

Supercritical CO₂-mediated Elaboration of Pd Supported Catalysts Using Amphiphilic Functional Copolymers

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ABSTRACT

Nowadays, the use of supercritical carbon dioxide as a green solvent develops more and more in various fields, such as extraction, separation, cleaning, but also in organic synthesis, polymer chemistry, inorganic chemistry, and materials chemistry to name a few. Simultaneously, palladium is used since many years as a heterogeneous catalyst to replace more expensive homogeneous catalysts, in particular for the catalysis of C-C bond formation. Many works were completed in order to develop new ligands of palladium to increase the stability of its nanoparticles while controlling their size. In this original work, we present the use of supercritical CO₂ as solvent for the elaboration of Pd supported catalysts.

First, a new palladium complex soluble in supercritical CO₂ has been prepared by ligand exchange, in Freon 113 or supercritical CO₂, between an amphiphilic functional copolymer and a metal precursor (palladium acetate Pd(OAc)₂). Then, the solubility behavior of this copolymer/Pd^{II} supramolecular complex has been studied in supercritical CO₂. The amphiphilic functional gradient copolymer used in this work, poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-acetoacetoxyethylmethacrylate) copolymer (poly(FDA-*co*-AAEM)), was purposely synthesized by controlled radical polymerization in trifluorotoluene or in supercritical CO₂. The fluorinated monomer units (FDA) impart CO₂-philic properties to the copolymer while the acetoacetoxy monomer units (AAEM) bring the complexing character to the copolymer. After reduction of the complex in soft conditions, well-dispersed small nanoparticles (2-6 nm diameter size range) were obtained inside the copolymer matrix.

The copolymer/Pd^{II} supramolecular complex was also used as an impregnation agent for the preparation of heterogeneous catalysts. Thus, a mesoporous silica material was impregnated by the complex in supercritical CO₂. After reduction, a composite material composed of nanoparticles of Pd (2-9 nm size) evenly distributed in the pores of the silica matrix was obtained. Finally, the catalytic activity of the prepared Pd@SiO₂ catalyst was evaluated in the Heck reaction.

INTRODUCTION

Nowadays, the use of supercritical carbon dioxide as a green solvent develops more and more in various fields, such as the extraction, separation, cleaning, decontamination, but also in organic synthesis, inorganic chemistry, and materials chemistry to name a few [1]. The facility of use of this solvent, like its harmlessness, its low cost and especially the possibility of varying the solubility of compounds thanks to its variable density by adjusting the pressure and the temperature make it a solvent of choice [2]. It began an important solvent for the synthesis of metal nanoparticles [3].

In their review, Aiken and Finke [4] list five general synthetic methods for nanoparticles formations: a) transition metal salt reduction, b) thermal decomposition and photochemical methods, c) ligand reduction and displacement from organometallics, d) metal vapor synthesis and e) electrochemical synthesis. The use of these methods allows the generation of metal particles of more or less big sizes according to the methods and operating conditions. In this work, we were interested by the exchange of ligand and the reduction of the complex formed to generate these nanoparticles. However this kind of synthesis generates the problem of stabilization because nanoclusters are only kinetically stable. They must be stabilized against aggregation in larger particles and, eventually, bulk material, their thermodynamic minimum. Stabilization can be accomplished in several manners: electrostatic stabilization, steric stabilization or electrosteric stabilization [5]. In this direction, various chemical molecules [6] can be employed to stabilize the nanoparticles during their syntheses, such as polymers [7, 8], dendrimers [9, 10], ionic liquids [11], perfluorinated chains [12].

Watkins and coll. were the precursors in the impregnation of metal particles in polymers under supercritical CO₂ (scCO₂). Many teams took as a starting point their work on the impregnation of PMP or PTFE by platinum [13], which made it possible to carry out the palladium impregnation in polymers such as HDPE [14, 15], PTFE or poly(arylenethynylene) [16]. These materials were then employed for various applications, such as hydrogenation or hydrodechlorination. In this example, the deposition of palladium is immediately followed by a reduction which can take place under hydrogen (under scCO₂ or not) or simply while heating under nitrogen. This kind of techniques employs the swelling effect of supercritical CO₂ with regard to polymers so that the palladium precursor can penetrate inside the matrix. At first, our interest is not in the impregnation of the polymeric matrix, but in the complexation of metal by copolymer. Hagio and coll. worked in this direction on the palladium catalyst immobilization by reducing metal palladium salts (Pd(OAc)₂ or Pd(NO₃)₂) in the presence of copolymers [17]. Initially, they incorporated palladium in copolymer then a reduction was performed under extremely soft conditions (room temperature and atmospheric pressure). However, these materials are prepared in organic solvent and present a polydispersity in size as well as an inhomogeneous distribution, but they are active as catalyst for standard reactions like Mizoroki-Heck coupling.

Since a few years, our team has developed new soluble amphiphilic copolymers in scCO₂. Some of them were already employed like macromolecular additives with scCO₂ to act as surfactant and sequestering agent of cobalt with an aim of nuclear decontamination [18]. In this work, we used amphiphilic gradient copolymers to play the role of palladium ligand. The function aceto-acetoxy (AAEM) plays the role of complexing group and the fluorinated chain alkyl (FDA) act as CO₂-philic group (Figure 1).

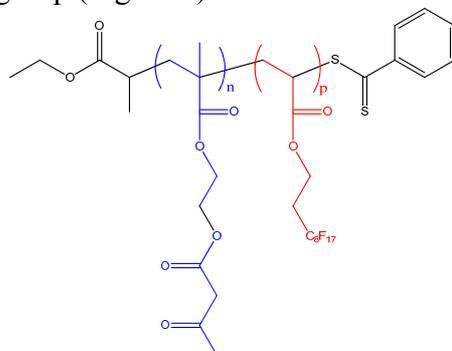


Figure 1 : Gradient amphiphilic copolymers poly(FDA-co-AAEM) used in this study.

Initially, we were interested in the complexation, in solvent or scCO₂, of a metal precursor (palladium acetate) by the copolymer and then we studied the behavior of this complex

Pd^{II}/copolymer in scCO₂ media. The supramolecular complex was then employed for various applications, such as catalysis (Heck reaction), generation of nanoparticles or impregnation of support such as commercial mesoporous silica.

MATERIALS AND METHODS

General :

1,1,2,2-Tetrahydroperfluorodecylacrylate (FDA, Atofina), methyl acrylate (MA, 99%, Aldrich) and acetoacetoxyethyl methacrylate (AAEM, Eastman, 97%) were purified by passing through activated basic (for FDA and MA) and neutral aluminum oxide (for AAEM). Azobis(isobutyronitrile) (AIBN) was recrystallized in methanol and dried under vacuum. α,α,α -Trifluorotoluene (TFT, Lancaster, 99%) was distilled before use. The chain transfer agent (CTA) 1-(ethoxycarbonyl)-ethyl dithiobenzoate was prepared in 82% yield with a procedure already described [19] (reaction time of 6 h). 1,1,2 Trichlorotrifluoroethane (F113, Aldrich, 99%), CO₂ (99.99,992%, SFE 5.2, Linde Gas SA, France), palladium (II) acetate (Pd(OAc)₂, 99.9%, Aldrich), mesostructured silica (MSU-H, Aldrich), 1,1,3,3-tetramethylguanidine (TMG, 99%, Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98% Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%, Aldrich), N,N-diisopropyléthylamine (DIPEA, 99%, Aldrich), triphenylphosphine (PPh₃, 99%, Aldrich), iodobenzene (BzI, 98%, Aldrich), triethylamine (Et₃N, 99%, Aldrich) were used as received unless otherwise stated.

Polymer synthesis :

The surfactant, poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-acetoacetoxyethyl methacrylate) (poly-(FDA-*co*-AAEM)), was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization to obtain a copolymer with a gradient architecture, predetermined molecular weight and narrow polydispersity index, as already described [20, 21]. The surfactant characteristics are the following: M_n = 25700 g/mol and AAEM molar fraction = 12.9%.

Complexation reaction:

- In Freon 113:

In a typical procedure, palladium acetate, copolymer and F113 were introduced in a round bottom flask, in the presence or not of a base. The flask was heated to 70°C in an oil bath during different time with magnetic stirring. At the end of the reaction, the reaction media was filtered on 0.2µm PTFE filter to eliminate insoluble salts and solvent was evaporated slowly under reduce pressure. The obtained complex of copolymer/Pd^{II} was dried overnight at 35°C under reduced pressure. The complex was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP – AES), after a complete dissolution in an acid solution, to determine the quantity of palladium.

- In supercritical CO₂:

The palladium acetate was introduced in the high pressure cell (V = 35 mL) with the copolymer or/and a base. The cell was pressurized with carbon dioxide at 250 bars and 40 °C, and the mixture was stirred with a magnetic stirring bar during desires time. At the end of the reaction, stirring was stopped, the high pressure cell was cooled to room temperature during few hours, and the cell was slowly depressurized (2-3 hours) with bubbling into a non-solvent, absolute ethanol. The obtained solid was dissolved into F113 and purified by filtration. F113 was then evaporated slowly under reduce pressure and the obtained complex of copolymer/Pd^{II} was dried overnight at 35°C under reduced pressure. The complex was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP – AES)..

Heck reaction:

In typical procedure, a stock solution of triphenylphosphine (0.12g, 0.08 eq), iodobenzene (1.50g, 1.00 eq), triethylamine (4.50g, 6 eq) and methyl acrylate (0.64g, 1.00 eq) in TFT (78.5g) was prepared in a Schlenk flask. After three freeze-thaw-pump cycles, 5mL of the stock solution was taken and introduced into a Radley reactor beforehand degased. The catalyst was then introduced under argon and the reactor was heated at 70°C during 48h under stirring. Samples were withdrawn under argon to follow the reaction and analyzed by ¹H NMR with deuterated benzene capillaries.

Cloud point:

Cloud-point measurements were carried out in a 15-mL, high-pressure, variable-volume view cell equipped with a sapphire window on the end for visual observations. The cell was equipped with a pressure transducer, a rupture disk, and an internal thermocouple and was thermostated by a water/glycol mixture delivered by a Lauda RE206 circulating pump. An ISCO 260D automatic syringe pump was used to deliver CO₂. Before each experiment, the cell was thoroughly cleaned with acetone and F113, and this was followed by copious venting with CO₂ until the residue was no longer present. The polymer was then weighted and transferred to the cell along with a clean stirring bar at a starting volume of 7.35 mL. Subsequently, the cell was sealed tightly and charged with CO₂ (at ca. 165 bar and 25 °C). The mixture was stirred for 20 min, and then the cell was heated gradually to 65 °C. Cloud points (one-phase/two-phase transition) were obtained by the slow lowering of the pressure of the cell after 20 min of stirring at a given temperature.

Characterization:

¹H NMR spectra were recorded with a Bruker 400-MHz spectrometer for copolymer characterization and Heck reaction. UV-vis analyses were performed on a VARIAN Cary 50 UV-vis spectrophotometer with a quartz cell (path length 10 mm) in F113 (concentration 1mg.mL⁻¹). In-situ UV-vis analyses were performed in scCO₂ using a high pressure cell (Mustang) fitted with optical fibers. DRX analyses were performed on the Balard characterization platform in Montpellier on a Philips EXPERT equipped with a diffractometric control PW 1710 with radiations Cu K α (1~1.5405 Å). For TEM analysis, samples were embedded in an epoxy resin and ultramicrotomed. TEM analyses were carried out on the Balard characterization platform in Montpellier on a JEOL 1200 EXII of 120 kV. Elemental analyses were performed by the Service Central d'Analyse (SCA) in Villeurbanne France.

RESULTS

Initially, the study of complexation was carried out in solvent, Freon 113, which is a good solvent of the fluorinated copolymer. Thus, we were interested in the mechanism of exchange between the copolymer and the ligand of the palladium precursor. This study was performed with and without a base.

We have tested the effectiveness of three strong bases: DBN (1,5-diazabicyclo[4.3.0]non-5-ene), DIPEA (diisopropylethylamine) and TMG (tetramethylguanidine). This reaction of exchange of ligand is favored in the presence of a base (Figure 2).

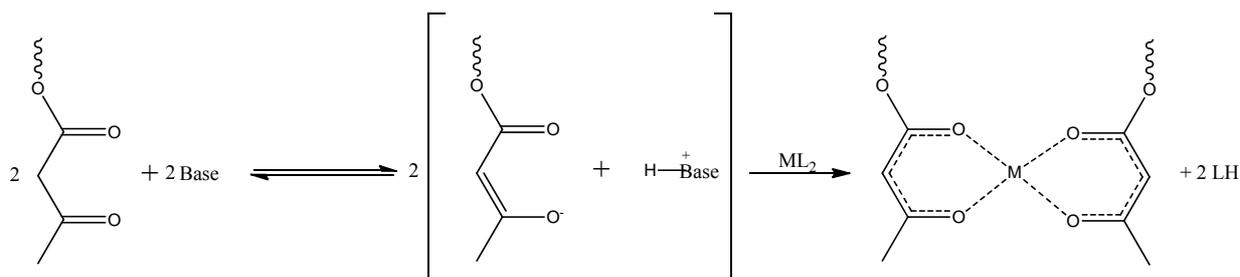


Figure 2 : Enolate formation in the presence of a base followed by metal complexation.

The quantity of introduced palladium precursor was fixed to a molar ratio $[AAEM]/[Pd]$ of two, which corresponds in our work to a simple load.

The comparison of the use of these three bases in simple load shows that the totality of palladium is complexed during the use of a base, which is validated by the presence in UV of the three characteristic bands (378-261-235 nm) of the absorbance of Pd^{II} complexes [22].

This same copolymer was then used as chelating agent in $scCO_2$. Experimental conditions were fixed so that the copolymer and the palladiated precursor were soluble in CO_2 SC (at $40^\circ C$, the cloud point of the copolymer is approximately 130 bars, see Figure 3).

Just as previously, the reactions were carried out with and without bases. Initially, the choice of the bases was dictated by their basic character. Indeed, the three bases used are relatively strong bases ($pK_a > 10$), like triethylamine already used in the literature. But this choice was made because they are little or not reactive with CO_2 . Indeed, bases such as primary or secondary amines are known to react with CO_2 to form carbamates. But bases like the DIPEA, DBN or the DBU are inert with CO_2 in absence of water, whereas the TMG is very reactive with CO_2 in the presence of water and has a low reactivity in the absence of water.

The best results were obtained with the use of TMG as a base. Indeed, after 24h of reaction in $scCO_2$ media, the rate of complexation reaches 90% in the presence of TMG. Performing the reaction of exchange between palladium acetate and poly(FDA-*co*-AAEM) in the presence of TMG in $scCO_2$ allows to obtain similar complexation yields to those obtained during the use of the organic solvent F113 in simple load.

The reaction of exchange of ligand being effective in solvent medium and $scCO_2$ medium, the synthesized palladiated copolymers were characterized in $scCO_2$ via the determination of its cloud point and by UV-visible analysis. The complex copolymer/ Pd^{II} obtained is always soluble in $scCO_2$, with a cloud point pressure only slightly higher than the cloud point of the parent copolymer (Figure 3). The use of the Mustang reactor allowing in-situ UV analysis made it possible to visualize the band at 378nm characteristic of a Pd^{II} complex in $scCO_2$.

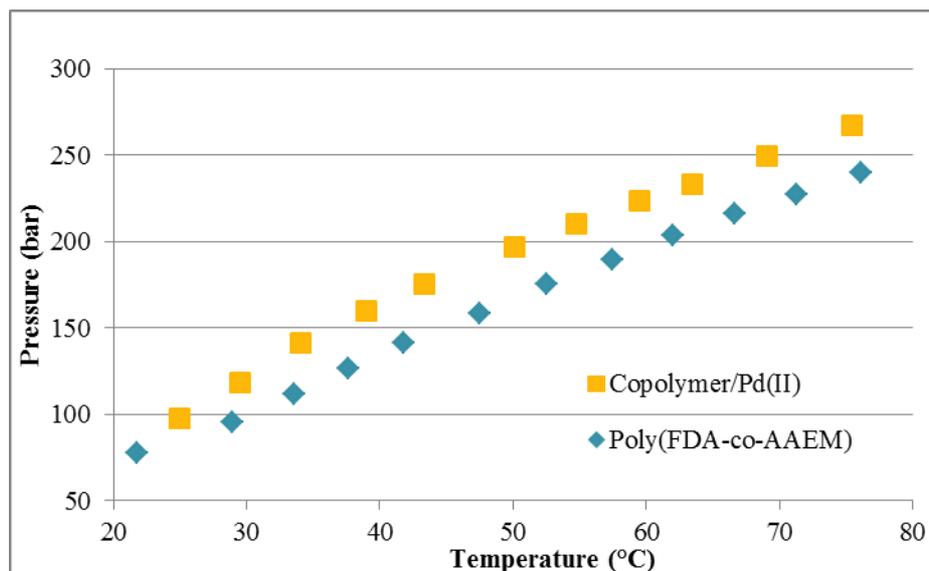


Figure 3 : cloud point of copolymer and copolymer/Pd^{II}.

After the preparation of these new palladium complexes, they were tested for a standard reaction in order to evaluate their catalytic activity. For this purpose, the reaction of C-C coupling of the Heck type between iodobenzene and methyl acrylate in conventional solvent (Figure 4) was used.

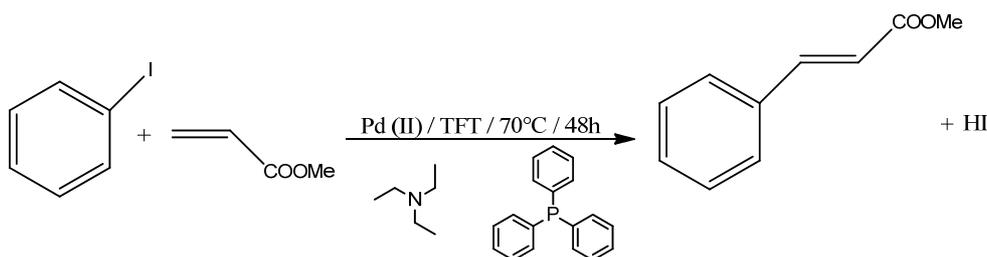


Figure 4 : Heck C-C coupling reaction between iodobenzene and methyl acrylate.

Whatever the procedure of preparation of the catalysts (in solvent medium, or in $scCO_2$ medium), and whatever the base used, the reaction of Heck was effective only if the mass percentage of palladium in the catalyst was higher than a threshold value of about 1wt%. Moreover, the comparison with the reaction catalyzed by palladium acetate, classically used for this reaction, showed that we obtain comparable conversion yields, but with slower kinetics, possibly because of steric hindrance around the palladium and/or diffusion limited reactions.

Secondly, we generated palladium nanoparticles starting from palladiated copolymers by hydrogenation. The generation of this kind of nanoparticles stabilized by polymer has been studied for a long time, whether it is in $scCO_2$ or in conventional solvent medium, and many works report their preparation. However, the originality of this study comes from the mechanism of preparation of the nanoparticles. Indeed, the first stage consists of an exchange of ligand between a palladiated precursor and the copolymer, followed by a reduction, whereas in the majority of the published works, the authors carried out the impregnation of a material by a low molecular weight metal precursor (soluble or not in CO_2).

Hydrogenation was chosen to generate small nanoparticles under soft conditions in order to preserve the copolymer.

TEM observations allow highlighting the presence of the palladium nanoparticles, their monodispersity, as well as the homogeneity of the hybrid material Pd⁰/copolymer.

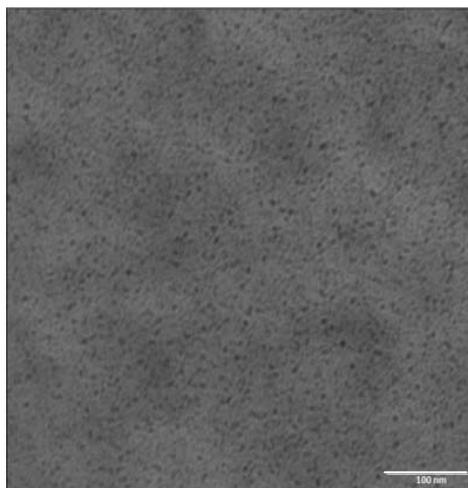


Figure 5 : TEM image of palladium nanoparticles generated into copolymer poly(FDA-co-AAEM). (scale is 100nm).

The presence of palladium nanoparticles in the copolymer was correlated by EDX and DRX analysis. The intermediate size ranging was determined between 3 and 6 nm.

The palladiated copolymer was finally used as precursor for the impregnation of a mesoporous material, commercial silica. The interest of the use of such a precursor is double. First of all by its capacity to generate small metal nanoparticles thanks to the presence of the copolymer which plays the role of steric stabilizer. Secondly, this fluorinated precursor is soluble in scCO₂ with practically no concentration limitation, whereas the commercially available precursor, Pd(acac)₂, has a solubility of only 10⁻⁵ mol. L⁻¹ in scCO₂. These two observations show the interest of such a supramolecular complex for the impregnation of a support by using scCO₂ as solvent.

TEM observations revealed that the nanoparticles of palladium, obtained after hydrogenation of the silica impregnated with the Pd^{II}/copolymer complex, present a monodispersity with an intermediate size of 4-6 nm. Moreover, the Pd⁰ nanoparticles are present inside the channels of the mesostructured silica, which is confirmed by BET analysis of the impregnated silica, showing a reduction in specific surface as well as porous volume.

We saw previously that the palladiated copolymer complex present a catalytic activity when the palladium rate is higher than 1wt%. This was confirmed when testing the heterogeneous catalysts silica/Pd⁰ thus generated in catalysis for the C-C coupling of Heck type. The results obtained with this kind of catalyst showed a real dependence between the conversion yield and the weight fraction of palladium: after 24 hours of reaction, the yield was 0% for 0.18%wt of Pd but it reached 80% for 0.80wt% of Pd.

CONCLUSION

Initially, we used amphiphilic gradient copolymers as ligand for Pd^{II}, and then we characterized this new complex, in particular by determining its cloud point curve in scCO₂. The obtained palladiated copolymer complex was used for various applications, such as catalysis, synthesis of nanoparticles, and impregnation of porous material. The synthesis of nanoparticles enabled us to show that the copolymer acts as a steric stabilizer of Pd⁰ generated during hydrogenation, which makes it possible to obtain small particles

(intermediate size 5nm) homogeneously distributed in the copolymer matrix. Moreover, the use of this supramolecular complex as precursor for the impregnation of commercial mesoporous silica allows the formation of the same nanoparticles inside the channels of the silica support. Lastly, the prepared supramolecular complexes are catalytically active for Heck reaction when the palladium load is higher than 1wt%. The kinetics of the Heck reaction is slower than during the use of a traditional catalyst (Pd(OAc)₂), but yields can be comparable, in particular when tetramethylguanidine (TMG) is used during the reaction of ligand exchange. Moreover the impregnation of these copolymers in MSU-H silica, followed by hydrogenation, leads to active supported catalysts, since after 48h of Heck reaction the conversion yield of methyl acrylate reaches 95%.

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REFERENCES

1. Bourne, R. A. and Poliakoff, M., *Mendeleev Communications*, Vol. 21, **2011**, p. 235.
2. Beckman, E. J., *The Journal of Supercritical Fluids*, Vol. 28, **2004**, p. 121.
3. Zhang, Y. and Erkey, C., *The Journal of Supercritical Fluids*, Vol. 38, **2006**, p. 252.
4. Aiken, J. D., III and Finke, R. G., *J. Mol. Catal. A: Chem.*, Vol. 145, **1999**, p. 1.
5. Cookson, J., *Platinum Metals Review*, Vol. 56, **2012**, p. 83.
6. Chaudret, B. and Philippot, K., *Oil & Gas Science and Technology - Revue de l'IFP*, Vol. 62, **2007**, p. 799.
7. Dassenoy, F., Philippot, K., Ould Ely, T., Amiens, C., Lecante, P., Snoeck, E., Mosset, A., Casanove, M.-J. and Chaudret, B., *New Journal of Chemistry*, Vol. 22, **1998**, p. 703.
8. Mayer, A. B. R., Mark, J. E. and Morris, R. E., *Polym. J. (Tokyo)*, Vol. 30, **1998**, p. 197.
9. Scott, R. W. J., Wilson, O. M. and Crooks, R. M., *The Journal of Physical Chemistry B*, Vol. 109, **2004**, p. 692.
10. Badetti, E., Caminade, A.-M., Majoral, J.-P., Moreno-Manas, M. and Sebastian, R. M., *Langmuir*, Vol. 24, **2008**, p. 2090.
11. Lara, P., Philippot, K. and Chaudret, B., *ChemCatChem*, Vol. 5, **2013**, p. 28.
12. Moreno-Manas, M., Pleixats, R. and Villarroya, S., *Chemical Communications*, Vol. 0, **2002**, p. 60.
13. Watkins, J. J. and McCarthy, T. J., *Chemistry of Materials*, Vol. 7, **1995**, p. 1991.
14. Wu, B. Z., Chen, H. Y., Wang, J. S., Tan, C. S., Wai, C. M., Liao, W. and Chiu, K., *J Hazard Mater*, Vol. 227-228, **2012**, p. 18.
15. Wang, J. S. and Chiu, K., *Chemosphere*, Vol. 75, **2009**, p. 629.
16. Hasell, T., Wood, C. D., Clowes, R., Jones, J. T. A., Khimyak, Y. Z., Adams, D. J. and Cooper, A. I., *Chemistry of Materials*, Vol. 22, **2010**, p. 557.
17. Hagio, H., Sugiura, M. and Kobayashi, S., *Organic Letters*, Vol. 8, **2006**, p. 375.
18. Chirat, M., Ribaut, T., Clerc, S., Charton, F., Fournel, B. and Lacroix-Desmazes, P., *Industrial & Engineering Chemistry Research*, Vol. 52, **2012**, p. 538.
19. Severac, R., Lacroix-Desmazes, P. and Boutevin, B., *Polymer International*, Vol. 51, **2002**, p. 1117.
20. Ribaut, T., Lacroix-Desmazes, P., Fournel, B. and Sarrade, S., *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 47, **2009**, p. 5448.
21. Ribaut, T., Oberdisse, J., Annighofer, B., Stoychev, I., Fournel, B., Sarrade, S. and Lacroix-Desmazes, P., *Soft Matter*, Vol. 5, **2009**, p. 4962.
22. Dell'Anna, M. M., Mastroilli, P., Rizzuti, A., Suranna, G. P. and Nobile, C. F., *Inorganica Chimica Acta*, Vol. 304, **2000**, p. 21.