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Phase-Equilibrium Measurements of the Polystyrene/Styrene/Carbon Dioxide Ternary System at Elevated Pressures Using ATR-FTIR Spectroscopy

*Michael Görnert, Gabriele Sadowski**

Summary: In this paper a novel ATR-IR spectroscopic setup for phase-equilibrium studies of polymer systems in supercritical carbon dioxide is presented. A calibration procedure for the spectroscopic investigations has been developed and verified. The results of isothermal phase-equilibrium measurements of the polystyrene/styrene/carbon dioxide ternary system are presented and compared to results of well-established cloud-point measurements. The phase behaviour was determined at 338.15 K, at two pressures (10 MPa and 15 MPa), and for two polystyrene samples having different molecular weights (6 kg/mol, 105 kg/mol) and narrow molecular-weight distributions.

Keywords: ATR-FTIR; high pressure; phase equilibrium; polymer

Introduction

Supercritical carbon dioxide has become an interesting alternative to organic solvents for polymerization processes (e.g.[1–3]). However, scale up and final process design need the knowledge not only of the kinetics of the several reaction steps but also of the phase behavior in the system monomer/polymer/carbon dioxide as function of various process conditions.[4–6] In this work we consider the polystyrene/styrene/carbon dioxide ternary system.

Experimental data for the binary subsystem styrene/carbon dioxide is available for a wide temperature and pressure range.[7–9] Data for the solubility of carbon dioxide in polystyrene are also published at different temperatures.[10–14] However, depending on the measurement method and sample preparation, the results of these experiments vary considerably. For the ternary system almost no experimental data is available in literature.

Chair for Thermodynamics – Dep. Biochemical and Chemical Engineering, University of Dortmund, Emil-Figge-Str. 70, 44227 Dortmund, Germany
Fax: +49 (231) 755 2572;
E-mail: g.sadowski@bci.uni-dortmund.de

The aim of this work is the measurement of the phase equilibrium in the polystyrene/styrene/carbon dioxide ternary system. Two different experimental setups were used for the experimental investigation. Cloud-point measurements were performed using a variable-volume view cell; whereas the concentrations of the coexisting phases were determined by means of a high-pressure ATR-IR probe.

Materials

Carbon dioxide (Air Liquide, 99.995 vol-%) was used as obtained without further treatment.

Styrene (Merck, for synthesis) was degassed before use by freezing in liquid nitrogen and removing the atmosphere with a vacuum pump. The frozen styrene was melted at room temperature under vacuum. This procedure has been repeated at least twice. Additional stabilizer (4-tert-butylpyrocatechol) was added to a concentration of 30 ppm to suppress polymerization of styrene while the experiment.

Polystyrene samples for phase-equilibrium measurements with a narrow molecular-

weight distribution were kindly supplied from BASF ($M_w = 6$ kg/mol, $M_w/M_n = 1.05$; $M_w = 105$ kg/mol, $M_w/M_n = 1.06$). For the calibration of the IR analysis an atactic polystyrene (M_w approx. 50 kg/mol) from Polysciences Inc. was used. All polymers were used without further purification.

Variable-Volume View Cell

Cloud-point measurements of the ternary system were performed using a variable-volume view cell (NWA analytische Messgeraete GmbH). The inner volume of the cell can be varied between 30 ml and 60 ml by means of a movable sapphire piston that is driven by a hydraulic system. To avoid temperature influence, the pressure is measured in the hydraulic system and transformed to system pressure. A sapphire window allows for observing the whole inner volume of the cell. All experiments were performed by visual observation. The cell is equipped with a magnetic-coupled drive and with a Pt-100 resistance thermometer. The maximum temperature of the cell is 453.15 K, the maximum pressure is 70 MPa.

Autoclave with High-Pressure ATR-IR Probe

Experiments to determine the composition of the coexisting phases we performed in an experimental setup that allows for in-situ IR-spectroscopic measurements of the polymer-rich phase as well as for external analysis of a sample from the carbon-dioxide-rich phase by gravimetric and volumetric measurements.

The core of the setup is a double-jacketed Büchi ''Limbo 350'' high-pressure autoclave as shown in Figure 1. It is designed for a maximum pressure of 30 MPa, maximum temperature of 473 K and has 200 ml of nominal volume. A magnetic-coupled stirrer is integrated in the cover plate. The temperature of the autoclave is kept constant by a Lauda C12 CP thermostat and measured with a Pt-100 resistance thermometer, whereas the pressure of the system is measured by a WIKA P-10 pressure transmitter ($p_{max} = 40$ MPa, accuracy better than 0.05% of the maximum value at 293.15 K). The pressure transmitter is connected to the autoclave using a capillary extension to keep the temperature of the transmitter constant.

A Mettler Toledo (ASI) Sentinel DiComp ATR-IR probe ($p_{max} = 31$ MPa, $T_{max} = 473$ K) is integrated in the bottom of the autoclave. It is connected to a Mettler Toledo ReactIR 4000 FTIR spectrometer via a K4 conduit and sealed with a gold O-ring. The spectrometer is equipped with

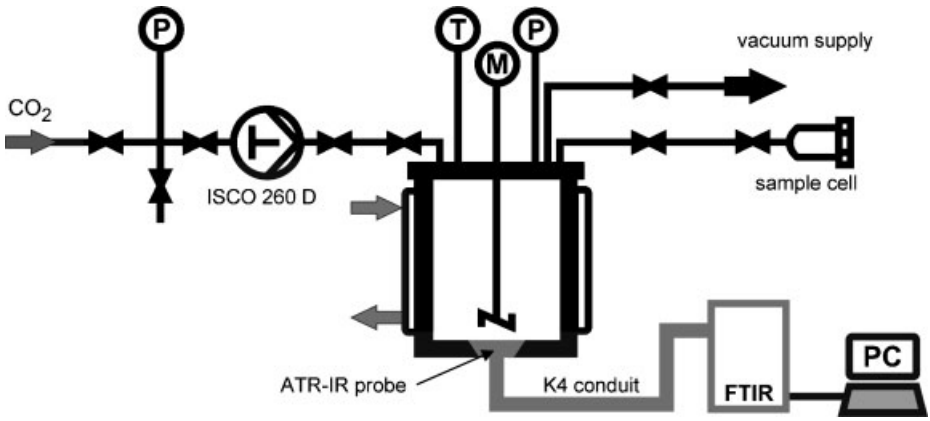

Figure 1.
High-pressure autoclave with integrated ATR-IR probe. The double-jacked autoclave is equipped with a magnetic-coupled drive as well as temperature measurement and pressure measurement. The ATR-IR probe that is embedded into the bottom is connected to the FTIR spectrometer by a K4 conduit.

a MCT detector, which is cooled with liquid nitrogen. The optical system is continuously flushed with dry and carbon-dioxide-free air. The data from the spectrometer is collected and visualized with the ReactIR 3.0 software and the calibration is performed with QuantIR 2.0 software from Mettler-Toledo.

All ATR-FTIR experiments were performed using a spectrum of dry air, taken at 338.15 K as reference background. The spectra were taken over the full MIR range from 600 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum is calculated from 128 interferograms using Happ-Genzel apodization.

Carbon dioxide can be fed with an accuracy of ± 0.16 g into each of the two equipments using an ISCO 260D syringe pump. To determine the mass of the carbon dioxide added, the density of carbon dioxide was calculated using the fundamental equation of state by Span and Wagner.[15] For that purpose the heating jacket of the pumps cylinder was kept at a constant temperature of 308.15 K using a Lauda RK20 KP thermostat. The pressure of the carbon dioxide in the pump is kept constant at 17.5 MPa before and after addition, and the volume change of the pump is detected.

Cloud-Point Measurements

Cloud-points of the ternary system were determined as reference for the IR-measurements. For that purpose the autoclave was filled with a solution of polystyrene, styrene, and carbon dioxide and equilibrated at 338.15 K. Starting from a homogeneous solution, the pressure was decreased with a rate of about $\Delta p = 2$ bar min^{-1} until phase separation did occur. After demixing, the pressure was increased again until the system became homogenous. The pressures at which phase separation occurs or the system gets homogenous again are the cloud point pressures of one concentration. The measurements were repeated at least tree times and were performed for different concentrations of carbon dioxide and polystyrene.

IR-Spectroscopic Measurements

Calibration

The ATR-IR technique is used here to analyze the concentration of the polymer-rich phase. A sophisticated calibration method for the ternary system is needed to calculate the mass fraction for each of the components. In prior experiments the influence of pressure and the molecular weight of the polymer on the IR spectra were investigated. In agreement to literature[16] it could be confirmed that the influence of the molecular weight of the polymer can be neglected. Although pressure has a small influence on the IR spectra, but its influence in the considered pressure range ($p =$ 7.5 MPa–15 MPa) is much smaller than that of composition and was also neglected here.

To calibrate the IR-probe, we considered a training set consisting of different (homogenous) mixtures of the ternary system with known concentrations at constant temperature and recorded the corresponding IR spectra according to the following calibration procedure.

A certain amount of polystyrene ($M_w \sim 50$ kg/mol) was fed into the ATR-IR autoclave and dissolved after evacuation in degassed styrene at room temperature (controlled via online IR measurements). After that the temperature was increased within four hours to a temperature of 338.15 K. At constant temperature carbon dioxide was added in small quantities and IR spectra were taken continuously every two minutes. The development of the IR absorption at characteristic wavelengths of the three components during addition of carbon dioxide is shown in Figure 2. After the IR-intensity of the components reached a constant value, the next amount of carbon dioxide was added. Due to adding of carbon dioxide the system pressure did increase up to the final pressure of about 10 MPa and 15 MPa, respectively. Since in the heterogeneous system the IR probe detects the polystyrene-rich phase, phase separation is indicated by an increase of the IR-intensity of polystyrene. The calibration measurements

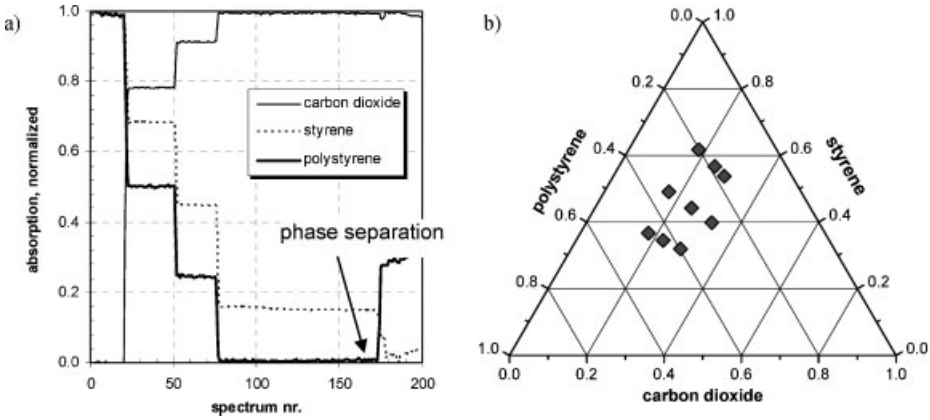

Figure 2.
Calibration of the IR spectroscopy. a) Development of the absorption profiles of each of the components during a calibration measurement. The data were normalized for better illustration. b) Data points used for the training set.

were finished at that point. This procedure was repeated three times with different polystyrene concentrations.

The training set used for calibration consists of three IR spectra at nine different homogenous concentrations (Figure 2b). Using this training set the system was calibrated using the Partial Least Squares (PLS) model with mean centering of the spectra. After optimization using the Predictive Residual Error Sum of Squares (PRESS) method,[17] seven factors for polystyrene, seven factors for styrene and eight factors for carbon dioxide are used to model the ternary system. Figure 3 shows the reproducibility of the mass fractions w of the components for the training set in comparison with the experimental data. The average relative deviation (ARD[1] in percent) of mass fractions w were 0.1470% for carbon dioxide, ARD = 0.1731% for styrene, and ARD = 0.3187% for polystyrene. The leave-one-out method showed similar good results.

It could be shown that a set of nine different concentrations, resulting from three experiments, was sufficient for the calibration. Using more data points did not improve the calibration quality significantly.

[1] $ARD = \frac{100}{n}\sum_{n}\frac{|w_{n,\exp}-w_{n,calc}|}{w_{n,\exp}}$

Phase-Equilibrium Measurements Using the IR-Technique

The measurement of the phase equilibrium was performed using polystyrene with narrow molecular weight distribution at constant temperature of 338.15 K and pressures of 10 MPa and 15 MPa, respectively. The measurements at the two pressures were performed within one experiment using the following procedure. Polystyrene was fed into the autoclave. The system was flushed with helium and evacuated at room temperature. Degassed and stabilized styrene was added to obtain a binary solution of approximately 15 mass-% polystyrene. After complete dissolution of polystyrene the temperature was increased up to 338.15 K within four hours. At constant temperature carbon dioxide was added stepwise up to a pressure of 15 MPa. While reaching equilibrium, IR spectra were taken every 20 minutes. Equilibrium was assumed when the concentrations of all components stayed constant for at least six hours. After that, the concentration of the polymer-rich phase was determined from the IR-spectra. To determine the composition of the carbon-dioxide-rich phase, we took samples (about 10 ml) which were analyzed by classical pVT-measurements and gravimetric determination of the styrene and polystyrene contents, respectively.

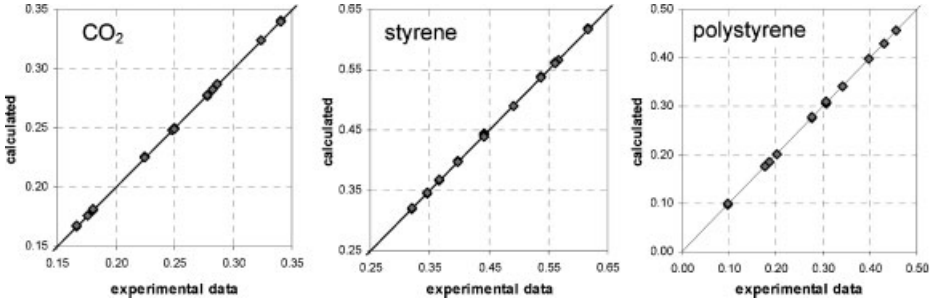

Figure 3.
Test of the reliability of the calibration function. Concentrations (in weight fraction) of the training-set are calculated from the IR-spectra are compared with training-set experimental data for each of the components carbon dioxide, styrene, and polystyrene.

Due to sampling the system pressure decreased to 10 MPa allowing for another phase-equilibrium measurement at the lower pressure. After analysis of the phase equilibrium the pressure was again increased up to 15 MPa by adding pure carbon dioxide. This enabled us to continue the measurements at the same temperature and pressure but at higher carbon-dioxide contents.

Results and Discussion

Figure 4 a) shows exemplarily the results of the cloud-point measurements at 338.15 K and at a polystyrene concentration of 15 mass-% in the initial carbon dioxide-free system as function of the carbon dioxide mass fraction. Here, each cloud-point pressure is an average of the results of the measurement by pressure increase and pressure decrease, respectively. These data were used to determine the phase boundary at 338.15 K and the pressures of 10 MPa and 15 MPa, respectively (shown in Figure 4b). Using this method, the concentration of carbon dioxide in the ternary system can be measured with an accuracy of ±0,75 mass-%.

Figure 5 compares the determined cloud-points with the results obtained using

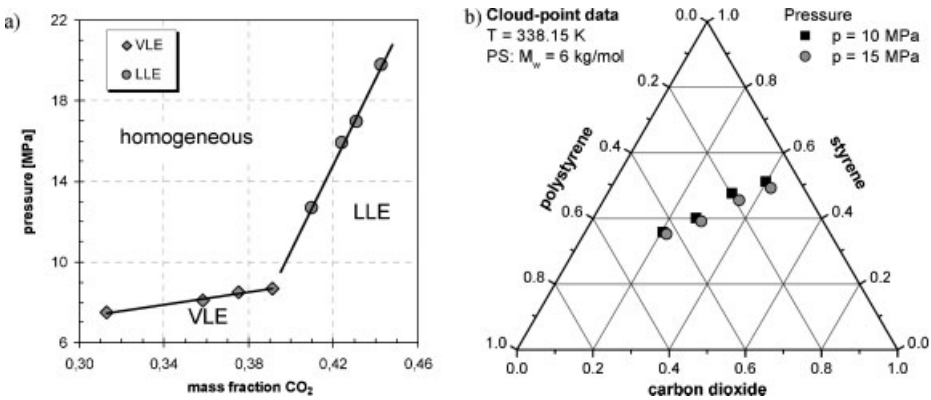

Figure 4.
Cloud point data of the PS ($M_w = 6$ kg/mol)/styrene/carbon-dioxide system at $T = 338.15$ K. a) Cloud-points at a polymer concentration of 15 mass-% in CO_2-free system. The circles represent the pressure, which is used for to determine the phase boundary at 10 MPa and 15 MPa shown in Figure 4 b). b) Phase behavior of the ternary system at $T = 338.15$ K, determined from four cloud-point experiments with different polymer concentrations in the initial binary solution.

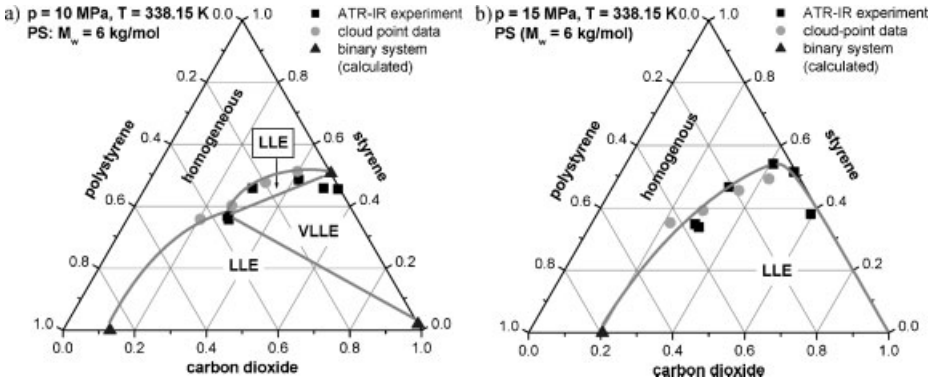

Figure 5.
Phase behavior of the polystyrene ($M_w = 6$ kg/mol)/styrene/carbon dioxide ternary system at 338.15 K [a) 10 MPa and b) 15 MPa], determined from cloud-point measurements (circles) and the ATR-IR experiment (squares). For better illustration binary data is calculated (triangles), and expected phase boundaries are plotted (lines).

the IR-spectroscopy for polystyrene samples of $M_w = 6$ kg/mol at 10 MPa and 15 MPa, respectively. Data points in the polymer-rich region are determined from IR measurements, concentrations of the coexisting polymer-lean phase are results of the pVT analysis. For a better evaluation of the experimental data of the ternary system, also binary data are included in Figure 5. They were obtained by modeling binary literature data[7–9,12–14] using the PC-SAFT equation of state.[18–20]

Figure 5 a) shows the results for 10 MPa. Here we can identify a VLLE region that has its origin in the VLE of the binary system styrene/carbon dioxide. This VLLE region is connected to two LLE regions. Only at low carbon dioxide concentrations the system is homogenous. The diagram in Figure 5 b) illustrates the results for 15 MPa. At this pressure the binary system styrene and carbon dioxide is supercritical[7] and therefore the three-phase region does not exist anymore.

Comparing the results from the cloud-point measurements and the analysis of the polymer- rich phase from the ATR-IR experiment, a good agreement of the two methods can be observed.

Figure 6 shows the results of the investigation for the ternary system at 338.15 K using polystyrene with a molecular weight

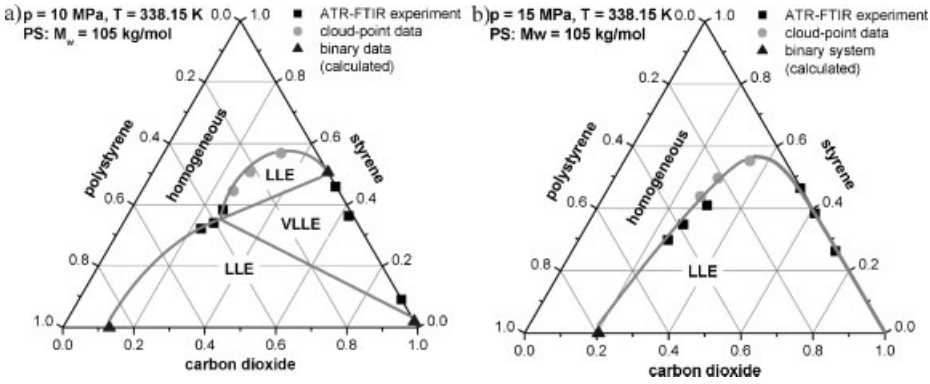

Figure 6.
Phase behavior of the polystyrene ($M_w = 105$ kg/mol)/styrene/carbon dioxide ternary system at 338.15 K, determined from cloud point measurements (circles) and the ATR-IR experiment (squares). For better illustration binary data is calculated (triangles), and expected phase boundaries are plotted as solid lines. a) phase behavior at 10 MPa, b) phase behavior at 15 MPa.

of $M_w = 105$ kg/mol at 10 MPa and 15 MPa, respectively. The agreement between IR analysis of the polymer-rich phase and the results of the cloud point measurement is again satisfying.

The experiment using polystyrene of $M_w = 105$ kg/mol shows distinct differences of the shape of the phase boundary at the two pressures. At 10 MPa (Figure 6a) the phase boundary shows a kink. Here we can again identify the VLLE region and the two LLE regions. At low carbon dioxide concentrations the system is homogenous. In contrast, the experimental data at 15 MPa shows a nearly continuous phase boundary that separates the homogenous region from the two-phase region.

Comparing the results at 10 MPa for polystyrene of $M_w = 6$ kg/mol (Figure 5a) and $M_w = 105$ kg/mol (Figure 6a) it is obvious that the LLE on top of the VLLE is much more pronounced at the system containing polystyrene of $M_w = 105$ kg/mol. In contrast the polymer molecular weight has only little influence on the lower LLE. Regarding the phase boundaries in general we observe that the solubility decreases with increasing molecular weight of the polymer.

Conclusion

We have used a novel high-pressure ATR-IR equipped autoclave which is suitable for phase-equilibrium measurements of the polystyrene/styrene/carbon dioxide ternary system. A calibration procedure for the IR analysis was developed that shows sufficient precision for quantitative analysis of the polymer-rich phase. Comparison to classical cloud-point measurements confirmed its reliability. The new technique is in particular advantageously when cloud-point measurements are not possible for any reason or -because it allows for time-dependent in-situ measurements - for studying kinetic effects.

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