RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Published on 26 May 2015. Downloaded by North Dakota State University on 07/06/2015 19:40:01.

Cite this: *RSC Adv.*, 2015, **5**, 46443

Received 22nd March 2015
Accepted 6th May 2015

DOI: 10.1039/c5ra05046d

www.rsc.org/advances

Oxidant free dehydrogenation of alcohols using chitosan/polyacrylamide entrapped Ag nanoparticles†

Deepak K. Kurhe, Thomson A. Fernandes, Tushar S. Deore and Radha V. Jayaram*

Silver nanoparticles encaged in a nanoporous chitosan/polyacrylamide interpenetrating polymer network (Ag@IPN) were synthesized and characterized by various techniques such as Fourier Transform Infra Red (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX), Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA) and ICP-AES. This material exhibits good catalytic activity for the oxidant free dehydrogenation of alcohols to the corresponding carbonyl compounds. The reusability of Ag@IPN for this reaction was compared with a chitosan–silver complex under the same reaction conditions. It was found that encaging silver nanoparticles in interpenetrating polymer networks (IPN) has improved their stability by avoiding leaching and aggregation.

1 Introduction

Oxidation of alcohols to carbonyl compounds is a fundamental transformation in synthetic organic chemistry.[1] Recently, transition metal catalyzed oxidation of alcohols using environmentally friendly oxidants such as oxygen,[2] hydrogen peroxide[3] has been reported. Transition metal catalyzed oxidant free dehydrogenation of alcohols is an atom economical method to convert alcohols into carbonyl compounds.[4] Though several homogeneous catalytic systems have been reported for this process, they often suffer from drawbacks such as air sensitivity, difficult catalyst synthesis and the requirement of additives.[5–7]

Supported transition metal catalyzed oxidant free dehydrogenation of alcohols is an environmental benign process as it avoids formation of H_2O,[8] produces H_2, which is a valuable energy source[9] and also suppresses over oxidation of reactants to carboxylic acids.[10] Transition metals such as, Ni,[11] Au,[12] Cu[13] and Rh[14] supported over various supports such as alumina, hydrotalcite and carbon have catalyzed the oxidant free dehydrogenation of primary and secondary alcohols into the corresponding aldehydes and ketones.

Recent drive towards sustainable and green chemical processes has lead to the use of biopolymers as catalyst supports.[15] Chitosan is an abundant natural hydrophilic biopolymer, which is widely used in pharmaceutical, food, biomedical[16] industries and catalysis.[17] As chitosan is a nontoxic, biodegradable polymer[18] which has good processability,[19] motivated its use as a support in an environment friendly heterogeneous catalysis. Also, the abundant amino and hydroxyl groups of the chitosan present unique affinity towards most transition metal species, making it an ideal solid support for applications in aqueous, organic and ionic liquid media.[20]

Kiyotomi Kaneda *et al.* have successfully carried out the oxidant free dehydrogenation of alcohols under heterogeneous condition using hydrotalcite supported silver nanoparticles. However, considering the growing consciousness of environmental issues chitosan supported silver nanoparticles catalyzed oxidant free dehydrogenation of alcohols is of considerable interest.

An interpenetrating polymer network (IPN) is a polymer comprising two or more networks which are at least partially interlocked on a polymer scale.[21] Materials formed from IPN's share characteristic properties of each network and have higher mechanical strength and stability than individual homopolymer network.[22] Also, IPN suppresses the reunion of nanoparticles, improves their distribution stability and uniformity in their networks.[23]

Thus it was intended to synthesize chitosan supported silver nanoparticles and improve the stability of silver nanoparticles by encaging them in IPN and use it as a catalyst for the oxidant free dehydrogenation of alcohols under oxidant free reaction conditions.

In this study, we synthesized chitosan supported silver nanoparticles by the reported procedure and formed interpenetrating polymer network with crosslinking polyacrylamide and chitosan. This silver-IPN catalyst (referred to as Ag@IPN) is

---

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai, 400 019, India. E-mail: rv.jayaram@ictmumbai.edu.in; Tel: +91 22 3361 2607

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra05046d

Published on 26 May 2015. Downloaded by North Dakota State University on 07/06/2015 19:40:01.

characterized by various spectroscopic and thermogravimetric techniques and used for the oxidant free dehydrogenation of alcohols under nitrogen environment. This catalyst showed the improved stability of silver nanoparticles in IPN than silver chitosan complex under the same reaction conditions.

2 Experimental

2.1 Materials and instrumentation

Low molecular weight chitosan (deacetylation 75–85%) was obtained from Sigma Aldrich (India) and used as received. All chemicals used in this study were of analytical grade and used as received without further purification. UV spectra were obtained using Shimadzu 1650PC (E) UV-Vis. Spectrophotometer. FTIR spectra were recorded using a FTIR spectrophotometer (Perkin Elmer Spectrum 100) as KBR pellets. Thermogravimetric (TGA) analysis of the samples was carried out with a heating rate of 10 °C $\min^{-1}$ and up to 700 °C under N_2 atmosphere with a Perkin Elmer instrument (STA 6000). Silver content in the materials was determined by ICP-AES analysis using a Varian AA240 analyzer. Scanning Electron Micrographs (SEM) and Energy Dispersive X-ray Analysis (EDX) were carried out using a FEI Quanta 200 ESEM FEG instrument. TEM imaging was done on 200 kV instrument (JEOL JEM 2100). XRD profiles were recorded on a Bruker AXS diffractometer with Cu-Kα radiation ($\lambda = 1.540562$ Å) over a 2θ range of 0–80°.

2.2 Catalyst preparation

Chitosan supported silver nanoparticles (Ag/chitosan) were synthesized by the reported procedure.[24] Chitosan (2.0 g) was dissolved in 50 mL acetic acid solution (1%). To this 5 mL aqueous solution of $AgNO_3$ (0.1 mol L^{-1}) was added and the solution was stirred at 30 °C overnight. At this stage, freshly prepared aqueous solution of $NaBH_4$ (5 times that of metal salt on mole basis) was added and stirred for 2 h. This solution was mixed with 0.2 mL 10% H_2SO_4, 0.4 mL of 25% glutaraldehyde solution and 0.4 mL 10% acetic acid solution to form solution I. Stirring with acetone for 30 minutes resulted in the precipitation of the Ag/cross linked polymer. The polymer was washed with distilled water repeatedly and dried under vacuum. Acrylamide (3.91 g), *N*,*N*′-methylenebisacrylamide (0.465 g) and potassium persulfate (0.08 g) were mixed in 10 mL distilled water to form solution II. Solution I was prepared again and solution I&II were mixed (chitosan : acrylamide = 0.8 : 1) and heated to 70 °C for 3 h to form interpenetrating polymer network gels which were washed with distilled water repetitively and dried under vacuum to get Ag@IPN.

3 Results and discussion

3.1 Catalyst characterization

The FTIR spectra of chitosan (a), Ag/chitosan (b) and Ag@IPN (c) are shown in Fig. S1.† The IR spectrum of chitosan absorption bands at 3444.49 cm^{-1} represents the $-NH_2$ and –OH groups. Absorption bands at 2993.99 cm^{-1} and 2856.11 cm^{-1} represent aliphatic groups. The absorption band at 1654.15 cm^{-1} is attributed to the $-CONH_2$ group of chitosan. In the FTIR spectrum of silver nanoparticle stabilized in chitosan (b), the absorption band 1654.15 cm^{-1} representing chitosan $-CONH_2$, disappeared and a new band appeared at 1629.78 cm^{-1}, which indicated the attachment of silver to nitrogen atom. The absorption band at 1655.24 cm^{-1} in Ag@IPN represents the amide stretching vibration from the crosslinked polyacrylamide.

Thermal studies of Ag/chitosan and Ag@IPN have been carried out (Fig. S2†). In case of Ag/chitosan (a) one stage decomposition with 36.45% weight loss was observed in the temperature range 200–400 °C, while in case of Ag@IPN (b) first stage decomposition was observed with 15.10% weight loss in the temperature range 200–300 °C. A second stage decomposition was observed with 30.04% weight loss in the temperature range 320–450 °C. This second stage decomposition in case of Ag@IPN can be attributed to the decomposition of amide groups and the degradation of the polymer main chains.[25]

The XRD pattern of Ag/chitosan (a) and Ag@IPN (b) is shown in Fig. 1. The XRD peaks at 2θ values around 38°, 44°, 64° and 77° could be assigned to the 111, 200, 220 and 311 crystallographic planes of the face centered cubic Ag crystals.[26]

The presence of well dispersed silver nanoparticles (60–75 nm) in the Ag@IPN was confirmed by SEM analysis (Fig. 2a). The silver content was found 4.49 wt% by EDX analysis (Fig. 2b).

Fig. S3(a–d)† shows the transmission electron micrographs of silver in chitosan (a&b) and chitosan-polyacrylamide IPN networks (c&d). These TEM images show that the silver nanoparticles are well dispersed without aggregation in the chitosan and chitosan-polyacrylamide IPN networks.

The silver content in Ag/chitosan and Ag@IPN as determined by ICP analysis was found to be 0.052 mmol g^{-1} and 0.024 mmol g^{-1} respectively.

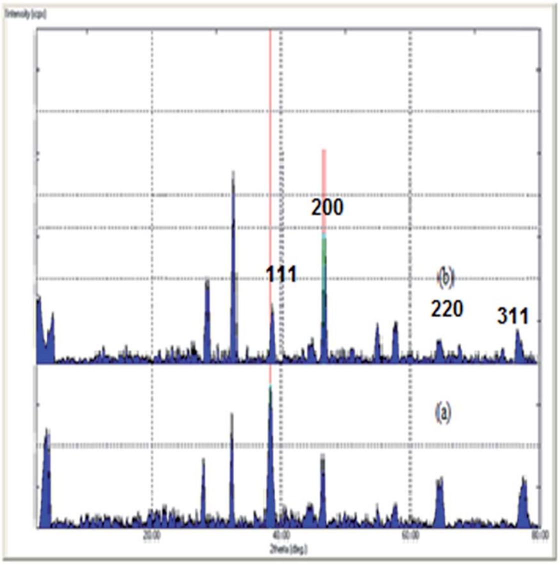
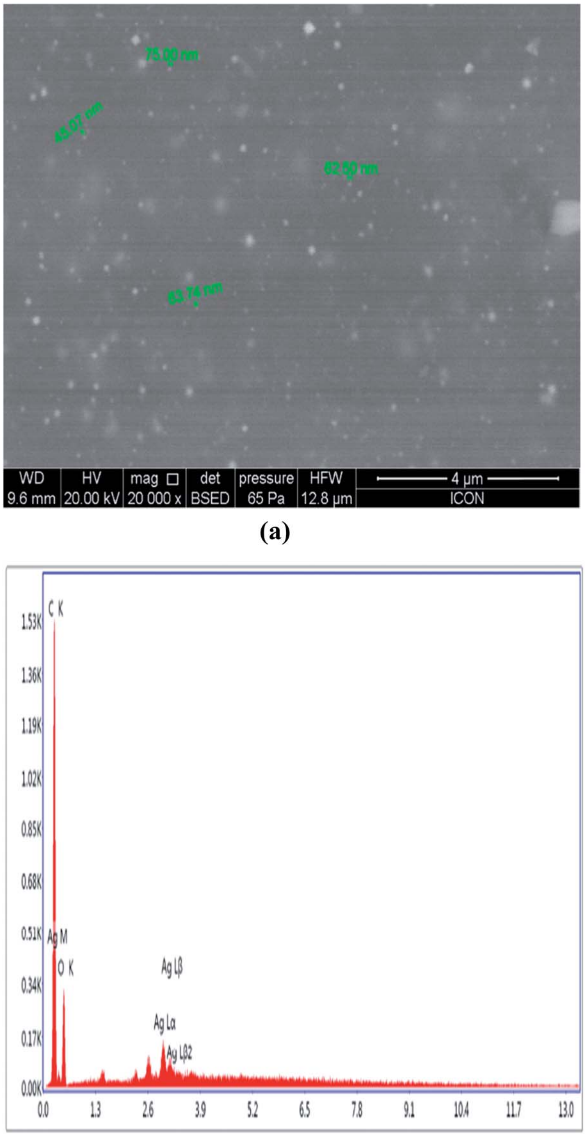


Fig. 1 XRD patterns of Ag/chitosan (a) and Ag@IPN (b).

Published on 26 May 2015. Downloaded by North Dakota State University on 07/06/2015 19:40:01.



(a)

(b)

Fig. 2 (a) SEM image of Ag@IPN. (b) EDX image of Ag@IPN.

The important parameters used to characterize nanostructure of crosslinked hydrogel networks are the polymer volume fraction in the swollen state ($V_{2,s}$), molecular weight of the polymer chains between two neighboring crosslinks ($\bar{M}_c$) and the corresponding mesh size (ξ).

$$Q = \frac{1}{V_{2,s}} \tag{1}$$

where $V_{2,s}$ is the volume fraction of the polymer in the swollen state.

Number average molecular weight between two adjacent crosslinks ($\bar{M}_c$) can be determined from the nominal crosslinking ratio X and the molecular weight of the repeating unit $\bar{M}_r$ of polyacrylamide ($\bar{M}_r = 71$) as

$$\overline{M}_c = \frac{\overline{M}_r}{2X} \tag{2}$$

The mesh size (ξ), or the correlation distance between two adjacent crosslinks, provides a measure of the space available between the macromolecular chains available for diffusion and movement of particles. This can be determined as follows.[27]

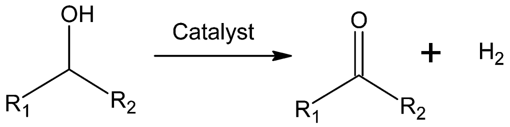
$$\xi = V_{2,s}^{-1/3}\left[C_n\left(\frac{2\overline{M}_c}{\overline{M}_r}\right)\right]^{1/2} l \tag{3}$$

where, C_n is the Flory characteristic ratio (C_n is 8.5 for polyacrylamide in water) and l is the carbon–carbon bond length (0.154 nm).

The polymer equilibrium swelling ratio (Q) and mesh size for polyacrylamide networks in Ag@IPN was determined by equilibrium swelling study and found to be 0.90 and 3.13 nm respectively. As mesh size for polyacrylamide networks in Ag@IPN is less than the size of silver nanoparticles, polyacrylamide networks will help in preventing the leaching of silver nanoparticles.

3.2 Catalytic activity

Catalytic activity of Ag@IPN was tested for the conversion alcohols to corresponding carbonyl compounds under oxidant free environment.



The conversion of 1-phenylethanol to acetophenone was selected as a model reaction. This conversion was carried out with different temperatures and quantities of the catalyst to obtain the optimized reaction conditions (Table 1). There was no difference in the conversion when catalyst loading was reduced from 0.1 mol% of Ag to 0.05 mol% Ag, but with 0.025 mol% Ag a low yield was observed. Hence 0.05 mol% of Ag was used for further studies (Scheme 1).

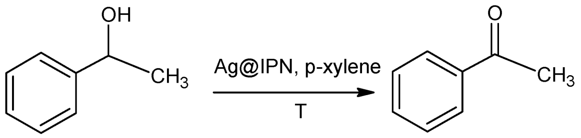
After optimizing the reaction conditions for the conversion of 1-ethylbenzene to acetophenone, the scope of the catalyst was tested for the reaction of various alcohols (Table 2). The catalytic system was found to be applicable to various aliphatic, aromatic and heteroaromatic alcohols.

Table 1 Optimization of reaction conditions

Entry	Catalyst (mol% of Ag)	Solvent	T (°C)	Time (h)	Yield[a,b] (%)
1	0.1	Toluene	90	12	72
2	0.1	Toluene	110	12	86
3	0.1	Toluene	110	24	93
4	0.1	*p*-Xylene	130	12	97
5	0.05	*p*-Xylene	130	12	97
6	0.025	*p*-Xylene	130	12	92

[a] Reaction conditions: 1-phenylethanol (1 mmol) and *p*-xylene (5 mL), catalyst (Ag@IPN). [b] Determined by GC.

Published on 26 May 2015. Downloaded by North Dakota State University on 07/06/2015 19:40:01.

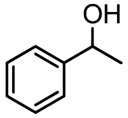
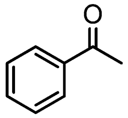
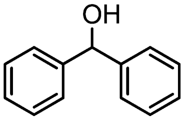
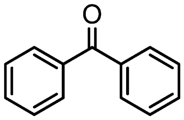
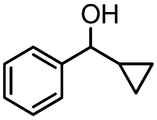
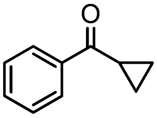
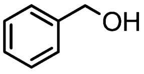
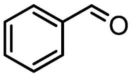
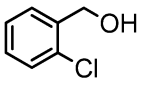
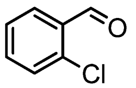
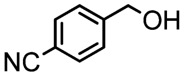
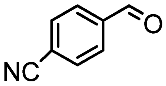
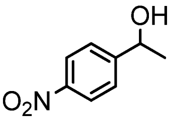
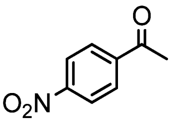
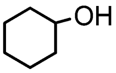
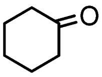
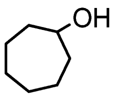
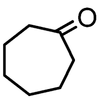
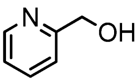
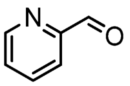
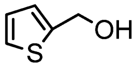
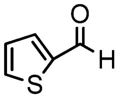
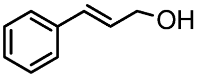
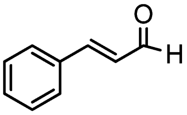


Scheme 1 Ag@IPN catalyzed conversion of 1-phenylethanol to acetophenone.

3.3 Catalyst reusability

In order to check the reusability of both Ag/chitosan and Ag@IPN, the conversion of 1-phenylethanol to acetophenone was repeated seven times with same amount of silver under optimized reaction conditions (Fig. 3). The catalyst was filtered off after each run and washed thoroughly with organic solvents. It was dried and fresh reaction was performed with new

Table 2 Synthesis of carbonyl compounds from alcohols catalyzed by Ag@IPN

Entry	Reactant	Product	Time (h)	Yield^{a,b} (%)
1			12	97
2			12	96
3			12	93
4			12	98
5			12	90
6			12	84
7			12	86
8			20	88
9			22	86
10			12	83
11			12	92
12			12	93

[a] Reaction conditions: alcohol (1.0 mmol), catalyst (0.05 mol% Ag), *p*-xylene (5 mL), temperature (130 °C). [b] Determined by GC.

Published on 26 May 2015. Downloaded by North Dakota State University on 07/06/2015 19:40:01.

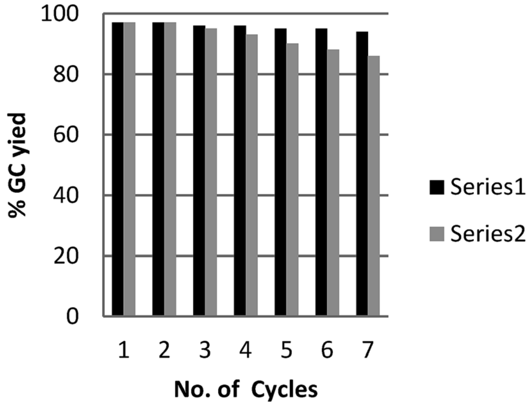


Fig. 3 Comparison of the recyclability of Ag/chitosan and Ag@IPN (black bars corresponds to Ag@IPN and grey to Ag/chitosan).

reactants under the same reaction conditions. By comparison, the activity of Ag/chitosan catalyst was reduced and after its 7th cycles a yield of 86% was obtained. However, with Ag@IPN catalyst 94% yield was obtained after its 7th cycle. Silver leaching of both catalysts was tested by ICP analysis after 7th cycle. The reusability study of both the catalysts was checked with 0.05 mol% of Ag. The Ag content was found to be 0.046 mol% in Ag@IPN and 0.035 mol% in Ag/chitosan after 7th cycle. This confirms that silver nanoparticles stability is improved in IPN networks by avoiding leaching.

4 Conclusions

In summary, silver nanoparticles encaged in chitosan/polyacrylamide interpenetrating networks. It was used as a catalyst for the oxidant free dehydrogenation of alcohols. Its reusability was compared with Ag/chitosan catalyst for the oxidation of 1-phenylethanol to acetophenone under same reaction conditions. It shows that encaging of silver nanoparticles in chitosan/polyacrylamide avoids leaching of silver nanoparticles. Thus, Ag@IPN catalytic system was expected to contribute to the development of environmentally benign oxidation process.

Acknowledgements

Author (DKK) is thankful to UGC for providing Research Fellowship (SAP) and BSR One time grant.

References

1 K.-ichi Fujita, N. Tanino and R. Yamaguchi, *Org. Lett.*, 2007, **9**, 109.

2 G. Csjernyik, A. H. Ell, L. Fadini, B. Pugin and J. E. Backvall, *J. Org. Chem.*, 2002, **67**, 1657.

3 R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, 2003, 1977.

4 G. Zhang and S. K. Hanson, *Org. Lett.*, 2013, **15**, 650.

5 J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Dalton Trans.*, 2007, 107.

6 J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans and L. A. Hulshof, *Organometallics*, 2006, **25**, 873.

7 G. B. W. L. Ligthart, R. H. Meijer, M. P. J. Donners and L. A. Hulshof, *Tetrahedron Lett.*, 2003, **44**, 1507.

8 W.-H. Kim, I. S. Park and J. Park, *Org. Lett.*, 2006, **8**, 2543.

9 R. Karvembu and S. Priyarega, *React. Kinet. Catal. Lett.*, 2006, **88**, 333.

10 T. Mistudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem.*, 2008, **120**, 144.

11 K. Shimizu, K. Kon, K. Shimura and S. S. M. A. Hakim, *J. Catal.*, 2013, **5**, 122.

12 W. Fang, Q. Zhang, J. Chen, W. Deng and Y. Yang, *Chem. Commun.*, 2010, **46**, 1547.

13 T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Commun.*, 2008, 4804.

14 Y. Sawama, K. Morita, T. Yamada, S. Nagata, Y. Yabe, Y. Monguchi and H. Sajiki, *Green Chem.*, 2014, **16**, 3439.

15 B. C. E. Makhubela, A. Jardine and G. S. Smith, *Appl. Catal., A*, 2011, **393**, 231.

16 S. Ekici and D. Saraydin, *Drug Delivery*, 2004, **11**, 381–388.

17 R. B. Nasir Baig and R. S. Varma, *Green Chem.*, 2013, **15**, 1839.

18 D. Wei, Y. Ye, X. Jia, C. Yuan and W. Qian, *Carbohydr. Res.*, 2010, **345**, 74.

19 D. Kuhbeck, G. Saidulu, K. Rajender Reddy and D. D. Diaz, *Green Chem.*, 2012, **14**, 378.

20 M. Zeng, C. Qi, J. Yang, B. Wang and X.-M. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 10041.

21 M. Shivshankar and B. K. Mandal, *Int. J. Pharm. Pharm. Sci.*, 2012, **4**, 1.

22 P. K. Suresh, S. K. Suryawani, D. Dewangan and P. Globale, *International Journal of Comprehensive Pharmacy*, 2011, **2**, 1–8.

23 Y.-L. Luo, Li-L. Chen, F. Xu and Q.-S. Feng, *Met. Mater. Int.*, 2012, **18**, 899.

24 J. An, Q. Luo, X. Yuan, D. Wang and X. Li, *J. Appl. Polym. Sci.*, 2011, **120**, 3180.

25 A. M. Al-Sabagh, N. G. Kandile, R. A. El-Ghazawy, M. R. Noor El-Din and E. A. El- Sharaky, *Egypt. J. Pet.*, 2013, **22**, 531.

26 M. B. Ahmad, J. J. Lim, K. Shameli, N. A. Ibrahim and M. Y. Tay, *Molecules*, 2011, **16**, 7237.

27 K. Zhan, H. You, W. Liu, J. Lu, P. Lu and J. Dong, *React. Funct. Polym.*, 2011, **71**, 756.