide Catalyzed by Chitosan-Supported Dendritic Sn Complexes

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Dendritic Sn complexes were successfully incorporated to chitosan by solid phase synthesis methodology. The polymer-supported catalysts exhibited promising catalytic performance for the Baeyer-Villiger oxidation of ketones in the presence of hydrogen peroxide. The influence of reaction temperature, reaction time, the amount of catalyst used, and solvents on the catalytic activity was investigated systematically. Notably, the catalysts can be prepared in large scale in a simple manner with low-cost materials and also can be recycled for times.

Keywords Baeyer-Villiger oxidation, chitosan, dendrimer Sn complex, hydrogen peroxide

#### 1. INTRODUCTION

Dendrimers are well-defined macromolecules with controllable structures. Their applications in catalysis have triggered increasing attention because the advantage of self and multi-unhindered active sites.<sup>[1]</sup> However, preparing as polymer, in most cases, dendrimers are used as homogeneous catalyst due to their great solubility in common used organic media. In recent years, considerable attention has been directed toward to the heterogeneous catalysis systems.<sup>[2–5]</sup> Heterogeneous reaction allows for the easy separation and recycling of the catalyst from the reaction mixture, which opens up the possibility of recycling and simpler reaction procedures.

In spite of the fact that the oxidative conversion of ketones/aldehydes to esters via the Baeyer Villiger reaction has been known for more than 100 years,<sup>[6]</sup> polymeranchored metal complexes are still of research interests and potentials. For the representative heterogeneous catalysts used to perform the Baeyer-Villiger reaction involve solid acids, Sn-MCM-41, sulphonatedresins, titaniumsilicalites, transition metal-functionalized hydrotalcites, hydrotalcite-supported Sb catalyst, Sn-synthesized hydrotalcites, and Fe-MCM-48.<sup>[7–17]</sup> Recenty, we reported a serial of supported Sn catalysts which demonstrated promising catalytic activities for Baeyer-Villiger oxidation of ketones with hydrogen peroxide.<sup>[18–22]</sup> The catalytic system we used is similar to those of Corma's,<sup>[16]</sup> but the preparation of the catalysts is much simpler.

In this article, we reported our preliminary investigation on the Baeyer-Villiger oxidation of ketones with hydrogen peroxide catalyzed by chitosan supported dendritic Sn complexes. We prepared the chitosan supported dendritic Sn complexes P-PAMAM ( $1.0 \sim 3.0$  G)-HBA-Sn(II) (where P = chitosan, PAMAM = polyamidoamine, and HBA = 4-hydroxybenzaldehyde, G = generation) by solid phase synthesis methodology. These catalysts showed high activity for the Baeyer-Villiger oxidation of ketones in the presence of hydrogen peroxide. Chitosan is available from the commercial sources. The catalysts can be prepared in large scale in a simple manner with low-cost materials, and are very convenient to be separated from the reaction mixture after the reaction. Moreover, the catalysts can be recycled.

## 2. EXPERIMENTAL

#### 2.1. Materials and Instruments

Chitosan was obtained from the chemical engineering factory in Yu-Huan Country of Zhejiang (molecular weight  $1.5 \times 10^5$ , deacetyl degree 93%). Chitosan was

Received 13 April 2011; accepted 11 May 2011.

This work was financially supported by the National Natural Science Foundation of China (No. 20474052) and the Specialized Research Fund for the Doctoral Program of High Education (No. 20050736001) from the Ministry of Education. We also thank the Key Laboratory of Eco-Environment-Related Polymer Materials (Northwest Normal University), Ministry of Education, for financial support.

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extracted with tetrahydrofuran (THF) for 24 hours using a Soxhlet apparatus, the chitosan was then dried in vacua at room temperature and stored in vacua at 110°C. Ethylenediamine (EDA), methyl acrylate (MA) were distilled before use.  $SnCl_2 \cdot 2H_2O$  and other reagents were commercially obtained and used without further purification.

Infrared (IR) spectra were recorded in KBr disks with a Nicolet AVATAR 360 FTIR spectrophotometer. Metal content was measured on an American ICPV-5600 analytic instrument. XPS analysis were obtained with the PHI-5702/ESCA/SAM system equipped with an Mg Ka (1253.6 eV) x-ray source. The binding energy (BE) of the C<sub>1s</sub> peak at 284.8 eV was taken as an internal standard. The reaction products of oxidation were determined and analyzed using Trace GC/MS 2000 system with  $25 \text{ m} \times 0.25 \text{ mm}$  SE-54 column, and Shimadzu GC-16A gas chromatograph with a  $3 \text{ m} \times 3 \text{ mm}$  OV-17 column.

#### 2.2. Synthesis of the Tin Complexes

## 2.2.1. Synthesis of the Chitosan Supported Polyamidoamine (P-PAMAM (1.0–3.0 G))

P-PAMAM (1.0–3.0 G) complexes were synthesized according to the literature.<sup>[23]</sup> Methyl acrylate (MA) and ethylenediamine (EDA) were used as substrates. The grafting reaction and propagation of dendritic polyamidoamine from the chitosan powder surface was achieved by repeating two processes: (1) Michael addition of MA to amino groups on the surface and (2) amidation of terminal ester groups by EDA.

Repeating the two reactions of Michael addition and amidation, the chitosan-supported dendrimers from second generation to third generation were also prepared. The reaction procedure is shown in Scheme 1.

## 2.2.2. Synthesis of the Complexes (P-PAMAM (1.0–3.0 G)-HBA-Sn (II))

An amount of 0.5 g first generation white power was added to the solution of HBA (0.5 g) in methanol (20 mL). The mixture was stirred at 50°C for 24 hours, then filtered and the product was repeatedly washed with methanol and dried. The first generation ligand yellow power (P-PAMAM-HBA (1.0 G)) was obtained.

The first generation ligand was added to the solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}(1.0 \text{ g})$  in THF (20 mL). The mixture was stirred at 50°C for 24 hours, then filtered and the product was repeatedly washed with THF. The first generation tin complex (P-PAMAM (1.0)-HBA-Sn (II)) was obtained. The reaction procedure is shown in Scheme 2. The other ligands with different generations and complexes were prepared using similar procedure.

#### 2.2.3. Baeyer-Villiger Oxidation of Ketones

The catalytic activity tests were carried out as described in the following procedure: ketone 0.1 mmol and 30%



SCH. 1. Procedure for the preparation of the chitosan-supported dendrimers.



SCH. 2. Procedure for the preparation of the tin complex of first generation.



SCH. 3. Baeyer-Villiger oxidation of ketones with hydrogen peroxide.

 $H_2O_2(2.0 \text{ eq} \text{ to the ketone})$  were dissolved in an appropriate of solvent (3.0 mL), and catalyst (3 mg) was added and heated to 50 or 70°C for 15 hours. The reaction procedure is shown in Scheme 3.

## 3. RESULTS AND DISCUSSION

## 3.1. Characterizations of the Ligands and Their Complexes

#### 3.1.1. IR Spectra

Figure 1 shows the IR of chitosan, P-PAMAM (2.0 G) and P-PAMAM (2.0 G)-HBA-Sn(II). The absorptions of



FIG. 1. Infrared spectrum of chitosan (a), P-PAMAM (2.0 G) (b), and P-PAMAM (2.0 G)-HBA-Sn(II) (c).

P-PAMAM (2.0 G) and P-PAMAM-HBA (2.0 G)-Sn(II) at 1649 cm<sup>-1</sup> and 1558 cm<sup>-1</sup>, are characteristic of C= ONHR, suggesting that polyamidoamine has grafted on chitosan. Meanwhile, we found that the color of the ligand changed into yellow from white after reaction. All these results showed that schiff-base ligand has formed.

## 3.1.2. ICP Analysis of the Complexes

The Sn content in the complexes is shown in Table 1. It can be seen from Table 1 that the Sn content of the tin complexes decreased with the increase of the generation. From the ideal structure of the dendrimer we know that Sn(II) ions can coordinate with the peripheral Schiff-base groups, the theoretical metal content of the complexes should increase with the increase of the generation. This unusual phenomenon may be due to the steric hindrance of higher generation dendrimer. On the other hand, the big cavity in the ligands can also trap many of the Sn(II) ions, which made the metal content of the complexes higher than theoretical value that was estimated from surface amino group determined by titration.

#### 3.1.3. XPS Analysis

In order to confirm the formation of the complexes, XPS of ligands and their complexes were investigated. Here we take the second generation ligand and the corresponding complex as example (Table 2).

TABLE 1 ICP data of complexes P-PAMAM (1.0~3.0 G)-HBA-Sn(II)

Catalyst	ICP data (%)		
$(1.0 \mathrm{G}) - \mathrm{Sn(II)}$	14.82		
$(2.0 \mathrm{G}) - \mathrm{Sn(II)}$	11.52		
$(3.0 \mathrm{G}) - \mathrm{Sn(II)}$	9.74		

TABLE 2 XPS date of the complex P-PAMAM (2.0 G)-HBA-Sn(II), ligand P-PAMAM (2.0 G) – HBA and the salt SnCl<sub>2</sub> · 2H<sub>2</sub>O

	biie	12 21120		
	Binding	g energy (		
XPS peaks	$SnCl_2 \cdot 2H_2O$	Ligand	Complex	$\triangle E_b$ (eV)
Sn <sub>3d(5/2)</sub>	487.5		486.5	-1.0
Cl <sub>2p</sub>	198.6		199.3	+0.7
1		401.5	402.4	+0.9
		400.1	401.4	+1.3
$N_{1s}$		399.0	400.0	+1.0
		397.7	398.7	+1.0
		533.6	533.5	-0.1
$O_{1s}$		532.6	532.4	-0.2
		531.3	530.7	-0.6

The binding energy is referred to  $C_{1s} = 284.80 \text{ eV}$ .

In comparison with  $SnCl_2 \cdot 2H_2O$ , the binding energy of the  $Sn_{3d(5/2)}$  in the complex decreases 1.0 eV; the change of  $Sn_{3d(5/2)}$  binding energy means the increase of its electron density. The oxygen peak in the complexes could be divided into three peaks due to C-O-C, CONH<sub>2</sub> and C-O-H. The binding energy of the complexes was decreased 0.1, 0.2, and 0.6 eV, respectively compared with those of the corresponding ligands. This means that the electron cloud in the oxygen atom may flow into the tin atom to form an O-Sn coordination bond. The nitrogen peak in the complexes could be divided into four peaks due to tertiary amino group, Schiff base, amide group and secondary amine. The binding energy of the complexes was increased 0.9, 1.3, 1.0, and 1.0 eV, respectively, compared with those of the corresponding ligands. This means that the electron cloud in the nitrogen atom may also flow into the tin atom to form N-Sn coordination bond. Compared with  $SnCl_2 \cdot 2H_2O$ , the binding energy of the  $Cl_{2p}$  in the complex increases 0.7 eV; the change means the decrease of its electron density. These results showed that the tin complexes were formed.

#### 3.2. Catalytic Properties Studies

#### 3.2.1. Effect of the Dendrimer Generation

In order to investigate the effect of the dendrimer generation on the catalytic conversion and selectivity, the reactions were carried out for 15 hours at 50°C in methanol. 2-Adamantanone was chosen as a model compound. We use 0.1 mmol of 2-adamantanone, 2.0 eq of 30% hydrogen peroxide and 3 mg of the different generation catalyst respectively in each of the experiment. The results are shown in Table 3.

As shown in Table 3, TON for 1–3 generation of the supported complexes is 14, 20, and 22, respectively under the identical reaction condition. It can be concluded that

IABLE 5				
Baeyer-Villiger oxidation of 2-adamantanone catalyzed				
by different generation catalyst				

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Cat.	Conv. (%)	Sele. (%)	TON	
1.0 G	93	100	14	
2.0 G	99	100	20	
3.0 G	90	100	22	

Condition: 2-adamantanone 0.1 mmol, cat. 5 mg, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), methanol 3 mL, 15 hours at  $50^{\circ}$ C.

the catalytic activity increased with the generation although the metal content decreased with the generation. The result suggests that the active center may be dispersed more efficiently in higher generation dendrimer complexes. In each case by the utilization of 1–3 generations of the dendritic Sn complexes, the selectivity to the product kept 100%. Among these complexes, the second generation P-PAMAM (2.0 G)-HBA-Sn(II) was found to exhibit the highest conversion of 2-adamantanone. So in the following test, we chose P-PAMAM (2.0 G)-HBA-Sn(II) as test catalyst to study the influence of temperature, reaction time, ratio of catalyst to substrate, solvent on the catalytic activity and the recycling of the catalyst.

#### 3.2.2. Effect of Organic Solvents

It is well known that reaction media generally have an obvious effect on various reactions. In this study, we also investigated the role of different solvents in the oxidation of ketones. The effect of organic solvents is shown in Table 4.

It can be seen from Table 4 that among the ten solvents, 1,4-Dioxane, ethanol and methanol gave almost complete conversion of 2-adamantanone. In contrast, the same result could be achieved in methanol at lower temperature. So, we chose methanol as the organic medium to fulfill the oxidation in the following experiments.

#### 3.2.3. Effect of Reaction Temperature

The reaction temperature gives great influence on the Baeyer-Villiger oxidation. We carried out the reaction at different temperatures ranged from 25 to 50°C. The conversion of 2-adamantanone varying with the reaction temperature was shown in Figure 2.

It is evident that the conversion gradually increased with the reaction temperature. A low temperature is unfavorable for the reaction. We found that 2-adamantanone has been converted into the corresponding lactone completely at  $50^{\circ}$ C. Therefore, a temperature of  $50^{\circ}$ C is the optimum reaction temperature.

TABLE 4 Catalytic oxidation of 2-adamantanone in different organic solvents

Entry	Solvent	Temp. (°C)	Conv. (%)	Sele. (%)
1	1,4-Dioxane	90	99	100
2	Toluene	90	27	90
3	nitrobenzene	90	44	95
4	chlorobenzene	90	21	93
5	ethylacetate	70	97	99
6	1,2-dichloroethane	70	34	97
7	Ethanol	70	98	99
8	Acetonitrile	70	91	98
9	methanol	50	99	99
10	THF	50	91	98

Condition: 2-adamantanone 0.1 mmol, cat. 5 mg, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), solvent 3 mL, 15 hours.

#### 3.2.4. Effect of Reaction Time

The influence of the reaction time on the reaction conversion was investigated by a series of oxidation reactions in which 2-adamantanone was still used as test substrate. The reaction was performed in methanol at  $50^{\circ}$ C. The result is shown in Figure 3. It can be seen that the conversion of 2-adamantanone was gradually increased with reaction time. The conversion of the substrate reached up to 82% at an early stage of 9 h. The substrate converted completely in 15 hours. From the result, it is suggested that the optimum reaction time is 15 hours.

#### 3.2.5. Effect of Ratio of Catalyst to Substrate

Different ratio of catalyst to substrate is used to investigate the corresponding variation of the oxidation. The reaction was carried out at 50°C for 15 hours in methanol.



FIG. 2. Relationship between conversion and the reaction temperature. Condition: 2-adamantanone 0.1 mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), cat. 5 mg, methanol 3 mL, 15 hours.



FIG. 3. Relationship between conversion and the reaction time. Condition: 2-adamantanone 0.1 mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), cat., 5 mg, methanol 3 mL, at 50°C.

The 2-adamantanone is still fixed to 0.1 mmol but with a different amount of catalyst. The result is shown in Figure 4.

It can be concluded from Figure 4 that when the amount of catalyst used is in the range of 1.0 to 5.0 mg, the conversion of 2-adamantanone was increased with increasing the amount of catalyst. The conversion reached 99% when the amount of catalyst is 5.0 mg. Hence, the optimum experimental condition is 0.1 mmol 2-adamantanone and 5.0 mg catalyst.

## 3.2.6. Recycling of the Catalyst

An important advantage of these chitosan supported dendritic tin catalysts is recycling. These complexes do not dissolve in the ordinary organic solvents, so the reaction is carried out under heterogeneous conditions. In order to verify if the catalysts could be reused, a series of experiments were carried out. The oxidation procedure is same with that previously mentioned. After the completion

100 80 Conversion (%) 60 40 20 0 ż ż á Ś Ω 1 Amount of catalyst (mg)

100 80 60 40 20 0ż 5 Recycling of catalyst (time)

FIG. 4. Effect of the amount of catalyst used on the conversion. Condition: 2-adamantanone 0.1 mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), methanol 3 mL, 15 hours at 50°C.

FIG. 5. Effect of recycling times on the conversion. Condition: 2-adamantanone 0.1 mmol, cat. 5 mg, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), methanol 3 mL, 15 hours at 50°C.

of each oxidation, the catalysts were separated by filtration. washed with methanol and then used for next oxidation reaction. The result is shown in Figure 5.

Figure 5 indicates that the catalyst P-PAMAM (2.0 G)-HBA-Sn(II) can be recycled for at least 6 times without appreciable loss in catalytic activity. The catalysts can also be stored for 3 years without any loss of capacity and activity, which means that the tin complexes have great stability.

## 3.2.7. Baeyer-Villiger Oxidation of Other Ketones

A variety of cyclic and acyclic ketones were also oxidized using chitosan supported dendritic Sn complexes at 70°C in different organic solvents. The result is listed in Table 5.

As shown in Table 5, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-tertbutylcyclohexanone, 4-tert-butylcyclohexanone, 3-methyl-2-pentanone, and 4-methyl-2-pentanone are transferred to the corresponding products in the Baeyer-Villiger oxidation catalyzed by P-PAMAM (2.0G)-HBA-Sn(II). The conversions are generally encouraging for most of the ketones examined. Besides cycloketones, the catalyst is also active for the oxidation of chain aliphatic ketones, such as 3-methyl-2-pentanone and 4-methyl-2-pentanone. For the two substrates, the conversions reach to 93% and 90%, respectively.

We found that the oxidation reaction did not proceed in the absence of the catalyst, or only in the presence of SnCl<sub>2</sub> or P-PAMAM-HBA (2.0 G). Then we can concluded that the activity point of the catalyst is Sn(II) ions that coordinated with the dendritic ligands.

The results show that this oxidation procedure is promising for cyclic and acyclic ketones and much cleaner than that of the traditional Baeyer-Villiger oxidation as it gives relatively higher substrate conversion and product selectivity.



Substrate	Solvent	Conv. (%)	Sele. (%)	TON	Product
	chorobenzene	72	97	14	o
o	chorobenzene	67	95	14	<b>o</b>
H <sub>3</sub> C	<b>O</b> ethanol	80	100	16	H <sub>3</sub> C
CH <sub>3</sub> O	ethanol	25	92	5	CH3
(H <sub>3</sub> C) <sub>3</sub> C	<b>O</b> ethanol	70	98	14	(H <sub>3</sub> C) <sub>3</sub> C
C(CH <sub>3</sub> ) <sub>3</sub>	ethanol	13	90	2	С(СН <sub>3</sub> )3
	chorobenzene	93	100	19	
, second	chorobenzene	90	100	20	

 TABLE 5

 Baeyer-Villiger oxidation of several ketones catalyzed by P-PAMAM (2.0 G)-HBA-Sn(II)

Condition: ketone 0.1 mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the ketone), cat.5 mg, solvent 3 mL, 15 hours at  $70^{\circ}$ C.

## 4. CONCLUSION

The chitosan supported dendrimer ligands and their dendritic tin complexes were synthesized by solid phase procedure. The complexes show high catalytic activities for the Baeyer-Villiger oxidation of ketones using environmentally friendly 30% hydrogen peroxide as oxidant. The reaction conditions were also well investigated. It can be concluded that the optimum reaction condition for the Baeyer-Villiger oxidation is 0.1 mmol ketone, 5 mg P-PAMAM (2.0 G)-HBA-Sn(II), 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to the

ketone), 3 mL solvent, 15 hours at 50°C. These complexes do not dissolve in the ordinary organic solvent, so the catalysts can be easily separated from reaction mixture, recycled and stored.

#### REFERENCES

 (a) Fischer, M. and Vogtle, F. (1999) Angew. Chem. Int. Ed., 38: 884–905; (b) Bosman, A.W., Janssen, H.M., and Meijer, E.W. (1999) Chem. Rev., 99: 1665–1688; (c) Helms, B. and Meijer, E.W. (2006) Science, 313: 929–923.

- [2] Annis, D.A. and Jacobson, E.N. (1999) J. Am. Chem. Soc., 121: 4147–4154.
- [3] Moszner, N., Volkel, T., and Rheinberger, V. (1996) Macromol. Chem. Phys., 197: 621–631.
- [4] Clair, N.S., Wang, Y., and Margolin, A.L. (2000) Angew. Chem. Int. Ed., 39: 380–383.
- [5] Fritschel, S.J., Ackerman, J.J.H., Keyer, T., and Stille, J.K. (1979) J. Org. Chem., 44: 3152–3157.
- [6] (a) Baeyer, A. and Villiger, V. (1899) Ber. Dtsch. Chem. Ges., 32: 3625–3633; (b) Baeye, A. and Villiger, V. (1900) Ber. Dtsch. Chem. Ges., 33: 858–864.
- [7] Strukul, G., Varagnolo, A., and Pinna, F. (1997) J. Mol. Catal. A, 117: 413–423.
- [8] Palazzi, C., Pinna, F., and Strukul, G. (2000) J. Mol. Catal. A, 151: 245–252.
- [9] Bernini, R., Mincione, E., Cortese, M., Saladino, R., Gualandi, G., and Belfiore, M.C. (2003) *Tetrahedron Lett.*, 44: 4823–4825.
- [10] Fischer, J. and Holderich, W.F. (1999) *Appl. Catal. A*, 180: 435–443.
- [11] Corma, A., Navarro, M.T., and Renz, M. (1996) Adv. Catal., 41: 253–334.
- [12] Corma, A., Navarro, M.T., and Renz, M. (2003) J. Catal., 219: 242–246.

- [13] Kaneda, K., Ueno, S., and Imanaka, T. (1995) J. Mol. Catal. A, 102: 135–138.
- [14] Liu, Y., Chen, C.L. and Xu, N.P. (2004) Chin. J. Catal., 25: 801–804.
- [15] Unnikrishnan, R.P. and Endalkachew, S.D. (2003) J. Mol. Catal. A, 191: 93–100.
- [16] Corma, A., Nemeth, L.T., Renz, M., and Valencla, S. (2001) *Nature*, 412: 423–425.
- [17] Hariharaputhiran, S., Elizabeth, G.N., Sridhar, B., and Ranjit, T. K. (2010) J. Mol. Catal. A, 330: 66–72.
- [18] Li, C.L., Wang, J.Q., Yang, Z.W., Hu, Z.A., and Lei, Z.Q. (2007) Catal. Commun., 8: 1202–1208.
- [19] Li, C.L., Yang, Z.W., Wu, S., and Lei, Z.Q. (2007) React. Funct. Polym., 67: 53–59.
- [20] Lei, Z.Q., Ma, G.F., and Jia, C.G. (2007) *Catal. Commun.*, 8: 305–309.
- [21] Lei, Z.Q., Ma, G.F., Wei, L.L., Yang, Q.L., and Su, B.T. (2008) Catal. Lett., 124: 330–333.
- [22] Lei, Z.Q., Zhang, Q.H., and Luo, J.J. (2005) Tetrahedron Lett., 46: 3505–3508.
- [23] Tsubokawa, N. and Takayama, T. (2000) React. Funct. Polym., 43: 341–350.