

Recycling of noble and/or critical metals by the use of complexing copolymers in supercritical CO₂

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ABSTRACT

Nowadays, noble and/or critical metals are extensively used in many areas, such as in the chemical industry (catalysis), in the automotive industry, and in the electronics, to name a few. Recovery and recycling of this kind of metals is a major aim in the field of sustainable development. Industrially, the recovery of such metals is often performed in strong acidic aqueous media, causing the destruction of the support of the metal and generating large amounts of aqueous effluents which have to be further treated.

In the frame of LABEX CheMISyst (Chemistry of Systems), our project aims at extracting nanoparticles of metals from a support in view to recycle metals without altering the support. Thus, new functional complexing copolymers soluble in supercritical CO₂ (scCO₂) are prepared and their behavior in scCO₂ is studied. Complexation and interactions between the copolymers and metal nanoparticles in scCO₂ are investigated by several analytical techniques. For instance, high pressure nuclear magnetic resonance (HP-NMR) spectroscopy and small-angle X-ray scattering (SAXS), using a specially designed SAXS high-pressure cell, are considered in this work. The on-going research on this project will be presented.

INTRODUCTION

Nowadays, noble and/or critical metals are extensively used in many areas, such as in the chemical industry (catalysis), in the automotive industry, and in the electronics, to name a few. For the automotive industry in particular (47% of the demand of PGM), the annual total platinum group metals (PGM) demand has grown steadily from just under 35 tons in 1980 to 292 tons in 2006. According to the European commission, the annual total platinum group metals (PGM) demand will rise by 50% in 2020 [1]. The increase of the demand correlated with the low availability of this kind of metal points out the necessity of recycling the PGM. Industrially, the recovery of such metals is often performed in strong acidic aqueous media, causing the destruction of the support of the metal and generating large amounts of aqueous effluents which have to be further treated.

In the same time, the use of supercritical carbon dioxide as a green solvent develops more and more in various fields, such as the extraction, separation, cleaning, and decontamination for example [2]. 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, in particular for the extraction [3]. Some studies have already been performed to recycle the PGM in supercritical CO₂. In their review, Wai [4] and Erkey [5] enumerate different chelating agent used for the extraction of ionic heavy metals from solid and/or liquid. More recently, Goto worked on the recovery of metals from spent catalyst with supercritical CO₂ (scCO₂) and a chelating agent, acetyl acetonate, bis(2,2,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) or a

complex between tributyl phosphate (TBP) nitric acid and water (TBP/HNO₃/H₂O) [6]. In their work, the extraction is thought to take place through the formation of a Pd(II) complex (Pd/ligand) soluble in scCO₂. So far as we look in the literature, we only found extraction of ionic species of PGM.

In the frame of LABEX CheMISyst (Chemistry of Systems), our project aims at extracting nanoparticles of metals from a support by amphiphilic copolymers in view to recycle metals without altering the support. In a first step, we were interested in palladium complexation.

Since a few years, our team has developed new soluble amphiphilic copolymers in scCO₂. Some of them were already employed as macromolecular additives in scCO₂ to act as surfactant and sequestering agent of cobalt with an aim of nuclear decontamination [7]. In this work, we used amphiphilic gradient copolymers comprising different functions as complexing groups and a fluorinated alkyl chain (FDA) as CO₂-philic group (Figure 1) to play the dual role of macromolecular ligand of palladium and steric stabilizer.

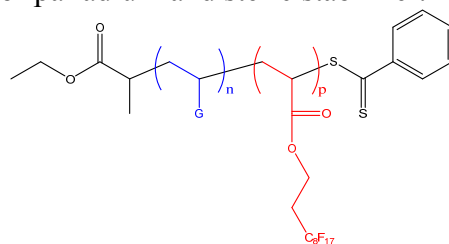


Figure 1 : Gradient amphiphilic copolymers poly(FDA-co-G), with G=complexing unit, used in this study.

Initially, we prepared new functional complexing copolymers soluble in supercritical CO₂ (scCO₂) and we studied their behavior in scCO₂. Complexation and interactions between the copolymers and palladium nanoparticles in scCO₂ are investigated by several analytical techniques. For instance, high pressure nuclear magnetic resonance (HP-NMR) spectroscopy and small-angle X-ray scattering (SAXS), using a specially designed SAXS high-pressure cell, are considered in this work. The on-going research on this project will be presented.

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 (reaction time of 6 h) [8]. 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), 1,1,3,3-tetramethylguanidine (TMG, 99%, Aldrich), butylamine (99%, Aldrich), 4-(diphenylphosphino)-styrene (DPPS, 97%, Aldrich), triphenylphosphine (PPh₃, 99%, Aldrich), were used as received unless otherwise stated.

Polymer synthesis:

All the polymers and copolymers were 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 [9, 10].

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. Pressure ¹H NMR spectra were performed in a high-pressure 5mm NMR tube and recorded with a Bruker 250-MHz spectrometer. 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). SAXS experiments were performed at ICSM, on a setup operating in transmission geometry. A Mo anode associated to a Fox2D multishell mirror (XENOCs) delivers a collimated beam of wavelength 0.710 Å. Two sets of scatterless slits delimitate the beam to a square section of side length 0.8 mm. A MAR345 imaging plate detector allows simultaneously recording scattering vectors q ranging from 0.25 nm⁻¹ up to 25 nm⁻¹. Absolute intensities were obtained by measuring a calibration sample of high density polyethylene (Goodfellow) for which the absolute scattering was already determined. All SAXS profiles are plotted in log–log scale in order to highlight the dependency of the intensity versus a power law of the scattering vector q .

RESULTS

The literature describes different functionalities used as complexing groups for palladium species. In order to screen those complexing moieties inserted in the copolymers, we prepared different amphiphilic copolymers by changing the CO₂-phobic units. Our first modification is obtained by performing the aminolysis of the end-RAFT-group of the PFDA homopolymer, as described in Figure 2. The impact of the size (M_n) of the homopolymer was also studied.

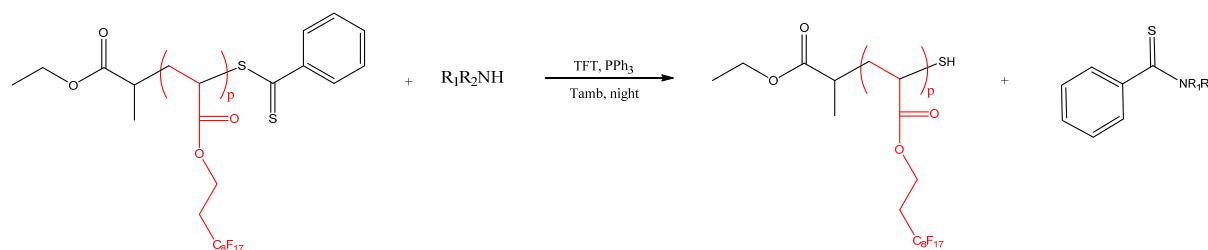


Figure 2 : End-RAFT-group aminolysis reaction.

Indeed, thiols are known to be good complexing groups for metals, particularly for the preparation of gold nanoparticles. In 2010, Liu and coll. used dodecanethiol as a complexing molecule to extract palladium nanoparticles from DMSO to hexane [11]. With the reaction of aminolysis on the PFDA obtained by RAFT, we obtained rapidly and easily a CO₂-soluble polymer functionalized by a thiol. The reaction is performed in the presence of a reducing agent (triphenylphosphine, PPh₃) to prevent the formation of disulfide bounds that will mask

the thiol-complexing unit. The cleavage of the dithioester can be easily observed by the discoloration of the reaction media, and is followed by ^1H NMR and UV-Vis analyses. The other functionality that we have introduced in the polymer is the phosphine. An amphiphilic copolymer named poly(FDA-co-DPPS) was prepared and characterized. The procedure of polymerization is adapted from the one already described in literature [9]. We also used the poly(FDA-co-AAEM) amphiphilic copolymer containing the acetoacetoxy ethyl methacrylate (AAEM) chain that we have already used successfully in the laboratory for the complexation of ionic Pd(II).

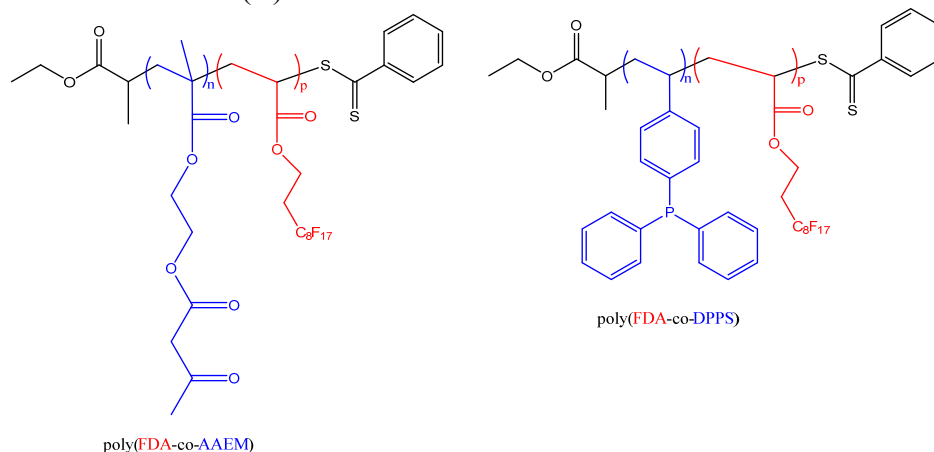


Figure 3 : Gradient copolymers prepared by RAFT used in this study (poly(FDA-co-AAEM): $M_n=25700\text{g}\cdot\text{mol}^{-1}$, 13%mol AAEM; poly(FDA-co-DPPS): $M_n=19900\text{g}\cdot\text{mol}^{-1}$, 22%mol DPPS).

These polymers were firstly characterized by determining their cloud point curves (Figure 4).

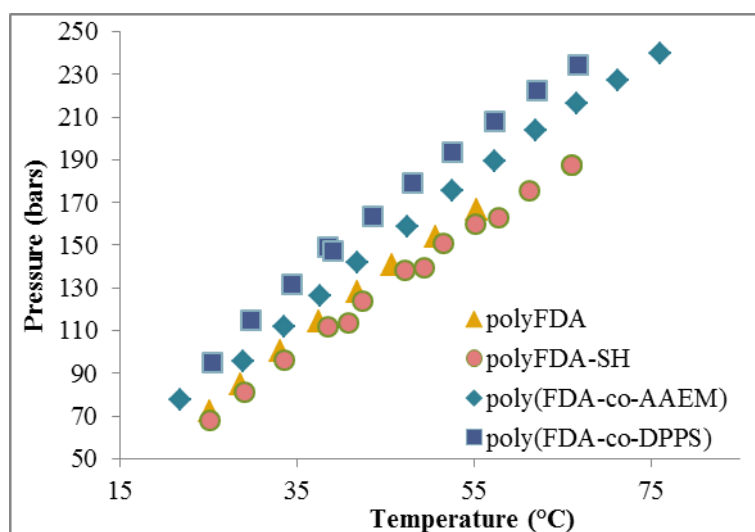


Figure 4 : Cloud point curves of different polymers used in this study (4% w/w of polymer versus CO₂).

The comparison of the cloud points of the homopolymer PFDA before and after aminolysis shows that the solubility in scCO₂ is almost unchanged. The presence of the end-RAFT-group has only little influence on the solubility. For the copolymers, as expected, the presence of the more polar complexing units in the gradient copolymer increases the cloud point pressure, *ie.* it decreases the solubility of the polymers in scCO₂. However, all the polymers remained soluble at relatively low pressure, making them suitable as ligands for extraction in scCO₂.

In the frame of the LabEx CheMISyst project, the characterization of the arrangement on the nanometer scale of the copolymers with and without palladium nanoparticles were performed by small angle X-ray scattering (SAXS). For this purpose, a new cell was designed with two

beryllium windows allowing the work in $scCO_2$ environment and the measure of X-ray diffusion (Figure 5). These analyses were carried out on two different setups. First, the polymers were analyzed on a laboratory scale SAXS at ICSM. Then, we performed SAXS analyses on synchrotron (SOLEIL) to increase the X-ray flow in order to determine the different parameters of arrangement of the polymers in $scCO_2$ (size, shape, aggregation) and to access a larger q range compatible with a dispersion of palladium nanoparticles in $scCO_2$.



Figure 5 : High-pressure SAXS cell.

The first results that we have obtained at ICSM are presented in Figure 6.

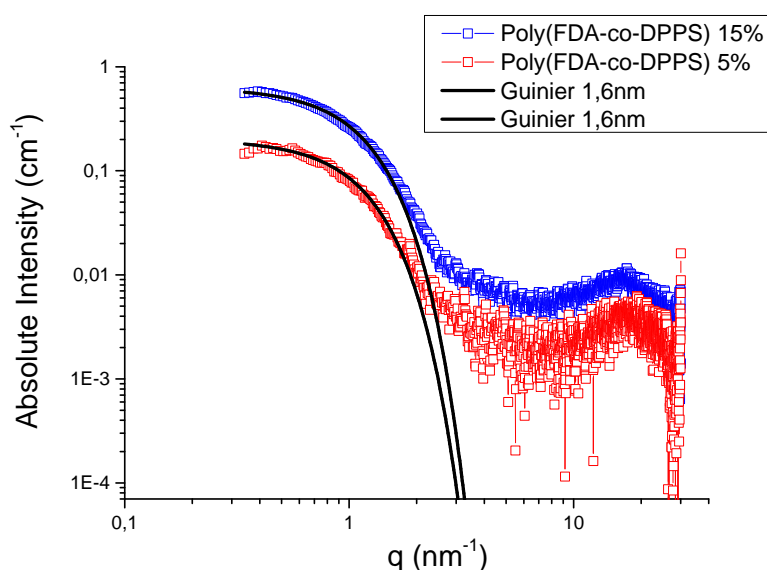


Figure 6 : Small angle X-ray scattering curve for 5wt% and 15wt% of poly(FDA-co-DPPS) in $scCO_2$ at 250bars and 40°C.

Curves representing the intensity (I) versus scattering vector (q) present a rise of diffusion in the small angles range showing that copolymers dissolved in $scCO_2$ (without NPs), at two different concentrations, form spheres of 1.6 nm of radius without any attractive or repulsive interaction. The continuous curves correspond to a simple Guinier model used to adjust the experimental curves. This model is only fitted in the range of small q values (for $q.R < 1$) and is expressed as follows:

$$I = I_0 \cdot e^{-\frac{q^2 R^2}{2}} \quad (1)$$

Here I_0 values are related to copolymer volume fraction (Φ), volume of scattering object (V_{ob}) and electronic contrast between CO_2 and copolymer ($\Delta\rho$) following this equation:

$$I_0 = \Phi \cdot V_{ob} \cdot \Delta\rho^2 \quad (2)$$

In the case of the system shown in Figure 6, values of I_0 changes from 0.63 to 0.20 when the copolymer concentration decreases from 15%wt to 5%wt. It means that the dilution has only an effect on the number of objects in suspension while their size remains unchanged. In order to complement the results obtained by SAXS, the laboratory is now equipped with a high pressure NMR tube to highlight the complexation of the palladium NPs by the polymer in $scCO_2$. This kind of study has already been carried out in the laboratory for the complexation of cerium oxide nanoparticles (CeO_2) by a phosphonated RAFT copolymer in water [12].

CONCLUSION

In the frame of the LabEx ChemISyst project, we have prepared new complexing polymers and gradient copolymers of different sizes and functionalities that we have characterized in $scCO_2$ medium. To study their arrangement and aggregation in $scCO_2$, a new cell with Be windows has been designed to carry out SAXS analyses either on a laboratory SAXS setup or on synchrotron SAXS. The first results point out the formation of sphere of 1.6 nm of radius without interaction. Use of high-pressure NMR is underway to validate the complexation of polymers with palladium nanoparticles.

Acknowledgments. The authors of this paper would like to thank Région Languedoc-Roussillon (Chercheur d'Avenir, Grant No. 2010-0-018, SUPERPOL project) and Labex Chemisyst (grant of Fabien Gasc) for financial support of this research. Bruno Corso (CEA) and Julien Cambedouzou (ENSCM) are acknowledged for their technical support during SAXS analyses at ICSM.

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