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H40-PCL-PEG unimolecular micelles both as anchoring sites for palladium nanoparticles and micellar catalyst for Heck reaction in water

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Abstract

A unimolecular micelle was employed both as anchoring sites for palladium nanoparticles and micellar catalyst for Heck reaction in water. In this system, the catalyst and substrates are concentrated in nanosize sites and therefore an efficient catalytic reaction occurs. The hyperbranched aliphatic polyester H40 has been functionalized with poly (caprolactone) (PCL) as hydrophobic core and polyethylene glycol (PEG) chains to obtain a water-soluble H40-PCL-PEG polymer which exhibits unimolecular micellar properties. The H40-PCL-PEG was effectively employed as a substrate for *in-situ* generation of Pd nanoparticles and also as a micellar catalyst. ¹H NMR, FT-IR, atomic absorption spectrometry (AAS), thermogravimetric analysis (TGA), x-ray diffraction (XRD) and transmission electron microscopy (TEM) were employed to characterize the synthesized catalyst. The application of palladium nanoparticles immobilized on H40-PCL-PEG (PdNPs@H40-PCL-PEG UMs) as an efficient nanocatalyst toward Heck reaction in different conditions was investigated. The catalyst were found to be very active in Heck reactions of aryl iodides, bromides and also chlorides with olefinic

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compounds in water at room temperature with short reaction time duration and high yields. The catalyst can be recycled several times by extraction, dialysis or ultracentrifuge methods without loss in activity.

Keywords: Hyperbranched polyester; Unimolecular micelle; Micellar catalyst; Palladium nanoparticles; Heck reaction.

1. Introduction

Despite the fact that water is cheap, safe, the most abundant and ecologically friendly solvent on earth, it is still relatively unexplored as a solvent for organic reactions [1-5]. The contrariety of some catalytic systems with water and the low water solubility of most organic compounds are the major factors restricting to perform organic reactions in aqueous media. However, there are a growing number of catalytic processes that use water as a reaction medium [6-10]. It has been demonstrated that surfactants can greatly raise both the activity and selectivity of the metal-based catalytic transformations in water because of the formation of micelles [11-13,5]. From the green chemistry view [14] the choice of amphiphile would ideally be, in the Anastas sense, "benign by design" [15]. In other words, its use on any scale would have minimal environmental consequences and ideally recyclable. It was recently shown that an amphiphilic block copolymer involving a ligand at the repeating unit of the hydrophobic block can be used instead of small organic surfactants in micellar catalysis [16]. For example, Schonfelder et al. have investigated the application of a novel class of amphiphilic, water-soluble diblock copolymers based on 2-oxazoline derivatives with pendant N-heterocyclic carbene/palladium catalysts in the hydrophobic block for Heck and Suzuki coupling in pure water [17].

The effect of surfactants and micelle forming agents on the rate of the cross coupling reactions may result from two sources, since surface tension at the boundary of the aqueous and organic phases decreases, a larger inter-phase area is produced which promotes mass transport, perhaps more important is the effect due to the appearance of micelles. In the presence of surfactants, above the critical micelle forming concentration (CMC), the concentration of water-insoluble olefins increased in the aqueous phase. The solubilized olefin is preferentially located in the hydrophobic part of micelles and if the catalyst can also be concentrated into that part then a very efficient catalytic reaction occurs [18-21]. At present, micellar catalysis has been applied in various organic syntheses, such as electrophilic substitution reaction, nucleophilic substitution reaction, oxidation reaction, hydrolysis, etc [22-26]. In 2011 Lipshutz et al introduced an environmentally benign surfactant, a diester composed of racemic R-tocopherol, methoxy poly (ethylene glycol) (MPEG), and succinic acid, and readily prepared as an effective nanomicelle-forming species for general use in metal-catalyzed cross-coupling reactions in water [27]. But multimolecular micelles are only thermodynamically stable above the CMC of the amphiphilic copolymers. When the concentration of the copolymer is above the CMC, the micelles are in dynamic equilibrium with the free copolymer molecules in solution, continuously breaking and reforming [28], but below the CMC, micelles disassemble. Developing unimolecular micelles based on amphiphilic copolymers with a dendritic or hyperbranched structure can be used to overcome the instability problem associated with multimolecular micelles [29,30]. For example, Meier et al. employed 5-arm star-shaped block copolymers with a poly(ethylene oxide) (PEO) core and a poly(e-caprolactone) (PCL) corona as templates for palladium nanoparticles [31]. Because of their covalent nature, unimolecular micelles do not disassemble upon dilution and are stable

toward environmental changes. Unimolecular micelles also offer other advantages, including narrow nanoparticle size distribution and high metal loading capacity. Moreover, the highly branched structure of the copolymers can provide many end groups for further functionalization [32,33]. Hyperbranched aliphatic polyester Boltorn H40 has received much attention in the design of amphiphilic hyperbranched block copolymers for different applications especially for drug delivery because of its globular structure, and high number of chain end functionalities [34,35].

In recent years our group has been working on the synthesis of micellar structures for controlled drug release [36-38] and the development of catalysts for useful new synthetic methodologies [39-42]. Herein, we report a novel approach toward applying the unimolecular micelles for catalytic purposes that utilizes H40 and PCL as the hydrophobic core and PEG as the hydrophilic corona.

2. Experimental

2.1. Materials

Hyperbranched aliphatic polyester Boltorn H40 was obtained from Perstorp Chemicals, and purified with acetone and tetrahydrofuran (THF). Poly (ethylene glycol) (PEG, Mn 2000 g/ mol) was purchased from Fluka and dried by azeotropic distillation using anhydrous toluene. ε-Caprolactone (CL) was purchased from Sigma and purified with calcium hydride (CaH₂) by vacuum distillation. Stannous octoate (Sn(Oct)₂, 95%), 4-(dimethylamino) pyridine (DMAP), N,N'-dicyclohexyl carbodiimide (DCC), maleic anhydride, and tin(II) chloride were purchased from Aldrich and used as received.

Dichloromethane (DCM) was dried over calcium chloride $(CaCl_2)$ and distilled. Triethylamine (TEA) was dried over CaH₂ and distilled. Dimethyl sulfoxide (DMSO) was

purified by distillation over P_2O_5 and CaH_2 . All other commercially available solvents and reagents were purchased from Merck or Aldrich Chemical Co. and used as received unless otherwise stated.

2.2. Instruments and characterization

AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (AAS) with a deuterium background corrector was used for determination of Pd (0). ¹H NMR spectra were recorded with a BRUKER DRX-300 AVANCE spectrometer, and CDCl₃ and DMSO- d_6 were used as solvent. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. A high resolution transmission electron microscopy (HR-TEM) analysis was performed by ZEISS EM- 900 at an acceleration voltage of 80 kV. Catalysis products were analysed using a Varian 3900 gas chromatograph (GC) (conversions were obtained using n-decane as an internal standard based on the amount of arylhalide employed relative to authentic standard product). Ultrasonic bath (EUROSONIC[®] 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvents. TGA was carried out using STA 1500 instrument at a heating rate of 10 °C min⁻¹ in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu K α radiation. CHN analysis was accomplished using a Vario EL analyzer.

2.3. H40-PCL-PEG Synthesis

The H40-PCL-OH was synthesized by $Sn(Oct)_2$ -catalyzed CROP of CL using H40 as macroinitiator. Typical polymerization procedure was as follows: H40 (0.85 g, 6.7 mmol hydroxyl groups) and CL (5.21 g, 4.85 mL, 46 mmol) were placed in a thoroughly dried silanized glass flask with a magnetic stirring bar. After the H40 was completely dissolved in the CL, a catalytic amount ([catalyst]/[macroinitiator] = 1:400) of Sn(Oct)₂ was introduced to

start the polymerization. The flask was evacuated, purged with nitrogen three times, sealed under vacuum, and then immersed in an oil bath at 120 °C for 24 h. After the reaction flask was cooled to ambient temperature, the reaction mixture was dissolved in dichloromethane, precipitated into cold methanol, filtrated, and dried under vacuum to obtain H40-PCL-OH. H40-PCL-OH with 2 mmol of -OH groups (the amount of H40-PCL-OH was calculated based on that 1 mol H40-PCL-OH contains 36 mol -OH groups, see ESI), maleic anhydride (2.2 mmol) and tin(II) chloride (5 wt % to H40-PCL-OH) were dissolved in dioxane (10 mL). The mixture was refluxed for 24 h to obtain H40-PCL-COOH. H40-PCL-COOH with 1 mmol of -COOH groups (the amount of H40-PCL-COOH was calculated based on that 1 mol H40-PCL-COOH contains 36 mol COOH groups, see ESI), 1 mmol PEG 2000, and DCC (1.1 mmol) were dissolved in anhydrous DMSO (20 mL) and stirred overnight at room temperature. Then DMAP (1 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for another 24 h. The product was dialyzed against DMSO for 3 h, then dialyzed against water for 24 h, during which the water was renewed every 3 h, and finally freeze-dried to obtain H40-PCL-PEG (Scheme 1) [43].

2.4. Micelle Formation and Palladium Loading

The H40-PCL-PEG (0.1 g) was dissolved in 5 mL of DMF. The solution was put into a dialysis tube (MWCO 8000-12000) and subjected to dialysis against 150 mL aqueous solution of PdCl₂ (0.05 M) for 8 h. An aqueous solution of NaBH₄ (180 mg in 0.5 mL of water) was then quickly added, and stirring was continued for 4 h. The palladium hybrid composite nanoparticles solution was further purified via dialysis against water for 24 h to obtain palladium nanoparticles immobilized on H40-PCL-PEG unimolecular micelles (Scheme 1).

The AAS and TGA were used to determine the amount of palladium in the synthesized catalyst.

2.5. Heck reaction in aqueous media using PdNs@H40-PCL-PEG UMs

At first aryl halide (1 mmol) and methyl acrylate or styrene (1 mmol) were dissolved in 2 ml water. This reactant mixture was then added to the solution of K_2CO_3 (1.2 mmol) in 1 ml of water under stirring condition. To this 0.1 mol% of Pd (0) nanocatalyst (PdNs-H40-PCL-PEG UMs) was added. The reaction was monitored by TLC (or GC if necessary). On completion of the reaction, the reaction mixture was transferred into ultracentrifuge and the phase below which contains catalyst was removed. Then, the mixture was extracted with CH₂Cl₂. The organic phase was dried over Na₂SO₄, filtered and evaporated in vacuum. The mixture was then purified by column chromatography over silica-gel or recrystallization to afford a product with high purity. Extraction with ethyl acetate or dialysis against water can also be applied to remove the catalyst. Characterization of the products was performed by comparison of their ¹H-NMR, and physical data with those of authentic samples.

3. Results and discussion

3.1. Synthesis and characterization of the catalyst

Our approach was guided by four imperatives: (i) the synthesized system should be amphiphile to act as micellar catalyst for organic reaction (ii) the support should encapsulate metal nanoparticles to control the size and uniform distributions of nanoparticles; (iii) the catalyst and substrates should concentrate in nanosize sites and iv) developing an efficient, environmental-friendly and benign synthetic process for the facile conversion of Heck cross coupling reaction.

The reason we used H40 as the core is because of its following advantages: similarity to dendrimers such as the existence of many functional groups that allow the modification for end use purposes and the possibility to form unimolecular micelles with stability against dilution after incorporation of hydrophilic shell, and much lower cost as compared with commercial dendrimers. Moreover, the encapsulated nanoparticles are confined in dendrimers by steric effects, and thus a substantial fraction of their surface is unpassivated and available to participate in catalytic reactions [44-48]. Also, we used PCL and PEG to afford amphiphilic copolymer which shows unimolecular micellar properties to act as micellar catalyst in organic reaction.

The synthesis of H40-PCL-PEG, subsequent formation of micelle and palladium loading have been outlined in Schemes 1. First, the H40-PCL-OH was prepared by the CROP (controlled ring opening polymerization) of CL using H40 as a macroinitiator.



Scheme 1. Synthesis of *PdNs@H40-PCL-PEG UMs*.

The ¹H NMR spectrum of H40-PCL-OH was shown in Fig. 1A. The major resonance peaks (a-d) are ascribed to the protons of methylene groups in the PCL main chains. Moreover, the signal at 3.64 ppm (e) that corresponds to the terminal methylene protons of the PCL (HOCH₂ \Box) is also identified. The signals at about 1.23 ppm and 4.10 ppm are assigned to the protons of methyl groups and methylene groups of the H40, respectively. The degree of polymerization (DP) for the PCL arms was found to be about 7, by calculating the relative integration of the peak at 3.64 ppm, which corresponds with the methylene group adjacent to the hydroxyl end group, and the peak at 4.04 ppm, which corresponds with the methylene protons adjacent to hydroxyl groups present in the polymer chain.

To achieve a high reactivity for further reactions, the next step was to convert hydroxyl groups of H40-PCL-OH to carboxyl groups. This was achieved by reaction between H40-PCL-OH and maleic anhydride in the presence of tin (II) in dioxane to obtain H40-PCL-COOH. After that, PEG segments were introduced to the hyperbrached polymer via the coupling reaction between -OH of PEG 2000 and -COOH of H40-PCL-COOH to form H40-PCL-PEG.

Fig. 1B shows ¹H NMR spectrum of H40-PCL-PEG. ¹H NMR spectra of H40-PCL-OH and H40-PCL-PEG reveal similar characteristic peaks for H40 and PCL. The peak at 5.6 ppm which was assigned as e is attributed to ($-CH=CH\Box$) of maleic anhydride. The characteristic peaks of PEG segments were observed at 3.7 ppm ($-O-CH_2-CH_2-$), the repeating unit of PEG.



Fig. 1. ¹H NMR spectra of H40-PCL in CDCl₃ and H40-PCL-PEG in DMSO-*d*₆.

The FT-IR spectra of the H40-PCL-OH, and H40-PCL-PEG have been shown in Fig. 2A and 2B, respectively, that also confirm the production of these compounds. The FT-IR spectrum of the H40-PCL-OH has a band characteristic for the ester carbonyl group at 1730 cm⁻¹ and two bands for hydroxyl at 3555 and 3411 cm⁻¹. These bands are associated to different hydrogen bonding interactions. The absorption band at 1102 cm⁻¹ in Fig. 2B is attributed to the characteristic C-O-C stretching vibration of the repeated $-OCH_2CH_2$ - units of polyethylene glycol backbone.



Fig. 2. FT-IR spectra of the H40-PCL-OH (A), and H40-PCL-PEG (B).

For the *in-situ* generation of palladium nanoparticles on the unimolecular micelle (Scheme 1), H40-PCL-PEG was dissolved in DMF. The solution was subjected to dialysis against aqueous solution of $PdCl_2$ and reduction into Pd nanoparticles was achieved upon addition of excess aqueous solution of NaBH₄. The solution immediately turned smoky. After dialysis and freeze drying, *PdNs@H40-PCL-PEG UMs* was obtained. Then AAS was used to calculate the weight percent of palladium in catalyst. The data showed that the amount of palladium loading on *H40-PCL-PEG UMs* is about 6.9 % wt.

The thermal properties of H40-PCL-PEG and *PdNs@H40-PCL-PEG* were characterized by TGA technique that was shown in Fig. 3A, 3B, respectively. No weight loss in the TGA curves in temperature range of 30–110 °C was observed showing to have achieved complete drying. The TGA profiles indicate that the main thermal degradation of H40-PCL-PEG occurs at 332 °C and that of *PdNs@H40-PCL-PEG* takes place at 320°C. Comparing the two curves demonstrates that the weight percent of palladium in synthesized catalyst is about 7% which is with agreement with AAS data.



Fig. 3. Weight loss as measured by TGA for *PdNAs@H40-PCL-PEG UMs* (A) and H40-PCL-PEG (B).

The diameters of the prepared Pd nanoparticles are 1-2 nm as determined from the TEM image shown in Fig. 4. This observation suggests the localization of Pd^{2+} ions within the *PdNs@H40-PCL-PEG UMs* because of the encapsulation of Pd^{2+} ions due to steric and electronic aspects. TEM image also shows that the diameter of micelles is around 28 nm which is the result of aggregation of unimolecular micelles.



Fig. 4. TEM image of PdNs@H40-PCL-PEG UMs.

The *PdNs@H40-PCL-PEG UMs* structure was also confirmed by XRD measurements (Figure 5). H40 exhibits a broad amorphous halo at around 2θ =17.1° [49]. As can be seen, two diffraction peaks at Bragg angles 2θ =21.5° and 23.1° could be observed, which was attributed to the diffraction of the (1 1 0) lattice plane and the (2 0 0) lattice plane of PCL, respectively [50]. A peak observed at around 2 θ value of 19° is due to organic moiety (PEG). The peaks at 2 θ values of about 39.9 is characteristic of face centered cubic (fcc) crystalline Pd, corresponding to the planes (1 1 1).

3.2. The catalytic activity of PdNs@H40-PCL-PEG UMs toward the Heck cross-coupling reactions

Various solvents, temperatures and catalyst amounts were employed in a model Heck coupling reaction between 4-methyl-iodobenzene and methyl acrylate and the conversion yields were measured by GC. The optimum results were obtained in water, at room temperature and by 0.1 mol% Pd.



Fig. 5. XRD pattern of *PdNs@H40-PCL-PEG UMs*.

We studied our amphiphilic polymer in a micellar catalytic variant of the Heck coupling reaction of different aryl halides and methyl acrylate or styrene under the above mentioned optimized conditions (Scheme 2 and Table 1). The course of the reaction was monitored by periodically taking samples and analyzing them by means of TLC (or GC if necessary). Characterization of the products was performed by comparison of their ¹H-NMR, and CHN data with those of authentic samples (see ESI). Moreover, melting points of the products were given in Table 1 and compared with the reported amounts.

The results demonstrate that aryl halides with either electron-withdrawing or electrondonating substituents react with olefins rapidly and generate the coupled products with excellent yields in aqueous medium at room temperature.



Scheme 2. Aqueous Heck coupling reaction of styrene and methyl acrylate with different aryl halides using *PdNs@H40-PCL-PEG UMs*.

The transformation of styrene with iodobenzene in neat water is considerably more complicated due to the higher hydrophobicity and lower water solubility of styrene (water solubility: 280 ppm) compared to methyl acrylate (water solubility: 52000 ppm) [57] but the presented system reveals excellent yields for both reactants. Actually, some of palladium nanoparticles placed in H40 and PCL which are hydrophobic part of unimolecular micelle. On the other hand, synthesized unimolecular micelle can act as micellar catalyst in organic reactions that concentrate organic substrates on its hydrophobic part. In our catalytic system, these two issues are combined; substrates and catalyst both are in hydrophobic part of micelle, so an efficient catalytic Heck reaction was achieved even for less reactive substrates.

The leaching of active metal species into solution is an important issue to be considered. To address this issue, in a separate experiment the catalyst was removed by ultracentrifuge after ~50% conversion at the reaction condition. Atomic absorption spectroscopy of the residue mixture confirms that the Pd content in the solution was below the detection limit (0.1 ppm). Moreover, further treatment of the residue mixture under similar reaction condition did not proceed significantly. Therefore, we may conclude that palladium leaching in the catalyst is negligible.

Entry	ArX	\mathbb{R}^2	Time (h)	Isolated yield	mp (°C)	Reported
				(%)		mp (°C)
1	H ₃ C-	Ph	1.5	99	116	112–115 [51]
2	H ₃ C-	CO ₂ Me	1	99	60-61	57-58 [52]
3	Br	Ph	1.5	98	123	124 [53]
4	Br	CO ₂ Me	1	99	39	36-38 [51]
5	O ₂ N-Br	Ph	1.5	98	155	155 [54]
6	O ₂ N-Br	CO ₂ Me	1	99	160	158-160 [55]
7	Сі	Ph	1.5	90	122	124 [53]
8	CI-CI	CO ₂ Me	1	93	37	36-38 [51]
9	O ₂ N-CI	Ph	1.5	92	157	155 [54]
10	O ₂ N-CI	CO ₂ Me	1	93	164	158-160 [55]
11	H ₃ C-CI	Ph	1.5	86	113	112–115 [51]
12	H ₃ C-CI	CO ₂ Me	1	89	60-61	57-58 [52]
13	H3CO-CI	Ph	1.5	85	135	134 [56]
14	H3CO-CI	CO ₂ Me	Í	87	88	89-90 [52]

Table 1. Aqueous Heck coupling reactions.

^a Reaction conditions: Aryl halide (1 mmol) and alkene (1 mmol), 2 ml water, K₂CO₃ (1.2 mmol) in 1 ml water, 0.1 mol% of Pd(0) nanocatalyst (*PdNs-H40-PCL-PEG UMs*).

3.3. Recycling PdNs@H40-PCL-PEG UMs.

By design, the preferred solubility of PdNs@H40-PCL-PEG~UMs in water, as opposed to common organic solvents used for extraction (e.g., hydrocarbons, Et₂O, and EtOAc), allows for recycling of the aqueous phase. A model Heck coupling reaction between 4-methyliodobenzene and methyl acrylate was studied, where each cycle was followed by a standard in-flask extraction of the product using minimal amounts of Et₂O (3 times), after which fresh substrate and catalyst were introduced. As illustrated in Table 2, after fifteen recycles, almost complete conversion to the desired product is realized.

Other methods for the recovery of catalyst are using ultracentrifugation or dialysis. Extraction or ultracentrifugation is the cheaper methods relative to dialysis.

No. of recycling	Conversion ^b (%)	-
	99	-
2	99	
3	99	
4	98	
5	97	
6	96	
7	96	
8	96	
9	96	
10	95	
11	95	
12	95	
13	95	
14	94	
15	94	_

Table 2. Effect of recycling on the catalytic efficiency of PdNs@H40-PCL-PEG UMs.^a

^a Reaction conditions: 4-methyl-iodobenzene (1 mmol) and methyl acrylate (1 mmol) 2 ml water, K_2CO_3 (1.2 mmol) in 1 ml of water, 0.1 mol% of Pd(0) nanocatalyst (*PdNs-H40-PCL-PEG UMs*).

^b Obtained by GC.

4. Conclusion

H40-PCL-PEG unimolecular micelles were employed as anchoring sites for palladium nanoparticles and also micellar catalyst for Heck reaction in water. H40-PCL-PEG unimolecular micelles can encapsulate nanoparticles due to both steric and electronic effects.

The deposition of Pd nanoparticles on *H40-PCL-PEG UMs* was confirmatively studied by AAS, XRD, TEM and TGA. The activity and efficiency of catalyst were examined in Heck reaction and these materials were found to be efficient and reusable catalysts in cross-coupling reactions of aryl iodides, bromides and also chlorides with olefinic compounds in short reaction time and high yields. Further efforts to extend the application of this catalyst in large variety of organic reactions in green conditions are currently in progress in our laboratory.

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References

[1] P. A. Grieco, Organic Synthesis in Water, Springer, New York, 1997.

[2] M.A. Abraham, L. Moens, Clean Solvents: Alternative Media for Chemical Reactions and Processing, ACS Symposium Series 819, Washington, DC, 2002.

- [3] U. M. Lindstroem, Organic Reactions in Water, Blackwell, Publishing Ltd., Oxford, UK, 2007.
- [4] H.C. Hailes, Org. Process Res. Dev. 11 (2007) 114-120.
- [5] P. H. Dixneuf and V. Cadierno, Metal-Catalyzed Reactions in Water, Wiley-VCH Verlag GmbH & Co. KGaA, 2013.
- [6] C.-J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68-82.
- [7] D. Sinou, Adv. Synth. Catal. 344 (2002) 221-237.
- [8] R. W. Eckl, T. Priermeier, W. A. Herrmann, J. Organomet. Chem. 532 (1997) 243-249.
- [9] W. W. Y. Leong, X. Chen, Y. R. Chi, Green Chem. 15 (2013) 1505-1508.
- [10] A. Corma, H. García, A. Leyva, J. Catal. 240 (2006) 87-99.
- [11] M. N. Khan, Micellar Catalysis, CRC Press, Boca Raton, USA, 2006.
- [12] T. Dwars, E. Paetzold, G. Oehme, Angew. Chem. Int. Ed. 44 (2005) 7174-7199.

[13] F. Szabo, B. Petho, Z. Gonda, Z. Novak, RSC Advances 3 (2013) 4903-4908.

[14] R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, Green Chemistry and Catalysis, Wiley-VCH: Weinheim, Germany, 2007.

- [15] P. T. Anastas, C. A. Farris, Benign by Design: Alternative Synthetic Design for Pollution
- Prevention, ACS Symposium Series 557, American Chemical Society, Washington, DC, 1994.
- [16] P. Persigehl, R. Jordan, O. Nuyken, Macromolecules 33 (2000) 6977-6981.
- [17] D. Schonfelder, O. Nuyken, R. Weberskirch, Des. Monomers Polym. 8 (2005) 117-134.
- [18] L. c. Leclercq, M. Lacour, S. H. Sanon, A. R. Schmitzer, Chem. Eur. J. 15 (2009) 6327-6331.
- [19] Y. Dror, J. Manassen, Stud. Surf. Sci. Catal. 7 (1981) 887-897.
- [20] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, J. Mol. Catal. A: Chem. 149 (1999) 1-6.
- [21] P. J. Quinn, C. E. Taylor, J. Mol. Catal. 13 (1981) 389-396.
- [22] E. Pandey, S. K. Upadhyay, Colloids and Surfaces A: Physicochem. Eng. Aspects 269 (2005) 7-15.
- [23] C. Siswanto, J. F. Rathman, J. Colloid Interface Sci. 196 (1997) 99-102.
- [24] L. G. Qiu, A. J. Xie, Y. H. Shen, Colloids and Surfaces A: Physicochem. Eng. Aspects 260 (2005)251-254.
- [25] T. Dwars, E. Paetzold, G. Oehme, Angew. Chem. Int. Ed. 44 (2005) 7174-7199.
- [26] K. Bica, P. Gartner, P. J. Gritsch, A. K. Ressmann, C. Schroder, R. Zirbs, Chem. Commun. 48 (2012) 5013-5015.
- [27] B. H. Lipshutz, S. Ghorai, A. R. Abela, R. Moser, T. Nishikata, C. Duplais, A. Krasovskiy, J. Org. Chem. 76 (2011) 4379-4391.
- [28] D. Hall, B. Pethica, M. Schick, Nonionic Surfactants, Marcel Decker Inc., New York, 1967.
- [29] A. Kikuchi, T. Nose, Macromolecules 29 (1996) 6770-6777.
- [30] S. Aryal, M. Prabaharan, S. Pilla, S. Q. Gong, Int. J. Biol. Macromol. 44 (2009) 346-352.
- [31] G. Kreutzer, C. Ternat, T. Q. Nguyen, C. J. G. Plummer, J. E. Manson, V. Castelletto, I. W.

- Hamley, F. Sun, S. S. Sheiko, A. Herrmann, L. Ouali, H. Sommer, W. Fieber, M. I. Velazco, H. A. Klok, Macromolecules 39 (2006) 4507-4516.
- [32] M. A. Meier, M. Filali, J.-F. Gohy, U. S. Schubert, J. Mater. Chem. 16 (2006) 3001-3006.
- [33] J. H. Zou, Y. B. Zhao, W. F. Shi, J. Phys. Chem. B 110 (2006) 2638-2642.
- [34] S. Luo, J. Xu, Z. Zhu, C. Wu, S. Liu, J. Phys. Chem. B 110 (2006) 9132-9138.
- [35] Y. Kitajyo, Y. Nawa, M. Tamaki, H. Tani, K. Takahashi, H. Kaga, T. Satoh, T. Kakuchi, Polymer 48 (2007) 4683-4690.
- [36] M. R. Nabid, S. J. T. Rezaei, R. Sedghi, H. Niknejad, A. A. Entezami, H. A. Oskooie, M. M. Heravi, Polymer 52 (2011) 2799-2809.
- [37] S. J. T. Rezaei, M. R. Nabid, H. Niknejad, A. A. Entezami, Int. J. Pharm. 437 (2012) 70-79.
- [38] R. Sedghi, H. A. Oskooie, M. M. Heravi, M. R. Nabid, A. H. Zarnani, J. Mater. Chem. B 1 (2013) 773-786.
- [39] M.R. Nabid, R. Sedghi, P.R. Jamaat, N. Safari, A.A. Entezami, Appl. Catal. A: Gen. 328 (2007)52-57.
- [40] M.R. Nabid, S.J. Tabatabaei Rezaei, Appl. Catal. A: Gen. 366 (2009) 108-113.
- [41] M.R. Nabid, Y. Bide, S.J. Tabatabaei Rezaei, Appl. Catal. A: Gen. 406 (2011) 124-132.
- [42] H. Ahmar, A. R. Fakhari, M. R. Nabid, S. J. T. Rezaei, Y. Bide, Sens. Actuators, B, 171–172 (2012) 611-618.
- [43] M. Zhao, R. M. Crooks, Angew. Chem., Int. Ed. 38 (1999) 364-366.
- [44] M. Zhao, R. M. Crooks, Adv. Mater. 11 (1999) 217-220.
- [45] L. K. Yeung, R. M. Crooks, Nano Lett. 1 (2001) 14-17.
- [46] V. Chechik, M. Zhao, R. M. Crooks, J. Am. Chem. Soc. 121 (1999) 4910-4911.
- [47] V. Chechik, R. M. Crooks, J. Am. Chem. Soc. 122 (2000) 1243-1244.
- [48] D. Schönfelder, O. Nuyken, R. Weberskirch, J. Organomet. Chem. 690 (2005) 4648-4655.
- [49] E. Zagar, M. Huskic, J. Grdadolnik, M. Zigon, A. Zupancic-Valant, Macromolecules 38 (2005)

3933-3942.

- [50] K.H. Lee, H.Y. Kim, M.S. Khil, Y.M. Ra, D.R. Lee, Polymer 44 (2003) 1287-1294.
- [51] L. R. Moore, K. H. Shaughnessy, Org. Lett. 6 (2004) 225–228.
- [52] C. Diebold, S. Schweizer, J-M. Becht, Org. Biomol. Chem. 8 (2010) 4834-4836.
- [53] A. Michaelis, H. Lange, Ber. Dtsch. Chem. Ges. 8 (1875) 1313–1316.
- [54] F. Luo, C. Pan, W. Wang, Z. Ye, J. Cheng, Tetrahedron 66 (2010) 1399-1403.
- [55] R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, R. Pleixats, A. Prastaro, R. M.
- Sebastia, R. Soler, M. Tristany, A. Vallribera, Org. Lett. 4 (2008) 561-564.
- [56] W. Ried, D. P. Schäfer, Chem. Ber. 103 (1970) 2225–2233.
- [57] S. Chen, X.Z. Zhang, S.X. Cheng, R.X. Zhuo, Z.W. Gu, Biomacromolecules 9 (2008) 2578-2585.

Graphical Abstract

H40-PCL-PEG unimolecular micelles both as anchoring sites for palladium nanoparticles and micellar catalyst for heck reaction in water



Highlights

- H40-PCL-PEG both as anchoring sites for metal nanoparticles and micellar catalyst.
- H40-PCL-PEG unimolecular micelles immobilized palladium nanoparticles.
- The catalyst and substrates are concentrated in nanosize sites.
- PdNPs@H40-PCL-PEG UMs as an efficient nanocatalyst toward Heck reaction in water.