Residual monomer reduction in polymer latex products by extraction with supercritical carbon dioxide

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**Residual monomer reduction in polymer latex products by
extraction with supercritical carbon dioxide**

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van de
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Niet alles draait om carrière en geld

Maar ook om liefde en vriendschap die je kunt geven,

Pas dan ben je ook geslaagd als mens voor de rest van je leven.

Table of Contents

Table of contents	i
Summary	iii
Samenvatting	v
Chapter 1 Introduction: Residual monomer reduction in polymer emulsion polymerization products: Limitations and challenges	1
Chapter 2 Partitioning of residual monomer between polymer and CO ₂ – A theoretical approach	9
Chapter 3 Experimental determination of the partition coefficient of monomers over polymer and supercritical carbon dioxide	27
Chapter 4 Mass transport phenomena in the supercritical carbon dioxide extraction of residual monomer from latex products	61
Chapter 5 Process design for the residual monomer reduction in latex with supercritical carbon dioxide	83
Chapter 6 High pressure carbon dioxide in the extraction of residual monomer from latex products: additional results and outlook	137
Notation	147
Dankwoord	155
Curriculum Vitae	157

Summary

Residual monomer reduction in polymer (latex) products by extraction with supercritical carbon dioxide

The increased awareness for environmental issues as well as for public health, demands “greener” processes as well as products. In the polymer industry, one of the major concerns relate to residual monomer in polymer (latex) products. Low molecular species are toxic. When monomer units diffuse out of their polymeric matrix, they contaminate the surrounding area. Decreasing the residual monomer level in polymer (latex) products is especially of great importance in food packaging, toys for children, etc. Conventional techniques to reduce residual monomer in polymer (latex) products are energy intensive, time consuming and not able to fulfill the increasingly stringent requirements for further reduction of residual monomer in polymer products, *i.e.* < 100 parts per million (ppm).

In this thesis the reduction of residual monomer in polymer (latex) products by extraction with supercritical carbon dioxide (scCO₂) is explored. The Peng-Robinson equation of state has been used to describe the binary phase diagram of CO₂ and styrene as well as of CO₂ and methyl methacrylate. The ternary phase diagram of CO₂-styrene-polystyrene as well as of CO₂-methyl methacrylate-polymethyl methacrylate has been estimated with the Perturbed Chain - Statistical Associated Fluid Theory. The partition coefficient of the distribution of monomer between CO₂ and CO₂ swollen polymer has been calculated.

In a high pressure autoclave the partition coefficient of the distribution of monomer between CO₂ and CO₂ swollen polymer has been determined experimentally at a range of temperatures and pressures. The experimental results demonstrate the partition coefficient is approximately independent of pressure and temperature. For the partitioning of styrene between CO₂ and CO₂ swollen polystyrene a value of 2 [kg PS/kg CO₂] has been found, while for the partitioning of methyl methacrylate between CO₂ and CO₂ swollen polymethyl methacrylate a value of 0.3 [kg PMMA/kg CO₂] has been determined.

Mass transport of monomer from the polymer phase to the CO₂ phase is governed by the shuttle effect. The monomer is hereby directly transferred from the polymer particles to the

CO₂ phase due to Brownian motion of the particles to and from the CO₂/H₂O interface. The main resistance against mass transfer has been demonstrated to be located in the polymer particles.

The countercurrent extraction process to reduce residual monomer in polymer (latex) products from 10⁴ ppm to 1 ppm in a column has been designed. Latex has been chosen as the continuous phase in which 1 mm CO₂ bubbles are dispersed with a hold up of 20 %. The column is operated at 100 bar and 35 °C. A column volume of 4.75 m³ applies for a throughput of 6000 kg PS latex (45% solids)/hr. The extraction process reducing the residual monomer costs 22 €/ton latex for a production capacity of 50 kt PS latex (45% solids)/yr. Continuous steam stripping only costs 12 €/ton latex to reduce the residual monomer level from 10⁴ to 100 ppm, whereas the purification costs of the CO₂-based extraction process are similar for a reduction to 100, 10 or 1 ppm. Reduction to lower levels of residual monomer, lower than 100 ppm, by means of steam stripping is hardly possible, mainly due to thermodynamic (and to some extent transport) limitations. The results of calculations for a residual monomer reduction from 10⁴ to 10 ppm with 100 °C steam point to a tremendous increase of the utility costs. The costs of a continuous steam stripping process are then more than 75 €/ton latex. The lowest residual monomer concentration in latex of 1 ppm can certainly only be achieved by extraction with (sc)CO₂.

Samenvatting

Verminderen van het restmonomeer gehalte in polymeren door middel van extractie met superkritisch kooldioxide

“Groene” processen en producten worden steeds belangrijker in het dagelijkse leven door de groeiende bezorgdheid om ons milieu, onze gezondheid en de beschikbaarheid van (fossiele) grondstoffen. Eén van de grootste aandachtspunten bij de productie van polymere materialen is het restmonomeer gehalte. Vooral in onder andere verpakkingsmateriaal voor voeding en in speelgoed is het verminderen van restmonomeer van groot belang. De technieken die nu gebruikt worden om restmonomeer in polymeer producten te verlagen zijn tijdrovend, kosten veel energie en kunnen het restmonomeer gehalte niet tot het gewenste niveau doen dalen, dat wil zeggen tot niveaus duidelijk lager dan 100 ppm.

In het in dit proefschrift beschreven werk is de extractie van restmonomeer uit polymeren door middel van superkritisch CO₂ (scCO₂) bestudeerd. Het binaire fasengedrag van zowel CO₂ en styreen als van CO₂ en methyl methacrylaat werd beschreven met de Peng-Robinson toestandsvergelijking. Het ternaire fasendiagram van CO₂-styreen-polystyreen en van CO₂-methyl methacrylaat-polymethyl methacrylaat werd in kaart gebracht met de Perturbed Chain - Statistical Associated Fluid Theory (PC SAFT). De verdelingscoëfficiënt van monomeer over de CO₂-fase en het polymeer gezwollen met CO₂ is berekend met het PC SAFT model.

De experimentele bepaling van de verdelingscoëfficiënt van monomeer over de CO₂ fase en het polymeer gezwollen met CO₂ werd uitgevoerd in een hoge druk cel bij verschillende drukken en temperaturen. De experimentele resultaten laten zien dat de verdelingscoëfficiënt nagenoeg onafhankelijk is van druk en temperatuur. De gemeten waarden van de verdelingscoëfficiënt wijken aanzienlijk af van de met PC SAFT berekende waarden. De reden voor deze verschillen tussen de berekende en gemeten waarden is waarschijnlijk het uitgangspunt bij de berekeningen. Bij de berekeningen is uitgegaan van een ideaal polymeer zonder verknopingen (entanglements). Voor de metingen zijn niet-behandelde reactorproducten gebruikt.

Het zogenaamde 'shuttle effect' domineert monomeer transport van de polymeer fase naar de CO₂ fase. De polymeerdeeltjes bewegen naar en van het CO₂/H₂O grensvlak ten gevolge van de Brownse beweging. Hierdoor ontstaat er een direct contact tussen het polymeerdeeltje en CO₂, waardoor monomeer direct wordt overgedragen naar het CO₂. De grootste weerstand tegen het monomeertransport ligt in de polymeerdeeltjes.

Het tegenstroom extractie proces om het restmonomeer gehalte in polymeer te verlagen van 10⁴ naar 1 ppm is ontworpen als een kolomproces. Latex is hierin de continue fase waarin 1 mm CO₂ druppels worden gedispergeerd met een volumefractie van 0,2. De extractiekolom is ontworpen voor een druk van 100 bar en een temperatuur van 35 °C. Voor het verwerken van 6000 kg PS latex (45% droge stof)/uur, is een kolomvolume van 4.75 m³ berekend. De kosten van de extractie van restmonomeer zijn geschat op 22 €/ton latex voor een productie capaciteit van 50*10³ ton PS latex (45% droge stof)/jaar. Het verminderen van restmonomeer van 10⁴ tot 100 ppm met stoomstrippen als continu proces kost slechts 12 €/ton latex. De kosten voor de extractie met CO₂ van 10⁴ ppm restmonomeer naar 100, 10 of 1 ppm blijven echter ongeveer gelijk. Mogelijkheden om het restmonomeergehalte met stoomstrippen verder te verlagen dan 100 ppm zijn zeer beperkt, omdat het proces zowel thermodynamisch als wat betreft monomeertransport in de polymeerdeeltjes is gelimiteerd. Een berekening voor het verlagen van restmonomeer van 10⁴ naar 10 ppm met stoom strippen toont een enorme stijging van de proceskosten, voornamelijk door de grote hoeveelheid stoom die verbruikt wordt. Het continue stoom strip proces kost dan maar liefst 75 €/ton latex. Een restmonomeer niveau van 1 ppm kan enkel worden bereikt door middel van extractie met scCO₂.

Chapter 1

Introduction: Residual monomer reduction in polymer emulsion polymerization products: Limitations and challenges

Introduction

Emulsion polymerization is frequently used in industry to produce e.g. adhesives, latex paints, coatings and rubbers (Gilbert, 1995). Emulsion polymerization is a free radical polymerization in a heterogeneous reaction system, yielding a colloidally stable dispersion of submicron polymer particles in an aqueous medium. The process is governed by a complex mechanism, see e.g. Gilbert (1995) and van Herk (2005). In many cases three time-separated stages can be distinguished in a batch process, *i.e.* particle nucleation, particle growth in the presence of monomer droplets and completion of the polymerization when the monomer droplets have been consumed. A simple description of the mechanism of emulsion polymerization has first been given by Harkins (1947) and later worked out by Smith and Ewart (1948). Many research groups have studied the emulsion polymerization process, see e.g. Hansen and Ugelstad (1982), Gilbert (1995), van Herk (2005), De la Cal *et al.* (2005) and De Cal *et al.* (2007). However, complete insight into the whole process has not been reached up to now. In general, emulsion polymerization yields a high molecular weight polymer product. Typical values of the degree of polymerization are mostly considerable larger than 10^3 . Molecular mass can e.g. be reduced by chain transfer agents. In the last stage of the process the rate of polymerization will decrease due to the decreasing monomer concentration inside the particles. Due to diffusion limitations in the particle phase the polymerization reaction will not proceed to completion. As a consequence, the polymer

latex product contains a significant amount of residual monomer inside the polymer particles, generally in the range of a thousand parts per million (ppm). Reduction of the residual monomer level in polymer latex products is essential for safe and non-toxic use. Moreover, increasingly stringent requirements demand for further reduction of residual monomer in polymer products. Various conventional techniques to reduce the residual monomer level in polymer latex products are energy intensive (e.g. steam stripping, Englund, 1981), time consuming (e.g. temperature increase) or even might change the product properties (e.g. addition of initiator). Most important, conventional techniques are not able to fulfill the stringent requirements as the result of thermodynamic and transport limitations.

Thermodynamic limitation

At high conversions ($X > 99\%$), i.e. high polymer volume fractions (ϕ_p), the activity coefficient of low molecular weight species molecularly dissolved in the polymer phase is very low. Consequently, monomer partitioning between the polymer phase and the vapor phase is characterized by very low monomer partial pressures in the vapor phase, see Equation 1 and Figure 1. Note that the activity coefficient decreases upon reduction of the volume fraction of low molecular weight species, e.g. residual monomer.

$$y_m * P_{\text{total}} = \gamma_m * x_m * P_m^{\text{sat}} \quad (1)$$

Figure 1 Monomer activity coefficient in a polymer solution as calculated with the Flory-Huggins model (Flory (1953)) for athermal polymer solutions;

$$\ln \gamma_A = \ln \left[1 - \left(1 - \frac{1}{m} \right) \Phi_P \right] + \left(1 - \frac{1}{m} \right) \Phi_P, \text{ m stands for the degree of polymerization.}$$

Reduction of the residual monomer to a level of a few ppm is in general not possible with steam stripping in equipment with a realistic size.

Transport limitation

The time constants for monomer transport in the polymer phase are very high. The diffusion coefficient (D_{mon}^p) of monomer in the polymer is in the order of magnitude of $10^{-15} \frac{\text{m}^2}{\text{s}}$, or even lower.

Pressurized carbon dioxide as alternative method to reduce residual monomer in polymer products

An alternative technique to reduce the residual monomer amount in polymer latex systems is the extraction with high pressure carbon dioxide (CO_2). Pressurized CO_2 has

several advantages to be used as extraction medium. At conditions above the critical temperature (304 K) and the critical pressure (73 bar) of CO₂ (Poling *et al.*, 2001), the physical properties lie between those of a liquid and a gas, combining favorable qualities of the liquid phase as well as the gas phase, see Table 1. For example, at high pressures a SCF has solubility and density properties close to those of a liquid, but with considerable larger diffusion coefficients and lower viscosity.

Table 1 Typical properties of gases, supercritical fluids (SCF) and liquids

property	gas	SCF	liquid
density (kg/m ³)	1	100-800	1000
viscosity (mPa.s)	0.01	0.05-0.1	0.5-1
diffusivity (m ² /s)	10 ⁻⁵	10 ⁻⁷	10 ⁻⁹

High pressure extraction with near supercritical or supercritical fluids (SCF) has been in use for several decades on an industrial scale (Kilzer *et al.*, 2011, Morgan, 2000, Araújo, 2002), *e.g.* for the decaffeination of coffee. Relatively small changes in the CO₂ pressure as well as in temperature result in large density changes favoring the extraction process. The most important advantage of using high pressure CO₂ is that CO₂ increases the fugacity of the monomer in the polymer phase (*i.e.* decreasing ϕ_p by swelling the polymer with CO₂), thereby increasing the monomer molar fraction in the gas or SCF phase, see Equation 1.

Note that as a result of swelling the polymer is softened and plasticized. Monomer transport rates (in terms of D_{mon}^p) in the polymer phase swollen with CO₂ increase from values $\leq 10^{-15} \frac{\text{m}^2}{\text{s}}$ to about $10^{-12} \frac{\text{m}^2}{\text{s}}$ or even higher (Alsoy and Duda, 1998), leading to improved monomer transport rates compared to *e.g.* steam stripping. Note that for highly amorphous or rubbery polymers, a maximum can be reached in the mass transfer rate with increasing pressure (Vandenburg, 2000). With increasing pressure, *i.e.* more CO₂ uptake in the polymer matrix, the softening point of the polymer, *i.e.* the glass transition temperature T_g , decreases. If T_g falls below the operation temperature in the extraction process, the polymer particles will become sticky and the extraction process is

hampered by fouling. Alessi *et al.* (2003) as well as Zhang and Handa (1998) reported the experimentally determined decrease in T_g of polystyrene (PS) as well as of polymethyl methacrylate (PMMA) with increasing pressure of CO_2 at a constant temperature, see Table 2.

Table 2 Decrease in the glass transition temperature (T_g) in CO_2 swollen polymers as a function of pressure (Alessi *et al.*, 2003, Zhang and Handa, 1998)

	P_{CO_2} [bar]				
	0	10	20	30	40
PS T_g [°C]	102	95	87	79	69
PMMA T_g [°C]	105	95	79	68	57

Moreover, due to the low polarizability of CO_2 , along with the lack of a dipole moment, nonvolatile polar molecules, surfactants and nearly all polymers are not or very sparsely soluble in (sc) CO_2 . Most commonly used monomers are moderately or well soluble in supercritical or liquid CO_2 .

So partitioning of monomer or other low molecular weight species (e.g. Diels-Alder adducts in styrene-butadiene based products) towards CO_2 is sufficiently good to allow application of supercritical or liquid CO_2 in an extraction process to reduce the level of residual monomer or other low molecular weight species.

Outline of this thesis

In the present work, aspects of thermodynamic phase behavior of PS as well as PMMA latex systems in a high pressure CO_2 atmosphere are reported in **Chapters 2** and **3**. **Chapter 4** discusses the mass transfer phenomena involved in the extraction of residual monomer with CO_2 . Based on experimental data (the partition coefficient (K_{mon}) for the distribution of monomer between the CO_2 swollen polymer and CO_2) as well as on

theoretically predicted parameters (dispersed phase hold up, droplet size) the design of an extraction process is described in **Chapter 5**. In Chapter 5 also an economic evaluation of the CO₂ based extraction process is given. The results of this evaluation are compared with the results of a cost estimation of a steam stripping process. In **Chapter 6** additional comments as well as the challenges and opportunities in field of extraction of residual monomer from polymer (latex) products with scCO₂ are presented.

References

- P. Alessi, A. Cortesi, I. Kikic, F. Vecchione, "Plasticization of polymers with supercritical carbon dioxide: Experimental determination of glass-transition temperatures", *J. Appl. Polym. Sci.*, **2003**, 88, 2189-2193
- S. Alsoy, J. L. Duda, "Supercritical devolatilization of polymers", *AIChE*, **1998**, 44, 3, 582-590
- P. H. H. Araújo, C. Sayer, J. G. R. Poço, R. Guidici, "Techniques for reducing residual monomer content in polymers: A review", *Polym. Eng. Sci.*, **2002**, 42, 7
- J. C. De La Cal, J. R. Leiza, J. M. Asua, A. Buttè, G. Storti, M. Morbidelli, "Emulsion polymerization", in "Handbook of polymer reaction engineering", J. T. F. Keurentjes, T. Meyer, Eds., **2005**, Wiley-VCH, Weinheim
- J. C. De La Cal, Chapter 6 in "Polymer reaction engineering", J. M. Asua, Ed., **2007**, Blackwell, Oxford
- S. M. Englund, "Monomer removal from latex", *Chem. Eng. Progr.*, **1981**, 55-59; and references therein
- R. G. Gilbert, "Emulsion polymerization, A mechanistic approach", *Academic Press*, **1995**
- Hansen, Ugelstad, Chapter 6 in "Emulsion polymerization, I. Piirma, Ed., *Academic Press*, **1982**, London
- A. M. van Herk, "Chemistry and technology of Emulsion polymerization", Ed., **2005**, Blackwell, Oxford
- A. Kilzer, S. Kareth, E. Weidner, "Neue Entwicklungen bei Reinigungs- und Trennprozessen mit über- und nahkritischen Fluiden", *Chemie Ingenieur Technik*, **2011**, 83, 9, 1405–1418
- E. D. Morgan, "III/Natural products/Supercritical fluid extraction", *Academic Press*, **2000**
- Z. Zhang, Y. P. Handa, "An in situ study of plasticization of polymers by high-pressure gases", *J. Polym. Sci., Part B: Polym. Phys.*, **1998**, 36, 977-982
- H. J. Vandenburg, "III/Polymers/Supercritical fluid extraction", *Academic Press*, **2000**

Chapter 2

Partitioning of residual monomer between polymer and CO₂

– A theoretical approach

Abstract

The efficiency of high pressure carbon dioxide to reduce residual monomer level in polymer products strongly depends on the monomer partitioning over the various phases involved in the separation process.

Phase behavior of the styrene – carbon dioxide as well as of the methyl methacrylate – carbon dioxide binary systems has been modeled with the Peng-Robinson equation of state. Monomer partitioning between the polystyrene or polymethyl methacrylate phase and the CO₂ phase has been estimated with the Perturbed Chain – Statistical Associated Fluid Theory (PC-SAFT).

Introduction

Extraction with supercritical or high pressure carbon dioxide ((sc)CO₂) is an interesting alternative to e.g. steam stripping to reduce the residual monomer level in polymer (latex) products. Knowledge of the phase behavior of the system monomer/polymer (latex)/(sc)CO₂ as a function of various operating conditions is a necessary prerequisite for process design.

Vapor-liquid phase equilibria at high pressure

For every component i in the mixture, the condition of thermodynamic equilibrium is the fugacity of a component is equal in all phases involved, see Equation 1 (Poling *et al.*, 2001, Prausnitz and Gmeling, 1979).

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} \quad (1)$$

The fugacity of a component in a mixture depends on temperature, pressure and composition of the particular mixture. The relation between fugacity, pressure, temperature and composition is expressed in the fugacity coefficient, Equations 2 and 3.

$$f_i^{(V)} = \varphi_i * y_i * P \quad \text{for the vapor phase} \quad (2)$$

$$f_i^{(L)} = \gamma_i * x_i * f_i^{O(L)} = \gamma_i * x_i * \varphi_i^{\text{sat}} * P_i^{\text{sat}} \quad \text{for the liquid phase} \quad (3)$$

The fugacity coefficient of the vapor and liquid phase can be calculated from vapor phase data, usually introduced by an equation of state¹. An equation of state is an algebraic relation between pressure, volume and temperature.

For liquids, the fugacity of component i in the liquid phase can also be calculated by another approach, the activity coefficient approach. The activity coefficient is expressed in Equation 4 (see Appendix A).

$$\left(\frac{\partial n * G^E}{\partial n_i} \right)_{P, T, n_j} = \mu_i^E = R T \ln \gamma_i \quad (4)$$

The activity coefficient must obey the Gibbs-Duhem criterion, *i.e.* $\sum x_i (d \ln \gamma_i)_{P, T} = 0$.

While liquid properties are generally not sensitive to pressure changes, pressure effects become only significant in high pressure systems, especially in systems containing supercritical components. The activity coefficient approach to determine the liquid fugacity coefficient is therefore not practical in high pressure systems. Describing high pressure phase equilibria, the fugacity coefficient of both the liquid and vapor phase is calculated with an appropriate equation of state. The fugacity coefficient of a component i in a mixture, derived from the chemical potential, is expressed in Equation 5 (Sadowski, 2003).

¹ At low pressures it is often assumed $\varphi_i^V = \frac{f_i}{y_i * P} = 1$ (Poling *et al.*, 2001)

$$R T \ln \varphi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{i \neq j}} - \frac{R T}{V} \right] dV - R T \ln Z \quad (5)$$

An typical Van der Waals type equation of state able to describe the pressure, volume, temperature relation for high pressure and supercritical fluids is the semi empirical equation of state reported by Peng and Robinson (1976). The Peng-Robinson equation of state expresses pressure as the sum of a repulsive term and an attractive term, Equation 6.

$$P = \frac{R T}{v-b} - \frac{a(T, \omega)}{v(v+b) + b(v-b)} \quad (6)$$

The parameter $a(T, \omega)$ reflects the temperature dependent intermolecular attraction. The parameter b reflects the Van der Waals hard sphere volume. For pure components, a and b can be estimated from the critical pressure (P_c) and the critical temperature (T_c), see Equations 7 and 8 (Peng and Robinson, 1976, Prausnitz and Gmehling, 1979).

$$a(T, \omega) = 0.45724 \frac{(R T_c)^2}{P_c} \left[1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2) (1 - \sqrt{T_r}) \right]^2 \quad (7)$$

$$b = 0.07780 \frac{R T_c}{P_c} \quad (8)$$

Applying Equation 5, the following expression for the fugacity coefficient of component i in a mixture has been derived (Peng and Robinson, 1976).

$$\ln \hat{\varphi}_i = \ln \frac{\hat{f}_i}{x_i P} = \frac{b_i}{b_{\text{mix}}} (Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2} B} \left(\frac{Z^* \sum_k x_k a_{ki}}{a_{\text{mix}}} - \frac{b_i}{b_{\text{mix}}} \right) \ln \left(\frac{Z+2.414 B}{Z-0.414 B} \right) \quad (9)$$

$$\text{where} \quad A = \frac{a_{\text{mix}} P}{R^2 T^2} \quad (10)$$

$$B = \frac{b_{\text{mix}} P}{R T} \quad (11)$$

$$Z = \frac{P v}{R T} \quad (12)$$

The mixture parameters used in Equation 9 follow from mixing rules, *e.g.*

$$a_{\text{mix}} = \sum_{i=1}^m \sum_{j=1}^m x_i * x_j * a_{ij} \quad (13)$$

$$b_{\text{mix}} = \sum_{i=1}^m \sum_{j=1}^m x_i * x_j * b_{ij} \quad (14)$$

Various expressions have been proposed to calculate the mixture coefficients a_{mix} and b_{mix} (Panagioutopoulos and Reid, 1985, Stryjek and Vera, 1986, Michelsen and Kistenmacher, 1990, Mathias and Klotz, 1991, Wong and Sandler, 1992). In the present work, the quadratic

mixing rule has been chosen to estimate the cross parameter a_{ij} , Equation 15 (Poling *et al.*, 2001).

$$a_{ij} = (a_i * a_j)^{0.5} * (1 - k_{ij}) \quad (15)$$

The cross parameter b_{ij} is often neglected due to its very small contribution to the description of phase equilibria. For simplicity, b_{mix} is expressed with a linear equation, Equation 16 (Han *et al.*, 1988).

$$b_{mix} = \sum_{i=1}^m x_i * b_i \quad (16)$$

Phase equilibria in polymer solutions

Thermodynamic modeling of phase behavior when polymers are involved, requires a model that is able to account for the dissimilarity in size between the different molecules, the polymer and solvent interactions and for the pressure dependence. The well known Flory-Huggins theory (Smith *et al.*, 2001, Prausnitz and Gmehling, 1979) is in general not able to describe the pressure influence. The Sanchez-Lacombe model (Sanchez and Lacombe, 1976) does take into account the requirements mentioned before, but a large set of parameters has to be determined. An alternative approach is the perturbed chain statistical associated fluid theory (PC-SAFT) equation of state (Gross and Sadowski, 2000, 2001), particularly developed for the thermodynamic modeling of systems containing both compressible components as well as chain-like molecules such as polymers. The PC-SAFT equation of state shows great similarity with the well known SAFT equation of state developed by Chapman *et al.* (1989). Both equations require three pure component parameters to describe a system: the number of segments, the size of the segments, and the energy related to the interaction of two segments. To describe a binary system, a binary interaction parameter k_{ij} is included correcting for the intermolecular interactions with respect to the pure components. Both models can be written as separate contributions to the Helmholtz energy, Equation 17,

$$A^{res} = A^{ref} + A^{pert} \quad (17)$$

The residual Helmholtz energy (deviation from the ideal gas state) of a system is the sum of the contributions of a reference system and a perturbation term. The reference system covers the repulsive interactions of the molecules, the perturbation term includes all kinds of attractive contributions, *e.g.* chain formation, dispersion, etc.. In contrast to the SAFT equation of state (Chapman *et al.*, 1989) where the reference system is the hard sphere system, the reference system in the PC-SAFT equation of state is the hard chain fluid system. In this way the dispersion term considers the attraction of chain molecules instead of that of unbounded segments, covering the influence neighboring segments of the same molecule on each other (de Loos, 2005). The different contributions to the residual Helmholtz energy in the PC-SAFT equation of state are summarized in Equation 18.

$$A^{\text{res}} = A^{\text{hc}} + A^{\text{disp}} + A^{\text{assoc}} \quad (18)$$

The association contribution to the Helmholtz energy accounts for specific short-range interactions, *e.g.* hydrogen bonding, dipole-dipole interactions.

For a detailed description of the PC-SAFT equation of state and its development, the reader is referred to literature (Gross and Sadowski, 2000, 2001).

Results and discussion of calculations

Vapor-liquid phase equilibria at high pressure

The vapor-liquid phase equilibria of styrene (Sty) – CO₂ as well as of methyl methacrylate (MMA) – CO₂ have been modeled with the Peng-Robinson equation of state. Table 1 lists the parameters used in the Peng-Robinson equation of state. The pure component parameters of Sty, MMA and CO₂ are taken from Poling (2001); binary interaction parameters are taken from Suppes and McHugh (1989) and Uzun *et al.* (2005).

Table 1 Peng-Robinson parameters as used for calculations. Pure component parameters are taken from Poling *et al.* (2001), binary interaction parameter k_{ij} taken from Suppes and McHugh (1989) and Uzun *et al.* (2005)

parameter	Sty	MMA	CO ₂
T_c [K]	647.05	563.95	304.25
P_c [10^5 Pa]	39.9	36.8	73.8
ω [-]	0.257	0.317	0.225
$k_{\text{Sty-CO}_2}$	0.046		
$k_{\text{MMA-CO}_2}$		0.033	

Experimental data for the binary systems Sty – CO₂ and MMA – CO₂ are available in literature (Suppes and McHugh, 1989, Uzun *et al.*, 2005). These data have been used to model the respective binary systems. Figure 1 shows the results of the modeling of the experimental liquid-vapor data for Sty-CO₂ (Suppes and McHugh, 1989) as well as for MMA-CO₂ (Uzun *et al.*, 2005).

Figure 1 Phase equilibrium data of the binary system Styrene-CO₂ (a). Symbols represent experimental data taken from Suppes and McHugh (1989) ♦ 35 °C, ▲ 55 °C. Lines represent calculations with the Peng-Robinson equation of state, — 35 °C, --- 55 °C; $k_{\text{Sty-CO}_2}=0.046$ (Suppes and McHugh, 1989); MMA-CO₂ (b). Symbols represent experimental data taken from Uzun *et al.* (2005), ♦ 35 °C, ▲ 60 °C. Lines represent calculations with the Peng-Robinson equation of state, 35 °C, — 60 °C; $k_{\text{MMA-CO}_2}=0.033$ (Uzun *et al.*, 2005).

The Peng-Robinson equation of state applies well in modeling liquid-vapor phase equilibria at high pressure. Knowledge of the phase behavior of the binary systems determines the

lowest possible operating pressure at a chosen constant temperature (or vice versa) to prevent phase separation of CO₂ and monomer during the extraction process. On the other hand it is noticed small changes in temperature and pressure should allow separation of CO₂ and monomer after the extraction process.

Phase equilibria in polymer solutions

Phase equilibrium of the ternary systems polystyrene (PS) – styrene (Sty) – CO₂ and polymethyl methacrylate (PMMA) – methyl methacrylate (MMA) – CO₂ has been modeled with the Perturbed Chain – Statistical Associated Fluid Theory (PC-SAFT) equation of state using the VLXE software of Laursen (2003). Table 2 shows the parameters used in the phase behavior calculations with the PC-SAFT equation of state. The pure component parameters were taken from the database of the VLXE software. The binary interaction parameters in the PS – Sty – CO₂ system were fitted to the cloud-point curve of the respective binary systems (Suppes and McHugh, 1989, Wissinger and Paulaitis, 1991). The binary interaction coefficients in the PMMA – MMA – CO₂ system were taken from literature (Görnert and Sadowski, 2008, Rajendran *et al.*, 2005, Lora and McHugh, 1999).

Table 2 PC-SAFT parameters as used for calculations

parameter	PS	Sty	PMMA	MMA	CO ₂
ϵ/k [K]	267	295.98	245	265.69	169.21
σ [Å]	4.107	3.712	3.6	3.624	2.785
m [-]	$M_w * 0.019$	3.08	$M_w * 0.019$	3.06	2.07

$k_{\text{Sty-PS}}$	0	$k_{\text{MMA-PMMA}}$	- 0.02
$k_{\text{PS-CO}_2}$	0.14	$k_{\text{PMMA-CO}_2}$	$-4.67*10^{-3} + 2.667*10^{-4}*T$ [K]
$k_{\text{Sty-CO}_2}$	0.1	$k_{\text{MMA-CO}_2}$	- 0.01

Note that the pure component parameters in Table 2, for both PS and PMMA, are parameters for pretreated polymers, *i.e.* PS and PMMA have been annealed above their glass transition temperature to remove any influence of the polymerization method as well as of contaminants. In the present study of the extraction of residual monomer from polymer

(latex) products, the polymers have not been pretreated in any way. It is very probable that pretreatment of the polymers changes physical interactions in comparison with untreated polymers.

Figure 2 shows the calculated phase behavior of the ternary system PS (100 kg/mol) – Sty – CO₂ at 18 °C for the pressures of 50 and 100 bar, respectively. The solid lines (phase boundary) as well as the dashed lines (tie lines) have been calculated with the PC-SAFT equation of state using the parameters listed in Table 2.

Figure 2 Phase behavior of the system PS ($M_w = 100$ kg/mol) – Sty – CO₂ at 18 °C, calculated with the PC-SAFT equation of state, concentrations are given in mass fractions. Solid lines represent phase boundaries, dashed lines represent tie lines; $k_{\text{Sty-CO}_2}=0.1$; $k_{\text{Sty-PS}}=0$; $k_{\text{CO}_2\text{-PS}}=0.14$. Triangles represent the borders of the VLLE region. a: 50 bar, b: 100 bar.

Figure 2a illustrates a homogeneous system at low CO₂ mass fractions at 50 bar. For higher CO₂ mass fractions the phase boundary is reached. A three phase region is formed due to the vapor-liquid equilibrium between Sty and CO₂ at 18 °C and 50 bar, as mentioned in the previous section. The triangles in Figure 2a represent the borders of the vapor-liquid-liquid equilibrium (VLLE) region. In the VLLE region a CO₂ vapor phase containing very small

amounts of Sty, is in equilibrium with a polymer rich liquid phase and a polymer lean liquid phase. Increasing the pressure to 100 bar, as shown in Figure 2b, a supercritical Sty-CO₂ mixture is formed. No three phase region exists anymore. A CO₂ rich vapor phase is in equilibrium with a polymer rich phase. Note that the slopes of the tie lines are more positive towards CO₂ at the higher pressure of 100 bar, indicating that more Sty dissolves in CO₂ compared to the system at the 50 bar. Choosing the operating conditions for the extraction of residual monomer from polymer (latex) products with high pressure CO₂, the binary phase behavior of CO₂ and monomer must be taken into account. A phase separation between monomer and CO₂ should be avoided.

Figure 3 shows the influence of temperature at a chosen constant pressure of 100 bar on the phase behavior of the PS (100 kg/mol) – Sty – CO₂ system.

Figure 3 Phase behavior of the system PS (100 kg/mol) – Sty – CO₂ at 100 bar, calculated with the PC-SAFT equation of state, pictures are based on mass fractions. Solid lines represent phase boundaries, dashed lines represent tie lines; $k_{\text{Sty-CO}_2}=0.1$; $k_{\text{Sty-PS}}=0$; $k_{\text{CO}_2\text{-PS}}=0.14$. a: 18 °C; b: 35 °C.

For the ternary system at a temperature of 18 °C as well as at 35 °C at 100 bar, no three phase regions appear in the phase diagram. For higher CO₂ mass fractions only a two phase region exist where the CO₂ rich vapor phase is in equilibrium with a polymer rich liquid phase. Phase separation between Sty and CO₂ appears at different compositions of monomer and CO₂ on increasing the temperature. Notice the slopes of the tie lines become more positive towards the polymer rich phase. Moreover, with increasing temperature the polymer rich phase contains more Sty, while the CO₂ rich phase contains less Sty. At constant pressure CO₂ extracts more Sty at a lower temperature than at higher temperatures. Note that at a low temperature and a high pressure the density of CO₂ is higher than at a high temperature and a high pressure.

Partitioning of Sty between CO₂-swollen PS and CO₂ has been calculated based on the monomer concentrations in both phases as predicted with the PC-SAFT equation of state. The partition coefficient is defined in Equation 19.

$$K_{\text{mon}} = \frac{c_{\text{mon}}^{\text{CO}_2}}{c_{\text{mon}}^{\text{pol}}} \left[\frac{\text{kg polymer}}{\text{kg CO}_2} \right] \quad (19)$$

The extraction of residual monomer in polymer products with high pressure CO₂ deals with very low monomer concentrations, *i.e.* less than 10⁴ parts per million (ppm). In Table 3 calculated partition coefficients for distribution of styrene between CO₂-swollen PS and CO₂ for various temperatures and pressures at low monomer concentrations in the CO₂-swollen polymer phase are collected. Partition coefficients were calculated with PC-SAFT and physical constants given in Table 2.

Table 3 Partition coefficient of Sty between CO₂-swollen PS (100 kg/mol) and CO₂, for a concentration of Sty in PS below 10⁴ ppm

Temperature [°C]	Pressure [bar]	Partition coefficient $\left[\frac{\text{kg PS}}{\text{kg CO}_2} \right]^*$
18	50	0.007
18	100	0.62
18	200	0.75
35	100	0.42
35	200	0.64
40	100	0.34

* see equation 20

The results in Table 3 demonstrate that increasing pressure at a constant temperature leads to higher values of the partition coefficient. The CO₂ density increases upon pressurizing the system, dissolving more monomer. The results in Table 3 also demonstrate that the partition coefficient decreases upon increasing temperature at a constant pressure. Due to the decreasing CO₂ density at higher temperatures, the partition coefficient also decreases as less monomer is dissolved in CO₂. An interesting issue is the partition coefficient at 18 °C and 100 bar is almost equal to the partition coefficient at 35 °C and 200 bar. For these two conditions the CO₂ density is approximately equal (*i.e.* 800 kg/m³). The partition coefficient therefore strongly depends on the temperature and pressure of the system, due to the changes in the CO₂ density. The partition coefficient of Sty at 18 °C and 50 bar is very low due to the phase separation between Sty and CO₂, as explained earlier.

Similar calculations have been performed predicting the phase behavior of the ternary system PMMA – MMA – CO₂ with the PC-SAFT equation of state using the parameters listed in Table 2. Table 4 summarizes the results of the calculations of the partition coefficient of MMA between CO₂-swollen PMMA and CO₂ at various temperatures and pressures.

Table 4 Partition coefficients of MMA between CO₂-swollen PMMA (100 kg/mol) and CO₂, for a concentration of MMA in PMMA below 10⁴ ppm

Temperature [°C]	Pressure [bar]	Partition coefficient $\left[\frac{\text{kg PMMA}}{\text{kg CO}_2} \right]^*$
35	50	0.014
35	100	2.1
35	200	4
40	100	1.7
50	100	1.5

* See equation 20

For the system PMMA – MMA – CO₂ the partition coefficient also increases when the pressure increases at a constant temperature (CO₂ density increases), and decreases when the temperature increases at a constant pressure (CO₂ density decreases). Note that at 35 °C and 50 bar MMA and CO₂ do not form a supercritical mixture which results in a very low partition coefficient.

The Gibbs-Helmholtz relation indicates the decrease of the partition coefficient with increasing temperature when $\Delta\Delta H_{\text{solution}} < 0$. The Gibbs-Helmholtz relation is expressed in Equation 21. The partition coefficient is written in terms of Gibbs free energies of solution, Equation 20.

$$K_{\text{mon}} = e^{\frac{-\Delta\Delta G_{\text{solution}}}{R T}} \quad \text{with} \quad \Delta\Delta G_{\text{solution}} = \Delta\Delta G_{\text{solution in CO}_2} - \Delta\Delta G_{\text{solution in CO}_2 \text{ swollen polymer}} \quad (20)$$

When the heats of solution are independent of temperature, Equation 21 holds, see also Chapter 3.

$$\ln \frac{K_{\text{mon}}^{T_2}}{K_{\text{mon}}^{T_1}} = -\frac{\Delta\Delta H_{\text{solution}}}{R} * \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (21)$$

Figure 4 illustrates the relation between the calculated partition coefficient and the temperature at 100 bar for the ternary systems PS – Sty – CO₂ (solid symbols) and PMMA – MMA – CO₂ (open symbols).

Figure 4 Partition coefficient of monomer between CO₂-swollen polymer and CO₂ at 100 bar in function of the temperature. Solid symbols represent styrene, open symbols represent MMA. Data points are fitted to $\ln K_{\text{mon}}^T = -\frac{\Delta\Delta H_{\text{solution}}}{R} * \left[\frac{1}{T} \right] + \text{constant}$ with $K_{\text{mon}} = \frac{C_{\text{mon}}^{\text{CO}_2}}{C_{\text{mon}}^{\text{pol}}}$, based on weight fractions.

The difference in heat of solution of Sty dissolved in CO₂ and the heat of solution of Sty dissolved in PS swollen with CO₂ at 40 °C and 18 °C is ~ 21 kJ/mol, see Equation 21. The difference in heat of solution of MMA dissolved in CO₂ and the heat of solution of MMA dissolved in CO₂ swollen PMMA at 50 °C and 35 °C is ~ 19 kJ/mol.

Note that the calculated partition coefficients for distribution of Sty between CO₂ swollen PS and CO₂ are generally lower than the partition coefficients for the distribution of MMA between CO₂ swollen PMMA and CO₂. This difference suggests that the molecular interactions between Sty and (sc)CO₂ are weaker than the MMA and (sc)CO₂ interactions, resulting in a lower affinity of Sty in (sc)CO₂. Kazarian *et al.* (1996a) studied the specific interactions of CO₂ with monomers to gain insight into interactions of CO₂ with polymers. With Fourier transform infrared (FTIR) spectroscopy, Kazarian and coworkers (1996a) demonstrated that CO₂ acts as a Lewis acid. An electron donor-acceptor complex between the carbonyl oxygen atom of MMA and the CO₂ carbon atom is formed, increasing solubility. For styrene there are no specific interactions with CO₂ as for MMA and CO₂. Similar observations have also been reported by Kazarian *et al.* (1996 b) and Shieh and Liu (2002).

Concluding remarks

The phase behavior of the binary systems Sty- CO₂ and MMA – CO₂ has been modeled with the Peng-Robinson equation of state. The calculated pressures approach the experimentally determined pressures (taken from literature) very well. The ternary systems PS – Sty – CO₂ and PMMA – MMA – CO₂ have been modeled with the Perturbed Chain – Statistical Associated Fluid Theory at various temperatures between 18 °C and 50 °C at various pressures between 50 bar and 200 bar. Monomer partitioning between the CO₂ swollen polymer phase and CO₂ strongly depends on the temperature and pressure. The partition coefficients for distribution of Sty between CO₂ swollen PS are generally lower than the partition coefficients for the distribution of MMA between CO₂ swollen PMMA and CO₂.

References

- W. G. Chapman, K. E. Gubbins, G. Jackson, M. Radosz, "SAFT: Equation of state model for associating fluids", *Fluid Phase Equilib.*, **1989**, 52, 31-38
- M. Görnert, G. Sadowski, "Phase-equilibrium measurement and modeling of the PMMA/MMA/carbon dioxide ternary system", *J. of Supercrit. Fluids*, **2008**, 46, 218-225
- J. Gross, G. Sadowski, "Application of perturbation theory to a hard-chain reference fluid: an equation of state for square-well chains", *Fluid Phase Equilibria*, **2000**, 168, 183-199
- J. Gross, G. Sadowski, "Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules", *Ind. Eng. Chem. Res.*, **2001**, 40, 1244-1260
- S. J. Han, H. M. Lin, K. C. Chao, "Vapor-liquid equilibrium of molecular fluid mixtures by equation of state", *Chem. Eng. Sci.*, **1988**, 43, 2327
- S. G. Kazarian, C. A. Eckert, J. C. Meredith, K. P. Johnston, J. M. Seminario, "Quantitative equilibrium constants between CO₂ and Lewis bases from FTIR spectroscopy", *J. Phys. Chem.*, **1996** (a), 100, 10837-10848
- S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, C. A. Eckert, "Specific intermolecular interaction of carbon dioxide with polymers", *J. Am. Chem. Soc.*, **1996** (b), 118, 1729-1736
- T. Laursen, Technical University of Denmark, **2003**, <http://www.vlxe.com>
- T. W. de Loos, "Polymer thermodynamics", in "Handbook of polymer reaction engineering", T. Meyer, J. Keurentjes, Eds., **2005**, Wiley-VCH, Weinheim
- M. Lora, M. A. McHugh, "Phase behavior and modeling of the poly(methyl methacrylate)-CO₂-methyl methacrylate system", *Fluid Phase Equilibria*, **1999**, 285-297
- P. M. Mathias, H. C. Klotz, J. M. Prausnitz, "Equation-of-state mixing rules for multicomponent mixtures: the problem of invariance", *Fluid phase equilibria*, **1991**, 67, 31
- M. L. Michelsen, H. Kistenmacher, "On composition-dependent interaction coefficients", *Fluid Phase Equilibria*, **1990**, 58, 229
- A. Z. Panagiotopoulos, R. C. Reid, "High-pressure phase equilibria in ternary fluid mixtures with a supercritical component", *ACS Div. Chem., Prep.*, **1985**, 30, 46
- D. Peng, D. B. Robinson, "A new two-constant equation of state", *Ind. Eng. Chem. Fund.*, **1976**, 15, 59-64
- B. E. Poling, J. M. Prausnitz, J. P. O'Connell, "The properties of gases and liquids", 5th ed., **2001**, McGraw-Hill Companies, Inc., USA
- J. M. Prausnitz, J. Gmehling, "vt-Hochschulkurs III: Thermische verfahrenstechnik phasengleichgewichte", *Thermische Verfahrenstechnik*, **1979**, 13, 3
- A. Rajendran, B. Bonavoglia, N. Forrer, G. Storti, M. Mazotti, M. Mordibelli, "Simultaneous measurement of swelling and sorption in a supercritical CO₂-poly(methyl methacrylate) system", *Ind. Eng. Chem. Res.*, **2005**, 44, 2549-2560

- G. Sadowksi, "Thermodynamik der polymerlösungen", Habilitationsschrift, Technischen Universität Berlin, 2000, **2003**, Shaker, Aachen
- I. C. Sanchez, R. H. Lacombe, "An elementary molecular theory of classical fluids. Pure fluids", *J. Phys. Chem.*, **1976**, 80, 2352-2362
- Y.-T. Shieh, K.-H. Liu, "Solubility of CO₂ in glassy PMMA and PS over a wide pressure range: the effect of the carbonyl groups", *J. Polym. Res.*, **2002**, 9, 107-113
- J. M. Smith, H. C. Van Ness, M. M. Abbot, "Introduction to chemical engineering thermodynamics", **2001**,
- R. Streyjek, J. H. Vera, "A cubic equation of state for accurate vapour-liquid equilibria calculations", *Can. J. Chem. Eng.*, **1986**, 64, 820
- G. J. Suppes, M. McHugh, "Phase behavior of the carbon dioxide-styrene system", *J. Chem. Eng. Dat.*, **1989**, 34, 310-312
- N. I. Uzun, M. Akgün, N. Baran, S. Deniz, S. Dinçer, "Methyl methacrylate plus carbon dioxide phase equilibria at high pressures", *J. Chem. Eng. Dat.*, **2005**, 50, 4, 1144-1147
- R. G. Wissinger, M. E. Paulaitis, "Molecular thermodynamic model for sorption and swelling in glassy polymer-CO₂ systems at elevated pressures", *Ind. Eng. Chem. Res.*, **1991**, 30, 5, 842-851
- D. S. H. Wong, S. I. Sandler, "A theoretically correct mixing rule for cubic equations of state", *AIChE Journal*, **1992**, 38, 671

Appendix A

The molar Gibbs free energy of mixing for an ideal system is the Gibbs energy of mixing per unit amount of mixture formed, defined as Equation A.1 (DeVoe, 2001)

$$G_m = H_m - T * S_m \quad (\text{A.1})$$

The enthalpy and entropy of 1 mole ideal mixture are written as, Equations A.2 and A.3.

$$H_m = \sum_i x_i * H_i^\circ \quad (\text{A.2})$$

$$S_m = \sum_i x_i * (S_i^\circ - R * \ln x_i) \quad (\text{A.3})$$

For an ideal solution $H_m = 0$, so

$$\Delta_{mix} G_m = -T * \Delta_{mix} S_m \quad (\text{A.4})$$

The molar Gibbs free energy of mixing in an ideal system then is, Equation A.5.

$$\Delta_{mix} G_m = R T * \sum_i x_i * \ln x_i \quad (\text{A.5})$$

For mixing pure substances to form a non-ideal solution, the deviation from an ideal solution is expressed in terms of excess molar mixing quantities at the same conditions of pressure, temperature and composition, see Equation A.6.

$$G_m^E = \Delta_{mix} G_{m(P,T,x)} - \Delta_{mix} G_{m,id(P,T,x)} = \sum_i x_i * (\mu_i - \mu_{i,id}) = \sum_i x_i * \mu_i^E = R T \sum_i x_i * \ln \gamma_i \quad (\text{A.6})$$

Note that the relation between the excess molar Gibbs energy and the activity coefficient follows from Equation A.7.

$$\begin{aligned} \mu_i^E &= \mu_i - \mu_{i,id} = (\mu_i - \mu_i^\circ) - (\mu_{i,id} - \mu_i^\circ) = R T \ln \frac{\hat{f}_i}{f_i^\circ} - R T \ln \frac{x_i * f_i^\circ}{f_i^\circ} \\ &= R T \ln \frac{\hat{f}_i}{x_i * f_i^\circ} = R T \ln \gamma_i \end{aligned} \quad (\text{A.7})$$

Chapter 3

Experimental determination of the partition coefficient of monomers over polymer and supercritical carbon dioxide

Abstract

The efficiency of high pressure carbon dioxide to reduce residual monomer in polymer products strongly depends on the monomer partitioning over the various phases involved in the separation process.

Phase behavior of the methyl methacrylate-carbon dioxide and styrene-carbon dioxide binary systems has been studied in a high-pressure variable volume optical cell and in a closed high pressure autoclave. The Peng-Robinson equation of state has been used to describe the pressure as a function of the composition in terms of monomer and carbon dioxide. Monomer partitioning between the polymethyl methacrylate or polystyrene phase and the carbon dioxide phase has been determined experimentally for a range of pressures and temperatures in a high pressure autoclave.

Introduction

Extraction with supercritical or high pressure carbon dioxide ((sc)CO₂) is an interesting alternative to e.g. steam stripping to reduce the residual monomer level in polymer (latex) products. Knowledge of the phase behavior of the system monomer/polymer (latex)/(sc)CO₂ as a function of various operating conditions is a prerequisite for process design.

Several authors already reported the results of phase behavior measurements of methyl methacrylate (MMA)-(sc)CO₂ (Lora and McHugh, 1999, Uzun *et al.*, 2005, Zwolak *et al.*, 2005, da Silva *et al.*, 2007) and of styrene (Sty)-(sc)CO₂ (Suppes and McHugh, 1989, Tan *et al.*, 1991, Akgun *et al.*, 2004, Zhang *et al.*, 2005) for a range of temperatures and

concentrations. In the present work experimental phase equilibria of the binary systems MMA-(sc)CO₂ and Sty-(sc)CO₂ at 35, 45 and 60 °C have been collected. Cloud-point measurements were performed using a high pressure variable volume optical cell. The concentrations of the coexisting phases were determined in a high-pressure autoclave with an online sampling system.

Phase behavior of the ternary system polystyrene (PS)-Sty-(sc)CO₂, for high monomer concentrations in the polymer phase, was studied by Görnert and Sadowski (2007) and Wu *et al.* (2002); polymethyl methacrylate (PMMA)-MMA-(sc)CO₂, for high monomer concentrations in the polymer phase, was also investigated by Görnert and Sadowski (2008). Wu *et al.* (2002) reported experimentally determined distribution coefficients of styrene between the corresponding polymer (molecular weight ~ 160 kg/mol) and the supercritical phase at 35 °C and 45 °C over the pressure range of 120-200 bar. Görnert and Sadowski (2007, 2008) presented isothermal measurements at 65 and 80 °C and pressures of 100 and 150 bar, for polymer samples having molecular weights of 6, 18 or 10 kg/mol, for both the PS-Sty-(sc)CO₂ and the PMMA-MMA-(sc)CO₂ system. In the present work experiments were performed at 35, 45 and 60 °C and 100, 140 and 180 bar, for polymer samples with molecular weights above 10 kg/mol and monomer concentrations in the polymer phase below 10⁴ ppm. The concentrations of MMA or Sty in the coexisting PS or PMMA and (sc)CO₂ phases were measured by means of a high-pressure autoclave with an online sampling system.

The experimentally determined monomer partition coefficient for distribution of monomer between the CO₂ swollen polymer and the (sc)CO₂ phase is used for design of extraction equipment for residual monomer reduction (see Chapter 5).

Experimental

Materials

Carbon dioxide (CO₂), grade 5.0 was obtained from Linde (The Netherlands). Prior to use CO₂ was led over a Messer Oxisorb filter to remove oxygen and moisture.

Styrene and methyl methacrylate monomer (purity $\geq 99\%$), obtained from Aldrich, were stored under argon. Additional inhibitor (4-tert-butylcatechol) was added to obtain a concentration of 10 parts per million (ppm) to suppress polymerization during the experiment.

Polystyrene beads (diameter 1 mm and 5 mm) and polymethyl methacrylate beads (diameter 0.5 mm), both with a molecular mass of about 10^5 kg/kmol, were kindly provided by BASF, Germany, and were used as received.

High-pressure variable volume optical cell

The high-pressure stainless steel optical cell (Sitec), see Figure 1, was temperature controlled by circulating oil in the heating jacket (PT100, ± 0.1 °C accuracy, **TIC**). The inner volume of the cell could be varied from 18 mL to 30 mL by means of a movable piston. The piston was driven by a hydraulic system. The pressure could be measured inside the cell, in direct contact with the mixture under investigation (HAEMI, circa 0.1 bar accuracy, **PI**). The maximum attainable temperature of the optical cell was 300 °C. The maximum pressure allowed was 300 bar. A sapphire window allowed for observing 80% of the inner volume of the cell. CO₂ was fed into the optical cell by a syringe pump (ISCO – model 260D, **FP**).

Figure 1 High-pressure variable volume cell. **FP** pump for liquid carbon dioxide, **PI** pressure indicator, **TIC** temperature indicator controller, **VI** volume indicator, **RD** rupture disk assembly.

Cloud-point measurements – Monomer was weighed in into an empty cell, after which the cell was closed. The volume of the cell was decreased to its lowest value of 18 mL CO₂ gas was fed to the reactor at room temperature (pressure ~ 30 bar) and the mixture was then stirred with a small magnetic stirrer bar at the bottom of the optical cell. The cell content was heated to a temperature of 35 °C and consecutively CO₂ was charged into the cell at a constant flow up to the pressure at which a homogeneous mixture was observed. These conditions were maintained for 10 minutes to allow for equilibration of the system. Starting from a homogeneous solution, the pressure was decreased by increasing the inner volume of the cell until the system starts to be turbid. After demixing, the pressure was increased until the system became homogeneous again. Decreasing and increasing the pressure of the system was repeated at least three times for one composition at the given temperature. Next, the temperature was increased to 45 °C. After equilibrium was reached, the same procedure of decreasing and increasing pressure was repeated for several times. Finally the temperature was increased to 60 °C and the procedure as described above was repeated.

High-pressure autoclave

The stainless steel (AISI 304L) reactor (modified “Andorra” high pressure autoclave, Premex, De Heer B.V.) with a volume of 100 mL, see Figure 2, was designed to withstand a maximum pressure of 300 bar at a maximum temperature of 300 °C. The system was stirred with a magnetic stirrer head (Premex Maxonmotor, **M**) equipped with a Rushton-Turbine impeller. A small cylindrical basket, made of 2 layers of gauze with 400 nm pores crossed over each other, was attached to the stirrer. CO₂ was fed into the reactor by a syringe pump (ISCO – model 260D, **FP**). The amount of CO₂ was calculated with the Modified Webb-Benedict-Ruben equation of state (MWBR EOS). Monomer was pumped into the autoclave by a high pressure pump for liquid chromatography (Shimadzu, **HPLC**). The temperature of the autoclave was controlled with an electrical circuit (3508 controller, Ordino Light, Pro Control B. V., **TIC1**). The pressure of the reactor was monitored with a calibrated pressure transducer (ATM, AE Sensors, accuracy circa 0.005 bar, **PI1**). Sampling from the top and bottom phase of the mixture in the autoclave was carried out using 2 independent Rolsi capillary sampler injectors (Mines ParisTech, **R**). The sampler-injectors were connected to

the autoclave through 0.1 mm inner diameter capillaries and were in direct contact with the top and bottom phase respectively. The outlet of the capillaries was closed by a movable microstem operated by an electromagnet. When the electromagnet was activated, the outlet of the capillary was opened so that an accurate amount of the sample could flow into an expansion room. The expansion room was crossed by the carrier gas of a gas chromatograph (2010, Shimadzu), which swept the sample into the gas chromatograph column (Factor Four VF-5 ms fused silica column, isothermal method at 50 °C). The sample volume could be accurately adjusted continuously from 0.1 to 1 μL with an electronic timer. Due to the small sample size no pressure drop in the autoclave was observed. The expansion room of the sampler was heated independently from the autoclave to allow the samples to remain in the vapor state or to vaporize liquid samples.

Figure 2 High-pressure autoclave. **FP** pump for liquid carbon dioxide, **M** magnetic stirring head, **RD** rupture disk assembly, **R** Rolsi, **PI** pressure indicator, **TI** temperature indicator, **VI** volume indicator, **TIC** temperature indicator controller.

Binary phase diagrams – The basket was removed from the stirrer. The autoclave was closed and gaseous CO_2 was fed into the vessel at room temperature (pressure ~ 30 bar). Next, the stirrer was turned on with a revolution speed of 300 rpm and the autoclave was heated to a temperature of 35 or 45 °C. When the desired temperature was reached, CO_2 was charged into the autoclave at a constant flow up to a pressure of 90 bar. Consequently, a known volume of monomer was pumped into the autoclave while stirring. After 10 minutes

stirring was stopped to allow phase separation in the vessel. Samples of the top and bottom phase were withdrawn every 12 minutes during 2 hours. Sampling was stopped and stirring was turned on again. Then an accurately known volume of monomer was added to the vessel content. After 10 minutes stirring was stopped again and sampling of top and bottom phase was started. This procedure was repeated several times.

Monomer partitioning over CO₂ swollen polymer and scCO₂ – An accurate amount of polymer was brought into the basket, an accurately known mass of monomer (10000 ppm or 100 ppm, based on polymer mass) was loaded into the autoclave. The autoclave was closed and the stirring was started with a speed of 150 rpm. Gaseous CO₂ was fed into the vessel at room temperature (pressure ~ 30 bar) after which the vessel was heated to a temperature of 35, 45 or 60 °C. When the desired temperature was reached, CO₂ was charged into the autoclave with a constant flow rate up to a pressure of 100 bar was reached. Samples of the vessel content, both top (R1) and bottom (R2), were withdrawn every 12 minutes. In preliminary trials it was observed that in about 2 hours phase equilibrium was reached (Appendix A). After at least 3 to 4 hours, sampling was stopped and the pressure of the autoclave was increased to 140 bar. Sampling was started again after the desired pressure was reached, also with a frequency of 1 sample per 12 minutes. The same procedure was repeated to increase the pressure of the autoclave to 180 bar.

Calibration of gas chromatographic analysis

Addition of an internal standard to the mixture under investigation will change the equilibrium pressure of the mixture. Therefore another method was chosen to calibrate the gas chromatograph. With a gas syringe an accurately known volume (known amount of moles) of CO₂ was injected into the gas chromatograph. Injected volumes were in the range from 0.01 to 5 µL. For every volume the injection was repeated 6 to 10 times. The peak area of the chromatogram were plotted as a function of the amount of moles CO₂ injected. The resulting plot was described with two separate equations with a 95 % confidence window (see Appendix B). The same procedure using a µL-sized syringe for liquids was followed to know the amount of moles of monomer in the sample.

Results and discussion

Phase behavior of the binary systems

The vapor – liquid equilibrium data are determined for the Sty-(sc)CO₂ and the MMA-(sc)CO₂ system at 35, 45 and 60 °C for monomer weight fractions in a range of 0.7 to 0.97. The results of the cloud-point measurements are collected in Figures 3 and 4 (solid symbols). The gas phase compositions corresponding to the cloud-points are calculated with the Peng-Robinson equation of state (eos) (Appendix D). To confirm the reliability of the high-pressure autoclave, the concentrations of the coexisting monomer and (sc)CO₂ phase are measured at 35 °C for Sty-(sc)CO₂ and at 45 °C for MMA-(sc)CO₂ (half open symbols). The experiments have been repeated several times. The equilibrium compositions shown have been calculated from the average of the results of the repeated experiments at the same conditions. For comparison, literature data of the Sty-(sc)CO₂ and MMA-(sc)CO₂ systems are included in the respective figures (open symbols).

Figure 3 Cloud-point data of the Sty-CO₂ binary system. □ 35 °C, data collected from Suppes and McHugh (1989), Tan *et al.* (1991), Zhang *et al.* (2005), ■ 35 °C, this work (solid symbols in the liquid (L) phase are data collected from the high-pressure optical cell, closed symbols in the gas (G) phase are calculated data; the half open symbols are experimental points of respectively the liquid and the gas phase measured in the high-pressure autoclave), ○ 45 °C, data collected from Tan *et al.* (1991), Zhang *et al.* (2005), ● 45 °C, this work (data in L were experimentally determined points, data in G were calculated), △ 60 °C, data collected from Akgün *et al.* (2004), ▲ 60 °C, this work (data in L were experimentally determined, data in G were calculated). Literature data are shown in terms of weight fractions, recalculated from the reported molar fractions. — Calculation with the Peng-Robinson equation of state; 35 °C, - - - - 45 °C, — 60 °C, $k_{\text{sty}/\text{CO}_2} = 0.046$ (Suppes and McHugh, 1989). The parameters $a(T)$, b and ω have been calculated from the critical properties of the components, see Appendix D.

The cloud-point measurements as well as the data from the high-pressure autoclave show good reproducibility, *i. e.* small experimental error (see Appendix C). Comparing cloud-points observed by Zhang *et al.* (2005) and the high-pressure autoclave equilibrium data (35 °C), a small deviation of only 0.51% exists.

The experimentally determined values of the monomer concentration in the coexisting phases overlap the cloud-point data as well as the data of Zhang *et al.* (2005), demonstrating the reliability of the high-pressure autoclave.

Some discrepancies exist between data collected in the present work and the previously published data of Suppes and McHugh (1989), Tan *et al.* (1991) and Akgün *et al.* (2004). The authors mentioned reported P-x-y data at different temperatures, with P being the pressure in the syringe pump. So the pressure was not recorded inside the equilibrium cell and therefore the pressure decrease due to the decrease in the fugacity of the monomer and (sc)CO₂ mixture on adding (sc)CO₂ was not taken into account (see Chapter 2).

In the present work the experiments have been performed with a pressure indicator directly in contact with the binary mixture.

Figure 4 Cloud-point data of the MMA-CO₂ binary system. □ 35 °C Zwolak *et al.* (2005), ■ 35 °C this work (data in L were experimentally determined points, data in G were calculated), ◇ 40 °C, data collected from Zwolak *et al.* (2005), da Silva *et al.* (2007), ● this work 45 °C (solid symbols in the liquid (L) phase represent data collected from the high-pressure optical cell, solid symbols in the gas (G) phase were calculated; the half open symbols are experimental points, respectively of the liquid and gas phase measured in the high-pressure autoclave), ▽ 50 °C, data collected from Zwolak *et al.* (2005), da Silva *et al.* (2007), Uzun *et al.* (2005), △ 60 °C, data collected from Zwolak *et al.* (2005), Uzun *et al.* (2005), ▲ 60 °C, this work (data in L were experimentally determined points, data in G were calculated). Literature data are shown in terms of weight fractions, recalculated from the reported molar fractions. — Calculations with the Peng-Robinson equation of state; 35 °C, - - - - 45 °C, — 60 °C; $k_{\text{MMA}/\text{CO}_2} = 0.033$ (Zwolak *et al.*, 2005). The parameters $a(T)$, b and ω have been calculated from the critical properties of the components, see Appendix D.

To the best of the authors' knowledge no experimental vapor-liquid equilibria for the MMA-(sc)CO₂ system at 45 °C are reported in literature. Therefore, in Figure 4, vapor-liquid data at 40 and 50 °C were included to check to what extent experimental data at 45 °C determined in the present work agree with the trends reported by Zwolak *et al.* (2005), da Silva *et al.* (2007) and Uzun *et al.* (2005).

The experimental error of the equilibrium data of the MMA-(sc)CO₂ system reported in the present work is very small (see Appendix C), *i. e.* the experiments are very reproducible.

The results at 35 and 60 °C from the present work and from Zwolak *et al.* (2005) and da Silva *et al.* (2007) are comparable. The discrepancy with the data at 60 °C from Uzun *et al.* (2005) is again probably due to the method of pressure indication. Uzun *et al.* (2005) measured the pressure outside the equilibrium cell, not taking into account the pressure decrease upon mixing MMA and (sc)CO₂, whereas in the present work the pressure is measured directly in the equilibrium cell. The 45 °C isotherm obtained from the cloud-point measurements matches the data of da Silva *et al.* (2007) and Zwolak *et al.* (2005) at 40 °C, whereas the equilibrium data from the high-pressure autoclave are found between 40 °C and 50 °C for higher weight fractions; below a weight fraction of CO₂ of 0.7, the data fit more at the 50 °C isotherm. Although the cloud-point measurements at 45 °C show a small experimental error, the reason why the data show correspondence with the 40 °C data of Zwolak *et al.* (2005) and da Silva *et al.* (2007) is unknown. It is believed that the equilibrium data set measured with the high-pressure autoclave is accurate and reliable for the higher weight fractions of CO₂, as the data are found right in between the 40 °C and 50 °C data from Zwolak *et al.* (2005) and da Silva *et al.* (2007). Following the trend of the curves of all data included in Figure 4, the experimental values of the pressure for CO₂ weight fractions below 0.7 are somewhat too high.

All pressures obtained in the present work are well correlated by the Peng-Robinson equation of state (eos) using one adjustable parameter, the binary interaction parameter k_{ij} (see Appendix D). The data collected by the other authors are also well described with the Peng-Robinson eos and the same value for k_{ij} (for clarity the data calculations with the Peng-Robinson eos found in literature are not included in the respective graphs. The reader is referred to the articles of Zwolak *et al.* (2005) and Uzun *et al.* (2005)). This observation also holds for the data determined in the experimental set-up measuring the pressure outside the equilibrium cell. So the Peng-Robinson eos seems to correlate every data set very well, due to the simple mixing rules imported in the Peng-Robinson eos. All reported correlations, including the present work, use the symmetrical Van der Waals mixing rules (Poling, 2001). The interaction parameter (a_{mix}) and the volume parameter (b_{mix}), calculated from critical

data, in the Van der Waals mixing rules have little sensitivity to small changes in pressure and weight fraction of the components.

For both the Sty-(sc)CO₂ as well as the MMA-(sc)CO₂ system it is observed that the monomer solubility in CO₂ decreases with increasing temperature, *i.e.* at higher temperatures, a higher pressure is needed to obtain a homogeneous mixture, see Figure 5. The relation between solubility and pressure is expressed in Equation 1.

$$y_m * P_{\text{total}} = \gamma_m * x_m * P_m^{\text{sat}} \quad (1)$$

Figure 5a illustrates the solubility of Sty and MMA in CO₂ at 35 °C, Figure 5b at 60 °C. Only the experimentally obtained data points are shown in the figures.

Figure 5 Phase separation pressure of Sty and MMA in (sc)CO₂ at 35 °C (a) and 60 °C (b). Open symbols represent Sty, solid symbols represent MMA.

The results in Figure 5 demonstrate that Sty-(sc)CO₂ isotherms are shifted to higher pressures than MMA-(sc)CO₂ isotherms. This behavior suggests that the molecular interactions between Sty and (sc)CO₂ are weaker than the MMA and (sc)CO₂ interactions, resulting in a lower solubility of Sty in (sc)CO₂. Kazarian *et al.* (1996a) studied the specific interactions of CO₂ with monomers to gain insight into interactions of CO₂ with polymers. With Fourier transform infrared (FTIR) spectroscopy, Kazarian *et al.* (1996a) demonstrated that CO₂ acts as a Lewis acid. An electron donor-acceptor complex between the carbonyl oxygen atom of MMA and the CO₂ carbon atom is formed, increasing solubility. Styrene does not possess a carbonyl oxygen atom and therefore no strong Lewis acid-base interactions with CO₂ exist. Other authors reported similar observations (Kazarian *et al.*, 1996 b, Shieh and Liu, 2002).

The difference in solubility of Sty and MMA in CO₂ is also explained by Equations 2 and 3 (DeVoe, 2001), see also Figure 6. Note that Equation 3 follows from Equation 2 using the Gibbs-Helmholtz relation with temperature independent heats of solution.

Figure 6 schematic representation of a monomer/CO₂ mixture.

The monomer distribution coefficient, *i.e.* the ratio of the monomer weight fraction in the vapor phase and the monomer weight fraction in the liquid phase, is expressed in terms of Gibbs free energies of solution, see Equation 2.

$$K_{\text{mon}} = e^{\frac{-\Delta G_{\text{solution}}}{R \cdot T}} \quad (2)$$

$$\ln \frac{K_{\text{mon}}^{T_2}}{K_{\text{mon}}^{T_1}} = -\frac{\Delta H_{\text{solution}}}{R} * \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (3)$$

The change in the heat of solution for a monomer solved in CO₂ at constant pressure is calculated through the partition coefficient (K_{mon}) of the monomer between the liquid and the vapor phase at a certain temperature. Figure 7 shows the relation between the partition coefficient and the temperature for both Sty-CO₂ (solid symbols) and for MMA-CO₂ (open symbols) at 65.5 bar. The data points calculated from experimentally determined compositions have been collected in Appendix E.

Figure 7 Partition coefficients for the distribution of monomer over the liquid phase and the vapor phase versus temperature at 65.5 bar. Open symbols represent Sty, solid symbols represent MMA. Data points are fitted to $\ln K_{\text{mon}}^T = -\frac{\Delta \Delta H_{\text{solution}}}{R} * \left[\frac{1}{T}\right] + \text{constant}$ with

$$K_{\text{mon}} = \frac{w_{\text{mon}}^{\text{vapor}}}{w_{\text{mon}}^{\text{liquid}}}$$

The difference in heat of solution ($\Delta \Delta H_{\text{solution}} = \Delta H_{\text{solution}}(\text{CO}_2) - \Delta H_{\text{solution}}(\text{CO}_2 \text{ swollen polymer})$) for Sty dissolved in CO₂ is ~ - 38 kJ/mole, whereas for MMA this difference is ~ - 60 kJ/mole.

Monomer partitioning over CO₂ swollen polymer and scCO₂

The monomer partitioning between CO₂ swollen polymer and (sc)CO₂ has been determined at 100, 140 and 180 bar at 35, 45 and 60 °C, by adding 10000 ppm and 100 ppm monomer. The amount of 10⁴ ppm and 100 ppm monomer to be added to the polymer/CO₂ mixture has been chosen to verify if the partition coefficient for distribution of monomer between CO₂-swollen polymer and (sc)CO₂ remains constant at the same conditions of temperature and pressure even when the amount of monomer present decreases. 100 ppm has been chosen as the experimental lower limit as it becomes more difficult to add an accurate amount of monomer when the amount to add decreases. While analyzing the CO₂ rich phase when only 100 ppm of monomer was added to the system, the resulting concentration of monomer in CO₂ was found to be much higher than 100 ppm. This result suggests that the received PS and PMMA polymer contain residual monomer. By means of several experiments and some iterations (see Appendix F) it was found that in the PS granules (~5 mm) about 500 ppm styrene and in the smaller PS beads (~1 mm) about 2600 ppm styrene was left after polymerization; in the PMMA beads (~0.5 mm) about 800 ppm residual MMA was found.

Monomer partitioning between the polymer particles and (sc)CO₂ is expressed in the partition coefficient:

$$K_m = \frac{C_m^{CO_2}}{C_m^{pol}} \left[\frac{\text{kg polymer}}{\text{kg CO}_2} \right] \quad (4)$$

Figure 8a shows the results for the determination of the monomer partition coefficient for Sty-PS-(sc)CO₂, Figure 8b graphically represents the results for MMA-PMMA-(sc)CO₂. The phase ratio is in the range 0.035 to 0.045 g polymer/g CO₂. Both cases for the addition of approximately 10000 ppm and 100 ppm of monomer are included.

Figure 8 Partition coefficient for distribution of styrene between (sc)CO₂ and PS (a, open symbols) and for distribution of MMA between (sc)CO₂ and PMMA (b, solid symbols). □, ■ 35 °C, ○, ● 45 °C, △, ▲ 60 °C.

For 100 bar the partition coefficient of Sty at 35 and 45 °C shows an unexpected deviation (Appendix F). At higher pressures the partition coefficient has an approximately constant value of 2 [kg PS/ kg CO₂]. The same results were obtained for a total of 10000 ppm and for approximately 3000 ppm (vide supra) styrene in the system. Also the particle diameter size did not influence the outcome. The partition coefficient of MMA between PMMA and (sc)CO₂ is ~0.3 [kg PMMA/kg CO₂] for every combination of pressure and temperature analyzed. The partition coefficients for 10000 ppm and approximately 1000 ppm (vide supra) MMA in the PMMA/(sc)CO₂ mixture are equal.

Theoretical predictions of the partition coefficient with the Perturbed Chain - Statistical Association Fluid Theory (PC-SAFT) eos, see Chapter 2, and the work of Görnert and Sadowski (2007 and 2008) suggest that the partition coefficient depends on the (sc)CO₂

density and on the solubility of the monomer in the (sc)CO₂ phase. The higher the density of the (sc)CO₂ phase, the higher the partition coefficient. The more soluble monomer (MMA) partitions more towards the (sc)CO₂ than the less soluble monomer (Sty). The experimental values of the partition coefficient in the present work neither show a significant dependence on (sc)CO₂ density, nor show the expected influence of monomer affinity for (sc)CO₂, *i.e.* the partition coefficient of Sty between PS and (sc)CO₂ is found to be higher than the partition coefficient of MMA between PMMA and (sc)CO₂.

The density profile of CO₂, see Figure 9, demonstrates that at low pressures CO₂ behaves more gas-like. The binary phase diagrams Sty-CO₂ (Figure 3) and MMA-CO₂ (Figure 4) also show a large miscibility gap between monomer and CO₂ in the lower pressure region, *i.e.* low solubility.

Figure 9 CO₂ density profile as a function of pressure for several temperatures. ▲25 °C, ■ 35 °C, ● 45 °C, ▼50 °C, ★60 °C, ◀70 °C, ▶80 °C, ◆90 °C; data are calculated with the Modified-Webb-Benedict-Ruben equation of state (Poling *et al.*, 2001).

At moderate pressures the CO₂ density increases rapidly with increasing pressure, especially for temperatures lower than 60 °C. At the same time the “solvency ability” of CO₂ increases with increasing pressure. Hence, more monomer dissolves in the CO₂ phase. At high pressures, CO₂ becomes more liquid-like, making its density and solubility behavior less sensitive to pressure changes. Increasing temperature decreases the CO₂ density and “solvency ability”, *i.e.* less monomer uptake. On the other hand, higher temperatures improve the monomer volatility, increasing the driving force for monomer uptake by CO₂. The experimental results demonstrate that the latter two effects rule each other out in the higher pressure region, keeping the partition coefficient approximately independent of pressure. Although Wu *et al.* (2002) found different values for the distribution coefficient of Sty between PS and CO₂, these authors reported similar findings about the constancy of the value with increasing pressure and temperature.

A second issue is that both Görnert and Sadowski (2007, 2008) and Wu *et al.* (2002) perform their measurements with annealed polymers, *i.e.* the polymer product is heated above the glass transition temperature to remove so-called history effects. By heating the polymer above the T_g, build-in defects and specific characteristics introduced by the preparation method of the polymer disappear and a smooth polymer product is obtained. The databank used in the PC-SAFT modeling is also based on the characteristics of annealed polymers to calculate its parameters. Already in the seventies of the previous century, van de Ven (1975) emphasized the influence of history effects in analyzing polymer products, describing colloidal interactions. Huvard *et al.* (1980) reported about the influence of annealing polyacrylonitrile (PAN) on CO₂ sorption. Huvard *et al.* (1980) observed that the sorption capacity of glassy PAN microspheres decreased by ~30% after annealing the microspheres in comparison to the “as made” microspheres. The author refers to Koros *et al.* (1978) and to Chan *et al.* (1978) who observed similar effects in CO₂ sorption in poly(ethylene terephthalate) and in polycarbonate, respectively. In the present work the polymers are used as received from industry, without annealing the product.

A third aspect concerns a possible explanation why the experimentally determined partition coefficient for Sty is higher than that for MMA, while the theory predicted it the other way around. Polymers can form physical or entangled networks including ion bridging from one

chain to another and hydrophobic and hydrophilic bonding (Goodwin and Hughes, 2008). Entanglements in amorphous polymers refer to the degree of topological constraint on the relative chain motion. An amorphous polymer, both in the glassy and rubbery state can often be idealized as a network of entangled strands linked at entanglement points. The entanglement network is characterized by, for example, the density of the entanglement points (Teerenstra *et al.*, 2003). Teerenstra *et al.* (2003) pointed out that not only the chain flexibility is important for the entanglement density, but also the chain diameter plays a significant role. These authors observed that a larger chain diameter decreases the entanglement density. The phenyl side groups of PS are larger than the alkyl groups of PMMA. Bucknall (2001) found that the degree of ductility of a polymeric material also depends on the entanglement density, both decreasing from polycarbonate to polyvinylchloride to PMMA to PS. For PS 1.35 bonds per nm³ are counted, for PMMA 1.50 bonds per nm³. Meijer *et al.* (2000) also reported an increase of the entanglement density from PS to PMMA. The findings of the authors mentioned are applicable to polymer films, polymer melts and diluted polymer samples. High-pressure CO₂ acts as a plasticizing agent, swelling the polymer, thereby decreasing the volume fraction of the polymer. The glass transition temperature of the polymer also decreases changing the polymer from the glassy to the rubbery state. The plasticization, characterized by increased segmental motion, chain mobility and inter-chain distance, is largely determined by polymer-solvent interactions and solvent size (Kazarian, 2000). As mentioned earlier, PMMA and (sc)CO₂ form an electron donor-acceptor complex (Kazarian *et al.*, 1996a) which results in an additional network link decreasing the distance between entanglements, *i.e.* increasing the entanglement density (Goodwin and Hughes, 2008, Brown, 2001). Therefore it is believed that it is easier to extract Sty from PS than MMA from PMMA due to the higher entanglement density of PMMA.

The same partitioning experiments as presented in Figure 8 have been performed with polymer beads equilibrated with water. The polymer beads were completely immersed in demineralized water for several days. Before the experiment started, the water attached to the surface of the polymer particles was removed. The results for monomer partitioning between polymer equilibrated with water and (sc)CO₂ and those between dry polymer and (sc)CO₂ are not significantly different. There exists no influence of traces of water in the polymer phase on the monomer partitioning between CO₂-swollen polymer and scCO₂.

Concluding remarks

A high-pressure optical cell and a high-pressure autoclave have been used to determine the binary phase behavior for Sty-CO₂ and for MMA-CO₂. The optical cell as well as the high-pressure autoclave are found to provide accurate results. In the high-pressure autoclave the monomer partition coefficients for distribution of monomer between CO₂-swollen polymer particles and (sc)CO₂ have been experimentally determined at various pressures between 100 and 180 bar at various temperatures between 35 and 60 °C. The experimental results demonstrate the partition coefficient is approximately independent of pressure and temperature. For Sty-PS-(sc)CO₂ a partition coefficient of 2 [kg PS/kg (sc)CO₂] is found for the different combinations of pressure and temperature, for MMA-PMMA-(sc)CO₂ a value of 0.3 [kg PMMA/kg (sc)CO₂] is observed.

References

- M. Akgün, D. Emel, N. Baran, N. A. Akgün, S. Deniz, S. Dinçer, "Styrene-carbon dioxide phase equilibria at high pressures", *J. Supercritical Fluids*, **2004**, 31, 27-32
- H. R. Brown, "Relation between the width of an interface between two polymers and its toughness", *Macromol.*, **2001**, 34, 11, 3720-3724
- C. B. Bucknall, "Blends containing core-shell impact modifiers Part 1: Structure and tensile deformation mechanisms", *Pure Appl. Chem.*, **2001**, 73, 6, 897-912
- A. H. Chan, D.R. Paul, "Effect of sub - T_g annealing on CO₂ sorption in polycarbonate", *ACS Preprints*, **1978**, 39, 230
- H. DeVoe, "Thermodynamics and Chemistry", **2001**, Prentice Hall, New York
- J. W. Goodwin, R. W. Hughes, "Rheology for chemists: An introduction", 2nd new ed., **2008**, Royal Society of Chemistry, Cambridge
- M. Görnert, G. Sadowski, "Phase-equilibrium measurements of the polystyrene/styrene/carbon dioxide ternary system at elevated pressures using ATR-FTIR spectroscopy", *Macromol. Symp.*, **2007**, 259, 236-242
- M. Görnert, G. Sadowski, "Phase-equilibrium measurement and modeling of the PMMA/MMA/carbon dioxide ternary system", *J. Supercritical Fluids*, **2008**, 46, 218-225
- G. S. Huvard, V. T. Stannett, W. J. Koros, H. P. Hopfenberg, "The pressure dependence of CO₂ sorption and permeation in poly(acrylonitrile)", *J. of Membrane Sci.*, **1980**, 6, 185-201
- S. G. Kazarian, C. A. Eckert, J. C. Meredith, K. P. Johnston, J. M. Seminario, "Quantitative equilibrium constants between CO₂ and Lewis bases from FTIR spectroscopy", *J. Phys. Chem.*, **1996** (a), 100, 10837-10848
- S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, C. A. Eckert, "Specific intermolecular interaction of carbon dioxide with polymers", *J. Am. Chem. Soc.*, **1996** (b), 118, 1729-1736
- S. G. Kazarian, "Review: Polymer processing with supercritical fluids", *Polym. Sci., Ser. C*, **2000**, 42, 78-101
- W. J. Koros, D. R. Paul, "CO₂ sorption in poly(ethylene terephthalate) above and below the glass transition temperature", *J. Polym. Sci., Polym. Phys. Ed.*, **1978**, 16, 1947
- K.-M. Krüger, G. Sadowski, "Fickian and non-fickian sorption kinetics of toluene in glassy polystyrene", *Macromol.*, **2005**, 38, 8408-8417
- M. Lora, M. A. McHugh, "Phase behavior and modeling of the poly(methyl methacrylate)-CO₂-methyl methacrylate system", *Fluid Phase Eq.*, **1999**, 157, 285-297
- H. E. H. Meijer, L. E. Govaert, R. J. M. Smit, "A multi-level finite element method for modeling rubber-toughened amorphous polymers" in R. A. Pearson, H. -J. Sue, A. F. Yee (Eds.) "Toughening of plastics: advances in modeling and experiments", **2000**, American Chemical Society, Washington D. C.
- B. E. Poling, J. M. Prausnitz, J. P. O'Connell, "The properties of gases and liquids", 5th ed., **2001**, The McGraw-Hill Companies, Inc., USA

- M. S. da Silva, M. Temtem, S. Henriques, T. Casimiro, A. Aguiar-Rocardo, "Phase behavior studies of 2-hydroxyethyl methacrylate and methyl methacrylate in high-pressure carbon dioxide", *J. Chem. Eng. Dat.*, **2007**, 52, 5, 1970-1974
- Y.-T. Shieh, K.-H. Liu, "Solubility of CO₂ in glassy PMMA and PS over a wide pressure range: the effect of the carbonyl groups", *J. Polym. Res.*, **2002**, 9, 107-113
- G. J. Suppes, M. McHugh, "Phase behavior of the carbon dioxide-styrene system", *J. Chem. Eng. Dat.*, **1989**, 34, 310-312
- C.-S. Tan, S.- J. Yarn, J.- H. Hsu, "Vapour-liquid equilibria for the systems carbon dioxide-ethylbenzene and carbon dioxide-styrene", *J. Chem. Eng. Dat.*, **1991**, 36, 23-25
- M. N. Teernestra, P. A. M. Steeman, W. Iwnes, A. Vandervelden, D. R. Suwier, B. Van Mele, C. E. Koning, "On the entanglement density of differently N-substituted styrene-maleimide copolymers", *e-Polym.*, **2003**, 045, 1-12
- N. I. Uzun, M. Akgün, N. Baran, S. Deniz, S. Dinçer, "Methyl methacrylate plus carbon dioxide phase equilibria at high pressures", *J. Chem. Eng. Dat.*, **2005**, 50, 4, 1144-1147
- T. G. M. van de Ven, *PhD thesis*, **1975**, McGill University, Montreal, Canada
- J. Wu, Q. Pan, G. L. Rempel, "High pressure phase equilibria for a styrene/CO₂/polystyrene ternary system", *J. Appl. Polym. Sci.*, **2002**, 85, 1938-1944
- J. Zhang, L. Gao, X. Zhang, B. Zong, T. Jiang, B. Han, "Phase behaviors, density, and isothermal compressibility of styrene + CO₂, ethylbenzene + CO₂, and ethylbenzene + styrene+ CO₂ systems", *J. Chem. Eng. Data*, **2005**, 50, 1818-1822
- G. Zwolak, L. Lioe, F. P. Lucien, "Vapor-liquid equilibria of carbon dioxide plus methyl methacrylate at 308, 313, 323 and 333 K", *Ind. Eng. Chem. Res.*, **2005**, 44, 1021-1026

Appendix A

Concentration time history of monomer in CO₂, Figure A.1.a shows the profile for Sty in CO₂ at 35 °C and 100 bar, Figure A.1.b for MMA in CO₂. After about 2 hours the equilibrium concentration is set.

Figure A. 1 Concentration profile of a) Sty in CO₂ and b) MMA in CO₂.

Krüger and Sadowski (2005) studied the sorption kinetics of toluene in glassy polystyrene. Krüger reported the toluene mass uptake in polystyrene films of thicknesses between 20 and 100 µm at 100 °C while increasing the pressure from 0-400 mbar. The resulting curves show that sorption of toluene in polystyrene is very slow and can take several days or weeks before equilibrium is reached.

The reason equilibrium in this work is reached rather fast, only 2 hours, is ascribed to the preparation of the polymer samples. Krüger and Sadowski (2005) made the polymer films by increasing the polymer temperature above its glass transition temperature, thereby removing all influences of the polymerization process. In the present work the polymer particles are

used as received as it is this kind of polymer that in general is the reactor product applied in industry.

Appendix B

Figure B.1 and B.2 show the calibration plots of the peak area in the chromatogram as a function of the amount of moles CO_2 injected. The calibration has been described with two separate equations due to the behavior of CO_2 . Up till an amount of $1.3 \cdot 10^{-5}$ moles CO_2 injected, the resulting plot can be described with an exponential function, see Equation B.1.

$$y = p(1) * e^{(x*p(2))^{-1}} \quad (\text{B.1})$$

where $p(1)$ and $p(2)$ stand for the coefficients fitted to the plot ($p(1) = 6.17 \cdot 10^{-6}$ and $p(2) = 0.24 \cdot 10^{-6}$ respectively).

Figure B.1 Peak area as a function of the amount of moles CO_2 injected ($<1.3 \cdot 10^{-5}$ moles CO_2) into the gas chromatograph. The open symbols represent the measured peak areas of an accurately known amount of moles CO_2 injected. The solid line represents the calibration line fitted to the data, $y = p(1) * e^{(x*p(2))^{-1}}$

Once the amount of moles CO_2 injected surmounts $1.3 \cdot 10^{-5}$ moles CO_2 , the measured data points have been found to show a linear relation between the peak area and the amount of moles CO_2 injected, see Equation B.2 and Figure B.2.

$$y = p(1) + p(2) * x \quad (\text{B.2})$$

where $p(1)$ and $p(2)$ stand for the coefficients fitted to the plot ($p(1) = -0.35 * 10^{-4}$ and $p(2) = 1.1 * 10^{-11}$ respectively).

Figure B.2 Peak area in function of the amount of moles CO₂ injected ($>1.3 * 10^{-5}$ moles CO₂) into the gas chromatograph. The open symbols represent the measured peak areas of an accurately known amount of moles CO₂ injected. The solid line represents the calibration line fitted to the data, $y = p(1) + p(2) * x$

Appendix C

Experimentally determined cloud-points of Sty-(sc)CO₂ and MMA-(sc)CO₂ at 35, 45 and 60 °C are presented in Table C.1.a and C.2.a respectively. The pressure is the calculated mean of all the experiments at one condition $\pm$ the standard deviation. Liquid and gas phase compositions of Sty-(sc)CO₂ at 35 °C and of MMA-(sc)CO₂ at 45 °C are collected in Table C.1.b and C.2.b. The weight fraction of (sc)CO₂ is the calculated mean of all the experiments at one condition $\pm$ the standard deviation.

Table C.1.a Cloud-point data of Sty-(sc)CO₂

w_{CO_2}	P [bar] at 35 °C	P [bar] at 45 °C	P [bar] at 60 °C
0.98	72.4 $\pm$ 0.8	87 $\pm$ 4	101 $\pm$ 1
0.89		827 $\pm$ 1	104 $\pm$ 1
0.86	69 $\pm$ 2	80 $\pm$ 2	104 $\pm$ 2
0.81	68 $\pm$ 2	81 $\pm$ 3	104 $\pm$ 1
0.69	66 $\pm$ 2	78 $\pm$ 1	99 $\pm$ 2

Table C.1.b Liquid and gas phase compositions of Sty-(sc)CO₂ at 35 °C

P [bar] at 35 °C	w_{CO_2} in the liquid phase	w_{CO_2} in the gas phase
72	0.934 $\pm$ 0.008	0.995 $\pm$ 0.0017
70	0.829 $\pm$ 0.034	0.994 $\pm$ 0.0004

Table C.2.a Cloud-point data of MMA-(sc)CO₂

w_{CO_2}	P [bar] at 35 °C	P [bar] at 45 °C	P [bar] at 60 °C
0.94	68 ± 0.3	80 ± 0.3	97 ± 0.9
0.87	6 ± 0.5	77 ± 0.6	96 ± 0.1
0.85	64 ± 0.4	74 ± 0.4	94 ± 0.4
0.76	60 ± 0.5	71 ± 0.5	91 ± 0.3

Table C.2.b Liquid and gas phase compositions of MMA-(sc)CO₂

P [bar] at 45 °C	w_{CO_2} in the liquid phase	w_{CO_2} in the gas phase
82.5	0.94 ± 0.0002	0.95 ± 0.0007
81	0.84 ± 0.0014	0.96 ± 0.0002
73	0.68 ± 0.0005	0.97 ± 0.0001
71	0.63 ± 0.0007	0.97 ± 0.00004

Appendix D

Tables D.1 and D.2 show the vapor-liquid equilibria of Sty-CO₂ and of MMA-CO₂ at 35 °C, 45 °C and 60 °C respectively. The composition of the liquid phase [L] is weighed into the equilibrium cell. The vapor phase [V] composition is calculated with the Peng-Robinson Equation of State, with a binary interaction parameter of 0.046 for Sty-CO₂ (Suppes and McHugh, 1989) and 0.033 for MMA-CO₂ (Zwolak *et al.*, 2005). Table D.3 gives the pure component parameters used in the Peng-Robinson eos.

Table D.1.a Vapor-liquid equilibria of Sty-CO₂ at 35 °C.

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
72.4	0.02	0.003	0.997	0.12	1.03
68.9	0.14	0.008	0.992	0.06	1.16
68.1	0.19	0.007	0.993	0.04	1.23
65.5	0.31	0.007	0.993	0.22	1.43

Table D.1.b Vapor-liquid equilibria of Sty-CO₂ at 45 °C

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
86.9	0.02	0.003	0.997	0.13	1.02
81.7	0.11	0.003	0.997	0.03	1.12
80.4	0.14	0.003	0.997	0.02	1.16
80.9	0.19	0.003	0.997	0.015	1.23
77.5	0.31	0.004	0.996	0.013	1.44

Table D.1.c Vapor-liquid equilibria of Sty-CO₂ at 60 °C

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
101.3	0.02	0.01	0.989	0.43	1.01
103.6	0.11	-	-	0.02	1.09
103.5	0.14	-	-	0.015	1.12
103.9	0.19	-	-	0.007	1.17
99.2	0.31	0.001	0.999	0.003	1.43

Table D.2.a Vapor-liquid equilibria of MMA-CO₂ at 35 °C

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
68.4	0.06	0.009	0.991	0.15	1.05
65.6	0.13	0.014	0.986	0.10	1.10
64.3	0.15	0.015	0.985	0.09	1.13
60.2	0.24	0.016	0.984	0.06	1.2

Table D.2.b Vapor-liquid equilibria for MMA-CO₂ at 45 °C

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
79.6	0.06	0.015	0.985	0.25	0.95
76.7	0.13	0.014	0.986	0.11	0.88
74.7	0.15	0.014	0.986	0.09	0.86
71.4	0.24	0.013	0.987	0.05	0.77

Table D.2.c Vapor-liquid equilibria for MMA-CO₂ at 60 °C

P [bar]	w _{Sty} [L]	w _{Sty} [V] calc	w _{CO₂} [V] calc	K _{Sty}	K _{CO₂}
96.7	0.06	0.014	0.986	0.23	1.05
95.7	0.13	0.014	0.986	0.11	0.88
94	0.15	0.015	0.985	0.10	0.86
90.0	0.24	0.015	0.985	0.06	0.77

Table D.3 Peng-Robinson parameters as used for calculations. Pure component parameters are taken from Poling *et al.* (2001), binary interaction parameter k_{ij} taken from Suppes and McHugh (1989) and Uzun *et al.* (2005)

parameter	Sty	MMA	CO ₂
T _c [K]	647.05	563.95	304.25
P _c [10 ⁵ Pa]	39.9	36.8	73.8
ω [-]	0.257	0.317	0.225

k _{Sty-CO₂}	0.046	k _{MMA-CO₂}	0.033
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Appendix E

Tables E.1 and E.2 give the vapor-liquid composition data for Sty-CO₂ and for MMA-CO₂ respectively, at 65.5 bar at different temperatures, calculated with the Peng-Robinson Equation of State. The partition coefficient is defined as the ratio of the monomer concentration in the vapor phase (y) over the monomer concentration in the liquid phase (x), *i. e.* $K_{\text{mon}} = \frac{y}{x}$. For the pure component parameters used in the Peng-Robinson eos, see Table D.3.

Table E.1 Vapor-liquid composition of Sty-CO₂ at 65.5 bar and 35, 45 and 60 °C

35 °C			45 °C			60 °C		
w _{Sty} (x)	w _{Sty} (y)	K _{Sty}	w _{Sty} (x)	w _{Sty} (y)	K _{Sty}	w _{Sty} (x)	w _{Sty} (y)	K _{Sty}
0.31	0.007	0.02	0.63	0.006	0.009	0.67	0.005	0.007

Table E.2 Vapor-liquid composition of MMA-CO₂ at 65.5 bar and 35, 45 and 60 °C

35 °C			45 °C			60 °C		
w _{MMA} (x)	w _{MMA} (y)	K _{MMA}	w _{MMA} (x)	w _{MMA} (y)	K _{MMA}	w _{MMA} (x)	w _{MMA} (y)	K _{MMA}
0.13	0.01	0.11	0.40	0.01	0.03	0.54	0.01	0.01

Appendix F

Experimentally determined monomer partition coefficient between polymer and CO₂. Table F.1 represents the results for Sty-PS-(sc)CO₂, Table F.2 shows the results for MMA-PMMA-(sc)CO₂.

Table F.1 Partition coefficient of Sty between PS and (sc)CO₂ [kg PS/ kg (sc)CO₂]

P [bar]	K at 35 °C	K at 45 °C	K at 60 °C
100	18 ± 10	9 ± 2.2	1.8 ± 0.1
140	2	2.5 ± 0.1	1.40 ± 0.01
180	1.0	1.8 ± 0.3	1.00 ± 0.02

Table F.2 Partition coefficient of MMA between PMMA and (sc)CO₂ [kg PMMA/ kg (sc)CO₂]

P [bar]	K at 35 °C	K at 45 °C	K at 60 °C
100	0.29 ± 0.002	0.25 ± 0.02	0.24 ± 0.01
140	0.38 ± 0.01	0.29 ± 0.02	0.32 ± 0.01
180	0.35 ± 0.01	0.3 ± 0.02	0.28 ± 0.01

The partition coefficient for the distribution of monomer between CO₂ swollen polymer and CO₂ has been calculated with Equation F.1

$$\frac{(\text{mol mon})^{\text{polymer}}}{(\text{mol mon})^{\text{CO}_2}} \quad (\text{F.1})$$

The monomer concentration in the polymer phase followed from a mass balance of the monomer, see Equation F.2.

$$(\text{mol mon})^{\text{added}} = (\text{mol mon})^{\text{CO}_2} + (\text{mol mon})^{\text{polymer}} \quad (\text{F.2})$$

The amount of moles of monomer added to the autoclave was accurately known (see section 'Materials and methods'). The monomer concentration in the (sc)CO₂ phase was measured. Without any addition of monomer to the polymer, the analysis of the (sc)CO₂ showed that

there was already monomer present in the polymer. The calculated partition coefficient, see Equation F.1, was set as starting value in the determination of the amount of monomer present in the polymer phase. The newly found number of monomer in the polymer phase was then added to the number found from the measurement and a new partition coefficient was determined. This iteration was repeated until a constant value for the partition coefficient had been found.

Chapter 4

Mass transport phenomena in the supercritical carbon dioxide extraction of residual monomer from latex products

Abstract

The mechanism of mass transport involved in the extraction of residual monomer from a latex product with supercritical carbon dioxide (scCO₂) has been studied. Monomer transport was found to be governed by the shuttle effect, based on Brownian motion of the polymer particles to and from the water/scCO₂ interface. Surface Gibbs free energy considerations were used to predict the position of the particles at the (sc)CO₂/H₂O interface. The main resistance against monomer transfer from the polymer particles to the (sc)CO₂ phase has been demonstrated to be located inside the polymer particles.

Introduction

Latex is a colloidally stable dispersion of submicron (~100 nm) polymer particles in water. The polymer particles contain residual monomer due to incomplete conversion. Supercritical or high-pressure carbon dioxide ((sc)CO₂) has been studied as extraction medium to reduce the residual monomer level in polymer based products. The present work focuses on the monomer transport mechanism from the submicron polystyrene or polymethyl methacrylate particles to the (sc)CO₂ phase.

Two mechanisms for transfer of monomer from latex particles to (sc)CO₂ operate in parallel. The resistance in series approach, *i.e.* solid-to-liquid-to-fluid (SLF) mass transfer, as well as a direct solid-to-fluid (SF) mass transfer model, also referred to as the shuttle effect (Beenackers and van Swaaij, 1993, Vinke *et al.*, 1993).

In the resistance in series approach, the monomer diffuses out of the polymer particles through the water (H₂O) phase into the (sc)CO₂ phase. The main resistance against mass transfer is located in the H₂O phase due to the low monomer solubility (Zhang and Ray, 1997), Figure 1.

Figure 1 The resistance in series mass transport approach. C_{mon} is the monomer concentration in the respective phases.

Describing the diffusion of monomer through the three phases, *i.e.* the polymer particles, the H₂O phase and the CO₂ phase, the film model has been used. The overall molar mass transfer flux of the monomer (ϕ_{mon}) is expressed in Equation 1.

$$\phi_{\text{mon}} = \left[\left(\frac{1}{k_m^p} \right)_{\text{P phase}} + \left(\frac{1}{k_m^{\text{H}_2\text{O}} * K_{\text{mon}}^{\text{polymer/H}_2\text{O}}} \right)_{\text{H}_2\text{O phase}} + \left(\frac{1}{k_m^{\text{CO}_2} * K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}} \right)_{\text{CO}_2 \text{ phase}} \right]^{-1} * a_p * \left(C_m^p - \frac{C_m^{\text{CO}_2}}{K_{\text{mon}}^{\text{polymer/H}_2\text{O}} * K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}} \right) \quad (1)$$

where k_m^i , $K_{\text{mon}}^{i/j}$ and a_p stand for the monomer mass transfer coefficient in phase i , the monomer partition coefficient between phase i and phase j and the specific mass transfer area of the polymer particles, respectively.

In the SF mass transfer approach, the polymer particles move through the H₂O phase towards the H₂O/CO₂ interface. The monomer diffuses out of the polymer particles directly into the (sc)CO₂ phase, see Figure 2.

Figure 2 The solid-to-fluid mass transfer approach (shuttle mechanism).

The dimension of the polymer particles, allows for Brownian motion in water and consequently can reside for some time at the $\text{H}_2\text{O}/(\text{sc})\text{CO}_2$ interface (Brilman *et al.*, 1998). At the $\text{H}_2\text{O}/(\text{sc})\text{CO}_2$ interface the polymer particle is in direct contact with the $(\text{sc})\text{CO}_2$ phase allowing direct diffusional transport of the monomer from the polymer particles to the $(\text{sc})\text{CO}_2$ phase. Alper *et al.* (1980) used the boundary layer model to describe mass transfer by the shuttle effect. After a certain contact time the particles near the interface have lost part of the initially present monomer. Dumont and Delmes (2003) emphasize that in many situations the contact time between particle and fluid is so short that the steady-state concentration gradient of the particles containing film does not have enough time to develop. Therefore, only unsteady-state models can be used to describe mass transfer.

Concentration leveling of the monomer in the polymer phase is related to time or the Fourier number, see Equation 2 and Figure 3.

$$\text{Fo} = \frac{D_m^p * t_{\text{contact, p}}}{d_{\text{particle}}^2} \quad (2)$$

Figure 3 Concentration leveling of the monomer in a polymer particle. r_p is the polymer particle radius, C_0 the initial monomer concentration in the polymer particle (at $t_{\text{contact}} = 0$), *i.e.* just before arriving at the $\text{H}_2\text{O}/\text{CO}_2$ interface, C_s the monomer concentration at the polymer particle surface, directly after arriving on the $\text{H}_2\text{O}/\text{CO}_2$ interface.

Chon *et al.* (2005) suggest that the residence time of polymer particles at the $\text{H}_2\text{O}/(\text{sc})\text{CO}_2$ interface ($t_{\text{contact}, p}$) can be regarded in terms of Brownian motion of the polymer particles in the water phase, see Equation 3. Chon *et al.* (2005) used Al_2O_3 nanoparticles to increase the heat conductivity of water and validated that Brownian motion of the nanoparticles is the key mechanism for thermal conductivity enhancement. Comparable observations are reported by other authors (Jang and Choi, 2004). $t_{\text{contact}, p}$ can be described as the ratio of the length scale of the interfacial region (Δs) and the Brownian velocity of the polymer particles (v_{Br}).

$$t_{\text{contact}, p} = \frac{\Delta s}{v_{\text{Br}}} \quad (3)$$

The length scale of the interfacial region is assumed to be $10 \mu\text{m}$ (Kemmere *et al.*, 2002); Δs is of the same order of magnitude. The Brownian velocity (v_{Br}) follows from Equation 4.

$$v_{\text{Br}} = \frac{k_b * T}{3 * \pi * \eta * d_{\text{particle}} * l_{\text{BF}}} \quad (4)$$

where k_b stands for the Boltzman constant, η for the water viscosity and l_{BF} for the mean free path of the particle in water ($l_{\text{H}_2\text{O}} = 0.17 \text{ nm}$ (Jang and Choi, 2004)).

For $Fo < 0.1$, mass transport in the polymer particles can be regarded to be in a semi-infinite medium. Then the penetration theory applies for mass transport, Equation 5 (Welty *et al.*, 2001, Bird *et al.*, 2002).

$$k_m^p = 2 * \sqrt{\frac{D_m^p}{\pi * t_{\text{contact}, p}}} \quad (5)$$

For $Fo > 0.1$, intraparticle mass transport can be described with Equation 6 (van den Akker and Mudde, 1997), see Figure 3.

$$Sh = \frac{k_m^i * d_{\text{particle}}}{D_m^i} = 6.6 \quad (6)$$

The mass transfer resistance depends on the specific area of the $H_2O/(sc)CO_2$ interface. Joly-Vuillemin and Bellefon (1999) suggest that the polymer particles partially cover the $H_2O/(sc)CO_2$ interface. The effective specific mass transfer area is then defined as:

$$a_{\text{eff}} (SF) = a_{ij} * \theta \quad \text{for the shuttle effect} \quad (7)$$

$$a_{\text{eff}} (SLF) = a_{ij} * (1-\theta) \quad \text{for the SLF approach} \quad (8)$$

Note that θ_{max} is 0.74, *i.e.* the maximum fractional surface coverage by spherical particles in a three dimensional closest packing.

As mentioned earlier the SLF model is diffusion limited due to the low monomer solubility in water (Zhang and Ray, 1997). The partitioning of monomer between the particles and the water phase is very low towards the water phase, $K_{\text{mon}}^{\text{polymer}/H_2O}$ is in the order of magnitude of 10^{-3} kg polymer/kg H_2O (Kemmere *et al.* 2005, González *et al.*, 2007). In comparison with the SF mass transfer model, phase equilibrium of monomer between the particles and (sc) CO_2 cannot be reached within a short time. The shuttle effect is therefore dominating the mass transfer. The mass transfer-in-series contribution is assumed to be negligible.

Interfacial properties

Interfacial properties, more specifically interfacial tension between the phases involved is an important quantity associated with mass transfer. The interfacial tension, related to the specific interfacial Gibbs energy, is the excess Gibbs energy per unit area due to the

formation of an interface (Van Krevelen, 1997). The interfacial tension is closely related to the cohesion energy of a system (O'Neill *et al.*, 1998).

In 1907, Pickering observed that solid particles could adhere to a liquid-liquid interface thereby stabilizing emulsions (Pickering, 1907). Finkle *et al.* (1923) suggested the emulsions were stabilized because the particles were partially wetted by the two liquids involved. The ability of solid particles to adhere to a liquid-liquid interface has been described by Colver *et al.* (2006) in terms of energy contributions.

Torza and Mason (1970) reported a thermodynamic approach to predict the morphology of two immiscible liquids suspended in a liquid immiscible with both other liquids. Based on the pioneering work of Torza and Mason (1970), numerous authors were able to thermodynamically predict the morphology of composite latex systems, see *e.g.* Sundberg *et al.* (1990), Chen *et al.* (1991) and Sundberg and Sundberg (1993).

In all cases reported, the thermodynamically preferred morphology is the one that has the lowest interfacial Gibbs free energy. The driving force to obtain the preferred morphology at fixed pressure and temperature, the Gibbs free energy change (ΔG) of the process, can be expressed as (Hiemenz and Rajagopalan, 1997):

$$\Delta G = \sum_i \gamma_i * A_i - \gamma_0 * A_0 \quad (9)$$

where γ_i , A_i , γ_0 and A_0 stand for the interfacial tension of the i^{th} interface and its corresponding interfacial area, the interfacial tension of the original polymer suspended in water and the corresponding interfacial area, respectively.

In the present work, the position of polystyrene (PS) and polymethyl methacrylate (PMMA) latex particles in a biphasic (sc)CO₂/H₂O environment has been predicted using the theory of Torza and Mason (1970) as well as the theory of Colver *et al.* (2006).

Torza and Mason (1970) defined the spreading coefficients (S_i) of a three-phase system, which yields the same result as an analysis based on minimizing the Gibbs free energy, as:

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad (10)$$

By convention, phase 1 must be the phase for which $\gamma_{12} > \gamma_{23}$, so that $S_1 < 0$. Then complete engulfment, *i.e.* core-shell morphology, occurs when $S_2 < 0$ and $S_3 > 0$. If $S_2 < 0$ and $S_3 < 0$, the engulfment is only partial and leads to hemispherical morphologies. When $S_2 > 0$ and $S_3 < 0$, separated structures are preferred. Removing the restriction that $\gamma_{12} > \gamma_{13}$, a fourth less common morphology can be predicted as a special case of core-shell, *i.e.* inverted core-shell, when $S_1 > 0$, $S_2 < 0$ and $S_3 < 0$. Figure 4 shows all possible structures and their spreading coefficients.

Figure 4 Engulfment and spreading coefficients according to the theory of Torza and Mason (1970).

In the present work, two systems have been investigated; a polystyrene (PS) latex and a polymethyl methacrylate (PMMA) latex are both submitted to extraction with (sc)CO₂. Interfacial tension between polymer particles and (sc)CO₂ decreases with increasing pressure due to the adsorption of (sc)CO₂ at the interface (Jaeger *et al.*, 1996, Otake *et al.*, 1994).

Table 1 gives the interfacial tensions between H₂O and CO₂ (Tewes and Boury, 2004, Owens and Wendt, 1969, da Rocha *et al.*, 2001, Kvamme *et al.*, 2007, Dhanuka *et al.*, 2006), H₂O and polymer (Sundberg *et al.*, 1990, Webber *et al.*, 1997) as well as between CO₂ and polymer at 100 bar and 35 °C, without any surfactant in either phase. The spreading coefficients are also collected in Table 1. The interfacial tension between CO₂ and polymer has been calculated by fitting data of Otake *et al.* (2004), who correlated the CO₂ density to the interfacial tension between CO₂ and PS as well as between CO₂ and PMMA.

The spreading coefficients have been calculated according to Torza's theory (Torza and Mason, 1970). To fulfill the condition $\gamma_{12} > \gamma_{23}$, PS, H₂O and CO₂ were designated as phase 1, 2, 3 respectively. In case of PMMA, CO₂ was taken as phase 1 and PMMA as phase 3.

Table 1 Interfacial tensions at 100 bar and 35 °C between H₂O and CO₂ (Kvamme *et al.*, 2007 *et al.*), between H₂O and polymer (Sundberg *et al.*, 1990, Webber *et al.*, 1997) and between CO₂ and polymer (Otake *et al.*, 2004). The spreading coefficients have been calculated with the Torza theory (Torza and Mason, 1970). The systems do not contain surfactant molecules.

polymer	Interfacial tensions [mN.m ⁻¹]			Spreading coefficients		
	$\gamma_{CO_2-H_2O}$	$\gamma_{CO_2-polymer}$	$\gamma_{H_2O-polymer}$	S ₁	S ₂	S ₃
PS	30	5.4	40.1	- 15.5	- 64.7	4.7
PMMA	30	5.1	25.4	- 9.7	- 50.3	- 0.5

The calculated spreading coefficients predict complete wetting of polymer particles in CO₂ for PS, *i.e.* CO₂ completely wets the polymer particles, and an intermediate structure, *i. e.* the polymer particles are partially wetted by the CO₂ and partially by the H₂O, for PMMA.

As mentioned before, latex is a dispersion of submicron polymer particles in water, colloidally stabilized by surface active agents. Surfactants consist of both a hydrophilic part and a hydrophobic part. Upon addition of a surfactant to a system of two immiscible phases, the surface active agent is adsorbed at the interface. When the surfactant molecules replace molecules from the original interface, the interaction across the interface is now between the hydrophilic group of the surfactant and the polar phase on one side of the interface and between the hydrophobic group of the surfactant and the apolar phase on the other side of the interface. The newly formed interactions are much stronger than the original interaction between the dissimilar polar and apolar molecules, consequently the interfacial tension is significantly reduced by the presence of the surfactant (Rosen, 2004, Chatteraj, 2001). Rosen (2004) also compared several surfactants in the performance of reducing the interfacial tension. Every type of surfactant, *i.e.* non-ionic, ionic or electrosteric, has a certain efficiency in adsorbing at the interface between two phases, depending on the

investigated system, thereby decreasing the interfacial tension. Harrison *et al.* (1996) also reported about the effect of different surfactants on the interfacial tension between two phases.

The latex systems investigated in the present work are stabilized by sulfate group containing surfactants. For simplicity, sodium dodecyl sulfate (SDS) has been chosen as surfactant to perform the calculations of Torza (Torza and Mason, 1970). Table 2 shows the interfacial tensions between H₂O/SDS and CO₂ (Dhanuka *et al.*, 2006), H₂O/SDS and polymer (Sundberg *et al.*, 1990, Sundberg and Sundberg, 1993) and CO₂ and polymer, as well as the spreading coefficients. Otake *et al.* (2004) reported about the interfacial tension at the CO₂/polymer interface in the presence of tetradecanoic acid (MA), demonstrating the surface activity of carboxylic surfactants. At the same CO₂ density, the interfacial tension between CO₂ and polymer/MA is approximately half the value of the interfacial tension between CO₂ and polymer without surfactant. Addition of SDS to the system CO₂/polymer will also decrease the interfacial tension as compared to the system without surfactant. However, due to the lack of any experimental data, the interfacial tension of the surfactant free system is used in the calculation of the spreading coefficients.¹

In order to fulfill the requirement $\gamma_{12} > \gamma_{23}$, polymer, H₂O and CO₂ were designated as phase 1, 2 and 3, respectively.

Table 2 Interfacial tensions at 100 bar and 35 °C between H₂O/SDS and CO₂ (Dhanuka *et al.*, 2006), between H₂O/SDS and polymer (Sundberg *et al.*, 1990, Sundberg and Sundberg, 1993) and between CO₂ and polymer (Otake *et al.*, 2004). The spreading coefficients have been calculated with the Torza theory (Torza and Mason, 1970). The water systems contain sodium dodecyl sulfate (SDS) as surfactant.

polymer	Interfacial tensions [mN.m ⁻¹]			Spreading coefficients		
	$\gamma_{CO_2-H_2O/SDS}$	$\gamma_{CO_2-polymer}$	$\gamma_{polymer-H_2O/SDS}$	S ₁	S ₂	S ₃
PS	4	5.4	13.2	- 14.6	- 11.8	3.8
PMMA	4	5.1	10.7	- 11.8	- 9.6	1.6

¹ The interfacial tension between CO₂ and polymer without surfactant is already so small, that using this value instead of the slightly smaller interfacial tension between CO₂-polymer/surfactant, does not change the result of the calculation of the spreading coefficients. In both cases, the same morphology has been predicted.

The calculated spreading coefficients predict complete wetting of the polymer particles in CO₂ for both PS and PMMA.

The position of the polymer particles in the CO₂/H₂O interfacial region predicted by the theory of Torza (Torza and Mason, 1970) was verified by the Pickering stabilization theory (Colver *et al.*, 2006). Colver *et al.* (2006) predict the polymer particle position with respect to a flat liquid-liquid interface and relative to the centre of the spherical polymer particle defining a dimensionless number, z_0 , see Equation 11 and Figure 5.

$$z_0 = \frac{z}{R} \quad (11)$$

Figure 5 Schematic representation for a sphere at a liquid-liquid interface.

The total Gibbs energy the system experiences is the sum of different energy contributions of the three interfaces (polymer-phase 1, polymer-phase 2, phase 1-phase 2). Division of the total Gibbs energy by $k_b * T$, results in the dimensionless total energy of the system, see Equation 12.

$$G_0 = \left[\frac{\pi * R^2 * \gamma_{21}}{k_b * T} \right] * [z_0^2 + 2 * (a - b) * z_0 + 2 * a + 2 * b - 1] \quad (12)$$

with $a = \frac{\gamma_{p1}}{\gamma_{21}}$ and $b = \frac{\gamma_{p2}}{\gamma_{21}}$. The minimum energy follows from the first derivative of G_0 with respect to z_0 , see Equation 13.

$$\frac{dG_0}{dz_0} = 2 * z_0 + 2 * (a - b) = 0 \quad (13)$$

The equilibrium position of the particle is, see Equation 14.

$$z_0^{\min} = b - a \quad (14)$$

There are three possible scenarios:

$z_0^{\min} \geq 1$ the particle will be completely in phase 1

$z_0^{\min} \leq -1$ the particle will be completely in phase 2

$-1 < z_0^{\min} < 1$ the particle will adhere at the interface of phase 1 and 2

The interfacial tensions between polymer and CO₂, polymer and H₂O as well as between CO₂ and H₂O at 100 bar and 35 °C (see also Table 1) are collected in Table 3. These interfacial tensions have been used in the calculation of the equilibrium position and energy of the polymer particle following the theory of Colver *et al.* (2006). CO₂ is designated as phase 1, H₂O as phase 2. The system does not contain a surface active agent. The polymer particles have a diameter of 100 nm.

Table 3 Interfacial tensions at 100 bar and 35 °C between H₂O and CO₂ (Kvamme *et al.*, 2007 *et al.*), between H₂O and polymer (Sundberg *et al.*, 1990, Webber *et al.*, 1997) and between CO₂ and polymer (Otake *et al.*, 2004). The equilibrium position of a polymer particle in a CO₂-H₂O system at 100 bar and 35 °C and the energy of the system have been calculated with the theory of Colver *et al.* (2006). There are no surfactants present in the system.

polymer	Interfacial tensions [mN.m ⁻¹]			Equilibrium position of the polymer particle [-] and energy of the system [-]			
	$\gamma_{polymer-CO_2}$	$\gamma_{polymer-H_2O}$	$\gamma_{CO_2-H_2O}$	a	b	z_0	G_0 [10 ⁶]
PS	5.4	40.1	30	0.18	1.34	1.16	38.5
PMMA	5.1	25.4	30	0.17	0.85	0.68	31.9

For PS, the theory of Colver *et al.* (2006) predicts that the PS particles will be completely wetted by the CO₂ phase ($z_0 \geq 1$). This result is comparable to the prediction of the position of the PS in the interfacial region with the theory of Torza and Mason (1970). The PMMA particles will adhere at the CO₂-H₂O interface ($-1 \leq z_0 \leq 1$) as has also been predicted by the theory of Torza and Mason (1970).

Table 4 shows the results of analogous calculations using the interfacial tensions between polymer and CO₂, polymer and H₂O/SDS as well as between CO₂ and H₂O/SDS.

Table 4 Interfacial tensions at 100 bar and 35 °C between H₂O/SDS and CO₂ (Dhanuka *et al.*, 2006), between H₂O/SDS and polymer (Sundberg *et al.*, 1990, Sundberg and Sundberg, 1993) and between CO₂ and polymer (Otake *et al.* 2004). The equilibrium position of a polymer particle in a CO₂-H₂O system at 100 bar and 35 °C and the energy of the system have been calculated with the theory of Colver *et al.* (2006). The water systems contain sodium dodecyl sulfate (SDS) as surfactant.

polymer	Interfacial tensions [mN.m ⁻¹]			Equilibrium position of the polymer particle [-] and energy of the system [-]			
	$\gamma_{polymer-CO_2}$	$\gamma_{polymer-H_2O+SDS}$	$\gamma_{CO_2-H_2O+SDS}$	a	b	z ₀	G ₀ [10 ⁶]
PS	5.4	13.2	4	1.35	3.3	1.95	33.2
PMMA	5.1	10.7	4	1.28	2.68	1.4	36.5

Again the equilibrium position predicted with the theory of Colver *et al.* (2006) corresponds to that predicted with the theory of Torza and Mason (1970). Using interfacial tensions given in Table 4 predicts completely wetted particles with CO₂ for polystyrene as well as for polymethyl methacrylate ($z_0 \geq 1$).

Interesting is that Colver *et al.* (2006) suggest that the Gibbs energy necessary to remove the particle from its equilibrium position has a value in the order of $10^6 \cdot k_b \cdot T$, meaning that the polymer particle is irreversibly trapped at its equilibrium position and cannot escape via simple Brownian motion. Figure 6 clarifies this suggestion graphically for a PMMA particle in a CO₂-H₂O system at 100 bar and 35 °C without surfactant. The respective energy barriers have been calculated according to Equations 15 and 16.

$$\Delta G_1 = G_0(z_0 = 1) - G_0(z_0 = b - a) \quad (15)$$

$$\Delta G_2 = G_0(z_0 = -1) - G_0(z_0 = b - a) \quad (16)$$

Figure 6 Gibbs energy profile of a 100 nm PMMA particle in a CO₂-H₂O interfacial region at 100 bar and 35 °C, without surfactant.

For the other systems, *i.e.* a PS particle in a CO₂-H₂O system at 100 bar and 35 °C without surfactant, a PMMA particle in a CO₂-H₂O system at 100 bar and 35 °C with surfactant, a PS particle in a CO₂-H₂O system at 100 bar and 35 °C with surfactant, similar graphs are obtained.

According to the theory of Torza and Mason (1970) as well as the theory of Colver *et al.* (2006), when PS or PMMA latex, stabilized with SDS as surface active agent, are submerged into a (sc)CO₂ environment, the polymer particles will be completely wetted by the (sc)CO₂. Moreover, the polymer particles are trapped in the (sc)CO₂ phase or in other words the particles irreversibly move from the H₂O phase into the (sc)CO₂ phase!

This conclusion has not been confirmed by our experimental observations. In a mixture of a PS latex, stabilized with SDS, and CO₂ at 100 bar and 35 °C, the polymer particles were “homogeneously” distributed throughout the mixture. No phase separation between the H₂O

phase and the CO₂ phase containing the polymer particles occurred, *i.e.* flotation of the polymer particles in the lighter CO₂ phase was not observed.

The calculated results have been obtained with interfacial tension data from literature, see Tables 1-4. The polymer films used in literature were all annealed at temperatures above their glass transition temperature to exclude any effect of the synthesis method or by impurities on the result of the measurement. Van de Ven (1975) emphasized the influence of history effects describing colloidal interactions in a PS latex. Huvard *et al.* (1980) also reported about the influence of annealing poly acrylonitrile (PAN) on CO₂ sorption. Huvard *et al.* (1980) observed that the sorption capacity of glassy PAN microspheres decreased by ~30% after annealing the microspheres. The author refers to Koros and Paul (1978) and to Chan and Paul. (1978) who observed similar effects in CO₂ sorption in poly(ethylene terephthalate) and in polycarbonate, respectively. It is believed that including history effects also has a profound effect on interfacial characteristics.

The interfacial tension between H₂O containing the surfactant SDS and CO₂ decreases with a factor 8 in comparison to the interfacial tension between surfactant free H₂O and CO₂, due to the orientation of the surfactant at the interface. The interactions between the polar part of the surfactant and H₂O on one hand and between the non polar part and CO₂ on the other hand are much stronger than the interactions between H₂O and CO₂, as explained earlier. In latex systems, the tail group of the surfactant is oriented inside the polymer particles. When all surfactant is located on the polymer particles, interaction between H₂O and CO₂ weakens in comparison to a surfactant orientation over the H₂O/CO₂ interface. Note that the polymer particles are surrounded by an electrical double layer of ions, changing the interaction with CO₂.

In either case of positioning of the polymer particles, *i.e.* at the H₂O/CO₂ interface or completely in the CO₂ phase, it should be realized that the particles are so small that the maximum fractional interface coverage of 74 % is reached.

Mass transfer resistance

In the solid-to-fluid (SF) mass transport approach, *i.e.* the shuttle effect, monomer diffuses directly from the polymer particles to the (sc)CO₂ phase. The residence time, $t_{\text{contact, p}}$ of one polymer particle at the H₂O/(sc)CO₂ interface, calculated with Equations 3 and 4 for 100 nm particles, is $3.8 \cdot 10^{-4}$ s. Within this time monomer is transferred from the polymer to the (sc)CO₂ phase. The overall resistance against mass transfer at the position where the polymer contacts the H₂O/CO₂ interface is expressed in Equation 17.

$$\left(\frac{1}{k \cdot a}\right)_{\text{overall}} = \left(\frac{1}{k \cdot a}\right)_{\text{polymer phase}} + \left(\frac{1}{k \cdot a \cdot K_{\text{mon}}^{\text{polymer/CO}_2}}\right)_{\text{CO}_2 \text{ phase}} \quad (17)$$

The specific area available for mass transport, a [m²/m³ polymer], for spherical particles applies. The partition coefficient $K_{\text{mon}}^{\text{polymer/CO}_2}$ is defined as the ratio of monomer concentration in the CO₂ phase and the monomer concentration in the polymer phase, see Equation 18.

$$K_m = \frac{C_m^{\text{CO}_2}}{C_m^{\text{pol}}} \left[\frac{\text{kg polymer}}{\text{kg CO}_2} \right] \quad (18)$$

When it is assumed that the polymer particle contacts the H₂O/CO₂ at one point, see Figure 7, mass transfer from the polymer particle through the interfacial region to the CO₂ phase is also possible.

Figure 7 Mass transfer from the polymer particle through the interfacial region to the (sc)CO₂ phase.

The overall resistance against mass transfer through the interfacial region is expressed in Equation 19, see also Figure 8.

Figure 8 Concentration profile of monomer in the polymer, water and CO₂ phase.

$$\left(\frac{1}{k \cdot a}\right)_{\text{overall}} = \left(\frac{1}{k \cdot a}\right)_{\text{polymer phase}} + \left(\frac{1}{k \cdot a \cdot K_{\text{mon}}^{\text{polymer/H}_2\text{O}}}\right)_{\text{H}_2\text{O phase}} + \left(\frac{1}{k \cdot a \cdot K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}}\right)_{\text{CO}_2 \text{ phase}} \quad (19)$$

The mass transfer coefficient of monomer in the H₂O phase is defined by the film theory, see Equation 1, averaged over the distance between the particle and the H₂O/CO₂ interface.

Example

It is assumed that residual monomer from PS latex and from PMMA latex is extracted by (sc)CO₂ in a countercurrent column. Latex has been chosen as the continuous phase, (sc)CO₂ is dispersed as 1 mm bubbles through the latex. Table 5 gives the parameters used to calculate the mass transfer resistance in each phase. The mass transfer coefficient of monomer in the polymer phase has been calculated according to Equation 5 ($Fo < 0.1$), for a diffusion coefficient of monomer in CO₂-swollen polymer of $10^{-12} \frac{\text{m}^2}{\text{s}}$. The concentration leveling in a 1 mm CO₂ bubble, *i.e.* when $Fo = 0.1$, requires 7 s; the mass transfer coefficient of monomer in the CO₂ bubble has then been calculated with Equation 5 for CO₂ instead of polymer. The mass transfer coefficient of monomer in water has been calculated for distances from the H₂O/CO₂ interface to the surface of the polymer particle of 1 to 10 nm.

Table 5 Parameters used in the prediction of the mass transfer resistance in the polymer particles, $\text{H}_2\text{O}/\text{CO}_2$ interfacial region and in the CO_2 bubble at 100 bar and 35 °C. (Kemmere *et al.*, 2005, González *et al.*, 2007)

polymer	$k_m^p \left[\frac{\text{m}}{\text{s}} \right]$	$D_m^{\text{CO}_2} \left[\frac{\text{m}^2}{\text{s}} \right]$	$k_m^{\text{CO}_2} \left[\frac{\text{m}}{\text{s}} \right]$	$k_m^{\text{H}_2\text{O}} \left[\frac{\text{m}}{\text{s}} \right]$	$K_m^{\text{P}/\text{H}_2\text{O}} \left[\frac{\text{kg H}_2\text{O}}{\text{kg P}} \right]$	$K_m^{\text{H}_2\text{O}/\text{CO}_2} \left[\frac{\text{kg CO}_2}{\text{kg H}_2\text{O}} \right]$
PS	$7 * 10^{-5}$	$1.4 * 10^{-8}$	$5 * 10^{-5}$	$4 * 10^{-1}$	$3 * 10^{-3}$	20
PMMA	$7 * 10^{-5}$	$6.8 * 10^{-8}$	$2.4 * 10^{-4}$	$4 * 10^{-1}$	$1.5 * 10^{-2}$	15

The partition coefficients of monomer between the polymer particles swollen with CO_2 and the (sc) CO_2 phase have been experimentally determined, see Chapter 3,

$$K_{\text{sty}}^{\text{PS}/\text{CO}_2} = 2 \left[\frac{\text{kg PS}}{\text{kg CO}_2} \right] \text{ and } K_{\text{MMA}}^{\text{PMMA}/\text{CO}_2} = 0.3 \left[\frac{\text{kg PMMA}}{\text{kg CO}_2} \right].$$

Table 6 collects the resulting mass transfer resistances in the polymer as well as in the CO_2 phase respectively, see Equation 17. Calculations have been performed including the specific surface area with relation to the surface area of the CO_2 bubble.

Table 6 Time constants for the mass transfer resistance in the polymer and CO_2 phase at the contact point of polymer particle and $\text{H}_2\text{O}/\text{CO}_2$ interface

polymer	$\left(\frac{1}{k * a} \right)_{\text{polymer phase}} [\text{s}]$	$\left(\frac{1}{k * a * K_{\text{mon}}^{\text{polymer}/\text{CO}_2}} \right)_{\text{CO}_2 \text{ phase}} [\text{s}]$
PS	2.3	1.67
PMMA	2.3	0.02

Table 6 shows the mass transfer resistance in extraction of residual monomer from PS latex as well as from PMMA latex with (sc) CO_2 is for the major part inside the polymer particles.

Table 7 gives the calculated resistance against mass transfer inside the polymer particle, through the $\text{H}_2\text{O}/\text{CO}_2$ interfacial region as well as in the CO_2 bubble not attached to the polymer particle, see Equation 19.

Table 7 Time constants for the mass transfer resistance in the polymer, H₂O and CO₂ phase

polymer	$\left(\frac{1}{k \cdot a}\right)_{\text{polymer phase}}$ [s]	$\left(\frac{1}{k \cdot a \cdot K_{\text{mon}}^{\text{polymer/H}_2\text{O}}}\right)_{\text{H}_2\text{O phase}}$ [s]	$\left(\frac{1}{k \cdot a \cdot K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}}\right)_{\text{CO}_2 \text{ phase}}$ [s]
PS	2.3	0.33	0.17
PMMA	2.3	0.07	0.1

The mass transfer resistance in extraction of residual monomer from PS latex as well as from PMMA latex with (sc)CO₂ is for the major part inside the polymer particles. Meier *et al.* (1997) reported similar observations studying steam stripping of PS latex. These authors demonstrated that diffusion resistance inside the latex particles can only be neglected when the residence time of the particles is significantly larger than the diffusion time of the transferred compounds inside the polymer particles. In the present work the residence time of a polymer particle at the H₂O/CO₂ interface, see Equation 3, is $4 \cdot 10^{-4}$ s. The time constant for monomer transport in the polymer particles to the CO₂ phase is 2.3 s, larger than that in water for PS and considerably larger than that for water in PMMA. The resistance against mass transfer in CO₂ is negligible. Therefore only the resistance inside the polymer particles has to be taken into account for the estimation of mass transfer rates of monomer from the particles to the CO₂ phase.

Concluding remarks

In the extraction with (sc)CO₂ to reduce residual monomer in a polymer latex, the shuttle mechanism has been found to govern mass transport. Due to Brownian motion the polymer particles move to and from the H₂O/CO₂ interface, improving mass transfer. According to the theory of Torza and Mason (1970) and Colver *et al.* (2006) the CO₂ completely wets the polymer particles in latex systems stabilized with ionic surfactants. Experimental observation of the behavior of latex submerged in a (sc)CO₂ environment did not confirm the theoretical predictions. History effects have been removed obtaining the specific literature data used in the theoretical considerations. The existence of an electrical double layer surrounding the polymer particles may also affect the calculated results. The main resistance against mass transfer has been demonstrated to be located inside the polymer particles.

References

- H. E. A. van den Akker, R. F. Mudde, E. Stammers, "Fysische transportverschijnselen: 200 vraagstukken", **1997**, 2nd ed., Delft University Press, The Netherlands
- E. Alper, B. Wichtendahl, W. D. Deckwer, "Gas absorption mechanism in catalytic slurry reactors", *Chem. Eng. Sci.*, **1980**, 35, 217-222
- A. A. C. M. Beenackers, W. P. M. van Swaaij, "Mass transfer in gas-liquid slurry reactors", *Chem. Eng. Sci.*, **1993**, 48, 18, 3109-3139
- R. B. Bird, W. E. Stewart, E. N. Lightfoot, "Transport phenomena", **2002**, 2nd edition, J. Wiley and sons Inc., New York
- D. W. F. Brilman, W. P. M. van Swaaij, G. F. Versteeg, "A one-dimensional instationary heterogeneous mass transfer model for gas absorption in multiphase systems", *Chem. Eng. Process.*, **1998**, 37, 471-488
- A. H. Chan, D. R. Paul, "Effect of sub- T_g annealing on CO₂ sorption in polycarbonate", *ACS Preprints*, **1978**, 39, 230
- D. K. Chattoraj, "Thermodynamics of adsorption at interfaces and the Gibbs surface excess", *PINSA*, **2001**, 67A, 6, 663-685
- Y-C. Chen, V. Dimonie, M. S. El-Aasser, " Interfacial phenomena controlling particle morphology of composite latexes", *J. Appl. Polym. Sci.*, **1991**, 42, 1049-1063
- Y-C. Chen, V. Dimonie, M. S. El-Aasser, "Effect of interfacial phenomena on the development of particle morphology in a polymer latex system", *Macromolec.*, **1991**, 24, 3779-3787
- C. H. Chon, K. D. Kihm, S. P. Lee, S. U. S. Choi, "Empirical correlation finding the role of temperature and particle size for nanofluid (Al₂O₃) thermal conductivity enhancement", *Appl. Phys. Lett.*, **2005**, 87, 153107
- P. J. Colver, T. Chen, S. A. F. Bon, "Supracolloidal structures through liquid-liquid interface driven assembly and polymerization", *Macromol. Symp.*, **2006**, 245-246, 34-41
- V. V. Dhanuka, J. L. Dickson, W. Ryoo, K. P. Johnston, "High internal phase CO₂-in-water emulsions stabilized with a branched nonionic hydrocarbon surfactant", *J. Colloid Interface Sci.*, **2006**, 298, 406-418
- E. Dumont, H. Delmas, "Mass transfer enhancement of gas absorption in oil-in-water systems: a review", *Chem. Eng. Process.*, **2003**, 42, 419-438
- P. Finkle, H. D. Draper, J. H. Hildebrand, *J. Amer. Chem. Soc.*, **1923**, 45, 12, 2780-2788
- L. M. González, O. Suárez-Iglesias, J. L. Bueno, C. Pizarro, I. Medina, "Limiting binary diffusivity of aniline, styrene, and mesitylene in supercritical carbon dioxide", *J. Chem. Eng. Data*, **2007**, 52, 1286-1290
- K. L. Harrison, K. P. Johnston, I. C. Sanchez, "Effects of surfactants on the interfacial tension between carbon dioxide and polyethylene glycol", *Langmuir*, **1996**, 12, 2637-2544
- P. C. Hiemenz, R. Rajagopalan, "Principles of colloid and surface chemistry", 3th ed., **1997**, Marcel Dekker, Inc., New York

- G. S. Huvard, V. T. Stannett, W. J. Koros, H. P. Hopfenberg, "The pressure dependence of CO₂ sorption and permeation in poly(acrylonitrile)", *J. Membrane Sci.*, **1980**, 6, 185-201
- P. T. Jaeger, J. v. Schnitzler, R. Eggers, "Interfacial tension of fluid systems considering the nonstationary case with respect to mass transfer", *Chem. Eng. Technol.*, **1996**, 19, 197-202
- S. P. Jang, S. U. S. Choi, "Role of Brownian motion in the enhanced thermal conductivity of nanofluids", *Appl. Phys. Lett.*, **2004**, 84, 21, 4316-4318
- C. Joly-Vuillemin, C. Bellefon, "Solids effects on gas-liquid mass transfer in three-phase slurry catalytic hydrogenation of adiponitrile over raney nickel", *Chem. Eng. Sci.*, **1999**, 51, 10, 2149-2158
- J-Y. Jung, J. Y. Yoo, "Thermal conductivity enhancement of nanofluids in conjunction with electrical double layer (EDL)", *Int. J. Heat Mass Transfer*, **2009**, 52, 525-528
- M. F. Kemmere, M. Cleven, M. A. van Schilt, J. T. F. Keurentjes, "Process design for the removal of residual monomer from latex products using supercritical carbon dioxide", *Chem. Eng. Sci.*, **2002**, 57, 3929-3937
- M. F. Kemmere, M. van Schilt, M. Jacobs, J. T. F. Keurentjes, "Reduction of residual monomer in latex products using high pressure carbon dioxide", in "Supercritical carbon dioxide in polymer reaction engineering", M. F. Kemmere, T. Meyer, Eds., **2005**, Wiley-VCH, Germany
- W. J. Koros, D. R. Paul, "CO₂ sorption in poly(ethylene terephthalat) above and below glass transition", *J. Polym. Sci., Polym. Phys. Ed.*, **1978**, 16, 1947
- D. W. van Krevelen in "Properties of Polymers"; 3rd Ed., Amsterdam: Elsevier, **1997**, Chapter 8
- B. Kvamme, T. Kuznetsova, A. Hebach, A. Oberhof, E. Lunde, "Measurements and modeling of interfacial tension for water + carbon dioxide systems at elevated pressures", *Comp. Mat. Sci.*, **2007**, 38, 506-513
- D. Meier, H.-J. Warnecke, J. Prüss, "Modelling of mass transfer of volatile organic compounds in polymer dispersions", *Chem. Eng. J.*, **1997**, 67, 45-53
- M. L. O'Neill, Q. Cao, M. Fang, K. P. Johnston, S. P. Wilkinson, C. D. Smith, J. L. Kerschner, S. H. Jureller, "Solubility of homopolymers and copolymers in carbon dioxide", *Ind. Eng. Chem. Res.*, **1998**, 37, 3067-3079
- K. Otake, M. Kobayashi, Y. Ozaki, S. Yoda, Y. Takebayashi, T. Sugeta, N. Nakazawa, H. Sakai, M. Abe, "Surface activity of myristic acid in the poly(methyl methacrylate)/supercritical carbon dioxide system", *Langmuir*, **2004**, 20, 6182-6186
- D. K. Owens, R. C. Wendt, "Estimation of the surface free energy of polymers", *J. Appl. Polym. Sci.*, **1969**, 13, 1741-1747
- S. U. Pickering, "Emulsions", *J. Chem. Soc. Transactions*, **1907**, 91, 2001-2021
- S. R. P. da Rocha, K. P. Johnston, R. E. Wetsacott, P. J. Rossky, "Molecular structure of the water-supercritical CO₂ interface", *J. Phys. Chem. B*, **2001**, 105, 12092-12104
- M. J. Rosen in "Surfactants and interfacial phenomena"; 3rd Ed., New York: John Wiley & sons, Inc., **2004**, Chapter 5

- D. C. Sundberg, A. P. Cacassa, J. Pantazopoulos, M. R. Muscato, "Morphology development of polymeric microparticles in aqueous dispersions. I. Thermodynamic considerations", *J. Appl. Polym. Sci.*, **1990**, 41, 1425-1442
- E. Sundberg, D. C. Sundberg, "Morphology development for three-component emulsion polymers: Theory and experiments", *J. Appl. Polym. Sci.*, **1993**, 47, 1277-1294
- F. Tewes, F. Boury, "Thermodynamic and dynamic interfacial properties of binary carbon dioxide-water systems", *J. Phys. Chem. B*, **2004**, 108, 2405-2412
- S. Torza, S. G. Mason, "Three-phase interactions in shear and electrical fields", *J. Colloid Interface Sci.*, **1970**, 33, 1, 67-83
- T. G. M. van de Ven, *PhD thesis*, **1975**, McGill University, Montreal, Canada
- H. Vinke, P. J. Hamersma, J. M. H. Fortuin, "Enhancement of the gas-absorption rate in agitated slurry reactors by gas-absorbing particles adhering to gas bubbles", *Chem. Eng. Sci.*, **1993**, 48, 12, 2197-2210
- J. A. Waters, "Predicting the surface morphology of composite latex particles", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **1994**, 83, 167-174
- S. E. Webber, P. Munk, K. P. Johnston, K. Otake, "Swelling of polystyrene latex particles in water by high-pressure carbon dioxide", *Langmuir*, **1997**, 13, 20, 3047-3051
- J. Welty, C. E. Wicks, R. E. Wilson, "Fundamentals of momentum, heat, and mass transfer", **2001**, 4th ed., Wiley, Chichester
- S. X. Zhang, W. H. Ray, "Modelling and experimental studies of aqueous suspension polymerization processes. 3. Mass transfer and monomer solubility effects", *Ind. Eng. Chem. Res.*, **1997**, 36, 1310-1321

Chapter 5

Process design for residual monomer reduction in latex with supercritical carbon dioxide

Abstract

Processes other than steam stripping or chemical conversion to reduce residual monomer in latex products are being intensively studied. One of the alternative processes is the extraction of residual monomer with high pressure carbon dioxide (CO_2). In the present work extraction of residual monomer from a latex product with supercritical carbon dioxide ((sc) CO_2) in a column has been studied. Operating conditions have been chosen at 35 °C and 100 bar. For reducing the residual styrene level in a polystyrene latex from 10^4 parts per million (ppm) to 1 ppm, a countercurrent mechanically agitated extractor with latex as continuous and (sc) CO_2 as the dispersed phase is suggested. Monomer partitioning was demonstrated to be a key issue for equipment design. Monomer transport was found to be governed by the shuttle effect, based on Brownian motion of the latex particles to and from the $\text{H}_2\text{O}/\text{CO}_2$ interface. The drift flux approach of Wallis was followed to determine the column flooding conditions. The influence of the dispersed phase hold up and the bubble size on the extraction efficiency has been analyzed. Column volumes of 4.75 m^3 are obtained for a throughput of 6000 kg latex/hr.

An economic analysis indicates that monomer extraction with (sc) CO_2 is a feasible process. Moreover, the performance compared to steam stripping can be improved, since lower final residual monomer levels can be attained.

Introduction

Emulsion polymerization is widely used in industry for the production of paints, coatings, adhesives and rubbers (Gilbert, 1995). The resulting latex is a dispersion of submicron (~ 100 nm) polymer particles in water. The free radical polymerization does not proceed to completion due to e. g. diffusion limitations of the monomer in the polymer particles. As a consequence, the polymer particles contain a significant amount of residual monomer, generally in the order of magnitude of a thousand parts per million (ppm). Legislation on the residual monomer level in polymer products is becoming increasingly strict. Reducing the residual monomer level is therefore a major incentive for the polymer producing industry. In practice, techniques such as steam stripping or a post polymerization temperature increase to reduce the residual monomer level are both energy intensive, time consuming and unable to meet future requirements (Englund, 1981). A novel method to reduce residual monomer in the latex particles based on high pressure or supercritical carbon dioxide ((sc)CO₂) extraction is being developed. Polymer particles swell with supercritical or liquid CO₂. The fugacity of the free monomer in the particles tremendously increases with the volume fraction of low molecular weight species in the polymer particles on addition of carbon dioxide. Moreover, high pressure CO₂ is an excellent extraction medium for various monomers as monomers have a relatively high solubility in CO₂, while (very) little water and practically no polymer dissolves in CO₂. Solubility and diffusivity of the monomer in (sc)CO₂ can easily be tuned by (small) changes in pressure and temperature. Due to the plasticizing effect the diffusion coefficient (D_m^p) of the monomer in the polymer particles increases from $\leq 10^{-15} \frac{\text{m}^2}{\text{s}}$ to $10^{-12} \frac{\text{m}^2}{\text{s}}$ or even higher (Alsoy and Duda, 1998).

High pressure or supercritical CO₂ behaves partly gas-like, *i.e.* high diffusivity and low viscosity, and partly liquid-like, *i.e.* high density. As the density of scCO₂ is similar to liquids, the monomer reduction with scCO₂ can be described as liquid-liquid extraction. Within liquid-liquid extraction the countercurrent arrangement is the best compromise between the objectives of a high extract concentration and a high extraction efficiency (De Haan, 2007). De Haan (2007) gives a comprehensive overview of industrial liquid-liquid extractors and provides some guidance for selecting an appropriate extraction column. Based on this guidance two types of extractors are discussed here: unagitated columns and mechanically

agitated columns. Unagitated columns are very simple and cheap, but suffer from a low efficiency. Spray towers are the most simple unagitated columns but due to poor phase contacting and severe backmixing in the continuous phase the equivalent of more than one or two theoretical stages or transfer units is hardly achieved (De Haan, 2007, Perry, 1999). In packed columns phase contacting is improved and backmixing is reduced. To avoid coalescence of the dispersed phase, it is required that the packing material is wetted by the continuous phase. Applying a sinusoidal pulsation to the contents of the column, sieve-plate or packed extraction columns improve efficiency (Scholtens, 2001). Maximizing the dispersion of one phase in the other (*i.e.* minimizing “droplet” size) and minimizing backmixing is also achieved by equipping the extractor with mechanically moving internals. The Scheibel column, rotating disk contactor, asymmetric rotating disk contactor, Oldshue-Rushton multiple mixer column and the Kuhni column employ rotary agitation. The Karr column reciprocates the plates, consuming less energy but agitating evenly well in comparison to rotating devices.

For simplicity, in the present work (sc)CO₂ extraction of residual monomer from a polystyrene latex in an empty, non agitated column has been designed for latex as the continuous and (sc)CO₂ as the dispersed phase. It is assumed that there is intensive phase contact and that backmixing in the column is low, see the section ‘Monomer transport’. To keep in mind that the (sc)CO₂ phase is dispersed, the extractor is referred to as a bubble column. After extraction at least one additional separation step is required to separate the (sc)CO₂/monomer mixture, thereby allowing recycling of (sc)CO₂.

Figure 1 schematically shows the extraction equipment, excluding the separation process on the extract phase.

Figure 1 Schematic view of an extraction column for residual monomer reduction in a latex with (sc)CO₂.

Calculations have been conducted based on experimentally and theoretically determined parameters, *e.g.* the partition coefficient, bubble size, dispersed phase hold up, etc., for a reduction of residual monomer from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm, respectively.

Partitioning

The key issue for equipment design is partitioning of the monomer between the CO₂-swollen latex particles and the (sc)CO₂ phase. Partitioning is expressed in the partition coefficient:

$$K_m = \frac{c_m^{CO_2}}{c_m^{pol}} \left[\frac{\text{kg polymer}}{\text{kg CO}_2} \right] \quad (1)$$

Note that the partition coefficient in general depends on concentrations, *i.e.* K_m is not a constant.

The partition coefficient governs the amount of (sc)CO₂ needed for extraction, as indicated by the mass balance over one stage of a countercurrent extraction column, see Equation 2 (McCabe, 2001), and Figure 2.

$$\phi_{CO_2} = \phi_P * \frac{C_{m, n-1}^p - C_{m, n}^p}{C_{m, n}^{CO_2} - C_{m, n+1}^{CO_2}} \left[\frac{m^3}{hr} \right] \quad (2)$$

$$\text{with } C_{m, n}^{CO_2} = K_m * C_{m, n}^p \quad (3)$$

Figure 2 Flowrates and concentrations in a theoretical stage in extraction equipment.

Swelling the polymer particles with (sc)CO₂, decreases the volume fraction of polymer in the polymer phase (*i.e.* the polymer particles). The polymer volume fraction completely remains in the reduced state during the extraction process in the column as the polymer particles are swollen with (sc)CO₂. Consequently, the monomer partition coefficient does not change from stage to stage, but can be assumed to be a constant.

Monomer transport

Two mechanisms for transfer of monomer from latex particles to (sc)CO₂ operate in parallel: the resistance in series approach, *i.e.* solid-to-liquid-to-fluid (SLF) mass transfer as well as a direct solid-to-fluid (SF) mass transfer model, also referred to as the shuttle effect (Beenackers, 1993, Vinke, 1993).

In the resistance in series approach, the monomer diffuses out of the polymer particles through the H₂O phase into the (sc)CO₂ phase. The main resistance against mass transfer is located in the H₂O phase due to low monomer solubility (Zhang, 1997), see Figure 3.

Figure 3 The resistance in series mass transport approach.

Describing the diffusion of monomer in through the three phases, *i.e.* the polymer particles, the H₂O phase and the CO₂ phase, the film model has been used. The overall molar mass transfer flux of the monomer (ϕ_{mon}) is expressed in Equation 4.

$$\phi_{\text{mon}} = \left[\left(\frac{1}{k_m^P} \right)_{\text{P phase}} + \left(\frac{1}{k_m^{\text{H}_2\text{O}} * K_{\text{mon}}^{\text{polymer/H}_2\text{O}}} \right)_{\text{H}_2\text{O phase}} + \left(\frac{1}{k_m^{\text{CO}_2} * K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}} \right)_{\text{CO}_2 \text{ phase}} \right]^{-1} * a_p * \left(C_m^P - \frac{C_m^{\text{CO}_2}}{K_{\text{mon}}^{\text{polymer/H}_2\text{O}} * K_{\text{mon}}^{\text{H}_2\text{O/CO}_2}} \right) \quad (4)$$

with k_m^i the monomer mass transfer coefficient in phase i , $K_{\text{mon}}^{i/j}$ the monomer partition coefficient between phase i and phase j , a_p the specific mass transfer area of the polymer particles.

In the SF mass transfer approach, the polymer particles move through the H₂O phase towards the H₂O/CO₂ interface. The monomer diffuses out of the polymer particles directly into the (sc)CO₂ phase, see Figure 4.

Figure 4 The shuttle mechanism.

The submicron polymer particles follow Brownian motion and consequently can reside for some time at the (sc)CO₂/H₂O interface (Brilman, 1998). At the (sc)CO₂/H₂O interface the polymer particle is in direct contact with the (sc)CO₂ phase allowing direct diffusional transport of the monomer from the polymer particles to the (sc)CO₂ phase. Alper *et al.* (1980) used the boundary layer model to describe mass transfer by the shuttle mechanism. However, in case of a system with particles with a limited amount of material to be transferred, stationary models cannot be applied. After a certain contact time the particles near the interface have lost part of the initially present monomer. Dumont *et al.* (2003) emphasizes that in many situations the contact time between particle and fluid is so short that only unsteady-state models can be used to estimate the mass transfer coefficient in the SF approach.

Concentration leveling of the monomer in the polymer phase is related to time or the Fourier number, see Equation 5 and Figure 5.

$$Fo = \frac{D_m^P * t_{\text{contact, P}}}{d_{\text{particle}}^2} \quad (5)$$

with $t_{\text{contact, P}}$ the contact time of the polymer at the H₂O/CO₂ interface, d_{particle} the polymer particle diameter.

Figure 5 Concentration leveling of the monomer in a polymer particle. r_p is the polymer particle radius, C_0 the monomer concentration at $t_{\text{contact}} = 0$, C_s the monomer concentration at the polymer particle surface.

Chon *et al.* (2005) suggest that the residence time of polymer particles at the H₂O/(sc)CO₂ interface can be regarded in terms of Brownian motion of the polymer particles in the H₂O phase, see Equation 6. Chon *et al.* (2005) used Al₂O₃ nanoparticles to increase the heat conductivity of water and validated that Brownian motion of the nanoparticles is the key mechanism for thermal conductivity enhancement. Comparable observations are reported by other authors (Jang, 2004).

$$t_{\text{contact}, p} = \frac{\Delta s}{v_{\text{Br}}} \quad (6)$$

Δs is the distance a polymer particle travels through the H₂O phase towards the H₂O/CO₂ interface. The length scale of the interfacial region is assumed to be 10 μm (Kemmere, 2002); Δs is of the same order of magnitude. v_{Br} is the velocity of the polymer particles due to Brownian motion, see Equation 7.

$$v_{\text{Br}} = \frac{k_b * T}{3 * \pi * \eta * d_{\text{particle}} * l_{\text{BF}}} \quad (7)$$

with k_b the Boltzman constant, η the H₂O viscosity, l_{BF} the mean free path of the particle in water ($l_{\text{H}_2\text{O}} = 0.17 \text{ nm}$ (Jang, 2004)).

For $Fo \leq 0.1$, mass transport in the polymer particles can be regarded to be in a semi-infinite medium. Then the penetration theory applies for mass transport, see Equation 8 (Welty *et al.*, 2001, Bird *et al.*, 2002).

$$k_m^p = 2 * \sqrt{\frac{D_m^p}{\pi * t_{\text{contact}, p}}} \quad (8)$$

For $Fo > 0.1$, *i.e.* developed concentration profile in the particle, intraparticle mass transport can be described with Equation 9 (van den Akker and Mudde, 1997), see Figure 5.

$$Sh = \frac{k_m^p * d_{\text{particle}}}{D_m^p} = 6.6 \quad (9)$$

Based on intrinsic properties, *i.e.* viscosity and surface tension, of the latex and (sc)CO₂, the (sc)CO₂ bubbles are assumed to behave as rigid spheres (Wesselingh, 1987, Slater, 1994). The monomer mass transfer coefficient in (sc)CO₂ then depends on the contact time of the polymer particle with the rising (sc)CO₂ bubble ($\sim 1 \text{ mm}$, specified by the sieve plate at the bottom of the column), see Equation 10.

$$Fo = \frac{D_m^{\text{CO}_2} * t_{\text{contact}, \text{CO}_2}}{d_{\text{CO}_2}^2} \quad (10)$$

with $D_m^{CO_2}$ the diffusion coefficient of monomer in the (sc)CO₂ phase and d_{CO_2} the diameter of a CO₂ bubble.

In a certain stage of the column, at the entrance of the (sc)CO₂ bubbles, the bubble needs a time $t_{\text{contact, CO}_2}$ for the average concentration in the bubble and the monomer concentration at the surface to become approximately equal, *i.e.* $Fo = 0.1$, see also Figure 5. In the neighboring stage, the bubble contacts polymer particles with a higher monomer concentration. Again, the bubble needs a time $t_{\text{contact, CO}_2}$ to reach $Fo = 0.1$. This cycle repeats itself till the bubble exits the column. Note that the concentration leveling of monomer in the (sc)CO₂ bubble can only develop when the (sc)CO₂ and the latex phase become efficiently mixed after every 7 seconds (follows from Equation 10 for $Fo = 0.1$; 1 mm CO₂ bubble). While rising through one transfer unit, CO₂ tends to coalesce, decreasing phase contact with the latex phase. After 7 seconds the CO₂ bubbles are assumed to redisperse, providing extensive mixing of the (sc)CO₂ and the latex phase at the beginning of each new transfer unit, see Figure 6.

Figure 6 Schematic view of one transfer unit in an extraction column for residual monomer reduction in a latex with (sc)CO₂.

In practice, intimate phase contact and reduced backmixing is achieved in a column including internals, *e.g.* a rotating disk contactor (RDC) or a Karr reciprocating column. Including

internals also supports the continuity of a small bubble size as well as of the width of the bubble size distribution (Gourdon, 1994, Kumar, 1994).

The mass transport coefficient of monomer in the (sc)CO₂ phase is then approximated according to Equation 11.

$$k_m^{\text{CO}_2} = 2 * \sqrt{\frac{D_m^{\text{CO}_2}}{\pi * t_{\text{contact, CO}_2}}} \quad (11)$$

The mass transfer resistance depends on the specific area of the H₂O/(sc)CO₂ interface. Joly-Vuillemin and Bellefon (1999) suggest that the polymer particles partially cover the H₂O/(sc)CO₂ interface. The effective specific mass transfer area is then defined as

$$a_{\text{eff}}(\text{SF}) = a_{ij} * \theta \quad \text{for the shuttle effect} \quad (12)$$

$$a_{\text{eff}}(\text{SLF}) = a_{ij} * (1-\theta) \quad \text{for the SLF approach} \quad (13)$$

Note that θ_{max} is 0.74, *i.e.* the maximum surface coverage by spherical particles in a three dimensional closest packing.

As mentioned earlier the SLF model is transport limited due to the resistance against monomer transport through the aqueous phase as a result of low monomer solubility in water (Zhang, 1997). In comparison with the SF mass transfer model, equilibrium cannot be reached within a short time. The shuttle effect is therefore dominating mass transfer. The mass transfer-in-series contribution is assumed to be negligible.

Equipment design

For extraction of residual monomer from a polystyrene (PS) latex by (sc)CO₂ an empty non agitated extraction column is chosen, referred to as a bubble column. Latex (containing 45 % solids) enters the column at the top with a throughput of 6000 kg/hr; the continuous latex flow is comparable to stripping a batch of 30 ton latex with steam in about 5 hours. Countercurrently 1 mm (sc)CO₂ bubbles (specified by the sieve plate at the bottom of the column) are dispersed into the latex. Both the latex and the (sc)CO₂ flow have been considered to move through the column with negligible axial dispersion and perfect radial

mixing, *i.e.* plug flow. Based on the results described in Chapter 3, the operating conditions of the bubble column have been chosen, leading to an operating pressure of 100 bar and an operating temperature of 35 °C. The partition coefficient of styrene between the PS latex and the (sc)CO₂ at the chosen operating conditions is 2 [kg PS/ kg (sc)CO₂]. The lowest (sc)CO₂ flow rate, *i.e.* when the incoming latex and the outgoing (sc)CO₂ are at phase equilibrium (McCabe, 2001), to reduce the residual styrene level in the PS latex from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm, is approximately¹ 1400 kg/hr, see Equation 14 and Figure 2. The lowest (sc)CO₂ flow rate applies in a column with an infinite number of stages.

$$\Phi_{\text{CO}_2, \text{lowest}} = \Phi_p * \frac{C_{m, 0}^p - C_{m, N}^p}{C_{m, 1}^{\text{CO}_2} - C_{m, N+1}^{\text{CO}_2}} \left[\frac{\text{m}^3}{\text{hr}} \right] \quad (14)$$

$$\text{with } C_{m, 1}^{\text{CO}_2} = K_m * C_{m, 0}^p \quad (15)$$

Note that for reducing the residual methyl methacrylate (MMA) in a polymethyl methacrylate (PMMA) latex the lowest (sc)CO₂ flow rate is about² 9000 kg/hr. More (sc)CO₂ is required to remove a similar amount of residual monomer from PMMA in comparison to the PS latex. This is due to the lower partition coefficient of MMA between PMMA latex and (sc)CO₂, *i.e.* $K_{\text{MMA}} = 0.3$ [kg PMMA/ kg (sc)CO₂] at 100 bar and 35 °C. The actual (sc)CO₂ flow rate has been calculated with Equations 14 and 3 and depends on the amount of monomer mass the extract phase may contain. A reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm corresponds (in this system) with ~200 mole Sty/m³ (sc)CO₂. The (sc)CO₂ flow leaving the extraction column contains 200 mole Sty/m³ (sc)CO₂ for the minimum flow rate of 1400 kg (sc)CO₂/hr. When it is specified that the outgoing (sc)CO₂ flow may contain only 90 mole Sty/m³, a (sc)CO₂ flow rate of 3050 kg/hr is required. To obtain an exiting (sc)CO₂ flow with a concentration of 50 mole Sty/m³ (sc)CO₂, 5500 kg (sc)CO₂/hr is necessary.

For designing the extraction column for residual monomer reduction in latex with (sc)CO₂ from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm, two approaches have been followed. In a first approach the number of theoretical stages required for the extraction have been determined based on the mass balance over one stage, see Equations 2 and 3. The mass

¹ The lowest CO₂ flow required for a residual styrene reduction in PS latex from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm are slightly different, *i.e.* 1337, 1349 and 1350 kg CO₂/hr, respectively. The value of the CO₂ flow indicated in the present work is somewhat higher to account for the CO₂ that dissolves in the H₂O phase.

² The lowest CO₂ flow required for a residual MMA reduction in PMMA latex from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm are slightly different, *i.e.* 8910, 8990 and 8999 kg CO₂/hr, respectively.

balance over one stage is extended with the McCabe-Thiele method (McCabe, 2001), see e.g. Figure 7. The equilibrium line is straight as the partition coefficient is a constant, see section ‘Partitioning’. The so-called operating line is always straight, the slope depends in general on the ratio of the liquid and the vapor (fluid) phase, *i.e.* the extraction performance. The monomer concentration in the entering latex phase as well as in the incoming (sc)CO₂ are known (*i.e.* $C_0^P = 10^4$ ppm and $C_{N+1}^{CO_2} = 0$ ppm). The required monomer concentration in the latex phase leaving the column has been chosen (*i.e.* $C_N^P = 1$ ppm) while the monomer level in the outgoing (sc)CO₂ depends on the ratio of the latex and the CO₂ phase.

Figure 7 McCabe-Thiele diagram for the extraction of residual monomer in latex with (sc)CO₂.

In a second approach the column dimensions have been determined with respect to a mass balance over the latex phase and the (sc)CO₂ phase, both in plug flow, in an infinitesimal slice of the column, see Figure 8 and Equations 16 and 17.

Figure 8 Schematic view of an infinitesimal piece Δx in an extraction column.

$$0 = \varphi_P * C_m^P|_{x+\Delta x} - \varphi_P * C_m^P|_x + \left[\frac{1}{k_m^P} + \frac{1}{K_m * k_m^{CO_2}} \right]^{-1} * a_{CO_2} * \theta * \varepsilon_{CO_2} * \pi * r_c^2 * \Delta x * \left[\frac{C_m^{CO_2}}{K_m} - C_m^P \right] \quad (16)$$

$$0 = \varphi_{CO_2} * C_m^{CO_2}|_x - \varphi_{CO_2} * C_m^{CO_2}|_{x+\Delta x} + \left[\frac{1}{k_m^P} + \frac{1}{K_m * k_m^{CO_2}} \right]^{-1} * a_{CO_2} * \theta * \varepsilon_{CO_2} * \pi * r_c^2 * \Delta x * \left[C_m^P - \frac{C_m^{CO_2}}{K_m} \right] \quad (17)$$

Designing an extraction column, the separation performance but also the hydrodynamic characteristics, namely the dispersed phase hold up and bubble size, are key parameters in determining the column capacity and the required column diameter to provide the desired throughput and performance. First the influence of the dispersed phase hold up on the column design is discussed, followed by the effect of the bubble size.

Dispersed phase hold up

The drift-flux model reported by Wallis *et al.* (Wallis, 1969) has been applied to describe the flow characteristics in the latex-(sc)CO₂ two-phase system. The drift flux is defined as the volume flux of the continuous phase with respect to the total volume flux (*i.e.* $v_d + v_c$). The drift-flux model is most importantly used to predict the flooding point (Xu, 1991). The drift-flux is proportional to the slip velocity. The slip velocity is the relative velocity of the dispersed

phase with respect to the continuous phase. The slip velocity is expressed in terms of the effective velocities of the continuous and dispersed phase:

$$v_s = \frac{v_d}{\varepsilon_d} - \frac{v_c}{(1 - \varepsilon_d)} \quad (18)$$

The superficial velocities of the dispersed as well as the continuous phase are defined as the ratio of the volumetric flux of the respective phase over the column area, see Equation 19.

$$v_i = \frac{\phi_{v,i}}{A_{\text{column}}} \quad (19)$$

For solid (rigid spheres)-liquid systems, Richardson and Zaki (1954) experimentally determined the relationship between the slip velocity and the single sphere terminal settling/rising velocity (v_∞), Equation 20. Note that the slip velocity is also a function of the volume fraction of the dispersed phase in the column.

$$v_s = v_\infty * (1 - \varepsilon_d)^{n-1} \quad (20)$$

In Equation 20, n is a function of the Reynolds number ($Re = \frac{v_\infty * d_{CO_2} * \rho_{\text{latex}}}{\mu_{\text{latex}}}$) for the rigid spheres, see Equations 21 to 24 (Richardson and Zaki, 1954).

$$Re < 0.2 \quad n = 4.65 \quad (21)$$

$$0.2 < Re < 1 \quad n = 4.35 * Re^{-0.03} \quad (22)$$

$$1 < Re < 500 \quad n = 4.45 * Re^{-0.1} \quad (23)$$

$$Re > 500 \quad n = 2.39 \quad (24)$$

The terminal rising velocity of one bubble is primarily controlled by buoyancy forces and the fluid drag, also a function of Re , Equation 25. The derivation for Equation 23 from the force balance is found in Appendix A.

$$v_\infty = \sqrt{\frac{4 * \Delta\rho * g * d_{CO_2}}{3 * \rho * C_D}} \quad (25)$$

For low Reynolds numbers, (*i.e.* $Re < 1$, creep flow) the drag coefficient is $C_D = \frac{24}{Re_{CO_2}}$ (Bird *et al.*, 2002).

Equations 18 and 20 become equal for two values of the dispersed phase hold up, a lower limit and an upper limit. The region between the hold up limits is assigned as stable working

region. The column diameter then follows from Equation 18 for a given flow as the superficial velocity depends on the cross-sectional area of the column.

Evaluating the drift-flux model for the latex-(sc)CO₂ system described above (1 mm CO₂ bubbles), the flooding point is assigned to a volume fraction of (sc)CO₂ in the column of $\varepsilon_d=0.3$. It is recommended that the actual value of the slip velocity should be taken at no more than 70% of the estimated slip velocity at the flooding point (Perry, 1999); in other words, the (sc)CO₂ hold up in the column is 0.2. Most liquid-liquid extraction columns are operated at dispersed phase hold ups of ε_d between 0.1 and 0.2 (Perry, 1999, Kumar, 1994).

Figure 9 shows the calculated (sc)CO₂ bubble residence times for a residual monomer reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm as a function of the fraction of the H₂O/CO₂ interface covered with polymer particles. The (sc)CO₂ hold up is 0.2, the diffusion coefficient (D_{sty}^{PS}) of styrene in PS is $10^{-12} \frac{m^2}{s}$, the (sc)CO₂ flow rate is a) 1400 kg/hr (Equations 14 and 15), b) 3050 kg/hr to 5500 kg/hr (Equations 2 and 3).

Figure 9 CO₂ bubble (1 mm) residence time for the extraction of Sty from PS at 35 °C and 100 bar in function of the fraction of the H₂O/CO₂ interface covered with polymer particles for different (sc)CO₂ flow rates. $K_{sty} = 2$ [kg PS/kg CO₂]; $\varepsilon_{CO_2} = 0.2$; $D_c = 1$ m; $D_{sty}^{PS} = 10^{-12} \frac{m^2}{s}$, — 100 ppm, - - - 10 ppm, 1 ppm residual monomer.

Figure 9 shows that the fraction of the H₂O/CO₂ interface covered with polymer particles affects the residence time of the CO₂ bubbles (and therefore also the column volume) tremendously. Note that in Figure 9 the horizontal axis has a range of $0.1 < \theta < 0.74$. The upper limit is $\theta_{\max} = 0.74$; the lower limit is arbitrarily chosen, according to the assumption that mass transport of monomer from polymer particles into the (sc)CO₂ phase is dominated by the shuttle effect. How many particles actually adsorb to the H₂O/CO₂ interface depends on the interfacial tensions between H₂O(with surfactant)/polymer, polymer/CO₂ and H₂O(with surfactant)/CO₂ (Torza and Mason, 1970) and on the frequency the polymer particles arrive at and move away from the H₂O/CO₂ interface. Predicting the number of particles adsorbed at the H₂O/CO₂ interface according to the theory of Torza (1970), the upper limit value of 0.74 has been found.

As expected, increasing the (sc)CO₂ flow rate, Figures 9a to 9c, decreases the monomer concentration in the exiting (sc)CO₂ flow, as well as the CO₂ residence time in the column (and therefore also the column volume). For the lowest (sc)CO₂ flow rate, Figure 9a, the actual column height is unrealistically high, *i.e.* 16 m for a residual monomer reduction from 10⁴ ppm to 100 ppm to 1600 m for a reduction from 10⁴ ppm to 1 ppm (at $\theta = 0.74$). For a flow rate of 3050 and 5500 kg (sc)CO₂/hr, Figures 9b and 9c, acceptable column heights (< 4 m) have been calculated. Columns with an aspect ratio of about 3 are recommended, but columns with an aspect ratio between 2 and 5 are also common (Seider, 2010). Based on the aspect ratio in Figure 9b, (sc)CO₂ flow rate of 3050 kg/hr, has been chosen as a base case in this work.

Tables 1 and 2 give the CO₂ bubble residence times in the column at some values of the fraction of the H₂O/CO₂ interface covered with polymer particles, for a (sc)CO₂ or dispersed phase hold up of 0.2 and 0.1. The (sc)CO₂ flow rate is 3050 kg/hr and the column diameter is taken as 1 m. The 1 mm (sc)CO₂ bubbles (specified by a sieve plate in the column) rise through the column with a velocity of 1 mm/s (*i.e.* the slip velocity or hindered rising velocity of the bubble swarm, calculated according to the drift flux approach, Equations 18 and 20). As mentioned in the introduction, the diffusion coefficient ($D_{\text{sty}}^{\text{PS}}$) of monomer in the polymer phase increases from $10^{-15} \frac{\text{m}^2}{\text{s}}$ to $10^{-12} \frac{\text{m}^2}{\text{s}} < D_{\text{sty}}^{\text{PS}} < 10^{-11} \frac{\text{m}^2}{\text{s}}$ due to the plasticizing effect of CO₂ (Alsoy, 1998). To analyze the effect of the transport constant of styrene in the polymer

phase, the CO₂ residence time has been calculated for $D_{sty}^{PS} = 10^{-12} \frac{m^2}{s}$ and for $D_{sty}^{PS} = 10^{-11} \frac{m^2}{s}$.

Table 1 (sc)CO₂ bubble residence time for operation with a CO₂ hold up (ϵ_d) of 0.2 for a residual monomer reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm as a function of the fraction of the H₂O/CO₂ interface covered with polymer particles. *

θ [–]	$D_{sty}^{PS} = 10^{-12} [\frac{m^2}{s}]$			$D_{sty}^{PS} = 10^{-11} [\frac{m^2}{s}]$		
	τ_{100} [s]	τ_{10} [s]	τ_1 [s]	τ_{100} [s]	τ_{10} [s]	τ_1 [s]
0.74	314	491	697	196	295	403
0.3	785	1276	1698	442	707	982

* operating conditions: 100 bar, 35 °C, $K_{sty} = 2$ [kg PS/kg CO₂], column diameter $D_c = 1$ m, $\phi_{CO_2} = 3050$ kg/hr, $d_{CO_2} = 1$ mm

Table 2 (sc)CO₂ bubble residence time for operation with a CO₂ hold up (ϵ_d) of 0.1 for a residual monomer reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm as a function of the fraction of the H₂O/CO₂ interface covered with polymer particles. *

θ [–]	$D_{sty}^{PS} = 10^{-12} [\frac{m^2}{s}]$			$D_{sty}^{PS} = 10^{-11} [\frac{m^2}{s}]$		
	τ_{100} [s]	τ_{10} [s]	τ_1 [s]	τ_{100} [s]	τ_{10} [s]	τ_1 [s]
0.74	589	982	1374	363	589	785
0.3	1571	2556	3436	982	1473	1963

* operating conditions: 100 bar, 35 °C, $K_{sty} = 2$ [kg PS/kg CO₂], column diameter $D_c = 1$ m, $\phi_{CO_2} = 3050$ kg/hr, $d_{CO_2} = 1$ mm

For a (sc)CO₂ hold up of 10%, a bubble residence time in the column more than twice the time at a hold up of 20% is necessary to absorb the desired amount of monomer. Consequently, the column height increases with approximately a factor 4, resulting in an aspect ratio far above 5. Table 3 provides the calculated column heights corresponding to the CO₂ residence times reported in Tables 1 and 2. Only the column heights at the highest

possible fraction of the H_2O/CO_2 interface covered with polymer particles ($\theta = 0.74$) are given.

Table 3 Column height for a residual monomer reduction from 10^4 ppm to 100 ppm, to 10 ppm and to 1 ppm as function of the dispersed phase hold up for $\theta = 0.74$.*

ε_{CO_2} [-]	$D_{sty}^{PS} = 10^{-12} \left[\frac{m^2}{s} \right]$			$D_{sty}^{PS} = 10^{-11} \left[\frac{m^2}{s} \right]$		
	$H_{c,100}$ [m]	$H_{c,10}$ [m]	$H_{c,1}$ [m]	$H_{c,100}$ [m]	$H_{c,10}$ [m]	$H_{c,1}$ [m]
0.2	1.6	2.5	3.6	1	1.5	2
0.1	6	10	14	3.7	6	8

* operating conditions: 100 bar, 35 °C, $K_{sty} = 2$ [kg PS/kg CO_2], column diameter $D_c = 1$ m, $\phi_{CO_2} = 3050$ kg/hr, $d_{CO_2} = 1$ mm

As a result, from here on the dispersed phase hold up of 0.2 is chosen in further designing the extraction column.

Tables 1 to 3 indicate that an increase of the diffusion coefficient of Sty in the polymer phase by only a factor 10 strongly affects the CO_2 residence time as well as the column volume. The transport coefficient (k_{sty}^{PS}) of styrene in PS improves from $7 * 10^{-5} \left[\frac{m}{s} \right]$ to $9.9 * 10^{-4} \left[\frac{m}{s} \right]$ when the diffusion coefficient (D_{sty}^{PS}) of styrene in PS increases from $10^{-12} \left[\frac{m^2}{s} \right]$ to $10^{-11} \left[\frac{m^2}{s} \right]$ (calculated with Equation 8 for 100 nm polymer particles). The polymer particles are depleted of monomer very fast when contacting a CO_2 bubble. From here on the column is designed for a diffusion coefficient of styrene in CO_2 swollen PS of $10^{-12} \left[\frac{m^2}{s} \right]$, the ‘worst case scenario’ upon swelling the polymer particles with CO_2 (Alsoy, 1998).

Bubble size

Kumar (1994) and Gourdon (1994) emphasize the importance of the drop-size distribution in designing extraction columns. The dispersed phase generally enters the column via a distribution plate (*i.e.* sieve plate). The inlet drop-size distribution is thus determined by the size of the sieve holes and dispersed phase throughput. Depending on the column type, a

steady drop-size distribution can be established, *i.e.* the drop-size distribution is practically independent of the axial position in the column length. Therefore, an average drop size is used to describe the extraction column. Kumar *et al.* (1996, 1994) give an overview of the unified correlations for predicting drop or bubble sizes of several kinds of liquid-liquid extraction columns. The predictions have been based upon experimental data obtained with a well defined column diameter and column height. Korchinsky (1994) found that smaller drops or bubbles require larger column diameters, because of a lower slip velocity relative to the continuous phase. At the same time smaller drops provide larger specific interfacial surface area, higher mass transfer rates and therefore columns become shorter. However, a larger column diameter results in more axial dispersion in the column, hence decreasing mass transfer (Godfrey, 1994). The axial mixing of the continuous phase is caused by the tendency of the droplets to concentrate in the center of the column and move up together with a core of continuous phase, which returns to the bottom through an annulus around the wall, see Figure 10.

Figure 10 Schematic view of the axial mixing of the continuous phase in an extraction column induced by the dispersed phase.

In the present work, the average bubble size as well as the column diameter have been defined, with respect to the flooding conditions according to the Wallis drift-flux model. From these data the corresponding CO₂ residence time and column height have been calculated. Table 4 collects the CO₂ residence time as well as the column height required for a residual monomer reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm for 3 different diameters of the CO₂ bubbles.

Table 4 CO₂ residence time and the corresponding column height for a residual monomer reduction from 10⁴ ppm to 100 ppm, to 10 ppm and to 1 ppm in function of the CO₂ bubble diameter for $\theta = 0.74^*$

d_{CO_2} [10 ⁻³ m]	τ_{100} [s]	τ_{10} [s]	τ_1 [s]	$H_{c, 100}$ [m]	$H_{c, 10}$ [m]	$H_{c, 1}$ [m]
0.5	98	147	216	0.5	0.75	1.1
1	314	491	697	1.6	2.5	3.6
2	589	942	1306	3	4.8	6.7

* operating conditions: 100 bar, 35 °C, $K_{sty} = 2$ [kg PS/kg CO₂], column diameter $D_c = 1$ m, $\phi_{CO_2} = 3050$ kg/hr, $D_{sty}^{PS} = 10^{-12}$ [m²/s], $\varepsilon_{CO_2} = 0.2$

Increasing the bubble diameter results in higher CO₂ residence times and larger columns, similar to the findings of Korchinsky (1994), as mentioned above. The mass transfer coefficient ($k_{sty}^{CO_2}$) of styrene in the CO₂ bubble decreases with increasing bubble size. Table 5 shows the required contact time of a CO₂ bubble with a polymer particle for a developed concentration profile in the CO₂ bubble, calculated with Equation 10, as well as the mass transfer coefficient ($k_{sty}^{CO_2}$) of styrene in a CO₂ bubble, calculated with Equation 11, with respect to the contact time for 3 different bubble sizes.

Table 5 Contact time of a CO₂ bubble with a polymer particle for a developed concentration profile in the CO₂ bubble, calculated with Equation 10, and the corresponding mass transfer coefficient of styrene in the CO₂ phase, calculated with Equation 11, as a function of the CO₂ bubble size for $\theta = 0.74^*$

d_{CO_2} [10 ⁻³ m]	$t_{contact, CO_2}$ [s]	$k_{sty}^{CO_2}$ [10 ⁻⁵ $\frac{m}{s}$]
0.5	2	10
1	7	5
2	29	2.5

* operating conditions: 100 bar, 35 °C, $K_{sty} = 2$ [kg PS/kg CO₂], column diameter $D_c = 1$ m, $\phi_{CO_2} = 3050$ kg/hr, $D_{sty}^{PS} = 10^{-12}$ [m²/s], $\varepsilon_{CO_2} = 0.2$

Large drops are internally well mixed, whereas small drops show an extra internal circulation modifying the rigidity of the drop, *i.e.* the Marangoni effect, suppressing the benefit of a

higher mass transfer rate in the dispersed phase (Bird, 2002). A bubble of 1 mm in diameter with a slip velocity of ~ 1 mm/s is considered to be of realistic dimensions.

With respect to the mass balance over one stage, see Equation 2, extended over the total height of the extraction column, the number of theoretical stages has been determined, see Figure 2. It has been found that 12 equilibrium stages apply to reduce the residual monomer in the latex from 10^4 ppm to 1 ppm. Knowing the number of stages required for the extraction as well as the column height, the height equivalent of a theoretical stage follows from Equation 26.

$$H_c = N_{ts} * H_{HETP} \quad (26)$$

Table 6 provides an overview of the operating conditions, design parameters and column dimensions for the reduction of residual styrene in a PS latex from 10^4 ppm to 1 ppm by extraction with $scCO_2$.

Table 6 Operating conditions, design parameters and column dimensions for the high pressure CO₂ extraction of residual monomer from 10⁴ ppm to 1 ppm.

Operating conditions	
pressure, P [bar]	100
temperature, T [°C]	35
latex throughput, ϕ_{latex} [kg/hr]	6000
CO ₂ throughput, ϕ_{CO_2} [kg/hr]	3050
partition coefficient, K_{sty} [kg PS/kg (sc)CO ₂]	2
diffusion coefficient of styrene in CO ₂ -swollen PS, $D_{\text{sty}}^{\text{PS}}$ [m ² /s]	10 ⁻¹²
Column dimensions	
column diameter, D_c [m] (+ 15% marge)	1.2
column height, H_c [m] (+ 15% marge)	4.2
number of theoretical stages, N_{ts}	12
height equivalent of a theoretical plate, H_{HETP} [m]	0.35
Design parameters	
dispersed phase hold up, $\varepsilon_{\text{CO}_2}$ [m ³ _{CO₂} /m ³ _{column}]	0.2
bubble diameter, d_{CO_2} [mm]	1

After the extraction, styrene (the extract) needs to be separated from (sc)CO₂ in order to recycle the extraction fluid. In a first step, by tuning the pressure of the styrene/CO₂ mixture, a great part of the styrene is liquefied containing a small amount of liquid CO₂. Note that in the binary phase diagram of styrene and CO₂ (Zhang, 2005, Chapter 3) one can see that depressurizing the homogeneous styrene/CO₂ mixture at 35 °C from 100 bar to 60 bar, a liquid phase containing 40% CO₂ and 60% styrene and a gas phase existing of ~99% CO₂ and ~1% styrene appear. In terms of flow rates and concentrations the mixture is separated into a gas stream of 3035 kg CO₂/hr containing 40 ppm styrene and a liquid stream of about 24 kg/hr styrene and 15 kg/hr CO₂. The CO₂ in the liquid phase is lost for the purpose of recycling. Decreasing pressure below 60 bar and/or increasing temperature above 35 °C

decreases the amount of liquid CO₂ in the waste stream. The concentration of styrene in the gaseous CO₂ leaving the separator is very small but the CO₂ still needs to be further purified before recycling. The energy consumption and equipment costs to separate the styrene/CO₂ mixture such that the liquid phase contains less CO₂, are much higher than adding 15 kg new CO₂/hr to the recycle stream. So the operating conditions of the separation step are 35 °C and 60 bar.³ It is suggested that in the top of separation vessel a demister is included to prevent entrainment of liquid droplets.

In a second step the styrene (~40 ppm) is suggested to be removed from the gaseous CO₂ flow by means of catalytic oxidation with oxygen (stoichiometric amount). The styrene/CO₂ mixture is led over a fixed bed of Platinum (Pt) catalyst on a silica or alumina support in a nitrogen-free environment. The styrene is completely converted into CO₂ and H₂O. The oxidation is exothermic but requires some heat to start. The operating conditions in the oxidation step have been chosen at 60 bar and 80 °C. The amount of catalyst needed has been estimated at 180 kg when the $M_{\text{cat}}/\phi_{\text{styrene} + \text{O}_2}$ ratio is approximately 1 g/molhr⁻¹ (for a production capacity of 50 kt PS latex (45% solids)/yr). For more information concerning the catalytic oxidation step the reader is referred to specialized literature (Seki, 2009, Evonik Industries, 2011).

The purified latex or raffinate phase contains 1 ppm styrene but is still swollen with CO₂ at a pressure of 100 bar. Depressurizing the CO₂-swollen latex is a key and delicate step as the colloidal stability of the latex may change under pressure relief, *i.e.* foaming, coagulation, etc.. These concerns are addressed in the next chapter.

Process flow diagram

Figure 11 shows the process flow diagram (PFD) for the reduction of the residual styrene content in a PS latex from 10⁴ ppm to 1 ppm by extraction with high pressure CO₂. The

³ In the available binary phase diagrams of styrene-CO₂ increasing the temperature to 75 °C (at 100 bar) (Suppes, 1989, Akgun, 2004) also creates a phase separation into a liquid phase containing 40 % CO₂ but it appears that the mixture existing out of 98% CO₂ is homogeneous at these conditions and phase separation will not occur. Accurate experimental data are necessary to verify this observation. When a phase separation of 40 % liquid and 99.5% gaseous CO₂ can be achieved at 75 °C and 100 bar, the recompression of the CO₂ recycle and therefore also the expensive compressor are no longer required. The overall cost and energy consumption decreases in comparison to the processes presented in the present section.

respective streams entering and leaving the various pieces of equipment are indicated in Figure 11a. The required work or power to heat or compress the streams are also given in this figure, based on the information in Table 6.

Figure 11a Process flow diagram for the reduction of residual styrene in polystyrene latex from 10^4 ppm to 1 ppm by extraction with scCO_2 at 100 bar and 35°C . a) heat exchanger 1, b) pump, c) extraction column, d) heat exchanger 2, e) heat exchanger 3, f) pressure reducer, g) separator with demister, h) heat exchanger 4, i) catalytic oxidation, j) compressor. Green line represents latex circuit; black line represents CO_2 circuit; red line represents the O_2 stream.

Two separate circuits are distinguished in the PFD: one for latex and one for (sc)CO₂. Latex enters the circuit at 1 bar and 15 °C. As the extraction conditions are 100 bar and 35 °C, the latex stream is heated (a) and pressurized (b). After extraction a purified latex product is obtained.

CO₂ follows a more complicated circuit. After extraction of the latex, a styrene/CO₂ mixture is obtained, leaving the extraction column at 35 °C and 100 bar. As previously mentioned, the separation step (g) requires a pressure decrease to 60 bar. In the Mollier diagram by Planck and Kuprianoff, see Appendix C, one can see that isentropic depressurizing decreases the temperature tremendously.⁴ Before separating the styrene from the CO₂, the mixture needs to be heated to 72 °C in order to allow the separator to operate at 35 °C and 60 bar. Before entering the oxidation vessel (i) an isobaric temperature increase from 35 °C to 80 °C is required. The purified CO₂ at 60 bar and 80 °C is mixed with some fresh CO₂ at 55 bar and 15 °C. The amount of fresh CO₂ is less than 1% of the total CO₂ required for extraction, so there will be no significant influence on the temperature and pressure of the recycled CO₂ stream. A compressor (j) isentropically pressurizes the CO₂ to 100 bar, increasing the temperature to 120 °C, see Mollier diagram, Appendix C. The energy flux of the CO₂ stream at 120 °C is very high, due to the relatively high heat capacity⁵ of dense CO₂, and can be used to heat the latex (a), the CO₂ at the oxidation vessel (h) and partly the CO₂ going to the styrene/CO₂ separator (d). Complementary heating the CO₂ at the separator is achieved by means of steam (e).

Figure 11b shows the complementary temperatures and pressures of the equipment in Figure 11a.

⁴ As the amount of styrene in the styrene/CO₂ mixture is so low, it has negligible influence on the behavior of CO₂.

⁵ At 100 bar at 35 °C the specific heat of CO₂ is 4.7 kJ/kg °C (deducted from the Mollier diagram, Appendix C).

Figure 11b Temperature and pressure profiles corresponding with the PFD of the reduction of residual styrene in polystyrene latex from 10^4 ppm to 1 ppm by extraction with scCO₂ at 100 bar and 35 °C shown in figure 7a. a) heat exchanger 1, b) pump, c) extraction column, d) heat exchanger 2, e) heat exchanger 3, f) pressure reducer, g) separator with demister, h) heat exchanger 4, i) catalytic oxidation, j) compressor. Green line represents the latex circuit; black line represents the CO₂ circuit; red line represents the O₂ stream.

Designing the (sc)CO₂-based extraction process, calculations have been performed assuming that the latex phase is swollen with (sc)CO₂, so the molecular diffusion coefficient of styrene in CO₂-swollen PS (D_{sty}^{PS}) is $10^{-12} \left[\frac{m^2}{s} \right]$. It is therefore suggested that the start-up of the extraction is performed semi-batch, *i.e.* (sc)CO₂ is bubbled through the partially filled column. Within a few cycles of the (sc)CO₂ flow, the latex is swollen with CO₂ and the actual continuous extraction process is started. At this point also the required operating temperatures and pressures of the equipment in every step are reached and the monomer extraction by (sc)CO₂ proceeds as described. Note that when the extraction column runs stationary, some extra column volume is needed to allow for swelling of the latex phase. To allow for a developed concentration profile in the polymer particles, *i.e.* $Fo \geq 0.1$, the contact time between the polymer particles and the (sc)CO₂ ($t_{contact, p}$) is 1 s, calculated according to

Equation 5 for 100 nm polymer particles and a diffusion coefficient ($D_{\text{CO}_2}^p$) of CO₂ in PS of $10^{-15} \text{ m}^2/\text{s}$.

Equipment sizing and costs

Table 7 summarizes the costs, characteristic dimensions and process parameters for the equipment as shown in Figure 11. The costs have been determined with the Aspen Process Economic Analyzer based on a production capacity of 50 kt PS latex (45% solids)/year. All equipment is made of stainless steel (316L) due to the corrosive properties of H₂O/CO₂ mixtures and the relatively high viscosity of the latex and the latex swollen with CO₂.

Table 7 Characteristic dimensions and purchased costs of equipment

Capacity : 50 kt PS latex (45% solids)/yr				
	Extraction column	Separator including demister	Oxidation vessel	
height [m]	4.2	1	1	
diameter [m]	1.2	0.1	0.1	
pressure [bar]	100	60	60	
temperature [°C]	35	35	80	
f.o.b. price* [k€]	614	45	45	
material costs [#] [k€]	175	51	51	

	Compressor	Pump
total power [kW]	31	20
f.o.b. price* [k€]	390	20
material costs [#] [k€]	40	12

	Heat exchanger (a)	Heat exchanger (d)	Heat exchanger (e)	Heat exchanger (h)
duty [kW]	80.5	76.3	80.5	60.5
A [m ²]	4.5	3.2	2.1	1.5
f.o.b. price* [k€]	39	34	18	22
material costs [#] [k€]	72	103	41	89

* f.o.b. price stands for free on board price, *i.e.* the price of the equipment without installation costs

[#] the material costs include piping, instrumentation, insulation, etc.

The total investment costs include materials for installation, *i.e.* piping, instrumentation, insulation, etc., and labor costs. Table 8 generates the investment costs for the high pressure CO₂ extraction of residual monomer from 6000 kg PS latex (45% solids)/hr ($\cong$ 50 kt/yr).

Table 8 Investment costs for the reduction of the residual monomer concentration in PS latex from 10⁴ ppm to 1 ppm by extraction with (sc)CO₂ at 100 bar and 35 °C for a production capacity of 50 kt PS latex (45% solids)/yr.

	costs [M€]	Depreciation over 5 years [k€/yr] [€/ton latex]		Depreciation over 10 years [k€/yr] [€/ton latex]	
f.o.b. price*	1.2				
material costs	0.7				
labor costs	0.2				
Total investment costs	2.1[M€]	417 [k€/yr]	8[€/ton latex]	208 [k€/yr]	4 [€/ton latex]

* f.o.b. price stands for free on board price, *i.e.* the price of the equipment without installation costs

Table 9 collects the utility costs of the extraction process for a production capacity of 50 kt PS latex (45% solids)/yr. The utility costs have been calculated based on price lists for steam and electricity from DACE (2009), the CO₂ price was delivered by Linde Gas Benelux, the costs for the Pt/Al₂O₃ catalyst has been estimated based on a price list from Evonik (2011). The costs for the O₂ used in the oxidation step are not included due to the low consumption. The start up costs for CO₂ have been included.

Table 9 Utility costs for the reduction of the residual monomer concentration in PS latex from 10⁴ ppm to 1 ppm by extraction with (sc)CO₂ 100 bar and 35 °C for a production capacity of 50 kt PS latex (45% solids)/yr. (see Figure 11a)

	unit price	amounts	Costs [k€/yr]	Costs [€/ton latex]
electricity	0.14 €/kWh	51 kW	57.1	1.14
CO ₂ *	20 €/ton	3.05 ton/yr	61 * 10 ⁻³	1 * 10 ⁻³
		15 * 10 ⁻³ ton/hr	2.4	0.05
steam (1 bar, 100 °C)	30 €/ton	128 * 10 ⁻³ ton/hr	31	0.61
catalyst	3500 €/kg	180 kg/yr	630	12.6
Total utility costs			720	14.4

* The CO₂ amount used in the extraction process is based on a production capacity of 50 kt PS latex (45% solids)/yr, without disruptions, *i.e.* cleaning of the equipment is performed once a year. In practice it is suggested the equipment is cleaned more often. The CO₂ start up cost of 61 €/start up cycle then has to be included in the overall utility cost. Note, however, that the CO₂ start up cost is negligible compared to the overall utility costs.

In the first 5 years of the (sc)CO₂ based extraction process reducing residual monomer level in PS latex from 10⁴ ppm to 1 ppm, the purification of the latex costs 22 €/ton latex. When the investment costs are recovered, the cost of the extraction of the residual monomer from the latex decreases to 14 €/ton latex.

Note that for a residual monomer reduction from 10⁴ ppm to 100 ppm or to 10 ppm, the costs for the purification of the latex are in the same range as for a reduction to 1 ppm. The higher the allowed residual monomer concentration in the latex phase after extraction, the less CO₂ required to perform the extraction, resulting in lower residence times needed, *i.e.* shorter columns. The difference in CO₂ needed to reduce the monomer concentration from 10⁴ ppm to 100 ppm, to 10 ppm or to 1 ppm, however, is small⁶, not affecting the total investment or utility costs.

Steam stripping

Englund (1981) gives an overview of several types of latex strippers. The author reports reducing the residual monomer level in latex with steam stripping is usually performed batch wise, due to its simplicity and ease of operation. A batch of latex is charged into a simple tank and steam is sparged through the latex at a certain flowrate, limited by foaming. Defoaming agents are often used to suppress foaming (Kelley *et al.*, 1978). Batch strippers normally operate at 80-90% efficiency, but the amount of steam needed is higher than for continuous countercurrent stripping. Englund (1981) states that for batch stripping the frequency by which fresh steam bubbles contact the polymer particles is rate limiting. The author refers to several patents for a description of a continuous countercurrent stripper. Batch wise stripping as well as continuous countercurrent stripping for the reduction of residual monomer level in PS latex from 10⁴ ppm to 100 ppm are shortly discussed here.

⁶ The amount of CO₂ required for residual monomer reduction in PS latex from 10⁴ ppm to 100, 10 or 1 ppm, are 3000, 3022 and 3024 kg/hr, respectively. The value of the CO₂ stream indicated in the present work is somewhat higher to account for the CO₂ that dissolves in the H₂O phase.

Batch operation

The steam flow rate required for stripping a batch of 30 ton (45 % solids) PS latex in approximately 5 hours (*i.e.* 6000 kg/hr) to reduce residual monomer from 10^4 ppm to about 100 ppm has been calculated according to Equation 27 (r_s from B. Odedra, Synthomer, UK, personal communication) .

$$\phi_{\text{steam}} = M_{\text{dry solids}} * r_s \quad (27)$$

r_s stands for the steam mass flow rate per kg dry solids.

Assuming that stripping is performed at 90% efficiency, the required steam flow rate is 1700 kg/hr, calculated with Equation 27. In 5 hours a total amount of 8500 kg steam is needed to reduce the residual monomer from 10^4 ppm to 100 ppm. The steam hold up in the latex is usually about 10-20 % [m^3 steam bubbles/ m^3 vessel) (Kantarci, 2005). The total liquid volume in the stripping vessel at 20 % steam hold up becomes 38 m^3 . Englund (1981) emphasizes that the batch stripping vessel is usually considerably larger than the liquid load to allow for foaming. Assuming that the stripping vessel is enlarged by 50 % of the liquid load, a tank of 57 m^3 is needed. To operate the stripping vessel in the homogeneous bubble flow regime, the superficial gas velocity needs to be smaller than 0.05 m/s (Kantarci, 2005). The superficial gas velocity is defined as the ratio of the volumetric flow rate and the cross-sectional area of the vessel. The density of steam at 100°C is 0.6 kg/m^3 (Perry, 1999). The tank diameter for a superficial gas velocity of 0.05 m/s then is 2.2 m; the height of the vessel is 14.5 m.

The latex batch, before stripping is started, is at 15°C (*i.e.* latex from the polymerization reaction is kept in a storage vessel). The steam at 100°C is partly used for heating the latex, *i.e.* 170 kg/hr or 850 kg steam during 5 hours of stripping (see Appendix D). So 10% of the steam is used as heating source. As 10% is a significant part of the steam consumption, it is added in the total steam flow required for stripping the latex.

Figure 12 illustrates the simple batch stripping vessel.

Figure 12 Batch stripping vessel

The steam containing the residual monomer has been chosen to be purified in a water treatment facility.

Continuously operated countercurrent stripping unit

Englund (1981) reports that the steam required to reduce residual monomer from 10^4 ppm to 100 ppm in a continuous countercurrent stripping vessel is less than the amount of steam used in the batch stripping vessel. Assuming a throughput of 6000 kg PS latex/hr, the number of theoretical stages is determined with the stage-to-stage calculation according to Equation 2. Note that the monomer partition coefficient (K_{mon}) for the distribution of styrene between the polymer particles and the steam decreases with decreasing residual monomer concentration in the polymer particles, *i.e.* $K_{\text{mon}} \downarrow$ when $N_{\text{ts}} \uparrow$, where N_{ts} stands for the number of theoretical stages. Table 10 shows the relation between the steam flow rate and the number of equilibrium stages.

Table 10 Required number of theoretical stages in function of the steam flow rate for a residual monomer reduction from 10^4 ppm to 100 ppm.

steam flow rate $\left[\frac{\text{kg}}{\text{hr}}\right]$	number of theoretical stages, N_{ts} [-]
1700	13
1500	17
1400	23
1300	44

Decreasing the steam flow rate increases the number of equilibrium stages needed to obtain the same reduction in residual monomer. A further decrease in steam flow rate results in unrealistic numbers of stages and is therefore not shown. Estimating the height equivalent to one theoretical stage to be 35 cm – the same value as has been found in the CO₂ extraction process – the stripping vessel is 15.4 m high for a steam flow rate of 1300 kg/hr. For a superficial gas velocity of 0.05 m/s (Kantarci, 2005) the column diameter has been calculated to be 2.2 m.

Figure 12a shows the process flow diagram (PFD) for reduction of residual styrene by continuous countercurrent stripping with steam.

Figure 12a Process flow diagram (PFD) for reduction of residual styrene from 10⁴ ppm to ~100 ppm by continuous countercurrent stripping with steam. a) pump, b) heat exchanger, c) stripper.

In the PFD a pump is included to pressurize the latex from 1 to 1.3 bar, to overcome the pressure drop inside the stripper. The latex flow is heated to the temperature of the stripping vessel, *i.e.* 100 °C by the steam flow entering the column for stripping the latex. Therefore somewhat more steam is required, *i.e.* 655 kg steam/hr for heating the latex (see Appendix

D). Figure 12b shows the complementary pressures and temperatures corresponding to the PFD, Figure 12a.

Figure 12b Temperature and pressure profiles for reduction of residual styrene from 10^4 ppm to about 100 ppm by continuous countercurrent stripping with steam corresponding to the PFD shown in figure 12a. a) pump, b) heat exchanger, c) stripper.

Similar to batch steam stripping the steam containing styrene is led to a water treatment facility.

In the stripping vessels discussed above the residual monomer level in the latex was reduced from 10^4 ppm to 100 ppm. For some latex products a reduction to 60 ppm residual monomer is possible (Araújo *et al.*, 2002). Reduction to lower levels of residual monomer is hardly possible mainly due to thermodynamic (and to some extent transport) limitations. The monomer activity coefficient in the polymer particles and as a consequence the equilibrium monomer vapor pressure are very low at high conversions ($X > 99\%$). Consequently, monomer partitioning between the polymer phase and the steam phase is very low towards the vapor phase, see Equation 28.

$$y * P_{\text{total}} = \gamma_m * x_m * P_m^{\text{sat}} \quad (28)$$

In contrast to the CO₂ extraction process, where the polymer phase is swollen with scCO₂ increasing the monomer activity coefficient in the polymer phase, the partition coefficient for steam stripping decreases with decreasing volume of the total amount of low molecular weight species in the polymer phase see Chapter 1, Figure 1. At low monomer volume fraction there is hardly any driving force for monomer anymore to diffuse to the vapor phase. Moreover, the molecular diffusion coefficient of monomer in the polymer phase is very low ($D_m^p = 10^{-15} \left[\frac{\text{m}^2}{\text{s}} \right]$), i.e. a high mass transfer resistance in the particle phase.

Table 11 shows steam flow rates as a function of the number of equilibrium stages for a monomer reduction from 10⁴ to 10 ppm not taking into account the thermodynamic as well as the transport limitation discussed above.

Table 11 Required number of theoretical stages in function of the steam flow rate for a residual monomer reduction from 10⁴ to 10 ppm.

steam flow rate $\left[\frac{\text{kg}}{\text{hr}} \right]$	number of theoretical stages, N_{ts} [-]
15000	13
12000	20
11000	45

Equipment sizing and evaluation

Table 12 summarizes the characteristic dimensions, process parameters and costs for the continuous steam stripping of residual monomer from PS latex, reducing the monomer level from 10⁴ ppm to about 100 ppm. The costs have been determined with Aspen Process Economic Analyzer based on a production capacity of 50 kt PS latex (45% solids)/yr. Stainless steel (316L) has been chosen as construction material.

Table 12 Characteristic dimensions and purchased costs of equipment

	column		heat exchanger		pump
height [m]	15.4	duty [kW]	411	total power [kW]	0.06
diameter [m]	2.2	A [m ²]	4.8	f.o.b. price* [k€]	17
pressure [bar]	1	f.o.b.price* [k€]	10	material costs [#] [k€]	11
temperature [°C]	100	material costs [#] [k€]	41		
f.o.b.price* [k€]	423				
material costs [#] [k€]	177				

* f.o.b. price stands for free on board price, *i.e.* the price of the equipment without installation costs

[#] the material costs include piping, instrumentation, insulation, etc.

The total investment costs include materials for installation, *i.e.* piping, instrumentation, insulation, etc., as well as labor costs. Table 13 gives the investment costs for the reduction of residual monomer from 10⁴ ppm to about 100 ppm with continuous steam stripping of 6000 kg PS latex/hr.

Table 13 Investment costs for the reduction of the residual monomer concentration in PS latex from 10⁴ ppm to 100 ppm with 100 °C steam for a production capacity of 50 kt PS latex (45% solids)/yr.

	costs [k€]	Depreciation over 5 years		Depreciation over 10 years	
		[k€/yr]	[€/ton latex]	[k€/yr]	[€/ton latex]
f.o.b. price*	450				
material costs	229				
labor costs	96				
Total investment costs	775 [k€]	155 [k€/yr]	3[€/ton latex]	77.5 [k€/yr]	2 [€/ton latex]

* f.o.b. price stands for free on board price, *i.e.* the price of the equipment without installation costs

Table 14 collects the utility costs of the steam strip process for a production capacity of 50 kt PS latex (45% solids)/yr. The utility costs have been calculated based on price lists for steam and electricity from DACE (2009).

Table 14 Utility costs for the reduction of the residual monomer concentration in PS latex from 10^4 ppm to 100 ppm with 100 °C steam for a production capacity of 50 kt PS latex (45% solids)/yr.

	unit price	amount	Costs [k€/yr]	Costs [€/ton latex]
electricity	14 ct/kWh	0.061 kW	0.07	0.001
steam	30 €/ton	1.96 ton/hr	469	9.38
Total utility costs			718.9	9.39

In the first 5 years of the steam stripping process reducing residual monomer level in PS latex (45% solids) from 10^4 ppm to 100 ppm, the cost of purifying the latex by stripping the residual monomer content with steam is 12 €/ton latex. When the investment costs are recovered, the cost of the stripping process decreases to 9 €/ton latex.

Note that when a residual monomer reduction from 10^4 to 10 ppm would be thermodynamically possible (within time limits), the utility costs of the steam consumption will tremendously increase as compared to the costs for a monomer reduction from 10^4 to 100 ppm.. For a steam flow rate of 15000 kg steam/hr, the utility costs for steam are 75 €/ton latex.

Extraction of residual monomer with (sc)CO₂ extraction in comparison to steam stripping

The purification costs per ton latex for the steam stripping process and the (sc)CO₂-based extraction process to reduce residual monomer in PS latex from 10^4 ppm to 100 ppm for a production capacity of 50 kt PS latex (45% solids)/yr, are respectively 12 and 22 €/ton latex in the period the investment costs are recovered. After a depreciation time of 5 years, the price for steam stripping is 9 €/ton latex, whereas the cost for the (sc)CO₂ based extraction process is 14 €/ton latex. The (sc)CO₂-based extraction process reduces the residual monomer level to 1 ppm for the same price as a reduction to 100 ppm or to 10 ppm. Steam stripping, however, reduces the residual monomer level in the latex to only about 100 ppm or somewhat lower, but certainly not to a level of 1 ppm.

Concluding remarks

Extraction with CO₂ to reduce residual monomer from 10⁴ ppm to 1 ppm in a countercurrent extraction process in a column has been designed. Latex has been chosen as the continuous phase in which 1 mm CO₂ bubbles are dispersed with a hold up of 20 %. The column is operated at 100 bar and 35 °C. The partition coefficient of monomer between the CO₂-swollen polymer particles and the CO₂ phase is a key parameter in the performance of the liquid-liquid extraction column in terms of the degree of residual monomer reduction. Due to the plasticizing effect of (sc)CO₂ the time constant for mass transport of monomer inside the polymer particles decreases tremendously compared to non swollen polymer particles. The mass transport mechanism is governed by the shuttle effect, due to the Brownian motion of the polymer particles from and to the H₂O/CO₂ interface. A column volume of 4.75 m³ applies for a throughput of 6000 kg PS latex (45% solids)/hr.

The extraction process reducing the residual monomer costs 22 €/ton latex for a production capacity of 50 kt PS latex (45% solids)/yr (for a reduction from 10⁴ to 100 ppm, to 10 ppm or to 1 ppm). Continuous steam stripping to reduce the residual monomer level in the latex from 10⁴ ppm to 100 ppm only costs 12 €/ton latex. The lowest residual monomer concentration in latex of 1 ppm can certainly only be achieved by extraction with (sc)CO₂.

References

- M. Akgün, D. Emel, N. Baran, N. A. Akgün, S. Deniz, S. Dinçer, "Styrene-carbon dioxide phase equilibria at high pressures", *J. Supercritical Fluids*, **2004**, 31, 27-32
- H. E. A. van den Akker, "Liquid-liquid spray columns – Hydrodynamic stability and reduction of axial mixing", PhD Thesis, **1978**, Eindhoven University of Technology, The Netherlands
- H. E. A. van den Akker, R. F. Mudde, E. Stammers, "Fysische transportverschijnselen: 200 vraagstukken", **1997**, 2nd ed., Delft University Press, The Netherlands
- E. Alper, B. Wichtendahl, W.-D. Deckwer, "Gas absorption mechanism in catalytic slurry reactors", *Chem. Eng. Sci.*, **1980**, 35, 217-222
- S. Alsoy, J. L. Duda, "Supercritical devolatilization of polymers", *AIChE*, **1998**, 44, 3, 582-590
- P. H. H. Araújo, C. Sayer, J. G. R. Poço, R. Guidici, "Techniques for reducing residual monomer content in polymers: A review", *Polym. Eng. Sci.*, **2002**, 42, 7
- A. A. C. M. Beenackers, W. P. M. Van Swaaij, "Mass transfer in gas-liquid slurry reactors, a review article", *Chem. Eng. Sci.*, **1993**, 48, 18, 3109-3139
- R. B. Bird, W. E. Stewart, E. N. Lightfoot, "Transport phenomena", **2002**, 2nd edition, J. Wiley and sons Inc., New York
- D. W. Brilman, W. P. M. van Swaaij, G. F. Versteeg, "A one-dimensional instationary heterogeneous mass transfer model for gas absorption in multiphase systems", *Chem. Eng. and Process.*, **1998**, 37, 471-488
- C. H. Chon, K. D. Kihm, "Empirical correlation finding the role of temperature and particle size for nanofluid (Al_2O_3) thermal conductivity enhancement", *Appl. Phys. Lett.*, **2005**, 87, 153107, 1-3
- A. B. De Haan, H. Bosch, "Fundamentals of industrial separations", **2007**, 2nd edition, The Netherlands
- Dutch Association of Cost Engineers (DACE), "Prijzenboekje", 27th ed., **2009**
- E. Dumont, H. Delmas, "Mass transfer enhancement of gas absorption in oil-in-water systems: a review", *Chem. Eng. and Process.*, **2003**, 42, 419-438
- S. M. Englund, "Monomer removal from latex", *Chem. Eng. Progr.*, **1981**, 55-59; and references therein
- J. van Deuren, T. Lloyd, S. Chhetry, R. Liou, J. Peck, Federal Remediation Technologies Roundtable, "Remediation technologies screening matrix and reference guide", 4th ed., **2002**, Washington
- R. G. Gilbert, "Emulsion polymerization, A mechanistic approach", Academic Press, **1995**
- J. C. Godfrey, M. J. Slater (Eds.), "Liquid-liquid extraction equipment", **1994**, J. Wiley and sons Inc., New York
- C. Gourdon, G. Casamatta, G. Muratet, "Population balance based modeling of solvent extraction columns" in "Liquid-liquid extraction equipment", eds. J. C. Godfrey, M. J. Slater, **1994**, J. Wiley and sons Inc., New York

- S. J. Jang, "Role of Brownian motion in the enhanced thermal conductivity of nanofluids", *Appl. Phys. Lett.*, **2004**, 84, 21, 4316
- C. Joly-Vuillemin, C. Bellefon, "Solids effects on gas-liquid", *Chem. Eng. Sci.*, **1999**, 51, 10, 2149-2158
- N. Kantarci, F. Borak, K. O. Ulgen, "Review: Bubble column reactors", *Proc. Biochem.*, **2005**, 40, 2263-2283
- E. L. Kelley, R. W. Harrison, B. B. Harris, "Defoamers: their theory and application with regard to the paint industry", *Polym., Paint and Colour J.*, **1978**, 168, 734
- M.F. Kemmere, M. Cleven, M. A. van Schilt, J. T. F. Keurentjes, "Process design for the removal of residual monomer from latex products using supercritical carbon dioxide", *Chem. Eng. Sci.*, **2002**, 57, 3929-3937
- A. Kumar, S. Hartland, "Empirical prediction of operating variables" in "Liquid-liquid extraction equipment", eds. J. C. Godfrey, M. J. Slater, **1994**, J. Wiley and sons Inc., New York
- A. Kumar, S. Hartland, "Unified correlations for the prediction of drop size in liquid-liquid extraction columns", *Ind. Eng. Chem. Res.*, **1996**, 35, 2682-2695
- W. L. McCabe, J. C. Smith, P. Harriott, "Unit operations of chemical engineering", **2001**, 6th edition, McGraww-Hill, New York
- J. H. Perry, Chapter 15, "Liquid-liquid extraction equipment" in "Chemical Engineer's Handbook", **1999**, McGraw-Hill, New York
- J. F. Richardson, W. N. Zaki, "Sedimentation and fluidization: part 1", *Trans. Inst. Chem. Eng.*, **1954**, 32, 35
- C. A. Scholtens, J. Meuldijk, A. A. H. Drinkenburg, "Production of copolymers with a predefined intermolecular chemical composition distribution by emulsion polymerisation in a continuously operated reactor", *Chem. Eng. Sci.*, **2001**, 56, 955
- W. D. Seider, J. D. Seader, D. R. Lewin, Widagdo, "Product and process design principles – Synthesis, analysis and evaluation", 3th ed., **2010**, John Wiley and sons Inc., USA
- T. Seki, B. Alfons, "Catalytic oxidations in dense carbon dioxide", *Chem. Rev.*, **2009**, 109, 6, 2409-2454
- M. J. Slater, "Rate coefficients in liquid-liquid extraction systems", in "Liquid-liquid extraction equipment", eds. J. C. Godfrey, M. J. Slater, **1994**, J. Wiley and sons Inc., New York
- G. J. Suppes, M. McHugh, "Phase behavior of the carbon dioxide-styrene system", *J. Chem. Eng. Dat.*, **1989**, 34, 310-312
- S. Torza, S. G. Mason, "Three-phase interactions in shear and electrical fields", *J. Colloid Interface Sci.*, **1970**, 33, 1, 67-83
- H. Vinke, P. J. Hamersma, J. M. H. Fortuin, "Enhancement of the gas-absorption rate in agitated slurry reactors by gas-absorbing particles adhering to gas bubbles", *Chem. Eng. Sci.*, **1993**, 48, 12, 2197-2210
- G. B. Wallis, "One-dimensional two-phase flow", **1969**, McGraww-Hill, New York
- J. Welty, C. E. Wicks, R. E. Wilson, "Fundamentals of momentum, heat, and mass transfer", **2001**, 4th ed., Wiley, Chichester

J. A. Wesselingh, "The velocity of particles, drops and bubbles", *Chem. Eng. Process.*, **1987**, 21, 9-14

M. Xu, J. A. Finch, A. Uribe-Salas, "Maximum gas and bubble surface rates in flotation columns", *Inter. J. Miner. Process.*, **1991**, 32, (3/4), 233

S. X. Zhang, W. H. Ray, "Modeling and experimental studies of aqueous suspension polymerization processes. 3. Mass transfer and monomer solubility effects", *Ind. Eng. Chem. Res.*, **1997**, 36, 1310-1321

J. Zhang, L. Gao, X. Zhang, B. Zong, T. Jiang, B. Han, "Phase behaviors, density, and isothermal compressibility of styrene + CO₂, ethylbenzene + CO₂, and ethylbenzene + styrene+ CO₂ systems", *J. Chem. Eng. Data*, **2005**, 50, 1818-1822

Appendix A

According to Newton's second law, three forces act on a (free falling) rigid sphere moving through a liquid (stationary momentum balance) (De Haan, 2007, McCabe, 2001):

$0 = \text{external force} - \text{buoyant force} - \text{drag force}$

$$0 = F_G - F_B - F_D \quad (\text{A.1})$$

The external force is in this case the gravitational force, the buoyant force is a force acting parallel with the external force but in opposite direction, and the drag force appears whenever there is relative motion between the spheres and the liquid.

$$F_G - F_B = m_{\text{sphere}} * g - V_{\text{sphere}} * \rho_{\text{liquid}} * g = \frac{\pi * d_{\text{sphere}}^3}{6} * (\rho_{\text{sphere}} - \rho_{\text{liquid}}) * g \quad (\text{A.2})$$

The drag force is caused by the shear stresses at the surface of a particle moving through a viscous liquid as well as in eddies in a possible wake and is generally described with a drag coefficient, Equation A.3.

$$F_D = C_D * A_{\perp} * \frac{1}{2} * \rho_{\text{liquid}} * v^2 = C_D * \left(\frac{\pi * d_{\text{sphere}}^2}{4} \right) * \frac{1}{2} * \rho_{\text{liquid}} * v^2 \quad (\text{A.3})$$

The force balance, Equation A.1, then becomes

$$0 = \frac{\pi * d_{\text{sphere}}^3}{6} * (\rho_{\text{sphere}} - \rho_{\text{liquid}}) * g - C_D * \left(\frac{\pi * d_{\text{sphere}}^2}{4} \right) * \left(\frac{1}{2} * \rho_{\text{liquid}} * v^2 \right) \quad (\text{A.4})$$

The terminal settling velocity is defined in Equation A.5:

$$v_{\infty} = \sqrt{\frac{4 * (\rho_{\text{sphere}} - \rho_{\text{liquid}}) * g * d_{\text{sphere}}}{3 * \rho_{\text{liquid}} * C_D}} \quad (\text{A.5})$$

For low Reynolds numbers, (*i. e.* $Re = \frac{v_{\infty} * d_{\text{dispersed phase}} * \rho_{\text{continuous phase}}}{\mu_{\text{continuous phase}}} < 1$, creep flow) the drag coefficient for rigid spheres is $C_D = \frac{24}{Re}$ (Bird *et al.*, 2002).

The terminal rising (*i.e.* = – settling velocity) velocity of a CO₂ bubble then becomes:

$$v_{\infty} = \frac{-(\rho_{\text{CO}_2 \text{ bubble}} - \rho_{\text{latex}}) * 9.81 * d_{\text{CO}_2}^2}{\mu_{\text{latex}}} \quad (\text{A.6})$$

Table A.1 gives the physical constants of the dispersed CO₂ phase as well as of the continuous latex phase used to calculate the terminal rising velocity (v_{∞}) of a CO₂ bubble.

Table A.1 Physical constants of CO₂ as well as of PS latex used to calculate the terminal rising velocity of a CO₂ bubble through the latex.

$\rho_{\text{CO}_2 \text{ bubble (35 } ^\circ\text{C, 100 bar)}}$	720 kg/m ³
ρ_{latex}	1020 kg/m ³
$d_{\text{CO}_2 \text{ bubble}}$	10 ⁻³ m
μ_{latex}	64 mPas

The terminal rising velocity becomes:

$$v_{\infty} = 3 * 10^{-3} \frac{\text{m}}{\text{s}} \quad (\text{A.7})$$

Note that the Reynolds number is indeed < 1, see Equation A.8.

$$\text{Re} = \frac{v_{\infty} * d_{\text{dispersed phase}} * \rho_{\text{continuous phase}}}{\mu_{\text{continuous phase}}} = \frac{3 * 10^{-3} * 10^{-3} * 1020}{64 * 10^{-3}} \cong 0.05 \quad (\text{A.8})$$

The rising velocity of the bubble swarm in the column according to Equation A.9 is:

$$v_s = v_{\infty} * (1 - \varepsilon_d)^{n-1} \quad (\text{A.9})$$

where n depends on Re, see Equations 21-24, and has a value of 4.65 for the Reynolds number of 0.05, see Equation A.8. For a CO₂ hold up of 20% [m³ CO₂ bubbles/m³ column] in the column, v_s becomes:

$$v_s = 3 * 10^{-3} * (1 - 0.2)^{4.65-1} \cong 1 * 10^{-3} \frac{\text{m}}{\text{s}} \quad (\text{A.10})$$

Appendix B

In this appendix the process flow diagram (PFD), Figures 11a and 11b, is explained into detail. The annotation used in this section corresponds to that in the respective figures.

1. Extraction column (c)

The extractor, 1.2 m in diameter and 4.2 m high, is operated at 100 bar and 35 °C. The overall heat balance over the extraction column is expressed in Equation B.1:

$$\phi_q(\text{column}) = \phi_{m, \text{CO}_2} * C_{p, \text{CO}_2} * \Delta T + \phi_{m, \text{latex}} * C_{p, \text{latex}} * \Delta T + \phi_q \quad (\text{B.1})$$

where $\phi_{m, i}$, $C_{p, i}$ and ϕ_q stand for the mass flow rate of phase i , for the specific heat of phase i and for the heat flow lost to the surroundings. To prevent temperature gradients inside the column due to cooling by the surrounding air, it is insulated with e.g. mineral wool. The air temperature is assumed to be 15 °C. The heat flow rate from the extraction column to the surroundings follows from Equation B.2. Note that the resistances against heat transfer from the liquid in the column to the wall of the column as well as from the wall to the surrounding air have been neglected.

$$\phi_q = U * A * \Delta T \quad (\text{B.2})$$

where U and A stand for the overall heat transfer coefficient and the column area respectively. Mineral wool has a thermal conductivity coefficient (λ) of $0.0523 \left[\frac{\text{W}}{\text{m} \cdot ^\circ\text{C}} \right]$ (Perry, 1999). An estimation of the overall heat transfer coefficient for mineral wool follows from Equation B.3,

$$U = \frac{\lambda}{\delta_{\text{insulation}}} \left[\frac{\text{W}}{\text{m}^2 \cdot ^\circ\text{C}} \right] = 1 \left[\frac{\text{W}}{\text{m}^2 \cdot ^\circ\text{C}} \right] \quad \text{for an insulation thickness of 5 cm} \quad (\text{B.3})$$

The resulting heat flow rate from the liquid in the column to the surrounding air then becomes:

$$\phi_q = 1 * \left(\frac{\pi * 4.2 * 1.2^2}{4} \right) * (35 - 15) [\text{kW}] \cong 0.32 [\text{kW}] \quad (\text{B.4})$$

Table B.1 gives the physical constants of latex as well as of CO₂ at 100 bar at 35 °C.

Table B.1 Flow rates and physical constants of latex as well as of CO₂ at 100 bar at 35 °C

	ϕ_m		ρ kg/m ³	C_p kJ/kg °C
	kg/hr	kg/s		
latex	6000	1.67	1020	2.9
CO ₂	3050	0.85	720	4.7

As the mass flow rate as well as the specific heat⁷ inside the column is known, the temperature loss to the environment easily follows from Equation B.5:

$$\Delta T = \frac{\phi_q}{\phi_{CO_2+latex} * C_{p, CO_2+latex}} = \frac{0.32}{2.52 * 3.5} \text{ °C} \cong 0.04 \text{ °C} \quad (B.5)$$

So heat loss from the extraction unit to the environment is negligible.

2. Pump (b)

6000 kg PS latex/hr is delivered at 15 °C at 1 bar. Before entering the extraction column the latex has to be pressurized to 100 bar and heated to 35 °C. For pressurizing the latex from 1 bar to 100 bar, a plunger pump has been chosen. The shaft work required for pressurizing the latex has been calculated with Equation B.6:

$$\phi_{w,shaft}(pump) = \phi_{m,latex} * \frac{P_2 - P_1}{\rho_{latex}} \quad (B.6)$$

where $\phi_{m,latex}$ and ρ_{latex} stand for the mass flow and density of latex, see Table B.1. The shaft work of the pump then becomes:

$$\phi_{w,shaft}(pump) = 1.67 * \frac{100-1}{1020} * 10^5 \text{ [W]} = 16.2 \text{ [kW]} \quad (B.7)$$

Pressurizing heated latex increases the chance on fouling inside the pump. Regularly cleaning has to be taken into account.

It is assumed the pump works at 80% of its efficiency, so

$$\phi_{w,tot}(pump) = \frac{\phi_{w,shaft}(pump)}{0.8} \cong 20.3 \text{ kW} \quad (B.8)$$

⁷ Inside the extraction column the total mass flow rate is 9050 kg/hr (= 2.52 kg/s) being 34 % CO₂, with a specific heat of 4.7 [kJ/kg °C] (deducted from Mollier diagram) and 66 % latex, with a specific heat of 2.9 [kJ/kg °C] (Perry, 1999). Then the specific heat of the CO₂/latex mixture is 3.5 [kJ/kg °C].

20% of the work the pump delivers is dissipated in heat. Assuming that all the heat dissipated is transferred to the latex, a temperature rise of the latex follows from Equation B.9.

$$\Delta T = \frac{0.2 * \phi_{w, \text{tot}} (\text{pump})}{\phi_{m, \text{latex}} * C_{p, \text{latex}}} \cong 0.8 \text{ }^{\circ}\text{C} \quad (\text{B.9})$$

The latex still has to be heated by 19.2 °C, see heat exchanger (a).

3. Compressor (j)

The energy balance for the adiabatically operating compressor is expressed in Equation B.10.

$$\phi_{w, \text{shaft}} (\text{compressor}) = \phi_{m, \text{CO}_2} * \Delta \left(u + \frac{p}{\rho} \right) = \phi_{m, \text{CO}_2} * \Delta h \quad (\text{B.10})$$

3050 kg CO₂/hr enters the compressor at 80 °C and 60 bar. The extraction conditions have been chosen at 35 °C and 100 bar, so CO₂ needs to be compressed and cooled. According to the Mollier diagram, Appendix C, isentropic compression (*i.e.* $s = 1.25 \text{ kcal/}^{\circ}\text{C}$) from 60 to 100 bar requires 29.3 kJ/kg (*i.e.* 7 kcal/kg).

$$\phi_{w, \text{shaft}} (\text{compressor}) = 0.85 * 29.3 \text{ [kW]} \cong 25 \text{ [kW]} \quad (\text{B.11})$$

At 80 % efficiency, the total power the compressor needs is

$$\phi_{w, \text{tot}} (\text{compressor}) = \frac{25}{0.8} \text{ [kW]} \cong 31 \text{ [kW]} \quad (\text{B.12})$$

At the same time due to the isentropic compression the temperature of the CO₂ rises to 120 °C. Isobaric cooling of the CO₂ flow from 120 °C to 35 °C, generates 256 kJ/kg (*i.e.* 61 kcal/kg), which can be used to heat the latex and CO₂ flow at other stages in the process, see PFD, Figure 11, heat exchanger a, d and h.

4. Separation vessel (g)

To separate (to some extent) styrene from the CO₂ leaving the extraction column, operating conditions of the separation vessel have been chosen at 35 °C and 60 bar. The gas flow

superficial velocity (v_s) has been taken at 0.5 m/s. Table B.2 gives the physical constants used in the calculation of the required vessel surface area.

Table B.2 Flow rates and physical constants used for the calculation of the vessel area perpendicular to flow at 35 °C at 60 bar.

$\phi_{m,CO_2 + styrene}$	3074 kg/hr	0.85 kg/s
ρ_{CO_2}	300 kg/m ³	
v_s	0.5 m/s	

The vessel area perpendicular to flow ($A_{separator, \perp}$) has been calculated with Equation B.13.

$$A_{separator, \perp} = \frac{\phi_{v, CO_2 + styrene}}{v_s} \quad (B.13)$$

where $\phi_{v, CO_2 + styrene}$ stands for the volume flow of the mixture CO₂/styrene.

$$A_{separator} = \frac{0.85}{300} * \frac{1}{0.5} [m^2] \cong 60 [cm^2] \quad (B.14)$$

Including a demister, the dimensions of the separation vessel have been estimated at 0.1 m in diameter and 1 m in height.

5. Oxidation vessel

In a second separation step the styrene (~40 ppm on weight base) is suggested to be removed from the gaseous CO₂ flow by means of catalytic oxidation with pure oxygen (stoichiometric amount). The styrene/CO₂ mixture is led over a fixed bed of Platinum (Pt) catalyst on a silica or alumina support in a nitrogen free environment. The styrene is completely converted into CO₂ and H₂O. The oxidation is exothermic but requires some heat to start. The operating conditions in the oxidation step have been chosen at 60 bar and 80 °C. The amount of catalyst needed has been estimated at 180 kg when the $M_{cat}/\phi_{styrene + O_2}$ ratio is approximately 1 g/molhr⁻¹ (for a production capacity of 50 kt PS latex (45% solids)/yr). For more information concerning the catalytic oxidation step the reader is referred to specialized literature (Seki, 2009, Evonik Industries, 2011).

Table B.3 shows the properties of the components in the oxidation vessel. The gas residence time ($\tau_{\text{CO}_2 + \text{styrene} + \text{O}_2}$) in the oxidation vessel is assumed to be 1 s (van Deuren, 2002).

Table B.3 Flow rates and physical properties of the $\text{CO}_2/\text{styrene}/\text{O}_2$ mixture in the oxidation vessel at 60 bar at 80 °C.

$\phi_{\text{m,CO}_2 + \text{styrene} + \text{O}_2}$	3035 kg/hr	0.84 kg/s
ρ_{CO_2}	110 kg/m ³	
$\tau_{\text{CO}_2 + \text{styrene} + \text{O}_2}$	1 s	

The oxidation vessel volume has been calculated according to Equation B.15.

$$V_{\text{oxidation vessel}} = \phi_{V, \text{CO}_2 + \text{styrene} + \text{O}_2} * \tau_{\text{CO}_2 + \text{styrene} + \text{O}_2} \quad (\text{B.15})$$

$$V_{\text{oxidation vessel}} = \frac{0.84}{110} * 1 [\text{m}^3] \cong 7.6 * 10^{-3} [\text{m}^3] \quad (\text{B.16})$$

Including some extra space inside the vessel to prevent gas build up at any time, the dimensions of the oxidation vessel have been estimated at 0.1 m in diameter and 1 m height.

6. Heat exchangers

At three different stages in the PFD heat exchangers are necessary:

- Heating 6000 kg PS latex/hr from 15 °C to 35 °C, see Figure 11b, heat exchanger a
- Increasing temperature of 3077 kg (styrene/ CO_2) mixture/hr from 35 °C to 72 °C, see Figure 11b, heat exchangers (d) and (e)
- Heating up 3045 kg (styrene/ CO_2) mixture/hr from 35 °C to 80 °C for the catalytic oxidation, see Figure 11b, heat exchanger (i)

The power each heat exchanger need is calculated as follows:

- Heating 6000 kg PS latex/hr from 15 °C to 35 °C requires a heat flow of (see Table B.1 for the physical constants of latex)

$$\phi_{q, \text{latex}} = \phi_{\text{m, latex}} * C_{p, \text{latex}} * \Delta T \quad (\text{B.17})$$

$$\phi_{q, \text{latex}} = 1.67 * 2.9 * 20 \text{ [W]} \cong 96.7 \text{ kW} \quad (\text{B.18})$$

Pressurizing the latex flow increases its temperature by 0.8 °C. Dimensioning the heat exchanger, only 80.5 kW is required to increase the temperature from 15 °C to 34.2 °C.

- According to the Mollier diagram an isobaric temperature increase of the styrene/CO₂ mixture (see Table B.2 for the physical constants) from 35 °C to 72 °C at 100 bar corresponds to 176 kJ/kg (*i.e.* 42 kcal/kg).

$$\phi_{q, \text{CO}_2} (\text{separator}) = \phi_{m, \text{CO}_2} * \Delta h \quad (\text{B.19})$$

$$\phi_{q, \text{CO}_2} (\text{separator}) = 0.85 * 176 \text{ [kW]} \cong 150 \text{ [kW]} \quad (\text{B.20})$$

- Increasing the temperature of the styrene/CO₂ mixture (see Table B.3 for the physical constants) from 35 °C to 80 °C at 60 bar requires 71 kJ/kg (*i.e.* 17 kcal/kg).

$$\phi_{q, \text{CO}_2} (\text{oxidation vessel}) = 0.84 * 71 \text{ [kW]} \cong 60.5 \text{ [kW]} \quad (\text{B.21})$$

As mentioned in the section 3, the CO₂ after compression provides a latent heat loss of 256 kJ/kg (*i.e.* 61 kcal/kg) upon decreasing the temperature from 120 °C to 35 °C at 100 bar. In the best scenario the CO₂ latent heat loss is used to heat other streams in the following order

- At the catalytic oxidation (71 kJ/kg = 17 kcal/kg), heat exchanger (h)
The respective temperatures of the heated and cooled CO₂ flow: 35 °C → 80 °C and 120 °C → 78 °C
- At the separator (~96.4 = 23 kcal/kg), heat exchanger (d)
The respective temperatures of the heated and cooled CO₂ flow: 35 °C → 48 °C and 78 °C → 50 °C, heat exchanger (d)
- Before the pump pressurizing the latex flow (~ 88 kJ/kg = 21 kcal/kg), heat exchanger (a)
The respective temperatures of the heated latex and cooled CO₂ flow: 15 °C → 34.2 °C and 50 °C → 35 °C

At the separator one extra heat exchanger is required heating the CO₂ flow from 48 °C to 72 °C. Steam at 100 °C and 1 bar is used for this purpose. The amount of steam required has

been calculated dividing the required power by the heat of vaporization of steam (Perry, 1999) at 100 °C, Equation B.22.

$$\phi_{\text{steam}} = \frac{\phi_{q,e}(\text{heat exchanger e})}{\Delta_{\text{vap}}h} \left[\frac{\text{kg}}{\text{hr}} \right] = \frac{80.5 * 3600}{2257.8} \left[\frac{\text{kg}}{\text{hr}} \right] = 128 \left[\frac{\text{kg}}{\text{hr}} \right] \quad (\text{B.22})$$

Dimensioning the different heat exchangers described above, has been performed according to Equation B.23.

$$\phi_{q,i}(\text{heat exchanger i}) = U * A * \Delta T_{\text{ln}} \quad (\text{B.23})$$

where ΔT_{ln} stands for the logarithmic mean temperature difference between the heated and cooled stream.

Table B.4 gives the physical properties as well as the resulting heat transfer area of the different heat exchangers (h), at the oxidation vessel, (d) at the separator, (a) to heat the latex, (e) at the separator.

Table B.4 Physical properties as well as the resulting heat transfer area for the heat exchangers (h), at the oxidation vessel, (d) at the separator, (a) to heat up the latex, (e) at the separator

heat exchanger i	$\phi_{q,i}$ [kW]	$U \left[\frac{\text{W}}{\text{m}^2 \cdot ^\circ\text{C}} \right]^8$	$\Delta T_{\text{ln}} [^\circ\text{C}]$	$A_i [\text{m}^2]$
h	60.5	1000	41.5	1.5
d	76.3	1000	24	3.2
a	80.5	1000	17.8	4.5
e	80.5	1000	38.8	2.1

7. Pressure reducer (f)

Before the styrene/CO₂ mixture enters the separator, its pressure is expanded from 100 bar to 60 bar. This process generates 21 kJ/kg (*i.e.* 5 kcal/kg) that is lost, see Equation B.24.

$$\phi_{q,\text{CO}_2}(\text{pressure reducer}) = 0.85 * 21 [\text{kJ/kg}] \cong 18 [\text{kJ/kg}] \quad (\text{B.24})$$

⁸ The overall heat transfer coefficient of CO₂ is estimated at 1000 $\left[\frac{\text{W}}{\text{m}^2 \cdot ^\circ\text{C}} \right]$, the same value as for H₂O (Perry, 1999) as the density of both components are very similar.

Appendix C

Appendix D

In a batch stripping vessel, steam at 100 °C is directly contacted with the cold latex of 15 °C. The steam therefore condenses at 100 °C. The amount of steam needed to heat the latex has been calculated with Equation D.1. Table D.1 shows the physical properties of latex.

Table D.1 Physical properties of latex

	ϕ_m		ρ	C_p
	kg/hr	kg/s	kg/m ³	kJ/kg °C
latex	6000	1.67	1020	2.9

$$\phi_{\text{steam}} = \frac{T * C_{p,\text{water}} * \phi_{m,\text{latex}}}{\Delta_{\text{vaph}}} \quad (\text{D.1})$$

$$\phi_{\text{steam}} = \frac{15 * 4.2 * 6000}{2257.8} \left[\frac{\text{kJ/hr}}{\text{kJ/kg}} \right] = 170 \left[\frac{\text{kg}}{\text{hr}} \right] \quad (\text{D.2})$$

In the continuous stripping process, the latex stream first needs to be heated before entering the column. The amount of steam required to heat the latex from 15 °C to 100 °C, see Equations D.3 to D.5.

$$\phi_q(\text{heat exchanger}) = \phi_{m,\text{latex}} * C_{p,\text{latex}} * \Delta T \quad (\text{D.3})$$

$$\phi_q(\text{heat exchanger}) = 1.67 * 2.9 * 85 \cong 411 \text{ [kW]} \quad (\text{D.4})$$

$$\phi_{\text{steam}} = \frac{411 * 3600}{2257.8} \left[\frac{\text{kJ/hr}}{\text{kJ/kg}} \right] = 655 \left[\frac{\text{kg}}{\text{hr}} \right] \quad (\text{D.5})$$

Chapter 6

High pressure carbon dioxide in the extraction of residual monomer from latex products: additional results and outlook

Abstract

In retrospect to the previous chapters, this final chapter gives a perspective on some challenges in the extraction of residual monomer from latex products with high pressure carbon dioxide.

Monomer partitioning

The partition coefficient (K_{mon}) of the distribution of monomer between CO_2 -swollen polymer and CO_2 is the key issue in the extraction of residual monomer from latex with scCO_2 . The phase behavior of a ternary system monomer- CO_2 -swollen polymer- CO_2 is often estimated by thermodynamic models based on the component properties. In Chapter 3 the large deviation between the experimentally determined and the theoretically predicted partition coefficient (K_{mon}) of the distribution of monomer between CO_2 -swollen polymer and CO_2 has been discussed. The polymers used in the present work have not been submitted to annealing before experimental data have been collected. The polymer properties found in literature as well as in the VLXE software (Laursen, 2003) databank, have been determined from polymers which have been tempered at temperatures above their glass transition temperature. The annealing process changes the polymer properties as it removes any history effects as well as contaminants (van de Ven, 1975, Huvard *et al.*, 1980). A proper design of an extraction process for residual monomer reduction (and reduction of the level of other low molecular weight species) from reactor products demands for partitioning data based on the actual products formed during the polymerization. This will almost always mean

that partition coefficients of residual monomer (and other relevant low molecular weight species) have to be determined by experiments.

Colloidal stability

One of the challenges in the reduction of residual monomer in polymer (latex) products by extraction with (sc)CO₂ is the release of CO₂ dissolved in the polymer particles. A rapid pressure decrease leads to loss of colloidal stability, *i.e.* bubble formation and even foaming, probably leading to surface coagulation/fouling. Foaming can be suppressed by introducing a defoaming agent to the reactor product (Kelley et al., 1978). However, the characteristics of the latex product can change, *i.e.* discoloration, hardness, etc.. Note that application of defoaming agents adds contaminants to the latex product.

It has been observed experimentally¹ that the first bottleneck in decreasing the pressure of a scCO₂ – latex mixture is the CO₂ phase transition point, when CO₂ changes from the supercritical to the gas phase. The formation of gas bubbles in the latex may cause foaming as a result of the presence of surface active species. Depending on the speed of the pressure decrease, foaming is severe or moderate. Once the pressure is below the supercritical pressure of 73 bar, decrease of the pressure can be controlled better than close to the critical pressure. Decreasing the pressure from about 5 bar to atmospheric pressure is also accompanied with some undesired phenomena. Note that particles are still swollen with CO₂ at these already low pressures. Release of CO₂ is governed by mass transport. The time constant for transport of CO₂ out of the particles to the gas phase is probably larger than the time constant for pressure decrease. So recording atmospheric pressure in the gas phase ignores the CO₂ present in the particles. Waiting for about 15 minutes allows CO₂ transport from the particles to the gas phase, leading to a pressure increase. Repeating the procedure of pressure decrease followed by CO₂ gas release from the particles is accompanied by fouling affixed to the wall of the vessel containing the latex. Also flocs of polymer were observed. Note that about 15 minutes after a constant pressure of 1 atmosphere has been reached a coagulum free latex could be isolated. Industrial removal of

¹ In the optical high pressure cell described in Chapter 3, latex was loaded with scCO₂ at 100 bar at 35 °C. After 1 hour the pressure was relieved through a valve at the top of the high pressure cell.

residual monomer with high pressure CO₂ demands for filtration after complete pressure release. Also cleaning of the equipment wall is necessary on a regular basis. The preliminary observations make clear that an accurately controlled pressure decrease is a prerequisite for a proper performance of a residual monomer reduction process based on (sc)CO₂-based extraction. Note that proper development of a pressure decrease procedure is also applicable for e.g. emulsion vinylchloride/polyvinylchloride systems in emulsion and suspension.

One of the alternative methods to allow for phase separation between the latex and the CO₂ dissolved in the latex, is to chemically bind the CO₂ by using a weak basic macroporous ion exchange resin. CO₂ reacts directly with primary or secondary amines generating their respective carbamate salts (Riley *et al.*, 1994), see Scheme 1 for the typical reversible reaction.

Scheme 1. Reaction of amines with CO₂.

The corresponding carbamate acid is not stable, only in the form of a sterically stabilized anion. The CO₂ dissolved in the latex can be captured by a proper amine when the latex/CO₂ mixture is led over a macroporous weak basic ion exchanger containing amine groups. Saha *et al.* (1999) as well as Samanta and Bandyopadhyay (2009) discuss the kinetics as well as the modeling of the absorption of CO₂ into aqueous solutions of the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP). Bonenfant *et al.* (2007) studied the CO₂ absorption capacities in aqueous 2-(2-aminoethylamino)ethanol (AEE) solutions. The authors mentioned reported experimental observations of CO₂ absorption in amine solutions from CO₂ containing gas streams. The pressure in such processes are low to moderate, < 100 bar. Nevertheless absorption of CO₂ by leading the latex/CO₂ mixture over an ion exchanger containing amine groups is a promising method to remove the CO₂ from the latex. Ion

exchange resins saturated with CO₂ by the reaction presented in Scheme 1 can be thermally regenerated after washing out the latex particles with an amount of water as small as possible. During the thermal regeneration the carbamate dissociates in CO₂ and the amine (note the analogy with the CO₂ absorption process during the production synthesis gas for ammonia synthesis).

Equilibrium between water and scCO₂: pH-effects

Water in contact with carbon dioxide is known to become acidic due to the formation and dissociation of carbonic acid, see Equation 1:

Organic species in an acidic medium can take up a proton, decreasing their solubility in CO₂. Thoews *et al.* (1995) measured the pH of water in contact with CO₂ by observing UV-VIS spectra of a pH indicator. The pH of water in equilibrium with scCO₂ at equilibrium has been found to be only slightly dependent of temperature in the range between 25 and 70 °C at pressures ranging from 70 to 200 bar. Toews *et al.* (1995) reported a pH of water in equilibrium with scCO₂ between 2.8 and 3. Increasing pressure at constant temperature decreases the pH. Increasing temperature at constant pressure increases the pH, due to the lower solubility of CO₂ in water at higher temperatures. The solubility behavior of CO₂ in water at supercritical conditions for CO₂ resembles that of liquid CO₂ in equilibrium with water. The partial molar volume of liquid CO₂ in water varies only slightly with pressure, hence the solubility of liquid CO₂ in water is rather independent of pressure. Li and Duan (2007) report similar observations.

During the extraction of residual monomer from latex products with scCO₂ the pH of the latex will decrease with respect to the pH of the reactor product. The colloidal stability of the latexes used in the experiments (*vide supra*), however, did not change. The latex used in the experiments varied in pH from 5 to 9.

Life Cycle Assessment

Green chemistry, low energy consumption, renewable resources, etc., are hot topics in process technology. The ecological footprint of a product or process has never been so emphasized as in the last two decades (Klöpffer, 2001-2006). Typically, a life cycle assessment (LCA) is made to identify, quantify, interpret and evaluate the environmental impact of a product or process. Van den Berg *et al.* (1995) defined LCA as a systematic evaluation of the environmental impact of products or activities from the resources entering the process to the ultimate waste disposal of the material. This so-called cradle-to-grave concept implies the identification and quantification of emissions and material consumption affecting the environment in all stages of the product life cycle. LCA is a diagnostic engineering tool which can be used to compare existing or novel products or processes or services with each other or with a standard.

Within LCA the definition of the system boundaries is very important. A functional unit determines which products or processes can be meaningfully compared to each other. Note, however, that in a comparative study, the compared products or processes are seldom exactly identical. Van den Berg *et al.* (1995) described two solutions for this problem: define a certain minimum level that all compared alternatives must obey, or leave qualitative differences between compared alternatives out of the LCA calculations and describe them in words. In either way, interpreting the LCA calculation results, one has to take into account the assumptions made in the functional unit definition.

In every LCA it is necessary to define which environmental impacts have to be taken into account. The International Organization for Standardization (ISO) published a series of standards, including only headlines for impact categories: resource use, ecological consequences and human health (ISO, 2007). In terms of more operational impact categories, several areas have been indicated, e.g. toxicity potential (human and/or ecotoxicity), energy consumption, global warming potential, acidification potential, land use, etc (Van den Berg *et al.*, 1995). In the next step, *i.e.* characterization, the contribution of individual impacts per impact category has to be calculated. To perform this characterization process objectively, the characterization results are normalized, *i.e.* the results are divided by the actual or predicted magnitude for each impact category. Applying weighting factors, a

single score or index for the total environmental impact of a product or process is obtained. In the last stage of LCA, all previous stages and the assumptions made therein need to be interpreted and evaluated. The robustness of the results needs to be tested, *i.e.* to check whether conclusions hold even if critical and/or approximate data are changed. Such evaluations typically cover sensitivity analysis, uncertainty analysis and data quality assessment. Nevertheless, discussions on the methodology followed, and especially on the choice of the functional unit, remains an important issue in the field of LCA.

Comparing the steam stripping process with the scCO₂-based extraction process to reduce residual monomer in latex products, the functional unit in an LCA can be assigned as the residual monomer level in the latex. In this way the environmental impacts of each separation process, *i.e.* steam stripping or extraction with scCO₂, can be unambiguously compared. The difficulty in interpreting the LCA results is hidden in the thermodynamic and transport limitations of the steam stripping process to reduce the residual monomer level. The monomer activity coefficient and as a consequence the monomer saturated vapor pressure in the polymer phase, respectively in the surrounding vapor phase are very low at high conversions ($X > 99\%$). Consequently, monomer partitioning between the polymer phase and the steam phase is very low towards the vapor phase, see Equation 2.

$$y_m * P_{\text{total}} = \gamma_m * x_m * p_m^{\text{sat}} \quad (2)$$

In contrast to the CO₂ extraction process, where the polymer phase is swollen with (sc)CO₂ increasing the monomer activity coefficient in the polymer phase with respect to the unswollen polymer, the partition coefficient decreases with decreasing monomer mole fraction in the polymer phase (ϕ_p), see Chapter 1, Figure 1. For low mole fractions of monomer there is no driving force for monomer transfer to the vapor phase. Moreover, the molecular diffusion coefficient of monomer in the polymer phase is very low ($D_m^p \leq 10^{-15} \left[\frac{\text{m}^2}{\text{s}} \right]$), *i.e.* there is high mass transfer resistance in the particle phase.

For some polymeric latexes a reduction to 60 parts per million (ppm) residual monomer has been reported (Araújo *et al.*, 2002). In the present work a final level of residual monomer in the latex product of 100 ppm has been chosen as the lowest level of the residual monomer in the latex with steam stripping. scCO₂ as extraction medium is able to reduce the residual monomer level in latex to 1 ppm with a slightly higher CO₂ flow compared to a residual

monomer reduction to 100 ppm. For a reduction of residual styrene in PS latex from 10^4 ppm to 100 ppm 3000 kg scCO₂/hr is needed with a concentration of 90 mol styrene/ m³ scCO₂ in the outgoing CO₂ flow. Under the same circumstances, 3025 kg scCO₂/hr is required to reduce the residual styrene level in PS latex from 10^4 ppm to 1 ppm.

Applying a LCA to study the environmental impact of the scCO₂ based extraction process compared to the steam stripping to reduce residual monomer in latex delivers knowledge on emission, energy consumption, etc.. However, the monomer reduction in latex with scCO₂ extraction to only 1 ppm may counter balance the impact factors.

Concluding remarks

The work described in this thesis covers several important aspects of residual monomer reduction in polymer products. High pressure or scCO₂ has the potential to decrease time constants for monomer transport in the polymer phase as well as to reach very low levels of the residual monomer concentration in polymers (1 ppm) with a relatively small equipment size. Performance compared with common techniques like steam stripping is better as the final residual monomer level aimed at becomes lower.

Although the implementation of high pressure or scCO₂ in residual monomer reduction needs to be further explored, the author of this thesis believes that the described CO₂ extraction-based process allows for the production of cleaner and greener polymer products. Consequently, the developed methodology also provides an technical answer to the increasingly stringent regulations in this respect.

References

- P. H. H. Aaújo, C. Sayer, J. G. R. Poço, R. Guidici, "Techniques for reducing residual monomer content in polymers: A review", *Polym. Eng. Sci.*, **2002**, 42, 7
- N. W. van den Berg, C. E. Dutilh, G. Huppes, "Beginning life cycle assessment: A guide into environmental life cycle assessment", **1995**, Leiden
- D. Li, Z. Duan, "The speciation equilibrium coupling with phase equilibrium in the H₂O-CO₂-NaCl system from 0 to 250 °C, from 0 to 1000 bar, and from 0 to 5 molality of NaCl", *Chem. Geology*, **2007**, 244, 730-751
- ISO 14001 Management Zone, UK, **2007**, <http://www.iso-14001.org.uk>
- E. L. Kelley, R. W. Harrison, B. B. Harris, "Defoamers: their theory and application with regard to the paint industry", *Polym., Paint and Colour J.*, **1978**, 168, 734
- W. Klöpffer, Ed., *Int. J. of Life Cycle Assessment*, **2001 - 2011**
- J. H. Perry, Chapter 16, "Adsorption and ion exchange" in "Chemical Engineer's Handbook", **1999**, McGraw-Hill, New York
- D. Riley, W. D. McGhee, T. Waldman, "Generation of urethanes and isocyanates from amines and carbon dioxide", *Am. Chem. Soc.*, **1994**, 122-132.
- K. L. Toews, R. M. Shroll, C. M. Wai, "pH – Defining equilibrium between water and supercritical CO₂. Influence on SFE of organics and metal chelates", *Anal. Chem.*, **1995**, 67, 4040-4043

Abbreviations

eos	equation of state
f.o.b.	free on board
MMA	methyl methacrylate
MWBR	Modified Webb Benedict Ruben
PMMA	polymethyl methacrylate
ppm	parts per million
PC-SAFT	perturbed chain-statistical associated fluid theory
PR	Peng -Robinson
PS	polystyrene
SF	solid-to-fluid
SLF	solid-to-liquid-to-fluid
Sty	styrene
VLE	vapor-liquid-liquid equilibrium

Symbols

a	first parameter in the Colver theory ($= \frac{\gamma_{p1}}{\gamma_{21}}$) [-] (Chapter4)
$a(T, \omega)$	attraction parameter used in the Peng-Robinson equation of state [Nm^4/mol^2]
a_{eff}	effective specific mass transfer area $[\frac{m_{ij}^2}{m_{ij}^3}]$
a_i	Peng-Robinson attraction parameter for pure component i [Nm^4/mol^2]
a_{ij}	cross attraction parameter used in Peng-Robinson equation of state [Nm^4/mol^2]
a_{ij}	total specific interfacial area $[\frac{m_{ij}^2}{m_{ij}^3}]$
a_{mix}	Peng-Robinson attraction parameter for a mixture [Nm^4/mol^2]
A	constant defined in equation 10, Chapter 2 [-]
A_i	area i [m^2]

A_i	interfacial area of the i^{th} interface [m ²]
A^{assoc}	Helmholtz energy covering the association contribution [J]
A^{disp}	Helmholtz energy covering the dispersion contribution [J]
A^{hc}	Helmholtz energy covering the hard chain contribution [J]
A^{pert}	Helmholtz energy covering the perturbation contribution [J]
A^{ref}	Helmholtz energy of the reference system [J]
A^{res}	residual Helmholtz energy [J]
b	second parameter in the Colver theory ($= \frac{\gamma_{p2}}{\gamma_{21}}$) [-] (Chapter 4)
b	volume parameter used in the Peng-Robinson equation of state [m ³ /mol]
b_i	Peng-Robinson volume parameter for pure component i [m ³ /mol]
b_{mix}	Peng-Robinson volume parameter for a mixture [m ³ /mol]
B	constant defined in equation 11, Chapter 2 [-]
C	constant factor
C_D	drag coefficient [-]
C_0	monomer concentration in the center of the polymer particle [$\frac{\text{mol}}{\text{m}^3}$]
$C_{P,i}$	specific heat of phase i [$\frac{\text{kJ}}{\text{kg} \text{ } ^\circ\text{C}}$]
C_s	monomer concentration at the surface of the polymer particle [$\frac{\text{mol}}{\text{m}^3}$]
C_{mon}^i	equilibrium monomer concentration in phase i [mol monomer / kg phase i]
D_c	column diameter [m]
d_i	diameter of sphere i [m]
d_{particle}	diameter of polymer particle [m]
D_m^i	diffusion coefficient of monomer m in phase i [$\frac{\text{m}^2}{\text{s}}$]
f_i	fugacity of a pure component i [Pa]
$\hat{f}_i$	fugacity of component i in a mixture [Pa]
f_i°	standard fugacity of component i [Pa]
$f_i^{(n)}$	fugacity of component i in phase n [Pa]
F_B	buoyant force [N]
F_D	drag force [N]

F_G	external force [N]
F_o	Fourier number [-]
g	gravitational force [m/s^2]
G_0	total energy of a solid-liquid-liquid system [-]
G_m	molar Gibbs free energy [$J \text{ mole}^{-1}$]
G_i°	standard molar Gibbs energy [$J \text{ mole}^{-1}$]
G_m^E	excess molar Gibbs energy [$J \text{ mole}^{-1}$]
ΔG	Gibbs free energy change [J]
ΔG_i	energy difference of phase I with respect to the minimal energy [-]
$\Delta_{\text{mix}} G_m$	molar Gibbs energy of mixing [$J \text{ mole}^{-1}$]
$\Delta_{\text{mix}} G_{m, \text{id}}$	molar Gibbs energy of mixing to form an ideal mixture [$J \text{ mole}^{-1}$]
$\Delta \Delta G_{\text{solution}}$	difference in Gibbs free energy of solution of monomer dissolved in CO_2 and of monomer dissolved in CO_2 swollen polymer [$J \text{ mole}^{-1}$]
h	enthalpy per kg [kJ/kg]
H_c	column height [m]
$H_{c, n}$	column height when n ppm residual monomer is reached
H_{HETP}	height equivalent of a theoretical plate [m]
H_m	enthalpy of mixing [$J \text{ mole}^{-1}$]
H_i°	standard enthalpy [$J \text{ mole}^{-1}$]
$\Delta \Delta H_{\text{solution}}$	difference in heat of solution of monomer dissolved in CO_2 and monomer dissolved in CO_2 swollen polymer [$J \text{ mole}^{-1}$]
k_b	Boltzman constant, $1.38 \cdot 10^{-23} [\frac{J}{K}]$
k_m^i	partial mass transfer coefficient of monomer in phase i [$\frac{m}{s}$]
k_{ij}	binary interaction parameter accounting for the interaction of unlike molecules [-]
K_i	partition coefficient of monomer i between (sc) CO_2 and polymer i [kg polymer/ kg (sc) CO_2]
K_{mon}	partition coefficient of monomer between (sc) CO_2 and polymer [kg polymer/ kg (sc) CO_2]
$K_{\text{mon}}^{T_i}$	partition coefficient of monomer between the (sc) CO_2 and polymer at temperature T_i [kg polymer/ kg (sc) CO_2]
l_{BF}	mean free path of base fluid ($l_{H_2O} = 0.17 \text{ nm}$) [m]
m	number of segments [-]

m_{sphere}	mass of sphere [kg]
M_i	mass of species i [kg]
M_w	weight averaged molecular weight [kg/mol]
N_{ts}	number of theoretical stages [-]
n	total number of molecules [-]
n_i	number of molecules of component i [-]
P	pressure [Pa]
P_A	attractive term of pressure [Pa]
P_c	critical pressure [Pa]
P_R	repulsive term of pressure [Pa]
P_{total}	total pressure of the system [bar]
$p(l)$	coefficient number l, defined in Appendix B, Chapter 3
p_m^{sat}	monomer saturated vapor pressure [bar]
R	gas constant [8.314 J mole ⁻¹ K ⁻¹]
Re	Reynolds number [-]
R_p	polymer particle radius [m]
r_p	polymer particle radius [m]
r_s	steam flow rate [kg steam/kg dry solids s] (from personal communication)
s	isentropy [kcal/°C]
Δs	distance a particle travels in the interfacial region [m]
S_i	spreading coefficient of phase i [-]
S_i°	standard entropy [J mole ⁻¹ K ⁻¹]
Sh	Sherwood number [-]
S_m	entropy of mixing [J mole ⁻¹ K ⁻¹]
$t_{\text{contact}, i}$	contact time of phase i [s]
T	temperature [K]
T_c	critical temperature [K]
T_g	glass transition temperature [K]
T_r	reduced temperature [-]
ΔT_{In}	logarithmic mean temperature difference [K]

u	internal energy [kJ/kg]
U	overall heat transfer coefficient [$\frac{W}{m^2 \cdot ^\circ C}$]
v	molar volume [m^3/mol]
v_{Br}	Brownian velocity of the polymer particles [$\frac{m}{s}$]
v_c	superficial velocity of the continuous phase [$\frac{m}{s}$]
v_d	superficial velocity of the dispersed phase [$\frac{m}{s}$]
v_i	molar volume of component i [m^3/mol]
v_s	slip velocity [$\frac{m}{s}$]
v_∞	hindered rising velocity of one bubble [$\frac{m}{s}$]
V	volume [m^3]
x_i	molar fraction of component i in the liquid phase [-]
X	conversion [-]
y_i	molar fraction of component i in the vapor phase [-]
w_i	weight fraction of component i [-]
Z	compressibility factor, defined in equation 12 [-]
z	particle's position with respect to the interface [m]
z_0	ratio of the particles position with respect to the interface over the particle radius [-]
z_0^{min}	particle's equilibrium position (= b - a) [-]

Greek letters

a_i	activity of component i [-]
δ_i	boundary layer thickness of phase i [m]
ϵ_d	dispersed phase hold up [$\frac{m^3 \text{ dispersed phase}}{m^3 \text{ column}}$]
ϵ/k	energy related to the interaction of two segments [K]
φ_i^I	fugacity coefficient of component i in phase I [-]
ϕ_i	mass flow rate of phase i [$\frac{kg}{hr}$] or [$\frac{kg}{s}$]
ϕ_q	heat flow [kW]

$\Phi_{w,shaft}$	shaft work [kW]
Φ_p	polymer volume fraction [-]
γ_i	activity coefficient of component i [-]
γ_{ij}	interfacial tension between phase i and j [$\frac{mN}{m}$]
γ_m	monomer activity coefficient [-]
λ	thermal conductivity coefficient [$\frac{W}{m \cdot ^\circ C}$]
η	dynamic viscosity of H ₂ O [Pa s]
μ_i	chemical potential of component i [J mole ⁻¹]
μ_i°	standard chemical potential of component i [J mole ⁻¹]
μ_i^E	excess chemical potential of component i [J mole ⁻¹]
$\mu_{i, id}$	chemical potential of component i of an ideal mixture [J mole ⁻¹]
ρ	density [$\frac{kg}{m^3}$]
σ	size of segments [Å]
τ_n	residence time of CO ₂ bubbles in the column when n residual monomer level is reached [s]
θ	fraction of the interfacial area covered with polymer particles [-]
ω	acentric factor [-]

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Curriculum Vitae

Marijke Aerts was born on January 2nd 1982 in Hasselt (Belgium). In 2000, she finalized her secondary education at Lyceum (Atheneum III) in Hasselt. In October of that year, she started studying chemistry at Hasselt University (Diepenbeek, Belgium). After completion of her second year candidature in 2002, she continued her education in chemical engineering at the Department of Chemical Engineering and Chemistry of the Eindhoven University of Technology (The Netherlands). She performed her MSc graduation project entitled "Synthesis of polyurethanes with carbon dioxide" in the Process Development Group. In August 2005 she received her MSc degree in Chemical Engineering. From October 2005 till December 2010, she performed a PhD graduation project in the Process Development Group under supervision of prof.dr.ir. J.T.F. Keurentjes and prof.dr. J. Meuldijk. The subject of the project was reduction of residual monomer in polymer latex products with high pressure carbon dioxide. The results of this research project sponsored by the Foundation Emulsion Polymerization, are summarized in this thesis. As from September 1st 2011, she is working as a process development engineer at Bodec Process Technology in Best (The Netherlands).