

SOLUBILITY OF HYPERBRANCHED POLYMERS IN SUPERCRITICAL CO₂

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The solubility in supercritical CO₂ of an hyperbranched polymer (poly(ethylene imine)) functionalized with fluoroalkyl chains, CO-CH₂-CH₂-C₈F₁₇ has been measured by FTIR spectroscopy at 313 K and 373 K between 6 and 35 MPa. Results are discussed in regard of the solubility of other macromolecules found in the literature.

INTRODUCTION

The use of supercritical CO₂ as solvent is of great interest due to its properties such as nonflammability, low toxicity, and relative chemical inertness [1]. The critical temperature of CO₂ is close to room temperature, and it is naturally abundant, which makes it attractive for processes such as polymerization, extraction, impregnation, encapsulation, etc... In these applications, one of the most important parameter to control the process is the solubility in supercritical CO₂. As it is well known, CO₂ dipole is almost zero, explaining the poor solubility for polar substances. Thus, the design of CO₂-philic molecules has attracted great interest during the last decade. In this context, it has been demonstrated that dendritic surfactants grafted with appropriate fluoroalkyl chains can be used to enhance dramatically the solubility of polar species in supercritical CO₂ [2]. More recently, a new hyperbranched polymer has been designed with a core constituted of poly(ethylene-imine) (PEI) and a shell composed of fluoroalkyl chains, CO-CH₂-CH₂-C₈F₁₇ (Figure 1)[3]. This molecule will be called PEI-CO-CH₂-CH₂-C₈F₁₇ in the following. The main advantage of this kind of polymers over dendritic surfactants is an easier way of synthesis. Thus, the aim of this work is to quantify the solubility in supercritical CO₂ of PEI-CO-CH₂-CH₂-C₈F₁₇. The solubility of PEI-CO-CH₂-CH₂-C₈F₁₇ has been measured in supercritical CO₂ at 313 K and 373 K for pressures between 6 and 35 MPa. For this purpose, an optical cell is used to measure the infrared absorption spectra. After a description of the experimental set up, the results of the hyperbranched polymer solubility are presented and discussed.

I - MATERIALS AND METHOD

CHEMICAL

The hyperbranched polymer used for the solubility measurements has a poly(ethylene imine) core (PEI= $C_2H_8N_2 (C_2H_5N)_n$) functionalized with fluoroalkyl chains ($-CO-CH_2-CH_2-C_8F_{17}$). The molar mass of PEI- $CO-CH_2-CH_2-C_8F_{17}$ is about $20\ 000\ g\cdot mol^{-1}$.

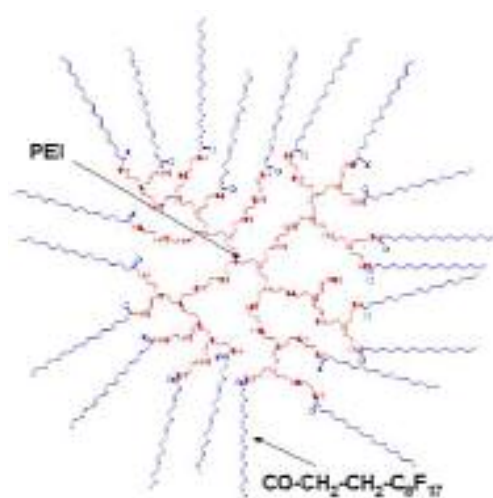


Figure 1: Representation of PEI- $CO-CH_2-CH_2-C_8F_{17}$

The structure was characterized by liquid NMR 1H and ^{13}C , and IR spectroscopy. CO_2 has a purity of 99.7% (TP Industriel, Air Liquide) with impurity composed of approximately 0.15 % N_2 , 0.06 % O_2 , 0.04 % H_2O , 0.02 % of hydrocarbons, CO , H_2 .

EXPERIMENTAL DETAILS

The infrared absorption measurements are performed with a Biorad interferometer (type FTS-60A). Single beam spectra recorded in the spectral range $400 - 6000\ cm^{-1}$ with $2\ cm^{-1}$ resolution are obtained by Fourier transformation of 50 accumulated interferograms. A special Titanium cell is used with two cylindrical silicon windows with a path length of 2.5 cm. A schematic view of the optical cell is shown in Figure 2a.

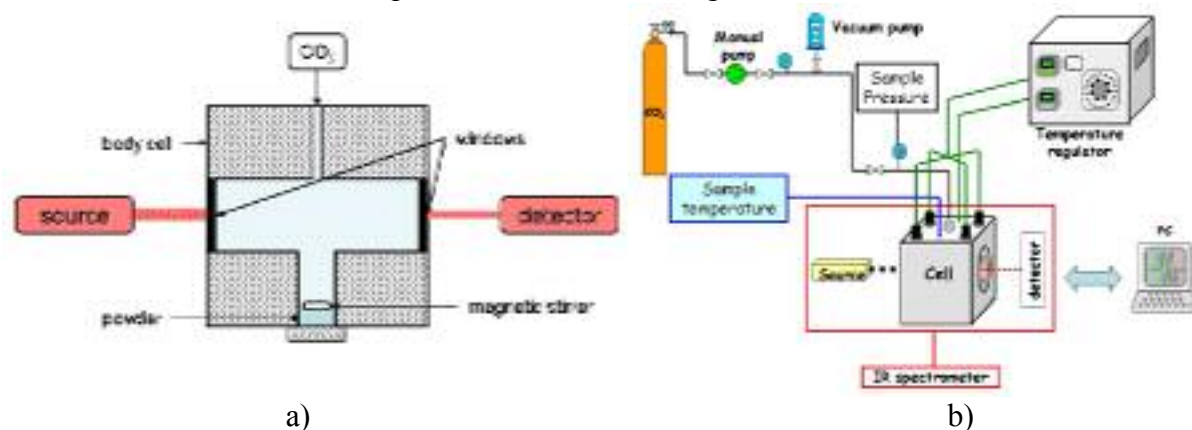


Figure 2: a) Schema of the high pressure high temperature cell; b) Experimental set-up

The cell volume is 5.5 cm³ and the homogeneity is ensured with a magnetic stirrer disposed at the bottom of the cell. The cell is connected via a stainless steel capillary to a hydraulic pressurising system which allows to adjust the pressure up to 50 MPa with an absolute uncertainty of ± 0.1 MPa with a relative error of $\pm 0.3\%$ (Figure 2b).

The heating is performed with four cartridge heaters disposed in the body of the cell in which two thermocouples are placed. The first one is located close to one cartridge in order to achieve a good temperature regulation and the second one is kept close to the sample area, to measure the temperature with an accuracy of about ± 0.5 K.

SOLUBILITY DETERMINATION METHOD

Infrared spectrometry is often used for in-situ characterisations in supercritical fluids. According to Beer-Lambert law, the integrated intensity of an infrared band allows to determine the concentration of a solute in solutions.

Beer-Lambert law: $A = \epsilon \cdot l \cdot c$ with A, sample absorbance without dimension, ϵ , molar extinction coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$), l, optical path length (cm) and c, sample concentration ($mol \cdot L^{-1}$).

In this study, a spectral domain is integrated to determine A which implies that ϵ is homogeneous to $L \cdot mol^{-1} \cdot cm^{-2}$.

The method of solubility determination consists of three steps:

1. Identification of a characteristic vibrational band,
2. Determination of the molar extinction coefficient for the considered bands, by checking that a small quantity of the product is completely solubilized in supercritical CO₂ at high density ($0.8 \text{ g} \cdot \text{cm}^{-3}$),
3. Determination of the solubility with an important mass of product by integrating the selected band.

For the last step, the values used for CO₂ density are reported in Table 1.

Table 1: Density values of CO₂ in $\text{g} \cdot \text{cm}^{-3}$ as a function of p and T [4]

P (MPa)	35	30	25	20	15	11	10	8.8	6
T = 313 K	0.935	0.910	0.879	0.839	0.780	0.684	0.629	0.429	0.150
T = 373 K	0.715	0.662	0.588	0.481	0.332	0.215	0.189	0.160	0.100

II - RESULTS AND DISCUSSION

CHARACTERISTIC VIBRATIONAL BANDS OF PEI-CO-CH₂-CH₂-C₈F₁₇

The first step of solubility determination is to notify which vibrational band can be investigated. After subtraction of neat CO₂ spectrum to the one of PEI-CO-CH₂-CH₂-C₈F₁₇, the obtained spectrum for characteristic vibrational modes is shown in Figure 3.

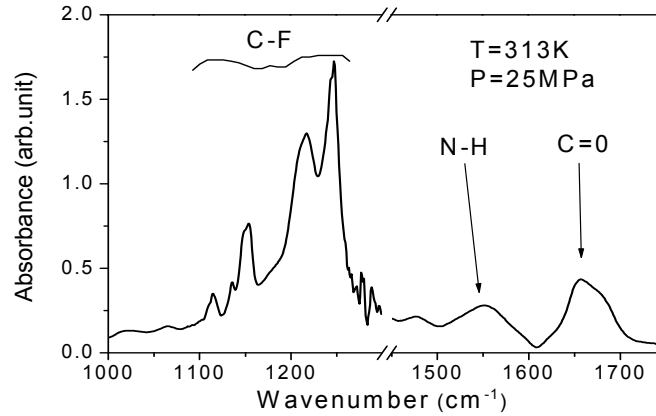


Figure 3: Spectrum of PEI-CO-CH₂-CH₂-C₈F₁₇ (T = 313K, P = 25 MPa)

Two spectral domains are chosen:

- 1123-1163 cm⁻¹: characteristics of C-F modes,
- 1634-1708cm⁻¹: characteristics of C=O modes.

N-H bands are not taken into account because of their low absorbance.

DETERMINATION OF MOLAR EXTINCTION COEFFICIENT

To determine the molar extinction coefficient of the characteristics C-F and C=O modes of PEI-CO-CH₂-CH₂-C₈F₁₇, a small quantity of polymer is introduced in the cell (m = 0.4 mg). When the characteristic band intensity does not increase with CO₂ pressure, it means that the initial quantity of product introduced in the cell is totally solubilised in CO₂. By integrating the area for each characteristic modes considered here, the following extinction molar coefficients are estimated:

- $\epsilon_{C-F} = 324\,477 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$
- $\epsilon_{C=O} = 655\,972 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$

ϵ is assumed to be independent of pressure and temperature.

DETERMINATION OF PEI-CO-CH₂-CH₂-C₈F₁₇ SOLUBILITY

In order to obtain an equilibrium between solid polymer and supercritical CO₂ phase, an excess quantity of PEI-CO-CH₂-CH₂-C₈F₁₇ (m=4.0 mg) is introduced in the cell. By integrating area for each spectral domain, the concentration of polymer solubilized in supercritical CO₂ is determined (Table 2).

Table 2: Values of solubility in g/g of CO₂ for PEI-CO-CH₂-CH₂-C₈F₁₇ as a function of pressure at 313 K and 373 K

P(MPa)	35	30	25	20	15	11
T = 313 K	4.1×10^{-4}	3.1×10^{-4}	1.8×10^{-4}	0.9×10^{-4}	0.3×10^{-4}	0
T = 373 K	$1.6 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	0	0	0	0

Figures 4 and 5 represent the evolution of FTIR spectra for C-F and C=O bands (after baseline correction) and the polymer solubility as a function of CO₂ pressure at 373 K.

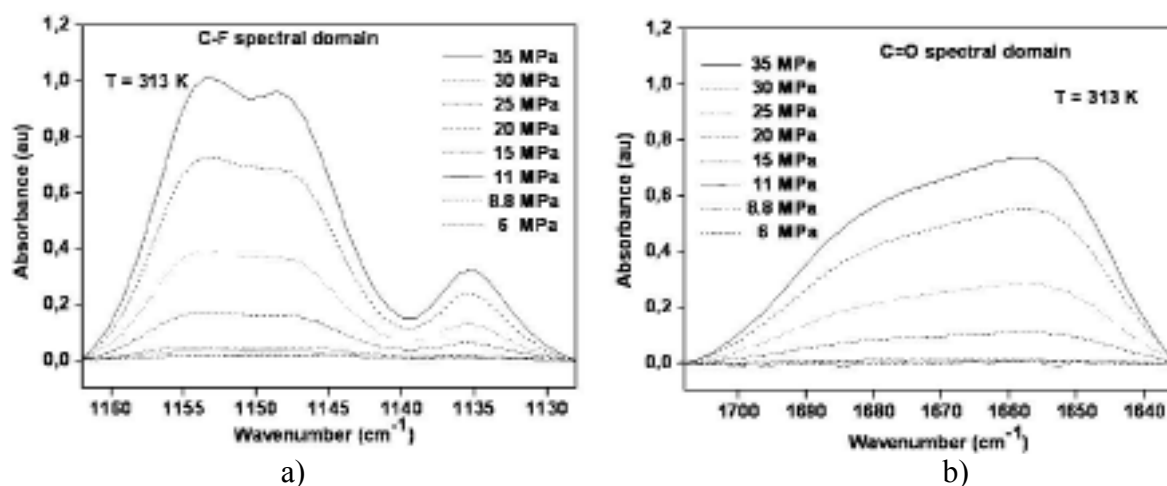


Figure 4: a) Evolution of FTIR spectra for C-F band as a function of CO₂ pressure at T=313K; b) Evolution of FTIR spectra for C=O band as a function of CO₂ pressure at T=313K.

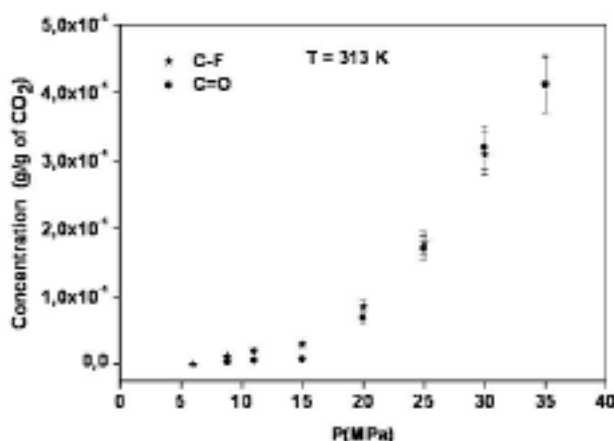


Figure 5: Solubility of PEI-CO-CH₂-CH₂-C₈F₁₇ for two bands at T=313K.

In these conditions, a very good agreement can be noticed between the solubility determined using both characteristics C-F and C=O modes which validates the experimental method. Errors are estimated to be about 10% for C-F and C=O spectral domain.

The solubility of this molecule is very low: for the greater density of CO₂ (0.935 g.cm⁻³), 0.04% in weight of CO₂ is solubilized. At 373 K, the polymer is not soluble in supercritical CO₂. To understand these results, data are compared with data from the literature.

In the literature, two types of macromolecules were studied: linear polymers [5] and dendrimers [2], [6]. These molecules have fluoroalkyl chains like in PEI-CO-CH₂-CH₂-C₈F₁₇. The solubility of these molecules is determined by cloud point measurement. To compare these results, a parameter which is called B, can be defined like the ratio of the CO₂-philic part molar mass to the non-CO₂-philic one. B values of these different types of molecules are

reported in Table 3. B seems to be a critical parameter to explain the solubility of the macromolecules in supercritical CO₂.

Table 3: Literature data concerning solubility of different types of polymers

Type of molecules	formula	B	Solubility in CO ₂	references
Hyperbranched polymer	PEI-CO-CH ₂ -CH ₂ -C ₈ F ₁₇	3.2	0.04% $\rho = 0.93$	This work
dendrimer	DAB-C ₂₀ O ₆ F ₄₁	9.5	soluble $\rho = 0.98$	[2]
Linear polymer	PS-b-PFDA	13	4 % $0.86 < \rho < 0.99$	[5]
dendrimer	PPI-C ₇ F ₁₅	13	soluble	[6]
Linear polymer	PS-b-PFDS	16	4 % $0.86 < \rho < 0.99$	[5]

A factor B close to 10 is linked to a relatively good polymer solubility in supercritical CO₂ at high density. PEI-CO-CH₂-CH₂-C₈F₁₇ present a factor B of 3.2; this low value could explain the low solubility in supercritical CO₂ even at high density.

CONCLUSION

The solubility in supercritical CO₂ of a new amphiphilic macromolecule with CO₂-philic tails, PEI-CO-CH₂-CH₂-C₈F₁₇, has been studied. With a density of 0.935 g.cm⁻³, PEI-CO-CH₂-CH₂-C₈F₁₇ solubility is of 0.04 % in weight of CO₂.

In order to improve the solubility of this macromolecule in supercritical CO₂, works are in progress to understand the solute-solvent interactions and so design new CO₂-philic macromolecules.

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