EXPERIMENTAL EVALUATION OF POLY(METHYL METHACRYLATE) SOLUBILITY IN SUPERCRITICAL MEDIA

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ABSTRACT

In the dispersion polymerization carried out in supercritical media, the partitioning of the polymer chains between continuous and dispersed phases represents a crucial aspect. In fact this partitioning is affecting both the particle formation mechanism and the relative importance of the reaction in the two phases, with deep impact on the final polymer properties. Aimed to quantify this aspect, in this work the solubility of poly(methyl methacrylate) (PMMA) chains in mixtures CO_2 – methyl methacrylate (MMA) is measured at different relative amounts of CO_2 and MMA, temperature of 65° C and pressure in the range of 130-140 bar. A stirred vessel equipped with a suitable sampling device is used and the collected polymer analyzed by GPC for total mass and degree of polymerization distribution.

INTRODUCTION

The use of supercritical carbon dioxide as a medium for polymer synthesis has become an area of great interest in the last few decades [1]. The advantages of using CO_2 are of chemical, environmental and economic nature. Moreover, since solvent separation occurs simply by depressurization, a solvent-free polymer is readily obtained.

Supercritical CO_2 is a good solvent for many non-polar, low molecular weight molecules such as the vinyl monomers typically used in free-radical polymerization. On the other hand, it is a poor solvent for most high molecular weight polymers [1]. This makes feasible the synthesis of these materials by heterogeneous processes only, like dispersion polymerization.

A good knowledge of the mechanisms involved in such process allows us to tune the reaction conditions so as to control carefully the properties of the final polymer. With this respect, a detailed study on the influence of the amount of monomer on the solubility of the polymer in the supercritical phase is therefore of interest, since probability of growth can be largely different for chains growing in the continuous or in the dispersed phase. The aim of this work is the experimental evaluation of the interphase partitioning of PMMA in a two-phase system where mixtures CO_2-monomer at constant pressure and temperature but different compositions are considered as continuous supercritical phase.

EXPERIMENTAL APPARATUS AND METHODOLOGY

Setup

The experimental setup used for our extraction experiments is shown in Figure 1. It is made of a carbon dioxide feeding line and of a stirred, stainless steel, double clamped

autoclave (NWA, Germany) with temperature control, digital temperature and pressure indicators and safety valve. The feeding line consists of a carbon dioxide cylinder with deep tube, a piston pump (NWA, Germany), a syringe pump (Isco, model 260D, USA) and a massflow meter (Rheonik, model RHM015GNT, USA).
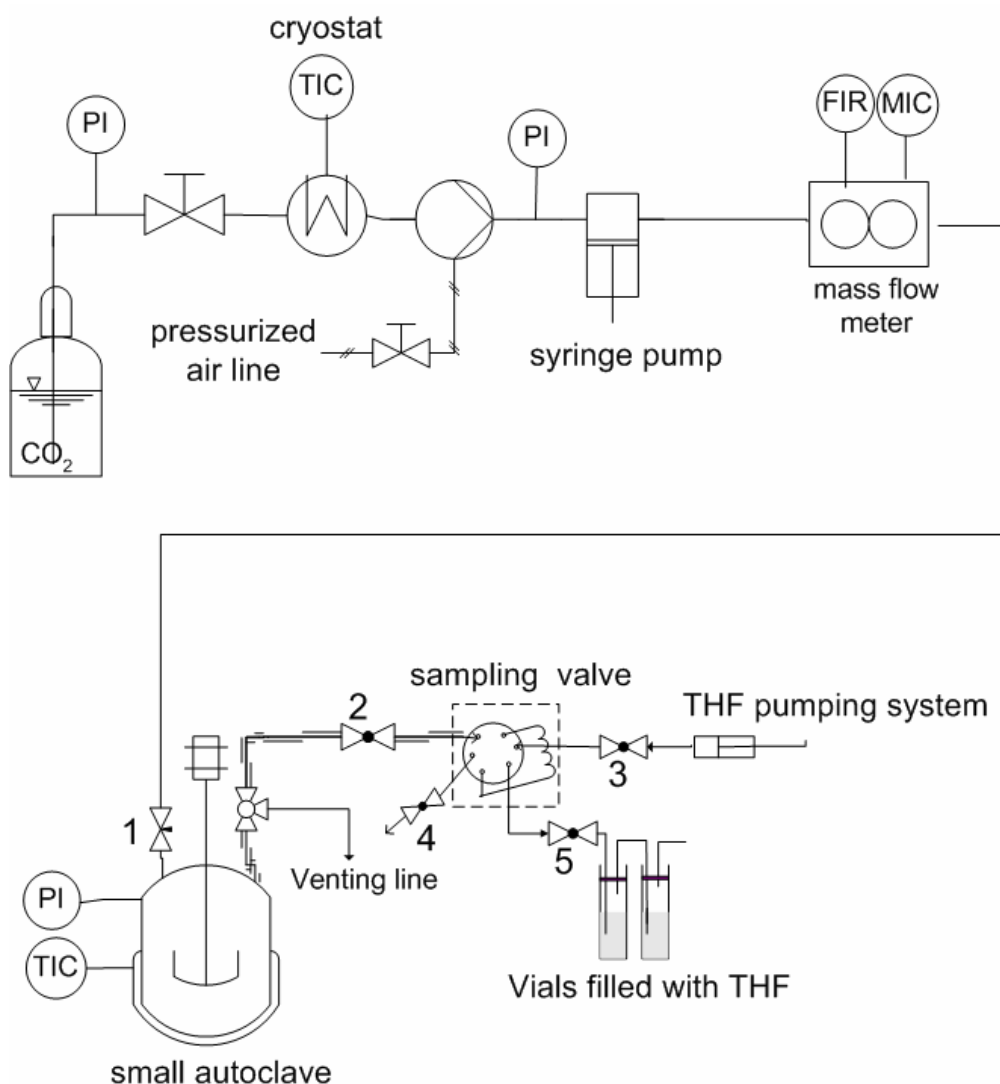
Figure 1: Sketch of the plant for the partitioning measurement

To perform a typical experiment, the vessel is connected to a two position sampling valve (VICI valve, model ET26UWTY, USA) modified to work at high pressure, high temperature and with tetrahydrofuran (THF). The sampling loop has a volume of 1 ml and the whole line from the reactor to the vials filled with THF is thermally insulated in order to prevent polymer precipitation while withdrawing the supercritical phase.

The analysis of the extracted material is carried out by gel permeation chromatography (GPC, Hewlett Packard series 1100, USA), with a special bench of 3 columns (Polymer Laboratories, two columns Plgel 5 μm MIXED-C and one OligoPore column, USA) suitable for separating both, high and low molecular weight materials. The eluent is THF (flow rate 1 cm^3/min) and the detector is UV working at a wavelength of 220 nm. All the measurements are carried out at constant temperature of 40°C.

Occasionally m.a.l.d.i.-m.s. (matrix-assisted laser desorption/ionization mass spectrometry) technique is applied to check the GPC results at low molecular weight. The 3-indolacrylic

acid matrix (Fluka, CH), a typical matrix for polymers, is hereby used in a concentration of 0.05 M. The detector is a reflector with a reflectron voltage of 23 kV, the detector voltage and the acceleration voltage respectively amount to 1.55 kV and 21 kV. The delay time is 200 ns. The available machine can measure up to a molecular weight of 30,000 g/mol.

Materials

High purity CO_2 (Pangas, CH, purity 4.5) and methyl methacrylate (MMA, Fluka, CH, purity>99.0%) are the solvents used in this work. Powder-like poly(methyl methacrylate) (PMMA, $M_n \approx 300.000$ g/mol) produced via dispersion polymerization in supercritical CO_2 is used for all experiments. A detailed description of the polymerization procedure can be found elsewhere [2]. Tetrahydrofuran (Merck, CH, purity 99.9%) is used to clean the sampling loop and ensure complete dissolution of the collected polymer.

Procedure

Since the final aim is to characterize the polymer present in the supercritical phase in terms of amount and molecular weight distribution (MWD), the GPC has to be used in a quantitative way. To do this a calibration is needed i.e. a correlation between the elugrams obtained and the polymer concentration in the samples. Several vials containing different and known concentrations of PMMA are prepared for this purpose and then analyzed by GPC. The area under the detector signal is then integrated and correlated to the injected concentration. The calibration curve shown in Figure 2 has been obtained in this way.
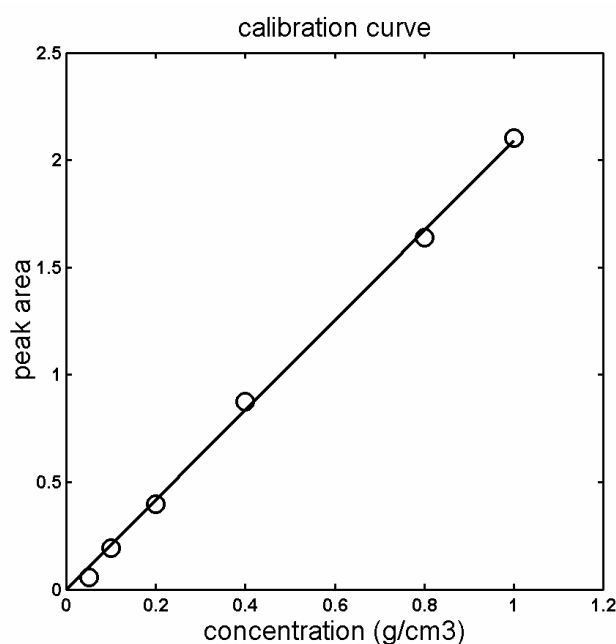
Figure 2: Calibration curve for GPC

For the extraction itself, first the polymer is treated overnight in a vacuum oven at a temperature of $60^{\circ}C$ to remove residual monomer and volatile impurities. Then a known quantity of polymer, usually around 10 g, is charged to the vessel and, in the case of mixture measurements, mixed with a weighted amount of MMA stabilized by hydroquinone to prevent further polymerization.

Afterwards the vessel is closed and carbon dioxide is fed to the system. The amount charged is controlled via mass flowmeter and valve 1 is closed when 70 g are reached (cf. Figure 1), which corresponds to a pressure of around 140 bar at the temperature of interest. The system is then stirred (around 300 rpm) and the heating is started. In a couple of hours the final temperature of $65^{\circ}C$ is reached and the system is then left for around 24 hours under these conditions to equilibrate the polymer chains partitioning in the two phases. Finally, stirring is stopped and the system is kept at rest for a couple of hours to allow the polymer to settle down and therefore prevent dragging of particles while sampling.

The withdrawal is then performed positioning the sampling valve on "load", i.e. opening valve 2 keeping 4 closed so as to fill the loop. Switching to the "injection" position keeping 3 closed and slowly opening the needle valve 5 enables to discharge the loop through the two vials filled with THF. The flow through the vials is kept extremely small so to give enough time to the gas to contact the solvent thereby enhancing the solvation of the polymer present in the supercritical phase in THF. The first vial is the one where the whole polymer is supposed to dissolve and the second one is basically there only to check that this assumption is correct. Since some of the polymer might have precipitated in the loop, giving rise to an underestimation of the extracted quantity, the emptied loop is also washed with THF and the solution collected in the first vial.

The volume of the vial is then measured and the polymer dissolved analyzed by GPC. Through the calibration, the polymer concentration in the THF solution is obtained and then, knowing the volume of liquid in the vial and of the sampling loop, the concentration of the polymer in the supercritical phase can be estimated.

RESULTS AND DISCUSSION

The polymer produced via dispersion polymerization in supercritical CO_2 exhibits a molecular weight distribution (MWD) with a tail down to chain lengths of the order of 5,000 g/mol, thus resulting in a high value of polydispersity.

The absence of polymer chains with smaller molecular weight has been further checked by m.a.l.d.i.-m.s. The last technique was used after a preliminary validation of the analytical procedure by analyzing PMMA oligomeric standards.

It is known from the literature [3] that the partition coefficient of the polymer chains between polymer and supercritical rich phases decreases rapidly with increasing chain length. Therefore the absence of low molecular weight material in the initial product lead to the expectation that no polymer should be extracted. However, the results of the experiments show that a significant amount of high molecular weight polymer is always solvated in the supercritical phase. Figure 3 shows a GPC chromatogram comparing the signal of the original polymer with the signal of the extracted material (experiment with 10w% of MMA with respect to CO_2). The shape of the small peak closely resembles the one of the original polymer, thus indicating that the partition coefficient is practically independent on chain length. This result seems to indicate that the partition coefficient could decrease with chain length for short chains only while reaching a constant, non-zero, plateau value at high molecular weight.
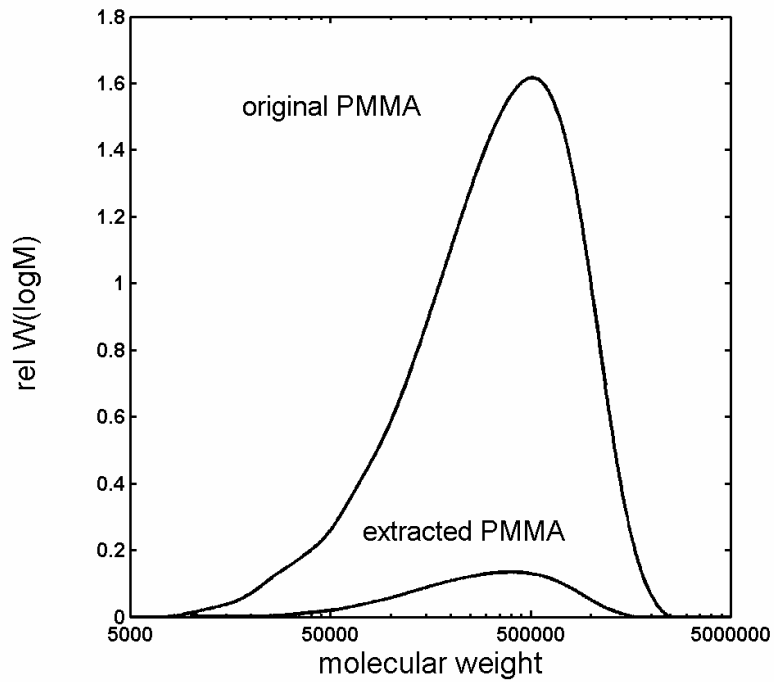
Figure 3: GPC chromatogram showing the comparison
between the original and the extracted polymer

To analyze the impact of monomer concentration on polymer solubility a series of experiments changing the initial amount of MMA have been performed and the results collected in Table 1. It shows how, the more MMA in the system, the more PMMA is extracted. This result is consistent with the fact that the polymer is completely soluble in its own monomer, which is acting as a cosolvent.

charged PMMA (g)	charged CO_2 (g)	charged MMA (g)	extracted PMMA (mg)
4.60	70.25	0	15.23
9.89	71.20	3.60	30.08
10.01	71.67	7.16	53.32
10.50	72.27	11.47	118.10

Table 1: Amount of extracted material versus amount of charged MMA

The modeling of these results using typical approaches developed for systems involving polymers (i.e. Sanchez Lacombe [4], EOS-Gex approach [5]) will be the next step of this project.

CONCLUSION

A notable partitioning of high molecular weight polymer has been found for PMMA in supercritical CO_2 at low pressure (140 bar) and temperature of $65^{\circ}C$. This result has a major impact on the quality of the polymer obtained in dispersion polymerization: since long chains are quite soluble in the continuous phase at high concentration of monomer, a significant amount of polymer could be produced in that phase, where a largely different growth probability is expected. Even though this partitioning becomes more and more in favor of the dispersed phase when a reaction is going on, the quite heterogeneous MWD typically obtained for these systems (cfr. Figure 3 "original PMMA") could be explained by a two loci reaction progress.

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