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## UNIVERSITÀ DEGLI STUDI DI TORINO

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# In situ cross-linked chitosan Cu(I) or Pd(II) complexes as a versatile, eco-friendly recyclable solid catalyst

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Cross-linked chitosan Ultrasound Heterogeneous catalysis, Cu-catalyzed azide/alkyne click reaction, Pd-catalyzed Suzuki reaction

## Abstract

Herein we report a simple ultrasound-assisted procedure to synthesize solid supported Cu(I) and Pd(II) catalysts. We prepared cross-linked chitosan derivatives (CS–Cu, CS–Pd) by reacting hexamethylene diisocyanate and chitosan in the presence of the metal salt. The in situ polymerization in water under sonochemical conditions was extremely fast and efficient. The catalysts were characterized by FT-IR, XPS, ICP-MS, and TGA. The Cu(I)-loaded polyurethane/urea-bridged chitosan was used for the azide/alkyne [3 + 2] cycloaddition, while those bearing Pd(II) complexes were used for Suzuki cross-couplings. In both reactions these novel catalysts permitted the use of simpler procedures and the possibility to reuse the catalyst several times with a minimal lost in activity. Our polyurethane/urea-bridged CS–Cu and CS–Pd complexes are superior in term of activity, recyclability and ease of preparation when compared to the adsorbed Cu or Pd/chitosan catalysts

## 1. Introduction

In synthetic organic chemistry, one of the most direct way to pursue Green Chemistry is the use of truly efficient catalytic reactions. To address these issues, highly active immobilized metal catalysts [1–3] are used to significantly facilitate these reactions and to benefit from a much simplified reaction workup. The hetero- geneous catalyst is often readily removed by filtration and can be successfully recycled several times with no detectable metal leaching or loss in activity. Polysaccharides have been widely applied as a suitable architecture for solid catalysts. Chitosan (CS), the N-deacetylated derivative of chitin, is an example of such polysaccharides that is widely distributed in living organisms. Because of the presence of a free-amino group, CS and its Schiff-base derivatives are considered to be suitable solid supports for the immobilization of a metal catalyst [4]. A limiting factor in the application of CS is its poor chemical resistance and mechanical strength, which significantly reduces the recycle life of this biopolymer. Physical and chemical modifications have been used to modify raw CS properties, in order to improve pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility. Modifications using cross-linking agents such as glutaraldehyde epichlorohydrin, diisocyanates or ethylene glycol glycidyl ether have commonly been investigated [5–13]. Diisocyanates are an important class of cross-linking agents for CS owing to their high reactivity towards amine as well as hydroxyl groups. However, the high reactivity of common diisocyanates with water and their insolubility in aqueous-acidic solutions represent an evident drawback. To the best of our knowledge, diisocyanates have so far been utilized to cross-link CS membranes [9,10], films [11], or to graft CS with synthetic or natural polymers [12,13]. Here we present a novel procedure for the preparation of in situ cross-linked CS–Cu(I) or Pd(II) complexes as recyclable solid catalysts.

The synthesis of CS-supported Pd(II) has already been reported in the literature as well as CS-imine derivatives used in C–C coupling reactions [14,15]. A study on the structure of CS supported ligand-free Pd(II) has already been published [16] and, based on our knowledge, only a few reports refer to their application in coupling reactions [17]. We have recently reported a number of Heck, Suzuki and Sonogashira reactions catalyzed by Pd(II)-loaded CS derivatives [18].

The physical properties of Cu–CS complexes are described in the literature [19,20]. Other authors have reported the use of CS- Schiff-base derivatives as Cu-chelating agents in heterogeneous catalysis [21,22]. A few publications have focused on the application of non-modified CS-supported copper [23,24]. Herein we describe the simple and rapid preparation of cross-linked CS supported Cu(I) or Pd(II) under ultrasound irradiation. The specific advantages of using sonication to remove the air bubbles in the bulk of CS derivatives and breaking agglomerates to achieve regular sized nanospheres, have been widely reported [23,25,26], as well as its influence in the formation of clustering of metal

nanoparticles in the presence of chitosan [27]. All these reactions go to completion in considerably shorter times and at lower temperatures, when compared to conventional methods, and positively influenced the formation of nanostructure [25,27]. Two different catalysts were prepared, characterized and applied in the Cu-catalyzed azide/alkyne [3 + 2] cycloaddition (CuAAC) as well as in Suzuki cross-coupling reactions. Their application under thermal conditions and under microwave irradiation was investigated.

## 2. Experimental

All chemicals were purchased from Sigma–Aldrich (solvents from Carlo Erba SpA) and were used without further purification. CS of medium molecular weight (from crab shells, 448877), 75–85% deacetylated was used as the support material. The FT-IR spectra were recorded with a Perkin-Elmer Fourier transform IR model 2000 spectrometer in the range of 4000–400  $\text{cm}^{-1}$  at a resolution of 0.2  $\text{cm}^{-1}$ . TG curves were recorded by the TA Instrument TGA 2050. The analyses were carried out at a constant heating rate of 10  $^{\circ}\text{C min}^{-1}$  from 50 to 700  $^{\circ}\text{C}$  under atmospheric conditions. The metal content in solution was determined by ICP-MS on a Quadrupole-ICP-MS X Series II (Thermo Fisher Scientific) after the digestion of CS–Pd(II) and CS–Cu(I) in  $\text{HNO}_3$  and aqua regia (1  $\text{HNO}_3$  /3  $\text{HCl}$ ). The oxidation state of the adsorbed palladium or copper was measured by X-ray photoelectron spectroscopy (XPS) with a Quantum 2000 (PHI Co., Chanhassen, MN, USA) with a focused monochromatic Al  $K_{\alpha}$  source (1486.7 eV) for excitation.

GC-MS analyses were performed on an Agilent Technologies 6850 Network GC System with 5973 Network Mass Selective Detector. NMR spectra were recorded on a Bruker 300 Avance (300 MHz and 75 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively) at 25  $^{\circ}\text{C}$ ; chemical shifts were calibrated to the residual proton and carbon resonance of the solvent:  $\text{CDCl}_3$  ( $\delta\text{H} = 7.26$ ,  $\delta\text{C} = 77.0$ ).

### 2.1. Preparation of cross-linked CS–Pd(II) and CS–Cu(I) catalysts (1–4)

CS (1.0 g) was dissolved in 0.1N  $\text{HCl}$  (68 ml) in a 250 ml three-neck round bottom flask at 60  $^{\circ}\text{C}$ . A solution of  $\text{Pd}(\text{OAc})_2$  (0.1 mmol) or  $\text{CuCl}$  (0.5 mmol) in 0.1N  $\text{HCl}$  (12 ml) was added and stirred until a clear solution was obtained. The mixture was sonicated (19.5 kHz, 30 W) and hexamethylene diisocyanate (HDI) (7.4 mmol, 1.2 ml) was added dropwise at room temperature and sonicated for about 90 min (60 W) at 50  $^{\circ}\text{C}$ . A whitish polymeric (CS–Pd(II)) or a bluishpale violet gel (CS–Cu(I)) were obtained. 0.5 N  $\text{NaOH}$  was added dropwise up to pH 10. The solid was filtered and washed with water, acetone and diethylether. The residue was dried over night at 50  $^{\circ}\text{C}$ . This procedure afforded

the two Pd(II)- and Cu(I)-loaded polyurethane/urea-bridged CS derivatives, 0.79 g (CS–Pd(II) **1**) and 0.81 g (CS–Cu(I) **2**) respectively.

In a variance of this procedure we replaced the HDI with HDACS (1 g) [25], obtaining the cross-linked CS derivatives **3** and **4**.

## 2.2. General procedure for CuAAC with cross-linked CS–Cu(I) catalyst 2

CS–Cu(I) **2** catalyst (5–10 mol%) was added to the solution of the azide (1 mmol) and the alkyne (1 mmol) in H<sub>2</sub>O/dioxane 8:2 (5 ml). The mixture was heated at 70 °C for 30 min. The mixture was filtered to remove the catalyst and the filter cake was washed twice with dioxane and three times with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to afford the triazole derivatives. The recovered catalyst was dried over night at 50 °C in a drying oven to be recycled.

When required the product was purified by flash column chromatography. All isolated products were confirmed by <sup>1</sup>H NMR and GC-MS and were demonstrated to be more than 99% pure.

## 2.3. General procedure for Suzuki cross-coupling with cross-linked CS–Pd(II) catalyst 1

The aryl halides (0.5 mmol) and the phenylboronic acid (0.55 mmol) were dissolved in H<sub>2</sub>O/dioxane 9:1 (7.5 ml). CS–Pd (II) catalyst **1** (1–0.5 mmol%) and triethylamine (1 mmol) were added.

The mixture was stirred at 70–100 °C (see Table 3) by conventional heating or under microwave irradiation (90–100 °C, max power 150 W). The mixture was filtered to remove the catalyst and the solid was washed twice with dioxane and three times with CH<sub>2</sub>Cl<sub>2</sub>. 1N HCl and water were added to the filtrate and the desired product was extracted with CH<sub>2</sub>Cl<sub>2</sub> without any further purifications.

The yield of biphenyl product from Suzuki cross-coupling was determined by GC-MS.

# 3. Results and discussion

## 3.1 Preparation and characterization of the catalysts 1–4

The cross-linked CS–Pd(II) **1** and CS–Cu(I) **2** were efficiently prepared by reacting the CS with HDI while the cross-linked CS derivatives **3** and **4** with hexamethylene 1,6-di(aminocarboxysulfonate) (HDACS) in water. The latter was chosen because it is stable under acidic conditions and easily activated by mild acidity and heat (60–80 °C) [28,29]. The polymeric gels **3** and **4**, however,

have been obtained in lower yield after a longer reaction time. Moreover, the reaction with HDSA was hardly reproducible. The lower viscosity of **3** and **4** also indicate a poorer reticulation degree then confirmed by IR analysis. The TGA analysis also showed a lower decomposition temperature. For all these reasons we decided to perform all our experiments only with catalyst **1** and **2**. All the reactions were performed in a high-power ultrasound bath. We suppose that the sonication breaks up intermicellar interaction and may promote the formation of clustering of metal nanoparticles. We observed that in absence of CuI or Pd(OAc)<sub>2</sub> the reaction failed even with a higher amount of the cross-linker. Nevertheless, when the metal salt was added afterwards the viscosity steadily increased until the formation of a turbid polymeric gel. This fact is not unprecedented, as reported in the literature, the addition of metals e.g. zinc strongly catalyzed the cross-linking reaction [30].

The IR spectra of plain CS, HDI cross-linked CS–Cu(I) **2** and HDACS cross-linked CS–Cu(I) **4** were compared (Fig. 1). It is expected that, with the increasing degree of reticulation, the bands at around 1650 and 1570 cm<sup>-1</sup>, assigned to amino I and amino II functional groups of CS, showed a better resolution. As depicted in Fig. 1, the IR spectra reveal feature which are consistent with moderate cross-linking for the derivative CS–Cu(I) **4** (HDACS derivative). The carbonyl resonance at 1700 cm<sup>-1</sup> becomes more prominent in the IR spectrum of HDI cross-linked CS–Cu(I) **2**, that evidences the presence of urea or urethane linkages in CS and an higher degree of reticulation. IR spectrum of HDI cross-linked CS–Pd(II) **1** was comparable to that of catalyst **2**, while when the CS was cross-linked with HDI in the absence of metal the IR was similar to that of plain CS, that means no reticulation.

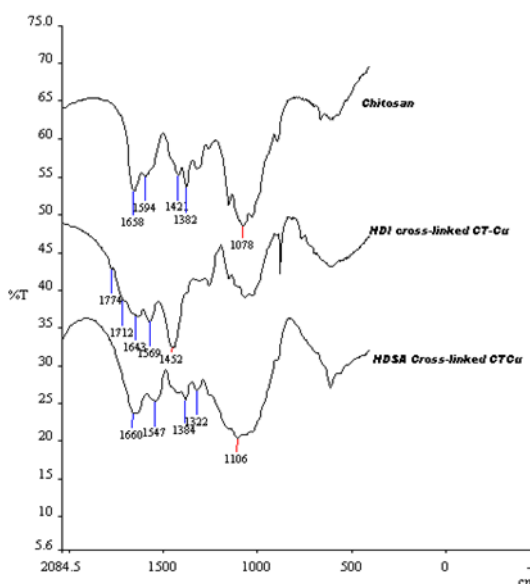
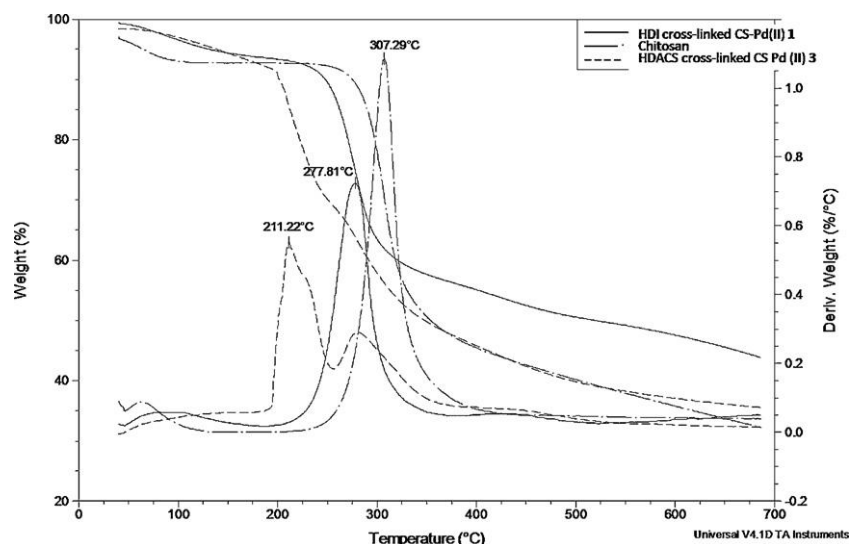


Fig1. IR spectra of chitosan, HDI cross-linked CS–Cu(I) **2** and HDACS cross-linkedCS–Cu(I)

Thermal gravimetric analysis (TGA) was used to measure and compare thermal stability. Due to the loss in hydrogen bonding caused by the derivatization of the amino group, the stability is expected to

decrease. As depicted in Fig. 2, TGA confirmed this assumption, while CS is stable up to 307 °C, cross-linked CS–Pd(II) **1** and cross-linked CS–Cu(I) **2** (that presented a comparable TGA profile) are stable up to 278 °C. The thermal decomposition temperature (heating rate 10 °C min<sup>-1</sup>) decreased to 211 °C when CS is cross-linked in the presence of HDSA. This indicates the higher thermal stability of HDI cross-linked CS.



**Figure 2.** Thermal stability of chitosan, HMDI cross-linked CS-Pd(II) **1** and HSACS cross-linked CS-Pd(II) **3**

In order to confirm the presence of the metals and the coordination of cross-linked CS with Cu or Pd, the catalysts were characterized by X-ray photoelectron spectroscopy (XPS). The binding energy of Cu 2p<sub>3/2</sub> in the cross-linked CS–Cu(I) **2** catalyst increased of 0.5 eV compared with CuCl. As described in Table 1, Pd 3d<sub>5/2</sub> signals of catalyst **1** could be divided into two varieties, indicating either the presence of two different Pd species, Pd(0) and Pd(II), or different coordination possibilities of Pd. The structure of the catalysts was not investigated by XPS because a preparation of the cross-linked CS without the metal was not successful. In the absence of this product, measurements of the differences in N1s and O1s binding energies in the polymer before and after the coordination of the metal could not be accomplished.

Samples	Pd 3d <sub>5/2</sub> eV	Cu 2p <sub>3/2</sub> eV
CuCl		931.9
cross-linked CS-Cu(I)		932.4
Pd(OAc) <sub>2</sub>	337.2	
cross-linked CS-Pd(II)	334.8	
	336.5	

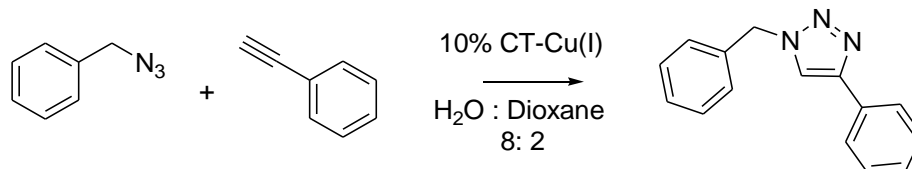
**Table 1.** XPS data for CuCl, Pd(OAc)<sub>2</sub>, and the novel catalysts (eV)

The weight content of metal in different complexes analyzed by ICP are 0.38% for cross-linked CS–Pd(II) **1**, and 1.10% for cross-linked CS–Cu(I) **2**.

### 3.2. CuAAC with cross-linked CS–Cu(I) catalyst **2**



The resulting cross-linked CS–Cu(I) catalyst **2** was applied in the Huisgen cycloaddition (Scheme 1). Benzyl azide, phenyl acetylene were mixed in H<sub>2</sub>O/dioxane 8:2 at 70 °C under magnetic stirring in the presence of 10 mol% cross-linked CS–Cu(I). The reaction was complete after 30 min. Filtration and solvent evaporation afforded pure triazole regioselectively and almost quantitatively.



**Scheme 1.** Synthesis of 1,2,3-triazole catalyzed by crosslinked CT-Cu(I) **2**

The reaction did not require any bases, ligands or reducing agents, and metal leaching was negligible, as shown by ICP-MS analysis of the triazole derivative. Compared to different copper supported catalysts the cross-linked CS–Cu(I) **2** showed higher reaction rate [31]. The reported Schiff-base CS–Cu-catalyst required 12 h to afford complete conversion of a similar click reaction [21]. Steric hindrance in either substrate can also reduce the reaction rate. Several additional experiments were carried out using the same conditions as listed in Table 2. After less than 30 min the yields were all uniformly high for aromatic alkynes and aliphatic alkynes, thus confirming the high catalytic activity of cross-linked CS–Cu(I) **2** (Table 2, Entries 3 and 4).

**Table 2:**

CuAAC catalyzed by cross linked CT-Cu(I) **2**.

Entry	Alkyne	Azide	Triazole	Yield [%]
1				95
2				94, 95 <sup>a</sup> , 93 <sup>b</sup> , 75 <sup>d</sup> , - <sup>d</sup>
3				95
4				96, 95 <sup>e</sup>
5				80 <sup>c</sup>

Reaction condition: alkyne, azide, crosslinked CT-Cu(I) **2** 10%, H<sub>2</sub>O: dioxane 8:2, 70°C, 30 min.

<sup>a</sup> Yield obtained with recycled catalyst

<sup>b</sup> Yield obtained with the two cycles/twice recycled catalyst

<sup>c</sup> The reaction was performed in ethanol

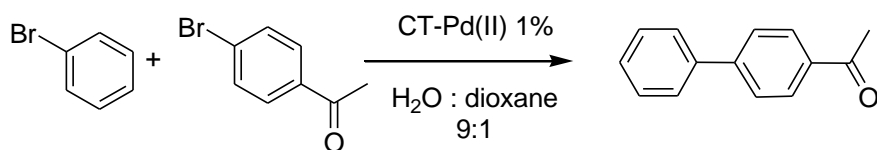
<sup>d</sup> The reaction was performed in toluene

<sup>e</sup> Yield obtained with cross linked CT-Cu(I) **2** 5%

Numerous control experiments indicated the efficacy and the robustness of the cross-linked CS-Cu(I) catalyst. After the completion of the reactions, the catalyst was filtered and washed twice with dioxane and three times with CH<sub>2</sub>Cl<sub>2</sub>. The recovered cross-linked CS-Cu(I) was reused for three cycles without any loss of activity (Table 2, Entry 2). The copper content was found to be almost the same in fresh and reused catalysts when checked by ICP-MS. The treatment of phenyl acetylene and benzyl azide with 5 mol% mol of cross-linked CS-Cu(I) demonstrates that the reaction can be performed at a lower catalyst concentration. This data was confirmed when the reaction was repeated with 3-butyn-2-ol and hexadecylazide (Table 2, Entries 4 and 5). The reaction yield was only moderately affected when the reaction was performed in ethanol, whereas, no conversion was observed in toluene (Table 2, Entry 2).

### 3.3. Suzuki cross-coupling with cross-linked CS-Pd(II) catalyst **1**

The catalytic activity of cross-linked CS-Pd(II) catalyst **1** was investigated. A model reaction with 4-bromoacetophenone and phenylboronic acid was optimized using different reaction conditions (Scheme 2). As shown in Table 3, the reaction was performed under conventional heating condition and under ultrasound or microwave irradiation. Satisfactory yields of biaryl product were obtained at 90 °C without the addition of a phase transfer catalyst. The catalytic activity of the complex with different amounts (1 or 0.5 mol%) was studied and comparable yields were obtained by increasing the reaction time. A yield of 90% was recovered with 0.5 mol% in 18 h at 90 °C. The reaction time was significantly reduced when the reaction was performed under microwave irradiation, thus confirming its promoting effect on the Suzuki cross-coupling in water. The feasibility of recycling the catalyst was also examined. After the reaction the catalyst was simply recovered by filtration and washed. However, a decrease of activity was observed until the third reuse.



**Scheme 2.** Suzuki cross-coupling catalyzed by cross-linked CS-Pd(I) **1**.

**Table 3.** Heterogeneous Suzuki coupling of 4-bromoacetophenone with bromobenzene

Entry	Catalyst <b>1</b>	Temp.	Time	Yield
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	(mol %)	(°C)	(h)	(%)
1	1	70	18	90
2	0.5	70	18	57
3 <sup>a</sup>	0.5	50	5	12
4	1	90	4	98
5	0.5	90	18	96
6 <sup>b</sup>	1	90	1	92
7 <sup>b</sup>	0.5	100	2	89
8 <sup>c</sup>	1	90	18	77
9 <sup>d</sup>	1	90	18	72

*Reaction conditions:* cross-linked CS-Pd(II) **1** H<sub>2</sub>O:dioxane 9:1;

<sup>a</sup>ultrasound irradiation (60W),

<sup>b</sup>microwave irradiation (150W),

<sup>c</sup>recycled catalyst,

<sup>d</sup>2<sup>nd</sup> recycle

#### 4. Conclusion

In conclusion we described the sonochemical preparation of solid cross-linked CS–Cu(I) or Pd(II) complexes. These are a series of polyurethane/urea-bridged derivatives that prove to be a versatile, efficient, eco-friendly and recyclable catalyst for azide/alkyne [3 + 2] cycloaddition and Suzuki cross-couplings.

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#### References

- [1] R. Akiyama, S. Kobayashi, *Chem. Rev.* 109 (2009) 594–642.
- [2] S.J. Shuttleworth, S.M. Allin, R.D. Wilson, D. Nasturica, *Synthesis* (2000) 1035–1074.
- [3] P. Hodge, *Chem. Soc. Rev.* 26 (1997) 417–424.

- [4] D.J. Macquarrie, J.J.E. Hardy, *Ind. Eng. Chem. Res.* 44 (2005) 8499–8520. [5] M. Ruiz, A.M. Sastre, E. Guibal, *React. Funct. Polym.* 45 (2000) 155–173.
- [6] Y.C. Wei, S.M. Hudson, J.M. Mayer, D.L. Kaplan, *J. Polym. Sci. A: Polym. Chem.* 30 (1992) 2187–2193.
- [7] W.S.W. Ngah, C.S. Endud, R. Mayanar, *React. Funct. Polym.* 50 (2002) 181–190.
- [8] M. Li, S. Cheng, H. Yan, *Green Chem.* 9 (2007) 894–898.
- [9] D.A. Devi, B. Smitha, S. Sridhar, T.M. Aminabhavi, *J. Membr. Sci.* 262 (2005) 91–99.
- [10] S.K. Choudhari, A.A. Kittur, S.S. Kulkarni, M.Y. Kariduraganavar, *J. Membr. Sci.* 302 (2007) 197–206.
- [11] C. Wenling, C. Mingyu, A. Qiang, G. Yandao, Z. Nanming, Z. Xiufang, *J. Biomater. Sci. Polym. Ed.* 16 (2005) 791–807.
- [12] R. Jayakumar, M. Prabakaran, R.L. Reis, J.F. Mano, *Carbohydr. Polym.* 62 (2005) 142–158.
- [13] M. Barikani, H. Honarkar, M. Barikani, *J. Appl. Polym. Sci.* 112 (2009) 3157–3165.
- [14] H.-F. Zhang, L. Zhang, Y.-C. Cui, *React. Funct. Polym.* 67 (2007) 322–328.
- [15] X. Xu, P. Liu, S. Li, P. Zhang, X. Wang, *React. Kinet. Catal. Lett.* 88 (2006) 217–223.
- [16] S.A. Johannesen, B.O. Petersen, J.Ø. Duus, T. Skrydstrup, *Inorg. Chem.* 46 (2007) 4326–4335.
- [17] V. Calò, A. Nacci, A. Monopoli, A. Fornaro, L. Sabbatini, N. Cioffi, N. Ditaranto, *Organometallics* 23 (2004) 5154–5158.
- [18] S.E.S. Leonhardt, A. Stolle, B. Ondruschka, G. Cravotto, C. De Leo, K.D. Jandt, T.F. Keller, *Appl. Catal. A: Gen.* 379 (2010) 30–37.
- [19] E. Chiessi, M. Branca, A. Palleschi, B. Pispisa, *Inorg. Chem.* 34 (1995) 2600–2609. [20] W. Sun, C.-G. Xia, H.-W. Wang, *New J. Chem.* 26 (2002) 755–758.
- [21] M. Chtchigrovsky, A. Primo, P. Gonzalez, K. Molvinger, M. Robitzer, F. Quignard, F. Taran, *Angew. Chem. Int. Ed.* 48 (2009) 5916–5920.
- [22] H. Wang, W. Sun, C. Xia, *J. Mol. Catal. A: Chem.* 206 (2003) 199–203. [23] X. Jin, J. Wang, J. Bai, *Carbohydr. Res.* 344 (2009) 825–829.
- [24] A.V. Kucherov, N.V. Kramareva, E.D. Finashina, A.E. Koklin, L.M. Kustov, *J. Mol. Catal. A: Chem.* 198 (2003) 377–389.
- [25] S.-Y. Zhang, J. Zhang, H.-Y. Wang, H.-Y. Chen, *Mater. Lett.* 58 (2004) 2590–2594.
- [26] G. Cravotto, S. Tagliapietra, B. Robaldo, M. Trotta, *Ultrason. Sonochem.* 12 (2005)

95–98.

[27] K. Okitsu, Y. Mizukoshi, T.A. Yamamoto, Y. Maeda, Y. Nagata, *Mater. Lett.* 61 (2007) 3429–3431.

[28] E.R. Welsh, C.L. Schauer, S.B. Qadri, R.R. Price, *Biomacromolecules* 3 (2002)1370–1374.

[29] S.-H. Chiu, T.-W. Chung, R. Giridhar, W.-T. Wu, *Food Res. Int.* 37 (2004) 217–223. [30] G.O. Aspinall (Ed.), *Spectroscopic Method in the Polysaccharides*, vol. 1, Academic Press, New York, 1982 (Chapter 4).

[31] B.H. Lipshutz, B.R. Taft, *Angew. Chem. Int. Ed.* 45 (2006) 8235–8238