

Innovative Decontamination of Textile in the Nuclear Industry Using Polymers in Supercritical Carbon Dioxide

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ABSTRACT

Cobalt ion is removed from a textile lab coat using supercritical carbon dioxide extraction. The process involves a macromolecular additive of well-defined architecture, acting both as a surfactant and a complexing agent. The extraction efficiency of cobalt reaches 97% when using a poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-vinylbenzylphosphonic diacid) gradient copolymer in the presence of a very tiny amount of water at 160 bar and 40 °C. The synergy of the two additives, namely the copolymer and water which are useless if used separately, is pointed out. The potential of the supercritical carbon dioxide extraction process using complexing macromolecular surfactant lies in the ability to modulate the complexing unit as a function of the metal as well as the architecture of the surface-active agent for applications ranging for instance from nuclear decontamination to the recovery of strategic metals.

INTRODUCTION

The laundry of contaminated textiles in the nuclear industry is performed in aqueous medium. This process generates contaminated aqueous effluents which have to be further treated. To reduce the amount of wastewater, supercritical carbon dioxide (scCO₂) is increasingly considered as an alternative solvent.[1-3] In this work, cobalt ion is removed from a textile lab coat by extraction using dense carbon dioxide. The process involves a macromolecular additive of well-defined architecture, acting both as a surfactant and a complexing agent. The influence of the architecture of the copolymers on their solubility and their self-assembly behaviour in scCO₂ will be shown. The influence of several experimental parameters on the extraction efficiency has been investigated: type of copolymer, presence of water, concentration of the additives, temperature, pressure, type of stirring (magnetic, ultrasound), nature of the contaminated matrix (cotton, polyester), nature of the counter-ion of cobalt (nitrate, acetate, chloride), number of washing cycles, and extraction time. Finally, a schematic view of the extraction mechanism will be proposed.

MATERIALS AND METHODS

Materials

The copolymers poly(1,1,2,2-tetrahydroperfluorodecylacrylate)-*b*-poly(vinylbenzylphosphonic diacid) (poly(FDA)-*b*-poly(VBPDA)) block copolymer and poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-vinylbenzylphosphonic diacid) (poly(FDA-*co*-VBPDA)) gradient copolymer were synthesized by reversible addition fragmentation chain

transfer (RAFT) polymerization to obtain copolymers of controlled architectures, predetermined molecular weight and narrow polydispersity index, as already described. [4-5]

The lab coat (textile) was provided by Sas Vanneville etFils, composition: 50/50 polyester/cotton. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Aldrich, 99.999%), CO_2 (99.99992%, SFE 5.2, Linde Gas SA, France) and all other chemicals were used as received unless otherwise stated. A high pressure, variable volume view cell (maximal volume of 15 mL) equipped with a sapphire window for visual observations is used for pressurized experiments. The cell is equipped with a pressure transducer, a rupture disk, and an internal thermocouple. The cell is thermostated by a water/glycol mixture delivered by a Lauda RE206 circulating pump. An ISCO 260D automatic syringe pump is used to deliver CO_2 .

Extraction Procedure in Supercritical Carbon Dioxide

On a piece of textile (20 mm diameter), 10 μL of an aqueous solution of cobalt nitrate (1 g/L of Co) was deposited with a micropipette to provide a sample with 10 μg of Co. The sample was dried overnight at 70 °C under vacuum. The sample was introduced in the high pressure cell ($V = 8.69\text{mL}$) with the copolymer additive or/and deionized water. The cell was pressurized with carbon dioxide at 160 bar and 40 °C, and the mixture was stirred with a magnetic stirring bar for 1h30 min at 1100 rpm. Then, 100 mL of CO_2 were passed through the cell at constant pressure (160 bar) at a flow rate of 5 mL/min. Finally, the cell was depressurized. The textile was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), after a complete dissolution in an aqueous sulphuric acid solution, to determine the quantity of residual cobalt. A control analysis was performed on the contaminated sample to ascertain that 10 μg of Co was initially present. The absence of copolymer on the sample at the end of the procedure was also checked by phosphorus analysis performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

RESULTS

Synthesis of copolymers

Several copolymers have been synthesized based on 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA) units as the CO_2 -philic units and different functional comonomers to impart extraction properties of metal ions: acetoacetoxyethyl methacrylate (AAEM) and vinyl benzyl diethyl phosphonate (VBPDE). AAEM units are already including the complexing group while VBPDE requires a further step (cleavage of the phosphonic ester groups) to give the diphosphonic acid complexing group. These copolymers have been synthesized by controlled radical polymerization in order to prepare copolymers of various controlled macromolecular architectures: block copolymers and gradient copolymers.[4-5] For instance, the structures and architectures of a block copolymer poly(VBPDA)-*b*-poly(FDA) and a gradient copolymer poly(VBPDA-*co*-FDA) are given in Figure 1.

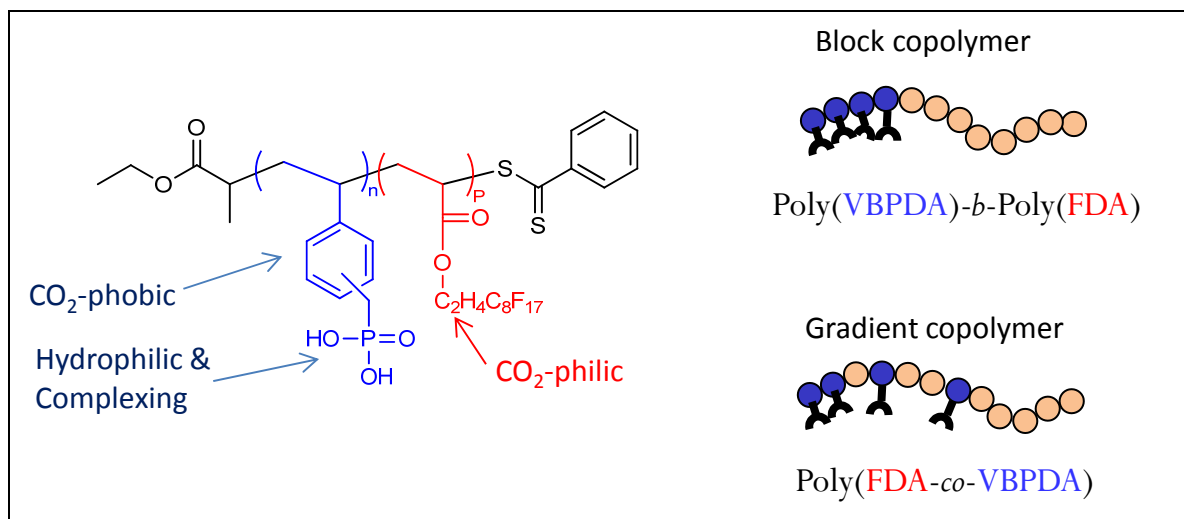


Figure 1: Formula and architectures of a block copolymer poly(VBPDA)-*b*-poly(FDA) and a gradient copolymer poly(VBPDA-*co*-FDA)

Solubility of copolymers in dense CO₂

The solubility of the copolymers in dense CO₂ has been assessed by cloud point measurements. In general, the gradient copolymers were found to be soluble at lower CO₂ pressure than their block copolymer analogues (copolymers of same composition and same molecular weight). Figure 2 illustrates this trend in the case of the copolymers of FDA and VBPDA. The gradient copolymer was soluble at a CO₂ pressure only a little bit higher than for a pure CO₂-philic PFDA homopolymer. The gradient architecture is especially of interest for several reasons.[4-6] First, gradient copolymers require only one synthetic step (in contrast to at least two steps for the synthesis of block copolymers). Second, the solubility properties in scCO₂ are better for copolymers with gradient architectures than with block architectures as illustrated in Figure 2. Finally, gradient copolymers can have surfactant properties (which random copolymers do not have specifically). Furthermore, it must be noticed that, unlike gradient copolymers synthesized by controlled free-radical copolymerization, random copolymers prepared by conventional free-radical copolymerization are heterogeneous in terms of molecular weight and composition. Therefore, the solubility and self-assembly of random copolymers in scCO₂ is somewhat less controlled than for gradient copolymers. In addition, the surfactant contains phosphonic diacid groups in order to interact with the metal ion (cobalt(II)) as well as to provide hydrophilic properties.

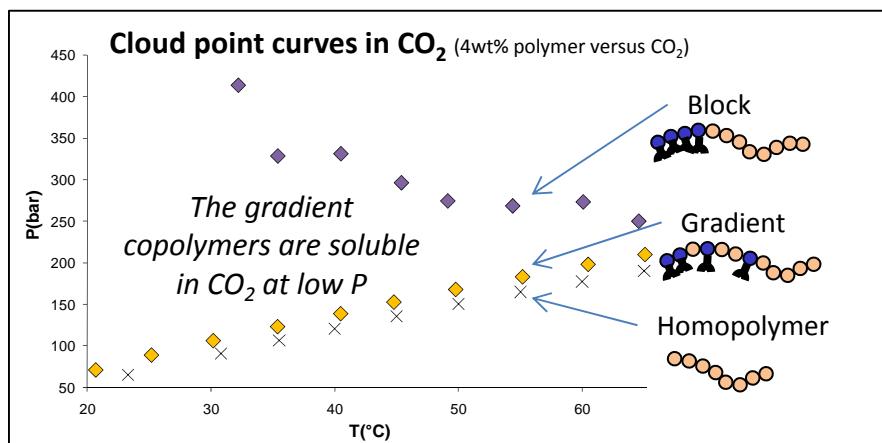


Figure 2: Cloud point curves of a PFDA homopolymer, a poly(VBPDA)-*b*-poly(FDA) block copolymer and a poly(VBPDA-*co*-FDA) gradient copolymer.

Extraction tests

The extraction procedure is detailed in the experimental part. Several experimental parameters have been screened such as the type of copolymer, the presence of water, the concentration of the additives, the temperature and pressure, the type of stirring (magnetic, ultrasound), the nature of the contaminated matrix (cotton, polyester), the nature of the counter-ion of cobalt (nitrate, acetate, chloride), the number of washing cycles, and the extraction time.

In Figure 3, some results are reported using the gradient copolymer poly(VBPDA-*co*-FDA). First, it shows that CO₂ alone is not able to extract considerably the cobalt ions. The result is even worse when a tiny amount of water is added to CO₂. Furthermore, unexpectedly, the gradient copolymer in CO₂ is not able to do the job. In contrast, the combination of the gradient copolymer and a tiny amount of water was shown to afford near quantitative extraction of the cobalt ions (close to 70% extraction).

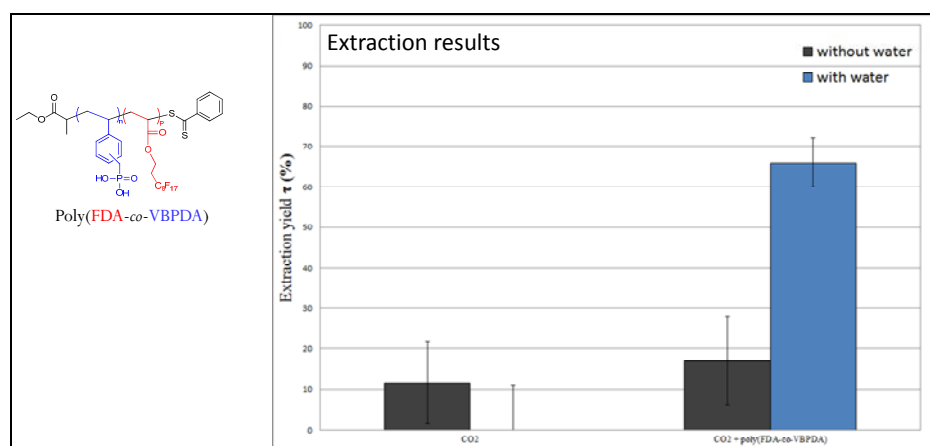


Figure 3: Extraction of cobalt ions in supercritical CO₂ at 40°C and 160 bar in the presence of a gradient copolymer poly(VBPDA-*co*-FDA).

Small angle neutron scattering of the ternary system polymer/water/CO₂ has shown that a microemulsion-like system was formed in the presence of the copolymer (Figure 4). Indeed,

for instance at $T=40\text{ }^{\circ}\text{C}$ and $P=350\text{ bar}$ and at a concentration of water above its saturation in CO_2 , the scattering data were consistent with the presence of some spherical aggregates ($N_{\text{agg}}=8.2$, $R=29\text{ \AA}$) solvated with D_2O ($W_c=[\text{D}_2\text{O}]/[\text{polymer}]=13$).[6]

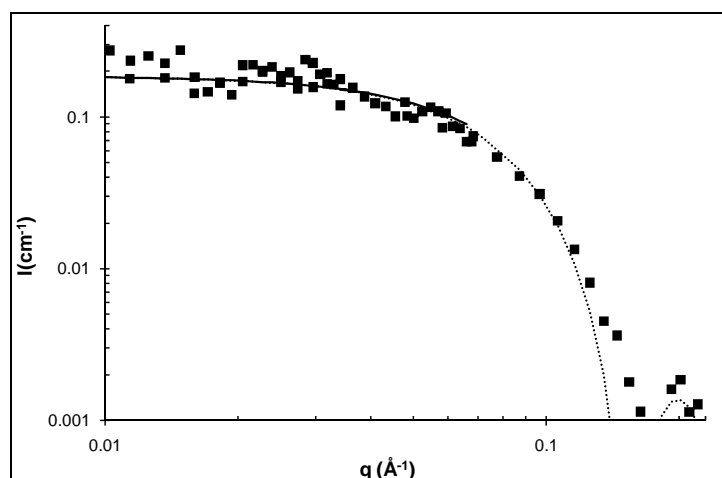


Figure 4: Small angle neutron scattering data for poly(FDA-co-VBPDA) gradient copolymer in CO_2 in the presence of D_2O .

Finally, after optimization of the process, including the addition of pyridine as co-extractant, a quantitative extraction yield of $97\% \pm 5\%$ of the cobalt ions was reached. The full detailed analysis of the influence of the different experimental parameters will be reported elsewhere.

A schematic view of the extraction mechanism can be proposed in Figure 5. It outlines that the extraction process requires both dispersed water (microemulsion) and a complexing group within the micelle to interact with the cobalt.[7]

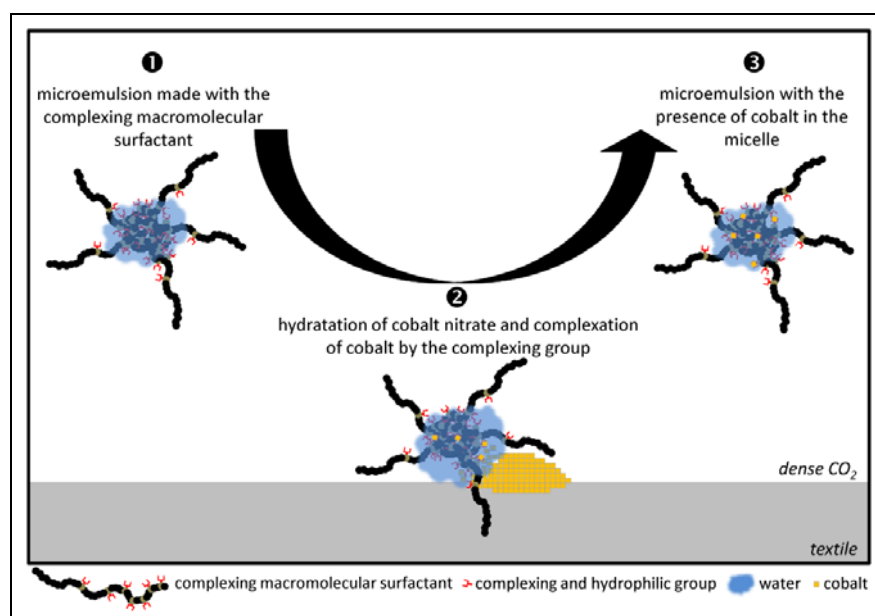


Figure 5: Schematic representation of the combined action of the complexing macromolecular surfactant and water in the supercritical extraction process.

CONCLUSION

A 97% extraction yield was obtained for cobalt-contaminated textile treated in supercritical carbon dioxide in the presence of a tiny amount of water using a macromolecular poly(FDA-co-VBPDA) gradient copolymer, acting as both a surfactant and a complexing agent. Our results pointed out the synergy of the two additives, the copolymer and water, which are useless if used separately. Beyond this, the presented strategy opens the route toward the development of a platform composed of a wide range of specific macromolecular additives by modulating the nature of the complexing unit as a function of the metal as well as by varying the architecture of the surface-active copolymer. Lastly, the use of such copolymers in other applications such as the recovery of critical metals which are nowadays more and more strategic is underway in our laboratory.

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