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Oligomers Partitioning in Supercritical CO_2

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ABSTRACT: A new experimental procedure for the evaluation of the partition coefficient of oligomers in supercritical carbon dioxide as a function of chain length is presented. After validating the technique through comparison with literature data, results involving polystyrene, poly(methyl methacrylate), and poly(vinylidene fluoride) are shown and discussed. The effect of chain end groups and of the presence of cosolvents is also analyzed. Most of the experiments are performed at a pressure of 150 bar and a temperature of 338 K, conditions which are typical for heterogeneous polymerization reactions carried out in supercritical media. The measured partition coefficients are well correlated by a simplified log−linear relationship proposed in the literature.

1. Introduction

The use of supercritical fluids in polymer synthesis and processing has gained considerable interest in the recent past.[1] Among the several advantages, the tunability of the solvent properties by changing the operating conditions is probably the most significant one with respect to applications. Different supercritical fluids have been tested, and carbon dioxide has certainly attracted the largest interest because of its low cost, chemical inertness, plasticization ability, and easily accessible critical point ($T_c = 304$ K and $P_c = 73.8$ bar).

In the field of polymer processing, supercritical CO_2 has been used as foaming agent and for polymer impregnation.[2−4] In the latter case, the CO_2 capability to depress the glass transition temperature of the polymer, thus enhancing the diffusion in and out of the polymer matrix, represents the key advantage. In polymer reaction, the supercritical fluid is used as dispersing medium in precipitation and dispersion polymerization. The majority of polymers are in fact insoluble in CO_2, and only fluorinated and silicon-based polymers are soluble enough to carry out a homogeneous reaction.[5−7]

The characteristics of the final product (e.g., the molecular weight distribution or the composition if a copolymer) are determined, in heterogeneous polymerization, by the environment where the chains are synthesized: the so-called reaction locus. In particular, it is important to know whether a radical generated in a certain phase grows and terminates in the same phase or whether it diffuses into another one.

In the typical case of most applications, where the polymer is largely insoluble in the continuous phase, the issue is to understand whether or not radicals generated in this phase are able to diffuse in the polymer phase before terminating. This is obviously quite relevant for the quality of the produced polymer since the propagation and termination rate constants are quite different in the supercritical and in the polymer phase. This, in turn, leads to different molecular weight distributions of the resulting polymer. To answer this question, the kinetics of interphase diffusion and termination for the radicals in the supercritical phase have to be compared. This can be done by considering the ratio $\Omega_{i,\mathrm{sc}}$ between the characteristic times of termination, $\tau_{\mathrm{term},i}$, and diffusion, $\tau_{\mathrm{diff},i}$, of an active chain of length i growing in the supercritical phase:[8]

$$\Omega_{i,\mathrm{sc}} = \frac{\tau_{\mathrm{term},i}}{\tau_{\mathrm{diff},i}} = \frac{D_{i,\mathrm{p}} D_{i,\mathrm{sc}}}{D_{i,\mathrm{p}} + c_i D_{i,\mathrm{sc}}} \frac{4\pi r_{\mathrm{P}} N_{\mathrm{P}}}{k_{\mathrm{term},i}[\mathrm{R}^\bullet]} \tag{1}$$

where $D_{i,\mathrm{p}}$ and $D_{i,\mathrm{sc}}$ are the diffusion coefficients of the radical of length i in polymer and in supercritical phase, respectively, c_i its partition coefficient between the two phases (ratio of the molar concentration in supercritical phase to that in polymer phase), r_{P} the particle radius, and N_{P} the concentration of the polymer particles per unit volume of supercritical phase. The product $k_{\mathrm{term},i}[\mathrm{R}^\bullet]$ is the pseudo-first-order rate coefficient of bimolecular termination and, in the general case of chain length dependent rate coefficients, is equal to

$$k_{\mathrm{term},i}[\mathrm{R}^\bullet] = \sum_{j=1}^{\infty} k_{\mathrm{term},i,j}[\mathrm{R}_j^\bullet] \tag{2}$$

where $k_{\mathrm{term},i,j}$ is the rate constant of termination between active chains of chain length i and j and $[\mathrm{R}_j^\bullet]$ the concentration of the latter radical in the supercritical phase. If $\Omega_{i,\mathrm{sc}}$ is larger than 1, the characteristic time of termination is larger than that of diffusion out of the supercritical phase, and the radical is captured by the polymer particles before terminating in the fluid phase. As a consequence, this radical spends most of its life in the particle, thus growing to a much larger extent than it would in the supercritical phase. Under these conditions, the role of the continuous phase in determining the final molecular weight becomes negligible. On the other hand, the radicals produced in the continuous phase terminate in this same phase when $\Omega_{i,\mathrm{sc}}$ is smaller than 1, thus producing relatively short chains which affect the quality of the final product.

The discussion above provides a motivation, although certainly not the only one, for estimating the partition coefficient of the polymer chains between the two phases as a function of the chain length. This, as apparent in

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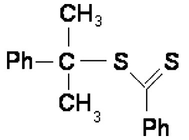

Figure 1. Chemical structure of the RAFT agent used.

eq 1, is then needed to estimate the parameter $\Omega_{i,\mathrm{sc}}$. In this work, an experimental technique for the measurement of this quantity is presented. After an initial validation by comparison with literature data for polystyrene (PS), the technique is applied to the same polymer at a different pressure and then to poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). Specific attention is directed to the effect of chain end groups on the oligomer solubility. For this, specific methyl methacrylate oligomers are synthesized via RAFT living polymerization, and their solubility in supercritical CO_2 is investigated. In the case of PMMA, both pure supercritical CO_2 and mixtures CO_2−monomer are considered in order to study the effect of a cosolvent (monomer in this case) on the partitioning of the oligomers.

2. Experimental Section

2.1. Materials and Analytical Techniques. Since the polymers considered in this work are expected to exhibit limited solubility in supercritical CO_2 at the selected operating conditions, only relatively short oligomers are considered. In particular, PMMA and PS samples have a maximum molecular weight of around 2500 g/mol while in the case of PVDF the highest molecular weight is of the order of 10 000 g/mol. All PS and one PMMA sample are prepared by mixing commercial oligomers typically used as standards for GPC calibration. Different ranges of nominal peak molecular weights, M_p, are considered: 580, 1660, 5000, and 9860 g/mol for PS and 620, 1310, 2220, 5200, and 11 100 g/mol for PMMA (Ercatech AG, Switzerland). Information about the chain end groups of these oligomers is taken from the certificates provided by the producer. Both have hydrogen atoms as ending groups.

The second sample of PMMA is produced in our laboratory via living free radical polymerization. Methyl methacrylate (Fluka, purity 99.0%) is mixed with 2,2′-azobis(isobutyronitrile) (AIBN) (Fluka, purity 98.0%) (molar ratio monomer/initiator = 800) and with the reversible addition−fragmentation transfer (RAFT) agent (synthesized in our laboratory, molecular structure shown in Figure 1) (molar ratio monomer/raft agent= 30), and the mixture is heated to 70 °C.

After about 10 h the reaction is stopped, and the mixture dried in air for several days. The obtained PMMA has molecular weights ranging from 400 to 2600 g/mol. The two end groups of the “living” PMMA chains are a dimethylphenyl group and a dithiobenzoate group (cf. Figure 1).

PVDF oligomers with a $-CH_2I$ group as chain terminator were kindly supplied by Solvay Solexis, Italy. The molecular weight distribution of the sample ranges from 700 to 10 000 g/mol.

Carbon dioxide (Pangas, Switzerland, purity 4.5), methyl methacrylate (Fluka, purity 99.0%), tetrahydrofuran (THF, Merck, Switzerland, purity 99.9%), and dimethylacetamide (DMA, Fluka, purity 98%) are used as supercritical medium and organic solvents.

The quantification of the extracted materials is carried out by gel permeation chromatography (GPC, Hewlett-Packard, series 1100), equipped with a bench of three columns, two for high molecular weight (Polymer Laboratories, Plgel 5 μm MIXED-C) and one for low molecular weight materials (Polymer Laboratories, OligoPore), and a UV detector (wavelengths: 240 nm for PMMA and methyl methacrylate, 260 nm for PS, 270 nm for PVDF, 345 nm for AIBN, and 510 nm for the RAFT agent). All measurements, except for PVDF, are carried out at constant eluent flow rate (THF, 1 mL/min) and column temperature of 40 °C. In the case of PVDF the solvent used is DMA with a flow rate of 0.7 mL/min, and the column temperature is set to 45 °C.

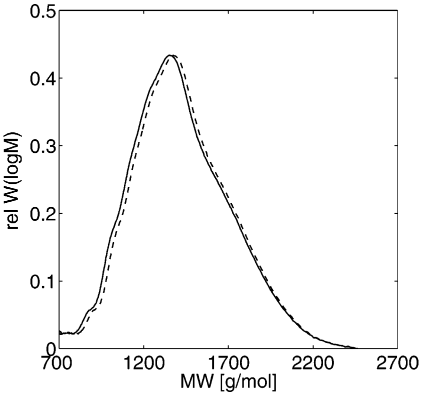

Figure 2. Comparison of estimated molecular weight distributions of PVDF using two different GPC calibrations.

Calibration curves for the GPC are obtained for PS and PMMA using polymer standards (Ercatech AG, Switzerland) with average molecular weight ranging from 600 to 1 500 000 g/mol and narrow molecular weight distribution. No commercially available standards of PVDF were found; hence, the PS calibration is used while applying the concept of “universal calibration”.[9,10] The required Mark−Houwink constants were reported in the literature for PS in DMA by Vilenchik et al.[11] and for PVDF in DMA by Lutringer and Weill.[12] However, the values reported were in both cases obtained at 25 °C while the GPC operating temperature for the PVDF experiments is 45 °C. Hence, before applying the obtained “universal calibration”, the effect of temperature on the Mark−Houwink constants was checked. For this reason a second “universal calibration” curve was generated using for PVDF again the values by Lutringer and Weill, while for PS a new set of Mark−Houwink constants obtained in DMA at 80 °C was used.[13] A PVDF sample was then injected in the GPC and analyzed using the two calibrations. The two obtained molecular weight distributions as shown in Figure 2 are practically superimposed. Therefore, the literature Mark−Houwink constants obtained at 25 °C are applied also at 45 °C. Note that the negligible effect of moderate temperature changes on the Mark−Houwink constants is also reported in the literature for the system PS−DMF and temperature range 25−45 °C.[14]

To ultimately validate the reliability of the GPC analysis, a comparison between the elugram of a mixture of polymer standards with the spectrum obtained by MALDI−MS (matrix-assisted laser desorption/ionization mass spectrometry)[15] is carried out. Hereby, the 3-indolacrylic acid matrix (Fluka), typical for polymers, is used at a concentration of 0.005 M. Other characteristic parameters are set as follows: reflection voltage = 23 kV, acceleration voltage = 21 kV, delay time = 200 ns. This technique measures the molecular weight of a polymer discriminating the chain lengths in terms of a single monomer unit up to 30 000 g/mol. The comparison of the results obtained by MALDI−MS and GPC is shown in Figure 3. For the MALDI spectrum (Figure 3a), all signals below 400 g/mol are due to sample-solvent impurities, while the polymer peaks start at 525 g/mol. From this point on, the peaks of the different oligomers follow at relative distance of 100 g/mol, which is the monomer molecular weight. The sensitivity of the analysis is sufficient to identify polymer chain lengths up to 17 monomer units. Also, the corresponding GPC spectrum (Figure 3b) exhibits, after some peaks below 400 g/mol which are assumed to be representative of low molecular weight impurities, the same series of peaks at relative distance of 100 g/mol. Moreover, polymer chains with maximum length of about 17−18 monomer units are found. This good agreement between the two results is considered the final validation of the chromatographic technique which is used in all further analysis.

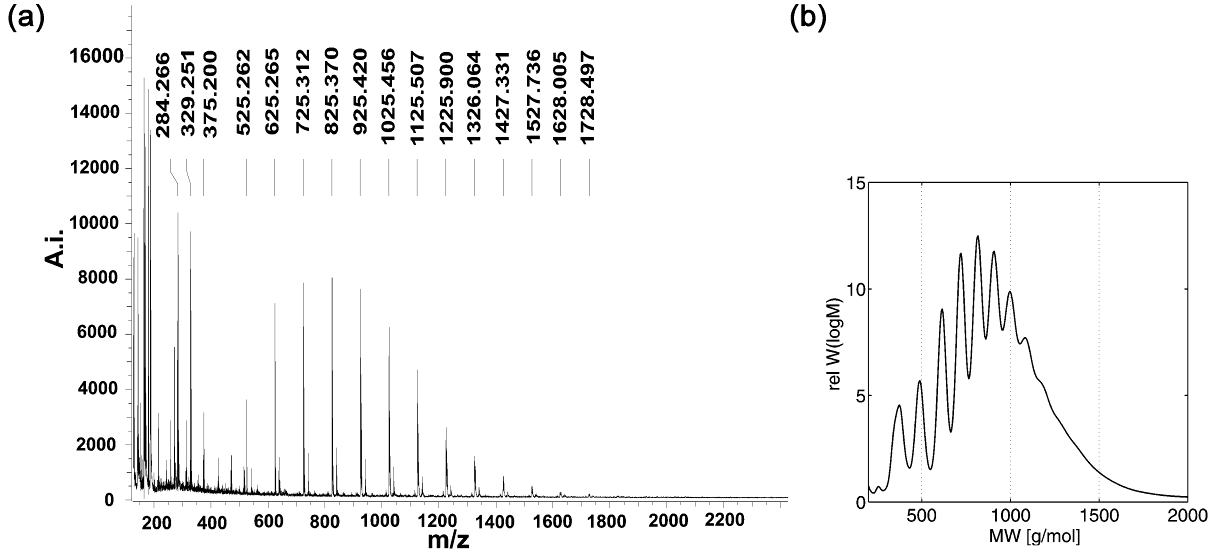

Figure 3. Comparison between MALDI−MS (a) and GPC plot (b) of the same sample.

2.2. Experimental Setup. Almost all experimental techniques previously presented in the literature for polymer extraction in supercritical fluids do not allow the measurement of an interphase partition coefficient for oligomers of a specific chain length. Typically they are designed to evaluate the solving power for low molecular weight materials (such as monomers, additives, or solvent residuals) or to estimate the limit of polymer complete solubility, the so-called cloud point curve.[1,16−18] The only available measurements of polymer partitioning between the supercritical and the polymer phase as a function of chain length were obtained by Reid and coworkers[19] using a technique based on a continuous operating mode. A stream of supercritical fluid was injected into a stainless steel column packed with the polymer to be extracted. After an initial transient, the leaving stream was assumed to be in equilibrium with the polymer packing in terms of polymer partitioning. To ensure this, the experiment was run at a low flow of CO$_2$ equal to 1 standard L/min ($\approx$2 g/min). The eluted stream was then depressurized and the precipitated polymer collected in a cold trap. This material, together with the original polymer, was subsequently analyzed by GPC to evaluate the chain length dependent partition coefficients. The procedure was applied to measure the partition coefficients of polystyrene oligomers at different conditions (pressure, temperature, fluid type). The experimental data were correlated by the following empirical relationship:

$$\log K_i = \log K_1 - \alpha\,(i - 1) \tag{3}$$

where i is the length, or degree of polymerization, of the considered chain, K_1 is the partition coefficient of the monomer ($i = 1$), and α is a constant. Note that the coefficients K_i are equivalent to the concentration-based partition coefficients used in eq 1, c_i. The only difference is that K_i is based on weight fractions and is defined as

$$K_i = \frac{w_{i,\mathrm{sc}}}{w_{i,\mathrm{p}}} \tag{4}$$

where $w_{i,\mathrm{sc}}$ is the mass fraction of the oligomer i in the fluid phase (g/g of solvent) and $w_{i,\mathrm{p}}$ that in the dispersed phase (g/g of *solvent-free* polymer). According to eq 3, the measured partition coefficients exhibit a linear dependence upon chain length when represented in a log−linear plot, as expected for liquidlike solvents such as supercritical fluids.[20] Reid and coworkers[19] examined the solubility of PS in supercritical CO$_2$ at 60 °C and 250 bar, and the best fit was obtained using $\alpha = 0.30$ and $K_1 = 0.125$.

This technique, even though convenient and reliable for the system PS−CO$_2$, cannot be adopted for all polymers. Problems are expected for polymers more prone to plasticization and swelling, such as PMMA in supercritical CO$_2$,[21] for which severe column clogging was observed shortly after the fluid flow was started.

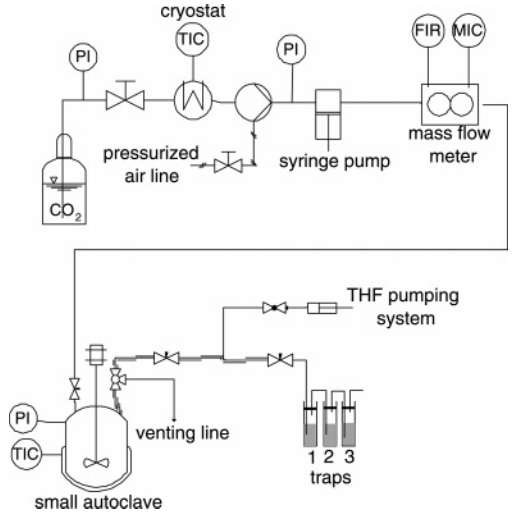

Figure 4. Sketch of the experimental setup.

To overcome this limitation, a different, batch-type equipment is designed. A sketch of the experimental setup is shown in Figure 4. The apparatus can be divided in three main parts: CO$_2$ feeding line, high-pressure vessel, and sampling line. The feeding line consists of a CO$_2$ cylinder with a deep tube, piston pump (NWA, Germany), syringe pump (Isco, model 260D), and mass-flow meter (Rheonik, model RHM015GNT). The vessel is a stirred, stainless steel, double-clamped autoclave (NWA, Germany) with temperature control, temperature and pressure gauges, and safety valve. The corresponding maximum temperature and pressure are 473 K and 300 bar, respectively. The main feature of the sampling system is a line, maintained at the same temperature of the autoclave, connecting the vessel to a suitable polymer collection device. The latter is made of a series of glass vials filled with a suitable polymer solvent (THF or DMA) and maintained at low temperature by a water-and-ice bath, through which the entire content of the autoclave is bubbled, so as to collect all the extracted polymer.

Previous attempts of sampling with a two-position valve (VICI, model ET26UWTY) modified to work at high pressure and high temperature and with THF and equipped with a sampling loop of 1 mL failed because the polymer collected (even by repeated, multiple samplings) was too small to give reliable and reproducible results.

Table 1. Parameters for the Calibration Curves Concentration vs Chromatogram Area

	a	*b*	*c*	*d*
PS	0	3.47×10^{-20}	-8.62×10^{-15}	4.85×10^{-7}
PMMA/methyl methacrylate	0	4.26×10^{-19}	-8.27×10^{-13}	4.96×10^{-6}
PVDF	0	0	5.03×10^{-13}	1.02×10^{-06}
AIBN	0	0	2.74×10^{-6}	1.11×10^{-2}
RAFT	1.74×10^{-11}	-2.29×10^{-8}	8.86×10^{-6}	3.50×10^{-3}

2.3. Sampling Procedure. Some precautions have to be taken to prevent dragging of nonsolubilized polymer particles while withdrawing the continuous phase. Various filters (sintered metal, Swagelok) of pore diameters ranging from 0.5 to 2 μm were mounted on the sampling line before the traps. However, each of them induced large pressure drops and flow irregularities difficult to control. Hence, the filters were dismounted, and the procedure adopted in this work is simply to sample very slowly and to use bulky polymer samples instead of powders. In the case of the oligomeric standards (PS, PMMA, PVDF), these are prepared dissolving a typical amount of about 0.8 g in THF/DMA and then drying under vacuum in order to obtain a small block of bulky material. The block is then introduced in a glass vial that fits into the vessel. For the PMMA sample prepared by living polymerization the polymer is synthesized in the same vial where it is then extracted. In the case of the experiments aimed at evaluating the solubility of the RAFT agent, two vials are charged in the vessel, one with about 0.1 g of RAFT agent and the second with about 1 g of bulk PMMA. Finally, when measuring the solubility of AIBN in sc-CO_2, about 1 g of initiator is charged in the glass vial inside the vessel.

2.3.1. Systems without Cosolvent. The main underlying assumption of the procedure adopted in the experiments without cosolvent is that the whole polymer dissolved in the continuous phase is recovered in the traps after the complete depressurization of the autoclave. To check this, a second small vial (without polymer), in the following referred to as "test vial", is introduced in the vessel as well. If part of the polymer precipitates in the vessel during sampling, traces of it would be found also in the test vial. Hence, its content is analyzed at the end of all experiments by washing the vial with THF. In all cases the corresponding GPC signal is found to be below the baseline noise, thus confirming that the amount of polymer precipitated during sampling can be neglected.

After inserting the vial with the polymer and the test vial into the vessel, a well-defined amount of carbon dioxide (controlled by the mass flow meter and suitable to reach the desired final pressure) is charged to the system. Then, the inlet valve is closed, the vessel stirred (60 rpm), and the heating started. After constant temperature is reached (usually 1 h), the system is left at least 2 h under stirring and an additional 1 h without stirring so as to reach equilibrium conditions and to allow complete polymer settling. To check this procedure, longer times were used and found to lead to the same results in terms of partition coefficients vs chain length. At the same time, traps 1 and 2 in Figure 4 (in this case the third trap is not used) are filled with a known amount of THF (DMA in the case of PVDF) and cooled by a water-and-ice bath. Then, the complete fluid content in the vessel is discharged by bubbling through the traps. This operation requires some care because the flow through the traps has to be small enough to ensure complete dissolution of the polymer originally in the supercritical phase. To check this, two traps in series are used: the negligible amount of polymer found in the second indicates that all the polymer has been recovered. Since, however, some polymer could have precipitated in the line during the slow sampling, the line is further washed with THF/DMA, and the resulting solution is collected in another trap ("wash trap") of known weight.

The same procedure is applied when measuring the solubility of AIBN in the supercritical phase and the partitioning of the RAFT agent between supercritical and polymer phase.

2.3.2. Systems with Cosolvent. In these experiments about 6 g of monomer (methyl methacrylate) is charged in the vessel together with polymer and CO_2. Moreover, trap 3 in Figure 4 is added at the end of the sampling line to ensure complete recovery of the monomer. Once all the components are loaded in the vessel, the procedure followed for heating, stirring, and depressurizing is the same as in the case without cosolvent. The sampling line is washed, also in this case, with THF after depressurization.

The main difference with respect to the case without cosolvent is in the quantification of the solubilized polymer. The assumption of complete recovery of the polymer in the traps is in fact not valid in this case since, during depressurization, methyl methacrylate precipitates in the vessel to some extent dragging part of the dissolved polymer. This complicates the analysis of this experiment as detailed in the following section. In this case, the test vial is not used, and the three traps (filled with THF) are analyzed by GPC also for methyl methacrylate.

The same analytical procedure is applied when measuring the solubility of AIBN in the mixture CO_2−methyl methacrylate.

2.4. Sample Analysis. Since the experiments require to characterize the polymer in the supercritical phase in terms of amount and molecular weight distribution, a quantitative GPC analysis is needed. Hence, a calibration curve, relating the area of the GPC peaks to the component concentration in the vial, is generated for each component under examination. After analyzing mixtures at given concentrations (1.0, 0.5, 0.25, 0.125, and 0.0625 mg/mL) of the materials described in section 2.1, calibration curves with the form $C = aA^4 + bA^3 + cA^2 + dA$ are obtained, where C indicates the polymer concentration in mg/mL and A the area of the peak in mV·mL. The parameters $a-d$ for the single polymers are reported in Table 1.

2.4.1. Systems without Cosolvent. All collected solutions (i.e., the contents of traps 1 and 2, wash trap, and test vial) are analyzed according to the following procedure. When the solubility of polymers is under investigation, the area below the GPC chromatograms is discretized as a series of rectangles with base length proportional to the molecular weight of the monomer unit (PS, 104 g/mol; PMMA, 100 g/mol; PVDF, 64 g/mol). By means of the corresponding calibration curve, these areas are converted into concentrations of the different oligomers in the solution. Given the volumes of the solutions recovered from the traps, the mass of the single oligomer i dissolved in the collected sample j, $m_{\mathrm{sc},j}^{i}$, is readily calculated. After checking the absence of polymer in the test vial, the total amount of oligomer i dissolved in CO_2, m_{sc}^{i}, is obtained by cumulating the distributions measured in the three traps:

$$m_{\mathrm{sc}}^{i} = \sum_{j=1}^{3} m_{\mathrm{sc},j}^{i} \tag{5}$$

From these values, the weight fraction of each oligomer in supercritical phase, $w_{i,\mathrm{sc}}$, is calculated since the total amount of charged CO_2 is known from the cumulative reading of the mass flow meter. Note that the GPC signal of trap 2 was always at least 1 order of magnitude smaller than those of trap 1 and of the wash trap.

To obtain the weight fraction of species i in the polymer phase, $w_{i,\mathrm{p}}$, a weighed amount of polymer after extraction, m_{pol}, is solubilized in a given volume of solvent, V_{sol}, and analyzed by GPC using the same approach discussed above. The resulting concentration values as a function of chain length, multiplied by V_{sol}, give the amount of each oligomer in the solution. These values divided by m_{pol} lead to $w_{i,\mathrm{p}}$ and, finally, to the estimation of the corresponding partition coefficients K_i defined by eq 4.

In the measurements of the solubility of AIBN the procedure presents some slight differences. No discretization of the GPC peak is needed, and the sum of the $m_{sc,j}$ over all the traps gives m_{sc} and subsequently w_{sc}. Since there is no real partitioning in this case and hence w_p is by definition equal to 1, the measured quantity is called solubility S in the following.

Also, when analyzing the partitioning of the RAFT agent between polymer and sc phase, no discretization of the GPC peaks is necessary. Again, the sum of the contributions of all traps gives w_{sc} while w_p is obtained by analyzing the polymer after the extraction experiment, integrating the peak corresponding to the RAFT agent, and dividing the obtained amount by m_{pol}.

2.4.2. Systems with Cosolvent. The discretization procedure of the GPC peaks described in section 2.4.1 is used also in this case. The GPC analysis of traps 1, 2, and 3 and of the wash trap leads to the evaluation of the methyl methacrylate amount leaving the vessel during depressurization. By subtracting it from the amount initially charged and assuming negligible the methyl methacrylate solubilized in the PMMA sample (PMMA less than 1 g), the portion of methyl methacrylate precipitated in the vessel is calculated. A problem arises when evaluating the oligomers solubilized in CO_2, m^i_{sc}. Since, while precipitating, the monomer entrains part of the oligomers solubilized in CO_2, the value of m^i_{sc} obtained by analyzing the GPC traces of the traps is smaller than the real solubilized amount. On the other hand, by assuming that (1) the relative amounts of oligomers with respect to monomer is the same in the material precipitated in the vessel and in that recovered from the traps and (2) the oligomers are equally entrained by the monomer during precipitation independently of their length, an estimation of m^i_{sc} and, therefore, of the partition coefficient becomes possible.

To test both these assumptions, some preliminary experiments were performed where also the monomer precipitated in the vessel was carefully collected and analyzed by GPC. The quantities of each oligomer obtained integrating the corresponding peaks were added to the amounts found in the traps, so as to evaluate the real value of m^i_{sc} and hence the partition coefficient K_i. The comparison between these values and the ones obtained under the assumptions mentioned above showed small differences which were in the range of the experimental uncertainty.

3. Results and Discussion

3.1. Validation of the Experimental Technique. To validate the developed experimental technique, the experiments reported by Kumar et al.[19] for PS at a pressure of 250 bar and a temperature of 333 K are first reproduced.

The typical GPC traces obtained in these experiments are shown in Figure 5. The continuous line corresponds to the original polymer, while the dashed and dotted lines represent the total of all extracted materials (the two traps plus the wash vial) obtained from two repeated experiments. Note that in this figure, as in all the following ones, the curves corresponding to the extracted quantities are multiplied by a factor equal to 125 to help their visualization. The minimum value on the molecular weight axis is 300 g/mol, which corresponds to the shortest oligomer in the original PS.

The obtained values of the partition coefficient K_i as a function of the oligomer chain length i for two repeated experiments (◇ and △) are compared in Figure 6 to the literature data (×, dashed line).[19]

Two conclusions can be drawn: (1) The new technique gives reproducible results (◇ and △ are very close to each other), and some discrepancy appears only at higher chain lengths, where the solubilities are very low.

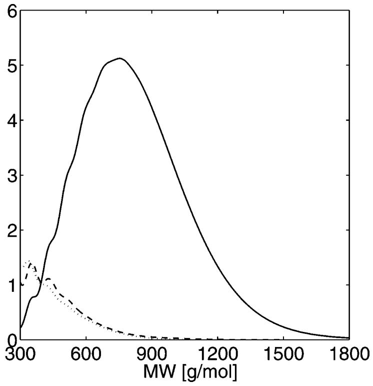

Figure 5. Measured molecular weight distributions obtained for the extraction of PS in CO_2 at $P = 250$ bar and $T = 333$ K. The solid line represents the GPC trace of the original polymer, while the dashed and the dotted lines represent the extracted polymer multiplied by a factor equal to 125.

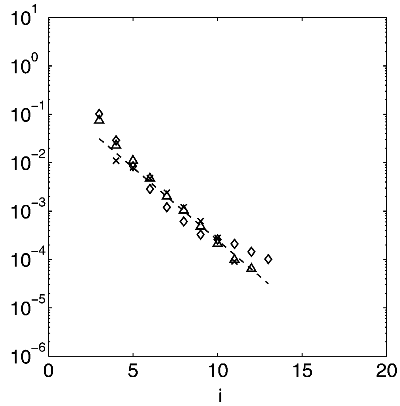

Figure 6. Experimental partition coefficient vs chain length of PS in CO_2 at $P = 250$ bar and $T = 333$ K: (△, ◇) this work, two repeated experiments; (× and best fitting curve (dashed)) Kumar et al.[19]

(2) The obtained results are in good agreement with the literature data, thus indicating the reliability of the selected experimental approach. It is worth noting that, with the developed technique, it is possible to measure the partition coefficient for chains with a maximum of 13 monomer units.

3.2. Polystyrene in Supercritical CO_2. A second set of measurements is performed with PS at a pressure of 150 bar and a temperature of 338 K. This specific pressure value is selected because it is closer to the operating conditions typically used in dispersion polymerization.[22,23] Moreover, to carry out a direct comparison, the same operating conditions are used in the following for the other polymers: PMMA and PVDF.

The values of the partition coefficient are shown in Figure 7 as a function of the chain length. The symbols (+ and ▽) represent the results obtained in two repeated experiments and confirm the good reproducibility of the developed technique. The dashed line is the same one shown in Figure 6 to reproduce the data obtained at higher pressure (250 bar). The analysis of these data leads to the conclusion that, at least within the explored pressure range, the solubility of PS in supercritical CO_2 is quite limited and the pressure (i.e., the solvent density) affects it only marginally.

3.3. Poly(methyl methacrylate) in Supercritical CO_2. The GPC traces measured for the PMMA sample obtained by mixing commercial oligomeric standards (see section 2.1) are shown in Figure 8. The continuous

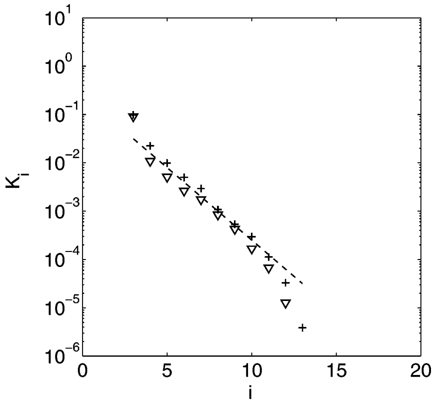

Figure 7. Experimental partition coefficient vs chain length for PS in CO_2 at P = 150 bar and T = 338 K: (+, ▽) two repeated experiments, dashed curve as in Figure 6.

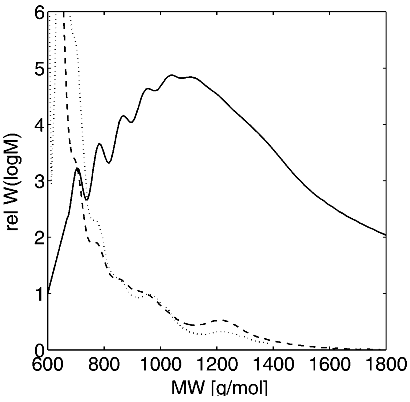

Figure 8. Measured molecular weight distributions obtained for the extraction of PMMA in CO_2 at P = 150 bar and T = 338 K: solid line, original polymer; dashed and dotted lines, extracted polymer multiplied by factor equal to 125.

curve refers to the original polymer, while the dotted and dashed curves are repetitions of the same experiment and refer to the overall extracted polymer. The experimental conditions are pressure of 150 bar and temperature of 338 K. The minimum value considered on the molecular weight axis is 600 g/mol because disturbances in the baseline at the selected detector wavelength (240 nm) appear at lower molecular weights. These disturbances are probably due to impurities in the eluent and could not be avoided. Hence, the signals of the eluted chromatograms are considered to be reliable only above 600 g/mol. Since the same value of the magnification factor is used in Figure 8 as well as in Figure 5, a direct comparison between the results for the two polymers is possible. The larger solubility of PMMA is evident because of the larger area below the molecular weight distribution of the extracted polymer and because of the better definition of the small peaks corresponding to the different oligomers. This improved resolution corresponds to a larger amount of injected polymer and, thus, of extracted material.

The corresponding partition coefficients are shown in Figure 9 as a function of chain length i, where the symbols (□ and ○) represent the results of two repeated experiments. When comparing these values with the dashed curve, representing the results obtained for PS at the same pressure, it is seen that the solubility coefficients for PMMA are almost 1 order of magnitude larger. This is in agreement with indications given by McHugh and co-workers,[17] who investigated the role of the polymer chain structure on its solubility in supercritical CO_2 by measuring cloud point curves under different conditions. They concluded that the solubility of nonpolar hydrocarbon polymers is enhanced by introducing polar groups in the polymer backbone, which is the case of PMMA with respect to PS. Moreover, indications that specific interactions between CO_2 and carbonyl groups present in the polymer backbone enhance the solubility of polymers were recently reported by Tan et al.[18] for the system poly(ether carbonate)−CO_2.

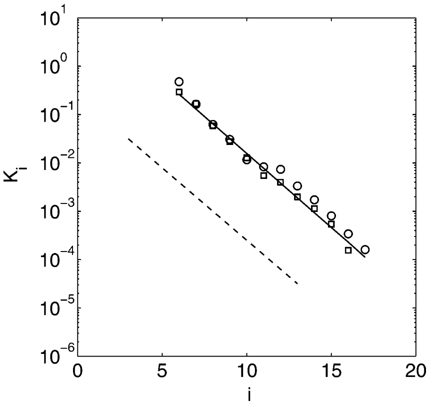

Figure 9. Experimental partition coefficient vs chain length for PMMA in CO_2 at P = 150 bar and T = 338 K for two repeated experiments (○, □): dashed line, best fitting curve for PS from Figure 6; solid line, best fitting curve for PMMA.

The values of K_1 and α (eq 3) are obtained by an optimization on all experimental partition coefficient data. The obtained parameter values for the system PMMA−CO_2 are K_1 = 8.99 and α = 0.307, and the straight line shown in Figure 9 is the resulting curve. The physical meaning of K_1 is the partition coefficient of a small amount of monomer in the presence of polymer and CO_2 and corresponds therefore to the monomer solubility at infinite dilution, for which no independent information is available. It is worth noting that the maximum soluble chain length is about 16−17 monomer units. Even though slightly larger than the value found for PS, it can be stated that only very short chains exhibit a measurable solubility in supercritical CO_2 for both the examined polymers.

It should be mentioned that the PMMA samples used in all the experiments reported above have hydrogen chain end groups (see producer certificates). However, in industrial polymerization processes initiators are used which leave fragments as chain end groups in the final product. The impact on oligomer solubility of mass and chemical nature of these chain ends cannot be neglected,[16] as also confirmed by the recent results reported by Bray et al.[24] for the system poly(vinyl acetate)−CO_2. In the following, further experiments are carried out to quantify this effect.

A relatively simple way for obtaining low molecular weight polymers with small polydispersity is to produce them via living free-radical polymerization.[25] The monomer polymerized is methyl methacrylate and the RAFT agent used (see Figure 1) leaves large end groups at both chain ends. Because of the nature of these end groups, a dimethylphenyl group and a dithiobenzoate group containing both aromatic rings, one expects the partition coefficients of these oligomers to be in between those of PMMA and PS. This is in fact confirmed by the measured values of K_i compared in Figure 10 (○ and ▽) with the best fitting curves for PMMA (solid line) and PS (dashed line[19]) (cf. Figure 9).

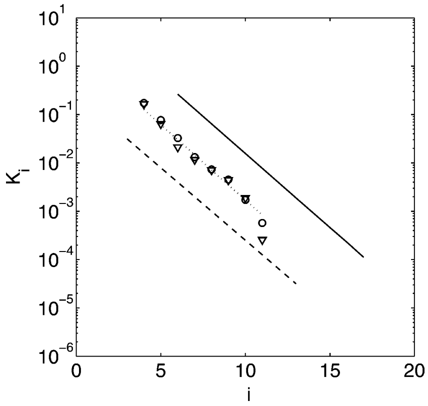

Figure 10. Experimental partition coefficient vs chain length for PMMA produced by RAFT living polymerization in CO$_2$ at P = 150 bar and T = 338 K for two repeated experiments (○, ▽): dotted line, best fitting curve; dashed line and continuous line as in Figure 9.

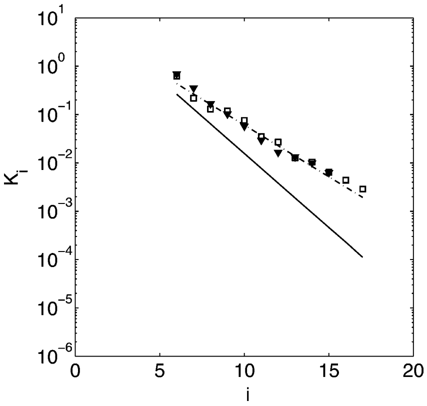

Figure 11. Experimental partition coefficient vs chain length for PMMA in methyl methacrylate-CO$_2$ at P = 150 bar and T = 338 K for two repeated experiments (□ and ▼): dashed–dotted line, best fit for PMMA in methyl methacrylate–CO$_2$; solid line, best fitting curve for PMMA in pure CO$_2$ (Figure 9).

Note that the molecular weight reported in Figure 10 considers *only* the methyl methacrylate units present in the chains. The contribution of the two chain end groups (about 180 g/mol) is subtracted from the molecular weight obtained by GPC. With this definition the maximum chain length for which the partition coefficient can be measured is 11.

To use eq 3 for reproducing this partition coefficients, K_1 and α are again both fitted directly on the experimental results. The computed values are $K_1 = 1.09$ and $\alpha = 0.312$. Note that K_1 in this case corresponds to the partition coefficient of a small amount of monomer in the presence of polymer, CO$_2$, and RAFT agent. It is therefore expected that the calculated K_1 value for this system is different from the one obtained for pure PMMA. Since the two end groups coming from the RAFT agent strongly affect the oligomers partitioning, it is in fact reasonable to assume that the presence of RAFT agent influences also the monomer behavior. To quantify the impact of the RAFT agent, its partitioning between supercritical and polymer phase is measured. The obtained value is $K_{\mathrm{RAFT}} \approx 0.03$, which is reasonable since the structure of the RAFT agent resembles the one of a styrene dimer, whose K value is 0.06 (see Figure 7 with i = 2). The difference in the two partition coefficients can be attributed to the presence of nonpolar groups, like the sulfur atoms and the methyl groups, which make the polymer less CO$_2$-soluble.[17] In conclusion, it is worth noting that the obtained value for α is very close to the one obtained for PMMA and for PS, showing that the effect of the end groups shifts simply the curve of the partition coefficients without affecting the dependence of the solubility on chain length.

The results reported above indicate that the impact of the chain end groups on the solubility of the oligomers is quite significant. A typical initiator for the polymerization in supercritical CO$_2$ is AIBN,[26] and care must be taken in extending to AIBN-terminated chains quantitative information on the solubility of similar chains but with different end groups. A useful information in this context is the solubility, S, of the pure initiator in supercritical CO$_2$ which is measured at the conditions of interest (pressure 150 bar and temperature 338 K) and found to be $S_{\mathrm{AIBN}} \simeq 1.3 \times 10^{-3}$ (weight fraction). This value is not too far from to the one obtained by Kumar et al.[27] for AIBN in supercritical ethane at pressure of 150 bar and temperature of 333 K (S = 0.006) and is considerably lower than the partition coefficients obtained for the shortest H-terminated PMMA chains (see Figure 9). Hence, it can be expected that short PMMA chains terminated by AIBN exhibit lower solubilities than the corresponding H-terminated methyl methacrylate oligomers.

3.4. Cosolvent Effect. The addition of a third component to solute–solvent systems can strongly affect the partition behavior at equilibrium conditions.[28–31] For example, the addition of a third component compatible with both solvent and solute can enhance the affinity of the solvent to the solute and hence lead to increased solubility. This is the so-called cosolvent effect. Since considerable amounts of monomer are present at the beginning of the polymerization process, it is interesting to study how this affects the partitioning of the growing polymer chains. For the system PMMA (high molecular weight)–CO$_2$–methyl methacrylate, a study performed by Lora and McHugh[29] evidenced an increase in solubility (decrease in the cloud point pressure at constant temperature) of PMMA after addition of methyl methacrylate. In the following this effect on oligomers is analyzed as a function of their chain length.

To quantify the cosolvent effect for oligomers, experiments in the presence of monomer at typical reaction concentrations (8.5% g of methyl methacrylate/g of CO$_2$) are performed. The temperature and pressure are the same as in the previous experiments, i.e., 338 K and 150 bar. The results in terms of partition coefficient vs chain length are shown in Figure 11, where the symbols (□, ▼) represent two repeated experiments and the dashed–dotted curve is the best fitting curve (eq 3). Also, in this case the values for K_1 and α are fitted on the experimental data, and the values obtained are 5.09 and 0.214, respectively. The discrepancy between the K_1 value obtained in this case and the one found for the system without cosolvent (K_1 = 8.99) is explained considering that here, instead of the solubility of the monomer at infinite dilution, the solubility of monomer in the presence of polymer, CO$_2$, and a large amount of monomer is obtained. In conclusion, the comparison of the partition coefficients measured with (dashed–dotted curve) and without (solid curve) cosolvent illustrates that the presence of methyl methacrylate increases the solubility of PMMA oligomers in the supercritical fluid and changes also the trend of solubility with chain length ($\alpha_{\mathrm{mon}} < \alpha_{\mathrm{pol}}$).

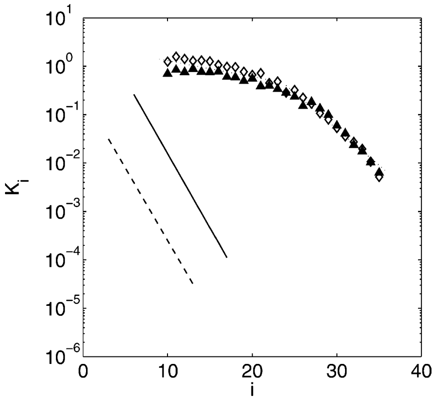

Figure 12. Experimental partition coefficient vs chain length for PVDF in CO_2 at P = 150 bar and T = 338 K for two repeated experiments (▲, ◇). Solid and dashed line represent the best fitting curves for the partition coefficient of PMMA in CO_2 and PS in CO_2 (Figure 9), respectively.

3.5. Poly(vinylidene fluoride) in Supercritical CO_2. Only few polymers are soluble in supercritical CO_2 at moderately high pressures and temperatures.[1,5,6] Among these the fluorinated ones are probably the most interesting because of their special characteristics.[32] As a representative of this category PVDF was chosen, and in the following the measurement of the partition coefficient of PVDF oligomers is reported. Indications on the relatively high compatibility of PVDF with CO_2 are reported in several literature studies on cloud point pressure and temperature.[33−35] PVDF in a concentration of 5 wt % is soluble in CO_2 at 393 K and pressures above 1700 bar.[34] In comparison, PMMA, used in the same amount, forms a homogeneous phase with CO_2 only at temperatures higher than 528 K and pressures above 2550 bar.[17] This leads to the expectation that the solubility of PVDF oligomers in CO_2 is larger than the one reported for PMMA in the previous section.

The results obtained at 338 K and 150 bar are shown in Figure 12 in terms of K_i as a function of chain length i (◇, ▲). In the same figure, the best fit curves for PMMA (continuous line) and PS (dashed line) are reported for comparison. As expected, PVDF exhibits a solubility at least 2 orders of magnitude larger than PMMA and PS and a maximum soluble chain length up to about 35 monomer units, corresponding to a molecular weight of around 2200 g/mol. It is also apparent that the chain length dependence of the partition coefficient is not anymore linear on the usual log−linear plot used for the other polymers, thus indicating that the empirical relationship (3) cannot be applied in this case. A possible explanation for this nonlinearity can be the presence of the iodine end group which might interact with CO_2 and influence strongly the behavior of the shortest chains.

4. Conclusion

An experimental technique for the evaluation of the partition coefficient of polymers in supercritical fluids as a function of chain length is proposed and validated. The operating conditions (pressure 150 bar, temperature 338 K) are chosen in order to represent typical reaction conditions. For all the systems under examination a satisfactory reproducibility of the experimental results is obtained, particularly when considering the small polymer amounts analyzed. It is found that the experimental error tends to increase for the largest and for the smallest soluble molecular weight for two different reasons. In the first case small changes in the user-defined GPC baseline cause large changes in the tail of the peaks and hence large experimental inaccuracies, while in the second case disturbances in the GPC chromatogram itself, given mainly by impurities in the solvents, affect the initial height of the peaks. The average error over all the collected data is about 20%.

In the case of PS, earlier experimental results by Kumar et al.[19] are well reproduced. The obtained results indicate that PS exhibit a very low solubility in sc-CO_2, with partition factors less than 10^{-4} already at chain lengths of about 12 monomer units. Experiments performed at different pressures (150 and 250 bar) indicate a very weak effect on solubility.

For PMMA oligomers terminated with hydrogen atoms, about 100 times larger partition coefficients are measured, thus confirming the expected larger compatibility of PMMA with sc-CO_2. The maximum chain length exhibiting partition coefficients above 10^{-4} is, however, around 18 monomer units, thus indicating a limited polymer solubility also in this case.

The effect of chain end groups has been found to be very strong for these short chains. In particular, PMMA oligomers prepared by RAFT living polymerization have been investigated. The two large end groups significantly affect the solubility, leading to a decrease of the partition coefficient and of the maximum soluble chain length.

Another interesting aspect is the effect of the monomer on the oligomer solubility, which is particularly relevant when considering reaction conditions. For this, the system PMMA−methyl methacrylate−CO_2 is investigated, and as expected, a relevant increase in the partition coefficients is observed.

Finally, the last system explored, PVDF oligomers with a $-CH_2I$ end group, exhibits much larger solubilities and maximum soluble chain length values than the other investigated polymers, thus confirming the strong affinity of fluorinated polymers to supercritical CO_2.

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Supporting Information Available: Values of the measured partition coefficients and oligomers mass fractions. This material is available free of charge via the Internet at http://pubs.acs.org.

Notation

A = area below the GPC signal [mV·mL]
C = polymer concentration in the traps [mg/mL]
c = concentration-based partition coefficient [−]
D = diffusion coefficient [cm^2/s]
k = bimolecular termination rate constant [$cm^3/(mol\ s)$]
K = mass-based partition coefficient of monomer [g/g]
i = chain length, i.e., number of monomer units [−]
m = mass [g]
M_p = nominal peak molecular weight [g/mol]
MW = molecular weight [g/mol]
N = concentration per unit volume of supercritical phase [$1/cm^3$]
P = pressure [bar]

rel $W(\log M)$ = distribution of molecular weight (GPC chromatogram of the molecular weight distribution)
r = radius [cm]
[$R^\bullet$] = concentration of radicals [mol/cm^3]
S = solubility [−]
T = temperature [K]
V = volume [cm^3]
w = mass fraction [−]
Greek Letters
α = slope of the log-linear correlation (eq 3) [−]
τ = characteristic time [s]
Ω = ratio between characteristic times [−]
Subscripts and Superscripts
1 = monomer
c = critical
diff = diffusion
i = chain length
mon = monomer
P = particle
p = polymer phase
pol = polymer
sc = supercritical phase
sol = solvent
term = termination

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