This article was downloaded by: On: 24 January 2011 Access details: Access Details: Free Access Publisher Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713597274

# The Influence of Pore Structures and Degree of Crosslinking on Catalytic Properties of Aminomethyl Polystyrene Resins Supported Dendritic Sn Complexes

Jiaqin Wang<sup>a</sup>; Renren Wang<sup>a</sup>; Zhe Zhang<sup>a</sup>; Cuilin Li<sup>a</sup>; Zhiwang Yang<sup>a</sup>; Ziqiang Lei<sup>a</sup> <sup>a</sup> Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, China

**To cite this Article** Wang, Jiaqin , Wang, Renren , Zhang, Zhe , Li, Cuilin , Yang, Zhiwang and Lei, Ziqiang(2008) 'The Influence of Pore Structures and Degree of Crosslinking on Catalytic Properties of Aminomethyl Polystyrene Resins Supported Dendritic Sn Complexes', Journal of Macromolecular Science, Part A, 45: 8, 672 – 679

To link to this Article: DOI: 10.1080/10601320802168934 URL: http://dx.doi.org/10.1080/10601320802168934

# PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# The Influence of Pore Structures and Degree of Crosslinking on Catalytic Properties of Aminomethyl Polystyrene Resins Supported Dendritic Sn Complexes

JIAQIN WANG, RENREN WANG, ZHE ZHANG, CUILIN LI, ZHIWANG YANG, and ZIQIANG LEI

Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, China

Received October, 2007, Accepted January, 2008

Seven different aminomethyl polystyrene resins supported dendritic Sn complexes were prepared by solid phase synthesis methodology. All the synthesized complexes show promising catalytic activities for the Baeyer-Villiger oxidation of ketones with hydrogen peroxide and affording the corresponding lactones or esters. The influence of different pore structures and the degree of crosslinking of the aminomethyl polystyrene resins on catalytic properties of the supported dendritic Sn complexes were well discussed.

Keywords: aminomethyl polystyrene; dendrimer; catalytic Baeyer-Villiger oxidation; pore structure; degree of crosslinking

#### 1 Introduction

Dendrimers were first synthesized by Tomalia and Newkone et al. (1, 2). With about two decades' development, dendrimers chemistry became one of the most fascinating and rapidly expanding areas of modern chemistry. Dendrimers are highly branched macromolecules and they are generally described to have a structure of spherical shape with a high degree of symmetry. Many of dendrimer supported metal complexes have been observed resulting from peripheral structure of dendrimers (3-8). However, solution-phase synthesis of dendrimers is often requiring long reaction times and tedious purifications. This disadvantage limited the preparation and the applications of the dendrimer-metal complexes. Several groups have reported the polymer supported dendrimers which were prepared by solid-phase synthesis methodology (9-15). However, all of these reported methods suffered from not only the complicated procedures for the preparation of the metal-containing dendrimers, but also the difficulty in the separation of the reaction mixtures. Solid-phase methodology, on the other hand, enables reactions to be driven to completion with the advantages of simple purification in that only filtration and washing are required to remove large excesses of reagents.

Immobilization of homogeneous catalysts onto polymer supports, through covalent attachment, has received wide attention because these materials offer advantage features of heterogeneous catalysis to homogeneous systems. The polymer-supported catalysts enhance their thermal stability, promising product selectivity, recyclability, as well as easy separation from reaction products leading to the operationally flexible. Such behavior prompted us to know the effect of structures of polymer supporters on catalytic properties of polymer supported complexes.

The Baeyer–Villiger oxidation is now frequently used for the synthesis of various lactones or esters. The reaction can also be applied in the synthesis of a wide variety of other chemicals, ranging from simple monomers used in the polyester industry to the more complex molecules that applied for the synthesis of pharmaceuticals (16). However, the traditional Baeyer-Villiger reactions have been commonly carried out by using peroxides or peracids as oxidants which potentially produce large amounts of harmful wastes. Much recent effort has been devoted to find chemically green oxidants along with the recyclable catalysts (17–23).

The palygorskite supported Sn(II) catalyst, which has shown promising catalytic activities for the Baeyer-Villiger oxidation of ketones with hydrogen peroxide, was first reported by our groups (24). Following this study, we use chloromethyl polystyrene and cellulose supported dendritic Sn complexes as another potential catalyst for the reaction

Address correspondence to: Ziqiang Lei, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China. Tel.: +86-931-7971687; Fax: +86-931-7970359; E-mail: leizq@nwnu.edu.cn

(25, 26). So we chose Baeyer–Villiger oxidation as the essential reaction to study the influence of different pore structures and the degree of crosslinking of the aminomethyl polystyrene resins on catalytic properties of the supported dendritic Sn complexes.

In this paper, we chose seven kinds of aminomethyl polystyrene resins with different pore structure or degree of crosslinking as the dendrimers supporters. We prepared seven groups of aminomethyl polystyrene resins supported dendritic Sn complexes named P-PAMAM-HBA ( $1.0 \sim 3.0$ G)-Sn(II) (where P = aminomethyl polystyrene resins, PAMAM = polyamidoamine, and G = generation). The ligands and the complexes were characterized by IR and ICP. Our aim is to find a way to select and use polymer supports, more reasonably, the influences of morphological structure of the supporters on the catalytic properties of the polymer-supported metal complexes were discussed. To the best of our knowledge, there is no literature reported on the research dealing with this subject.

#### 2 Experimental

#### 2.1 Reagents

Methyl acrylate (MA), AR, ethylenediamine (EDA), AR, were all obtained from a commercial source and purified before use.  $SnCl_2 \cdot 2H_2O$ , 4-hydroxybenzaldehyde (HBA) and other reagents were also obtained commercially and used without further purification. The characterization of three different aminomethyl polystyrene resins was shown in Table 1.

#### 2.2 Synthesis of the Metal Complexes

### 2.2.1 Grafting the Dendrimer to the Surface of Aminomethyl Polystyrene Resin

The metal complexes were prepared according to the literature (7, 25, 26). First, each of the three different structured

 Table 1. The characterization of seven different aminomethyl polystyrene resins

Entry	Loading (mmol/g)	Particle size (mesh)	Degree of crosslinking (DVB)	Pore structure
1	1.40	$100 \sim 200$	1%	Microporous <sup>b</sup>
2	1.15	$100\sim 200$	4%	Microporous <sup>b</sup>
3	1.13	$100\sim 200$	6%	Microporous <sup>b</sup>
4	1.50	$100\sim 200$	1%	Macroporous <sup>a</sup>
5	1.12	$100\sim 200$	4%	Macroporous <sup>a</sup>
6	1.13	$100\sim 200$	6%	Macroporous <sup>a</sup>
7	1.74	$100 \sim 200$	15%	Macroporous <sup>a</sup>

<sup>a</sup>The average diameter of this pore is 10 nm.

<sup>b</sup>Relative area is 500 g/m<sup>2</sup>.

aminomethyl polystyrene resins (0.5 g) was allowed to swell in THF (20 mL) for 48 h, respectively.

The second step, Michael addition of MA to amino groups on the surface of the resin: The swollen resin with peripheral amino groups, used as an initiator site, was added to the solution of MA (0.83 mL) in methanol (20 mL). The mixture was stirred at 50°C for 24 h, then filtered and the product was washed thoroughly with methanol.

Last, amidation of resulting terminal ester groups on the surface of the resin: after Michael addition, the resin was added to the solution of EDA (1.00 mL) in methanol (20 mL). The reaction mixture was heated to  $50^{\circ}$ C while stirring for 24 h, then filtered, and the product was washed with methanol five times. The supported dendrimer with the generation number of 1.0 (P-PAMAM (1.0G)) was obtained.

Repeating the above two reactions, the polymer-supported dendrimers from second generation to third generation were prepared.

## 2.2.2 Synthesis of the P-PAMAM-HBA $(1.0 \sim 3.0G)$

The supported 1.0G resin (0.25 g) was added to the solution of HBA (0.5 g) in methanol (20 mL). The mixture was stirred at 50°C for 48 h, then filtered, and the product was repeatedly washed with methanol until the filtrate became colorless. The supported first generation ligand (P-PAMAM-HBA (1.0G)) was obtained. Other ligands with different generation numbers were prepared with similar procedures.

# 2.2.3 Synthesis of the complexes P-PAMAM-HBA (1.0~3.0G)-Sn(II)

The 1.0G ligand (0.25 g) was added to the solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (2.0 g) in THF (20 mL). The mixture was stirred at 50°C for 48 h, then filtered and the product was repeatedly washed with THF and 1M HCl until the filtrate became colorless. The 1.0G supported dendritic tin complex (P-PAMAM-HBA (1.0G)-Sn(II)) was obtained. Other complexes with different generation numbers were prepared with similar procedures.

#### **3** Results and Discussion

#### 3.1 Characterizations of Synthesized Products

# 3.1.1 The IR Data of the Supported Dendritic Ligands and Resulting Complexes

The IR spectra of the aminomethyl polystyrene, polymersupported dendrimer, supported dendritic ligands and the resulting complexes were recorded with FT-IR using KBr pellet on a Nicolet AVATAR360 FT-IR spectrophotometer. The FT-IR data of macroporous aminomethyl polystyrene (15% DVB), the resulting supported dendrimers, the ligands, as well as the complex (G = 3.0) are shown in Figure 1.

As show in Figure 1, the IR spectra of aminomethyl polystyrene supported dendrimer, ligands and complexes show 674



**Fig. 1.** IR data of the resulting compounds (a) macroporous aminomethyl polystyrene (15% DVB); (b) P-PAMAM (3.0G); (c) P-PAMAM-HBA (3.0G); (d) P-PAMAM-HBA (3.0G)-Sn(II).

new absorptions peaks, which are characteristic of polyamidoamine and the tin complexes grafted on aminomethyl polystyrene resin. The absorption peak at  $3423 \text{ cm}^{-1}$  is characteristic of a secondary amino group. At the same time, several medium intensity bands appear at 2800-2985 cm<sup>-1</sup> due to the presence of CH<sub>2</sub> groups of polystyrene. The absorptions at  $1737 \text{ cm}^{-1}$ , which is characteristic of C==O, increased with an increasing of generation numbers. The absorptions at  $1171 \text{ cm}^{-1}$ , suggest the presence of Ph-O. All the absorption signals of the functional groups appear in the spectroscopy. It confirmed that the dendritic structures have been formed; and all the ligands and complexes we expected have also been well prepared.

## 3.1.2 ICP Analysis of the P-PAMAM-HBA (1.0~3.0G)-Sn(II) Complexes

ICP data of the P-PAMAM-HBA  $(1.0 \sim 3.0G)$ -Sn(II) complexes were analyzed on an American ICPV-5600 analytic instrument. All the analyses were carried out on standard

**Table 2.** The ICP data of the complexes Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G) Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G)

	ICP data (%)						
Catalyst	а	b	с	d	e	f	g
P-PAMAM-HBA (1.0G)-Sn(II)	21.64	10.19	11.96	7.10	11.43	14.48	7.89
P-PAMAM-HBA (2.0G)-Sn(II)	14.66	7.64	10.56	10.21	11.94	19.41	12.34
P-PAMAM-HBA (3.0G)-Sn(II)	13.68	5.26	5.94	17.21	11.81	14.61	12.90

$$\begin{array}{c} O \\ R-C-R \xrightarrow{Cat.} P \\ H_2O_2 \end{array} \xrightarrow{O} R-C-O-R$$

Sch. 1. Baeyer-Villiger oxidation of ketones.

conditions. The tin contents of the resulting complexes were shown in Table 2.

From the ideal structures of the ligands, we know that Sn (II) ions not only can coordinate with the peripheral Schiffbase groups, but also can coordinate with the inner nitrogen atoms. The theoretical metal content of the complexes should increase with the increase of the generation numbers. In fact, because of the steroic hindrance of higher generation dendrimer, the metal content of the polymer supported dendrimer complexes decreased with the increase of the generation numbers (38, 39). However, in Table 2, we can see that the Sn content of the macroporous aminomethyl polystyrene resin supported dendrimer complexes increased with the increase of the generation numbers. This may be due to the pore structure of the polymer supporters.

## 3.2 Catalytic Property Studies

A series of the Baeyer-Villiger oxidation reaction of 2-adamantanone were carried out to detect the different catalytic activity of the synthesized complexes. The results showed that different aminomethyl polystyrene resin supported P-PAMAM-HBA  $(1.0 \sim 3.0G)$ -Sn(II) have different catalytic activities, respectively. Several cyclic and acyclic ketones were oxidized to the corresponding lactones or esters (Scheme 1).

All the factors, including solvents, amount of catalysts used, reaction temperature, reaction time, as well as the



**Fig. 2.** The influence of different generation on the oxidation of 2-adamantanone Reaction conditions: 2-adamantanone 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq), methanol 3 mL, 24 h at 50°C. Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

recycling properties of catalysts, were investigated in the following.

# 3.2.1 The Catalytic Properties of Different Resins Supported Dendrimer Complexes P-PAMAM-HBA (1.0~3.0G)-Sn(II)

Oxidation of ketones was carried out in a 10 mL flask. A typical procedure for the Baeyer-Villiger oxidation of ketones is as follows: ketones (0.1 mmol) and 30% H<sub>2</sub>O<sub>2</sub>

(2.0 eq to the ketones) were dissolved in methanol or 1,4-dioxane (3.0 mL), a sample of the catalyst was added, the mixture was heated to  $50^{\circ}$ C or  $90^{\circ}$ C and stirred for 24 h. The percentage of conversion and product selectivity of oxidation were determined on a GC (instrument: Shimadzu GC-16A spectrophotometer) and a GC-MS spectrophotometer (instrument: QP-1000A GC-MS system). The results of oxidation of 2-adamantanone were shown in Figure 2.

**Table 3.** The influence of different solvent on the oxidation of 2-adamantanone by aminomethyl resin supported P-PAMAM-HBA (3.0G)-Sn(II) complexes. Reaction conditions: 2-adamantanone: 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30%H<sub>2</sub>O<sub>2</sub> (2.0 eq), solvent 3 mL, 24 h

Entry	Solvent	Catalyst	Temperature (°C)	Conv. (%)	TON	Sele. (%)
1	1,4-Dioxane	а	90	81	23	100
		b	90	54	16	100
		с	90	89	26	100
		d	90	83	24	100
		e	90	69	20	100
		f	90	68	20	100
		g	90	98	28	100
2	Nitrobenzene	а	90	54	16	100
		b	90	31	9	100
		с	90	76	22	100
		d	90	87	25	100
		e	90	36	10	100
		f	90	86	25	100
		g	90	98	28	100
3	Acetonitrile	а	70	53	15	100
		b	70	30	9	100
		с	70	24	7	100
		d	70	56	16	100
		e	70	34	10	100
		f	70	39	11	100
		g	70	32	9	100
4	Ethyl acetate	а	60	72	21	100
	2	b	60	70	20	100
		с	60	73	21	100
		d	60	85	25	100
		e	60	65	19	100
		f	60	78	23	100
		g	60	88	25	100
5	Ethanol	а	60	57	16	100
		b	60	74	21	100
		с	60	75	22	100
		d	60	60	17	100
		e	60	90	26	100
		f	60	85	25	100
		g	60	34	10	100
6	Methanol	а	50	97	28	100
		b	50	98	28	100
		c	50	97	28	100
		d	50	92	27	100
		e	50	95	27	100
		f	50	96	28	100
		g	50	95	27	100

Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). 676



**Fig. 3.** The relationship between TON and the reaction temperature. Reaction conditions: 2-adamantanone: 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq), methanol 3 mL, 24 h. Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn (II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

As shown in Figure 2, all the complexes perform promising catalytic activities in the Baeyer-Villiger oxidation of 2-adamantanone under normal conditions. We find that the catalytic activity was decreased with the increase of the generation numbers for the macroporous aminomethyl resin supported complexes, but the aminomethyl resin supported complexes have contrary results. In order to conveniently investigate the other differences of seven groups catalysts, the 3.0G complexes were taken as the model catalysts for the investigation of other factors.

Blank experiments performed at the same reaction conditions using 30% H<sub>2</sub>O<sub>2</sub> as oxidant catalyzed by the





**Fig. 5.** The relationship between TON and the reaction time. Reaction conditions: 2-adamantanone: 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq), methanol 3 mL, at 50°C. Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

dendrimer ligands showed no catalytic activities for the oxidation. But  $SnCl_2 \cdot 2H_2O$  have high catalytic activity with the presence of 30%  $H_2O_2$  for the Baeyer-Villiger oxidation of 2-adamantanone.

#### 3.2.2. The Solvent

According to our experimental results, the solvent has a great influence on the oxidation. In this way, the reactions were carried out at  $50^{\circ}$ C,  $60^{\circ}$ C,  $70^{\circ}$ C, and  $90^{\circ}$ C. Several organic solvents were examined for the oxidation of 2-adamantanone



Fig. 4. The effect of the amount of catalyst used on the TON. Reaction conditions: 2-adamantanone: 0.1 mmol,  $30\%H_2O_2$  (2.0 eq), methanol 3 mL, 24 h at 50°C. Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

**Fig. 6.** The effect of recycling times on the TON. Reaction conditions: 2-adamantanone 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq), methanol 3 mL, 24 h at 50°C. Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G). Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

Substrate	Cat.	Conv. (%)	Sele. (%)	TON	Product
$\square$	а	97	100	28	$\square$
	b	97	100	28	
	С	97	100	28	
0	d	92	100	27	- 00
	e	96	100	28	
	f	95	100	27	
	g	95	100	27	
0	а	23	100	7	О
l	b	25	100	7	
$\sim$	с	21	100	6	<u> </u>
$\setminus$ /	d	20	100	6	
	e	18	100	5	$\sim$
	f	32	100	9	
	g	27	100	8	
0	2	43	100	12	0
	a b	4J 67	100	10	Ĩ.
	U	60	100	19	
$\left( \right)$	d	09	100	20	
	d	20	100	7	
	e	25	100	/	
	I	27	100	8	
	g	36	100	10	
0	а	43	57	16	O II
	b	24	78	7	
CH <sub>3</sub>	с	25	80	7	$\frown$ $\rightarrow$ CH <sub>2</sub>
	d	41	100	12	
$\checkmark$	e	34	100	10	
	f	35	100	10	
	g	41	100	12	
0	а	56	100	16	О
Ц	h	59	100	17	
$\frown$	c	71	100	21	0
	d	45	100	13	
$\checkmark$	e	40	100	12	
ĊH <sub>3</sub>	f	59	100	17	Ť
	σ	29	100	8	CH3
0	5	2)	42	10	0
	a 1.	00	42	19	
$CH_3 - CH - CH_2 - C - CH_3$	D	85	100	25	$CH_3-CH-CH_2-O-C-CH_3$
CH <sub>3</sub>	C	89	100	26	CH <sub>3</sub>
	d	89	65	26	
	e	64	80	19	
	İ	5/	65	16	
	g	29	100	8	
O II	а	60	39	17	OII
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	b	72	83	21	CH <sub>3</sub> -CH <sub>2</sub> -CH-O-CH-O-CH <sub>3</sub>
$\operatorname{CH}_3$	с	83	81	24	$\operatorname{CH}_3$
-	d	73	53	21	-
	е	92	92	27	
	f	97	100	28	
	g	68	42	20	

 Table 4.
 Baeyer-Villiger oxidation of ketones catalyzed by P-PAMAM-HBA (3.0G)-Sn(II) complexes

Reaction conditions: ketones: 0.1 mmol, Sn:  $3.5 \times 10^{-3}$  mmol, 30% H<sub>2</sub>O<sub>2</sub> (2.0 eq to ketones), 1,4-dioxane 3 mL, 24 h at 90°C.

Aminomethyl resin (a: 1% DVB, b: 4% DVB, c: 6% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

Macroporous aminomethyl resin (d: 1% DVB, e: 4% DVB, f: 6% DVB, g: 15% DVB) supported P-PAMAM-HBA-Sn(II) (1.0G~3.0G).

using supported dendrimer complexes as catalyst. The results of TON, presented conversion and product selectivity data were concluded in Table 3.

It can be seen from Table 3 that the product selectivity remains 100% in all the examined solvents, but the product conversion is over 90% only in methanol, therefore, methanol was chosen as the organic medium to fulfill the oxidation in the following experiments.

### 3.2.3 Temperature

Effect of temperature on the catalytic performance has been studied at four different stages, that are 20°C, 30°C, 40°C and 50°C, the percentage conversion and product selectivity under different temperature are presented in Figure 3.

It is clear from Figure 3 that the conversion of 2-adamantanone were gradually increased while the reaction temperature ranged from 20°C to 50°C. There are slight differences between seven different pore structures and degree of crosslinking aminomethyl polystyrene resins supported dendritic Sn complexes.

# 3.2.4 The Influence of Ratio of Catalyst to Substrate

In order to optimize the reaction condition, different ratios of catalyst to substrate were used to investigate the corresponding variation of the oxidation result. The oxidation results were changed with the ratio. The results are shown in Figure 4.

It can be concluded from Figure 4 that the TON data of the oxidation was decreased when the amount of catalyst used was increased from 0.5 mg to 5.0 mg. However, when the amount of catalyst used was 3.0 mg, the reaction was finished over 85%. The results indicate that the effect of the amount of catalyst used on the TON data of seven groups of catalysts is reversible.

#### 3.2.5 Reaction Time

The effect of reaction time on the conversion of 2-adamantanone was also detailed in this system by a time controller. We removed 0.001 mL of reaction mixture at an identical interval from the reaction flask, and the reaction mixture was then immediately analyzed with GC. The results were shown in Figure 5.

Figure 5 shows that the TON data of 2-adamantanone increased with increasing the reaction time. During  $0 \sim 4$  h, the TON data of 2-adamantanone quickly increased. Under identical conditions, the reaction was finished completely at 24 h. At the same time, we can conclude from the data that pore structure or degree of crosslinking also has a slight effect on the catalytic properties of the complexes.

# 3.2.6 Recycling of the Catalyst

The recycling experiments were performed by separating the catalysts from the reaction mixture after the completion of each oxidation. The polymer-supported complexes separated by filtration were washed with methanol and subjected to another cycle with a fresh reaction mixture under the same reaction condition. The results were shown in Figure 6.

Figure 6 indicates that the macroporous aminomethyl resin with 15% DVB supported P-PAMAM-HBA(3.0G)-Sn(II) can be recycled at least 3 times without the obvious catalytic activity decrease, whereas, the other six catalysts could not be recycled because of remarkable decreasing of the conversions. We can conclude from this data that lower a degree of crosslinking gave poor recycled properties. On the other hand, the larger porous and higher degree of crosslinking results in more recycling times. The pore structures and degree of crosslinking have a tremendous influence on the catalytic of supported P-PAMAM-HBA (3.0G)-Sn(II) complexes. The result may be related to the position of the catalytic active center and the diffusibility of the solvents and the reactant through the supports.

# 3.2.7 The Baeyer-Villiger Oxidation of Other Ketones

Several selected cyclic and acyclic ketones, including 2-adamantanone, cyclopenanone, cyclooctanone, 2-methyl-cyclohexanone, 4-methylcyclohexanone, 4-methyl-2-pentanone and 3-methyl-2-pentanone were also oxidized in this oxidation system to give the corresponding lactones or esters. The results obtained in this study are summarized in Table 4.

The results in Table 4 showed that all three supported Sn-containing complexes show promising catalytic activity for the Baeyer-Villiger oxidation of these selected ketones. Under the same mild conditions, the complexes show higher catalytic activity for the oxidation of 4-methyl cyclohexanone, 4-methyl-2-pentanone, as well as 3-methyl-2-pentanone. However, among the seven Sn-containing complexes presented, the macroporous aminomethylated resin supported P-PAMAM-HBA (3.0)-Sn(II) catalyst gives better results in the oxidation. The results suggest that all of the synthesized complexes can be used as catalysts for the catalytic Baeyer-Villiger oxidation of ketones under mild reaction conditions.

# 4 Conclusions

In summary, the seven groups of aminomethyl resin supported dendrimer ligands and their dendritic complexes P-PAMAM-HBA ( $1.0 \sim 3.0$ G)-Sn(II) were synthesized by solid phase methodologies. The complexes show promising catalytic activities for Baeyer-Villiger oxidation of ketones using environmentally friendly 30% hydrogen peroxide as oxidant. The macroporous aminomethyl resin with 15% DVB degree of crosslinking supported dendritic complexes shows better catalytic properties among the seven complexes. The result may be related to the position of the catalytic active center, diffusibility of the solvents, and the reactant through the supports. The catalysts with a higher crosslinker support possess better recycling properties.

#### 5 Acknowledgments

The authors acknowledge support by the National Natural Science Foundation of China (20174031 and 20474052), Specialized Research Fund for the Doctoral Program of Higher Education (20050736001) and Key Laboratory of Eco-Environment-Related Polymer Materials

#### 6 References

- Tomalia, D.A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, G. and Smith, P. (1985) *Polym. J.*, **17(1)**, 117–132.
- Newkonme, G.R., Yao, Z.Q., Baker, G.R. and Gupta, V.K. (1985) J. Org. Chem., 50(11), 2003.
- 3. Astruc, D. and Chardac, F. (2001) Chem. Rev., 101(9), 2991-3024.
- Cordova, A. and Janda, K.D. (2001) J. Am. Chem. Soc., 123(34), 8248–8259.
- Yang, Z.W., Kang, Q.X., Ma, H.C., Li, C.L. and Lei, Z.Q. (2004) J. Mol. Cata. A-Chem., 213(2), 169–176.
- 6. Larsen, G. and Noriega, S. (2004) Appl. Catal. A-Gen., 278(1), 73-81.
- Krishna, T.R. and Jayaraman, N. (2004) *Tetrahedron*, 60(45), 10325–10334.
- Laurent, R., Caminade, A.M. and Majoral, J.P. (2005) *Tetrahedron Lett.*, 46(38), 6503–6506.
- Tsubokawa, N. and Takayama, T. (2000) *React. Funct. Polym.*, 43(3), 341–350.
- Dahan, A., Weissberg, A. and Portnoy, M. (2003) Chem. Commun., 10), 1206–1207.

- Dahan, A. and Portnoy, M. (2005) J. Polym. Sci. Pol. Chem., 43, 235–262.
- Bourque, S.C., Maltais, F., Xiao, W.J., Tardif, O., Alper, H., Arya, P. and Manzer, L.E. (1999) J. Am. Chem. Soc., 121(13), 3035–3038.
- 13. Chung, Y.M. and Rhee, H.K. (2002) Chem. Commun., (3), 238–239.
- 14. Chung, Y.M. and Rhee, H.K. (2003) CR. Chim., 6(7), 695-705.
- Touzani, R. and Alder, H. (2005) J. Mol. Cata. A-Chem., 227(1-2), 197–207.
- Bernini, R., Coratti, A., Fabrizi, G., Goggiamani, A., Fabrizi, G. and Goggiamani, A. (2003) *Tetrahedron Lett.*, 44(50), 8991–8994.
- Palazzi, C., Pinna, F. and Strukul, G. (2000) J. Mol. Catal. A-Chem., 151(1-2), 245–252.
- Bernini, R., Mincione, E., Cortese, M., Saladino, R., Gualandi, G. and Belfiore, M.C. (2003) *Tetrahedron Lett.*, 44(26), 4823–4825.
- Fischer, J. and Holderich, W.F. (1999) *Appl. Catal. A-Gen.*, 180(1–2), 435–443.
- Corma, A., Nemeth, L.T., Renz, M. and Valencia, S. (2001) *Nature*, 412, 423–425.
- 21. Corma, A., Navarro, M.T., Nemeth, L. and Renz, M. (2003) *J. Catal.*, **219(1)**, 242–246.
- 22. Unnikrishnan, R.P. (2003) J. Mol. Catal. A-Chem., 191(1-2), 93-100.
- 23. Strukul, G. (2001) Nature, 412, 388-389.
- Lei, Z.Q., Zhang, Q.H., Luo, J.J. and He, X.Y. (2005) *Tetrahedron Lett.*, 46(20), 3505–3508.
- Li, C.L., Yang, Z.W., Wu, S. and Lei, Z.Q. (2007) *React. Funct. Polym.*, 67(1), 53–59.
- Li, C.L., Wang, J.Q., Yang, Z.W., Hu, Z.A. and Lei, Z.Q. (2007) Catal. Commun., 8(8), 1202–1208.

2011