Universal Supercritical Binary Mixture for Polymer Fractionation

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ABSTRACT: Supercritical fluids are well known for their efficiency to fractionate polymers as a function of their molar mass, their architecture and their chemical composition, in the case of copolymers. We have used a supercritical solvent mixture, made of CO₂ and ethanol, to fractionate poly(ethylene oxide) (PEO) and polystyrene (PS). This mixture which can solubilize both polar (PEO) and nonpolar (PS) polymers, allows the obtention of a narrow molar mass distribution with possibility to select the molar mass value and the molar mass distribution of the extracted sample. The purification of a binary mixture of star and linear PEO has been also performed.

KEY WORDS Supercritical Fluid / Polymer / Fractionation / Star Architecture /

Several authors have studied the polymer fractionation with a supercritical fluid processing, during this last decay.^{1,2} The fractionation of polymer chains with narrow molar mass distribution or the extraction of residual monomers, catalytic system, are performed by adjustment of the fluid density which permits a modulation of the solutes solubility (it increases with density) and fluid selectivity (it decreases with density).^{3,4} So uniform and clean materials can be easily and quickly obtained in comparison with ionic polymerization or other separation techniques such as dialysis. As we have shown in a previous paper, by separating star and linear polymers of the same molar masses; the fractionation principle is based on the hydrodynamic volume of polymer chains difference.⁵

Carbon dioxide (CO₂) is generally used for these studies. Indeed it is recognized as a replacement fluid for environmentally objectionable organic solvents and can be used to reduce their use.⁶ So the investigation of binary mixtures of carbon dioxide with organic solvents is particularly studied in order to develop supercritical fluid processing technology.^{7,8}

The present report deals with the fractionation (with respect to the molar masses) of two chemically different polymers, the poly(ethylene oxide) (PEO, polar compound) and polystyrene (PS, nonpolar compound), with a supercritical solvent mixture made of CO₂ and ethanol. Other organic cosolvents have also been tested for the PS fractionation.

EXPERIMENTAL

The experimental apparatus (Figure 1) used for SCF fractionation, up 40 MPa and 400°C, essentially consists of a high pressure pump (minipump Model 396/2396) and a mass exchanger. The binary mixture (solvent + cosolvent) is pressurised in liquid phase up to the required pressure. Then it flows through a heat exchanger which brings the fluid to the working temperature and through the mass exchanger. The mass exchanger is a column of

0.8 cm diameter and 20 cm length. It is filled with a glass packed bed of 0.2 cm diameter and polymer. Silica wool is placed at the inlet and outlet of the column to avoid the dragging of polymer by the flowing fluid. The rate is adjusted by a micrometric valve located at the exit of the apparatus. We have worked either at constant temperature with an increasing pressure profile when fractionation as a function of the molar mass was investigated or at constant temperature and pressure to purify star polymers contaminated with linear impurities.

The weight compositions of the supercritical mixtures are determined during each experiment, by means of a flow-meter (CO₂ part) and a balance (cosolvent part). The flow-meter measures the CO₂ flow rate and the balance, the weight of cosolvent pumped during the experiment. Incertitudes for the flow-meter are about 0.4% and around 1 mg for the balance. Flow rates of CO₂ and cosolvent, used in each experiment, are given in the Table I.

The characterization of linear PEO and PS samples was performed by a size exclusion chromatography (SEC) with a refractive index detector. SEC were run with either a water-methanol (50 : 50, v/v) mixture for the PEO or toluene for the PS.

CO₂ is provided by Air Liquide. Its critical temperature and critical pressure are respectively 31°C and 7.38 MPa. Ethanol is a Prolabo product (99.9% purity) and other organic solvents, Aldrich products. The linear PEO samples come from Aldrich, the linear PS from Polymer Expert. Star PEO samples are synthesized in Laboratoire de Chimie des Polymères Organiques.

RESULTS AND DISCUSSION

Fractionation of PEO

Several linear PEO samples with molar masses from 1000 to 35000 g mol⁻¹ were mixed so as to make a compound with a very broad molar mass distribution (Table II).

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Figure 1. Schematic experimental setup used for the fractionation of polymers with a supercritical binary mixture.

Table I. Binary mixture flow rates used during experiments on PEO and PS fractionation

Mixture	CO ₂ flow rate	Cosolvent flow rate	Total flow rate
	kg h ⁻¹	kg h ⁻¹	kg h ⁻¹
CO ₂ -ethanol (94:6% in weight)	0.155	0.011	0.166
CO ₂ -ethanol (91:9% in weight)	0.162	0.014	0.176
CO ₂ -ethanol (70:30% in weight)	0.061	0.026	0.087
CO ₂ -ethanol (58:42% in weight)	0.072	0.054	0.124
CO ₂ -acetone (58:42% in weight)	0.072	0.054	0.124
CO ₂ -THF (70:30% in weight)	0.084	0.036	0.12
CO ₂ -THF (50:50% in weight)	0.061	0.061	0.122

We chose the nature of the cosolvent as a function of the known solubility in various solvents, in normal conditions of temperature and pressure.⁹ So we worked with a mixture made of CO₂ and ethanol (the ethanol ratio varying from 6 to 9% in weight) at 60°C and in a pressure range between 15 and 40 MPa (with 5 MPa pressure increments), during 90 min. We recovered six fractions which have been analyzed by SEC. From chromatograms, we can determine the maximum solubilized molar mass or "cut-off mass" (Mc) of each extracted fraction, at a given pressure. The cut-off mass corresponds to the molar mass of the slice that exhibits the lowest elution volume in the SEC eluogram. Then a calibration curve, showing the evolution of the molar mass of extracted chains with the pressure, can be established for a solvent system, at the working temperature.

Table II. Polymer characteristic (number average molar mass, average molar mass in weight, and molar mass distribution)

Polymer	M_n	M_w	Molar mass distribution
	g mol ⁻¹	g mol ⁻¹	
PEO	3050	7480	2.5
PS	4140	7160	1.7

Figure 2. Cut-off-mass of linear poly(ethylene oxide) in supercritical CO₂-ethanol (91:9 and 94:6) as a function of the pressure at 60°C. —●—, CO₂-ethanol (91:9 in weight); —■—, CO₂-ethanol (94:6 in weight).

Experiments were performed with a solvent mixture made of 94% of CO₂ and 6% of ethanol. This supercritical system does not allow an Mc increase with pressure (Figure 2). For this composition, only the chains of low molar masses are extracted (≈ 2000 g mol⁻¹): the mixture is too selective. From this experiment, we have determined the minimum composition of the solvent mixture. So we have tried a CO₂-ethanol mixture (91:9% in weight), for the second fractionation. In this case, we

Figure 3. SEC chromatograms of the parent PEO and representative fractions obtained after fractionation with the supercritical CO_2 -ethanol mixture (91:9 in weight) at 25, 35, and 40 MPa.

can observe a progressive increase of M_c with the pressure and so with the fluid density (as usually observed) that shows an efficient fractionation¹⁰⁻¹² (Figures 2 and 3). This experiment is not quantitative but just qualitative. It allows to determine M_c , for a given pressure. The distribution in mass of each recovered fraction has not been optimized ($I = 1.2 - 1.3$). So in order to decrease the I value, it is necessary to increase the extraction time or to reduce the pressure increments. The Figure 2 reports the calibration curve for the PEO- CO_2 -ethanol (91:9% in weight) system. It permits to define the optimum pressure to apply at 60°C , for the extraction of PEO of given molar mass. The ethanol ratio cannot be increased above 9% in weight because it would involve the system demixing, in our temperature and pressure conditions. We then become interested in the separation of PEO as a function of their architecture.

Star PEO samples have been the subject of a great interest because of peculiar properties in solution for biological applications such as coating or vectorisation. As described in the paper,^{13,14} star polymers are prepared *via* the so-called "core-first" method. This synthesis consists in anionic polymerization of oxirane by means of a plurifunctional metalorganic initiator (alcoholate initiator). As the initiation reaction is quantitative and the functionality of the initiator precisely defined, stars of predetermined size and functionality are directly accessible. However the PEO star samples are often contaminated with linear materials. These linear chains are induced by monofunctional alcoholate that results from the deprotonation of residual protonic impurities present in the reaction medium at the time of the initiation. So a fractionation step is required to eliminate linear PEO. We first tested a mixture made of 50% in weight of three-arm star ($M_p = 16600 \text{ g mol}^{-1}$) and 50% in weight of linear PEO ($M_p = 3300 \text{ g mol}^{-1}$). The fractionation using the CO_2 -ethanol mixture (91:9% in weight) as supercritical fluid was done at 60°C and 27 MPa. The value of the pressure to apply was drawn

Figure 4. SEC chromatograms of a binary mixture (50:50 in weight) made of linear ($M_p = 3300 \text{ g mol}^{-1}$) and star ($M_p = 16600 \text{ g mol}^{-1}$) PEO before and after fractionation at 27 MPa and 60°C .

Figure 5. SEC chromatograms of a star PEO ($M_p = 10900 \text{ g mol}^{-1}$) contaminated with linear PEO chains ($M_p = 3430 \text{ g mol}^{-1}$) before and after fractionation at 28 MPa and 60°C .

from the calibration curve established for linear chains (Figure 2). As evidenced in Figure 4, the extraction of linear PEO occurs as expected at 27 MPa. Another experiment on a three-arm star PEO ($M_p = 10900 \text{ g mol}^{-1}$) contaminated with linear chains ($M_p = 3430 \text{ g mol}^{-1}$), was investigated using the same supercritical mixture at 60°C and 28 MPa. In this case, linear impurity exhibits the same molar mass as that of the star branches. The study was carried out with an initial load of 500 mg. At these temperature and pressure, we have recovered 280 mg of linear chains (3430 g mol^{-1}), after a working time of 4 h (Figure 5).

In a previous paper,⁵ we had already reported a work on star and linear PEO separation, with supercritical

Figure 6. Cut-off-mass of linear polystyrene in supercritical CO₂-THF (50:50) and (70:30) as a function of the pressure at 150°C. —■—, CO₂-THF (50:50 in weight); —▲—, CO₂-THF (70:30 in weight).

1-chloro-1,1-difluoroethane (R142b). The same experimental approach has been employed in the present study, with a new solvent system, the CO₂-ethanol mixture. Similar results have been found, but here the separation of linear and star PEO is based on the difference in their molar masses rather than the difference in their chain structures. Moreover this solvent system has been investigated to fractionate another polymer, the PS.

Fractionation of PS

The polystyrene fractionation was first performed, with a mixture made of CO₂ and tetrahydrofuran (THF) (a good solvent of PS at the ambient). Experiments were realized on a broad linear polystyrene (Table II) at 150°C and in a pressure range from 15 to 40 MPa (with 5 MPa pressure increments), during 90 min. Around 10% in weight cosolvent, chromatograms do not present any significant evolution of the molar mass, and fractionation yields are low. So, the THF amount in the mixture was increased up to 30% and 50% in weight. The evolution of Mc with the pressure is presented on Figure 6. It clearly shows the continuous tunable effect of supercritical mixture to adjust solubility and selectivity. Indeed, the mixture 70:30 in weight permits a high selectivity for lower molar masses whereas the mixture 50:50 in weight allows a higher solubility with a lower pressure selectivity.

Properties of some solvents are modified in the supercritical domain like water which can dissolve organic solutes, this is because of the dielectric constant decrease.¹⁵ So, we have added a poor solvent like ethanol and acetone to CO₂ and studied their effects on the polystyrene fractionation. Experiments were performed with CO₂-ethanol (70:30 in weight), CO₂-ethanol (58:42 in weight) and CO₂-acetone (58:42 in weight) on the same polystyrene sample, under the same experimental conditions. First we present SEC chromatograms of the parent PS and of several representative fractions, in the case of the supercritical mixture CO₂-ethanol (58:42 in weight) fractionation (Figure 7).

Figure 8 shows that the fractionation efficiency increases with the cosolvent amount. This rise is significant when comparing the CO₂-ethanol (70:30 in weight) to the CO₂-ethanol (58:42 in weight) systems. Indeed with the CO₂-ethanol (70:30 in weight) super-

Figure 7. SEC chromatograms of the parent PS and of representative fractions obtained after fractionation with the supercritical CO₂-ethanol mixture (58:42 in weight) at 20, 25, 30, 35, and 40 MPa.

Figure 8. Cut-off-mass of linear polystyrene in supercritical CO₂-ethanol (58:42) and (70:30) as a function of the pressure at 150°C. —▲—, CO₂-ethanol (58:42 in weight); —■—, CO₂-ethanol (70:30 in weight).

Figure 9. Cut-off-mass of linear polystyrene in supercritical CO₂-THF (50:50), CO₂-ethanol (58:42), and CO₂-acetone (58:42) as a function of the pressure at 150°C. —◆—, CO₂-ethanol (58:42 in weight); —■—, CO₂-acetone (58:42 in weight); —▲—, CO₂-THF (50:50 in weight).

critical mixture, the solubilized molar mass increases slowly and weakly whereas the CO₂-ethanol (58:42 in weight) system enables to obtain a good Mc increment with the pressure comparable to the effect of the CO₂-THF (70:30 in weight) mixture. These results bear out that THF is a better cosolvent for PS than ethanol and acetone. Indeed at 40 MPa, the CO₂-THF (50:50) supercritical mixture solubilize molar masses three times high as CO₂-ethanol (58:42) and CO₂-acetone (58:42) systems (Figure 9). Nevertheless, these two last mixtures are competitive and can be used to fractionate samples of low molar masses (from 2000 to 10000 g mol⁻¹).

Experiments have shown that the chemical nature of the cosolvent can not be considered as the only key factor of the fractionation efficiency. The cosolvent amount is an important parameter which must be controlled and adjusted in order to optimise the compromise between solubility of the chains and selectivity. Moreover, whatever the cosolvent added to CO₂, a good (THF) or a poor solvent (ethanol, acetone) of the PS, it is its amount in the supercritical solvent mixture that will define the molar masses scale to fractionate and the efficiency of the separation. This original behavior can be interpreted as a cluster formation of the cosolvent¹⁶ when there is a low ethanol amount, as in the PEO solubility case. The PS solubility, which is insoluble in CO₂ and ethanol, could be explained by the formation of hydrophobic microdomains resulting from a complex between CO₂ and ethanol molecules.¹⁷

CONCLUSIONS

Fractionations with supercritical mixtures have been validated as a function of the polymer molar masses, with correct and even good yields in weight and in time, in comparison with the dialysis process.⁵ With a binary mixture, we have a supplementary degree of freedom. We can work, at constant temperature and pressure, and just modulate the cosolvent amount in order to extract chains of different lengths and different chemical natures such as for the copolymer fractionation. The more the cosolvent composition increases, the higher the solubilized molar masses.

It was found that ethanol used as a cosolvent in various amounts, can solubilize chemically different polymers such as polar (PEO) and nonpolar (PS) polymers. This allows to think that the CO₂-ethanol system could be used to fractionate whichever polymer. In each case, the only parameters to define would be the mixture composition and the fluid density. This supercritical solvent mixture could be considered as universal.

Now, we study with spectroscopic techniques, the microscopic organization of the mixture which enables to solubilize both hydrophobic and hydrophilic polymers.

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