

Phase Equilibrium Thermodynamics for a Polycarbonate Production Process using Supercritical Carbon Dioxide

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Abstract

Thermodynamic phase equilibrium data, which are relevant to the development of a novel production process for polycarbonates from CO₂ and epoxides, are presented. In this solvent-free process, CO₂ is coupled to epoxides using various transition-metal catalyst systems. Data on the performance of these systems are discussed. Additionally, the polycarbonate solubility in CO₂ and CHO is considered, both inside and beyond the P-T ranges that have been used for synthesis of the polycarbonate. Moreover, CHO-CO₂ vapour pressure isotherms have been measured and modelled. Experimental results indicate that following the pressure decay during the polymerisation reaction offers a feasible and reliable method for on-line monitoring of monomer conversion. Results are finally discussed in terms of their implication on the development of novel production processes for polycarbonates.

Introduction

Using various transition-metal catalyst systems, CO₂ is alternatingly coupled to epoxides in order to produce polycarbonates without the further need for additional solvents. Supercritical CO₂ is used both as a renewable reactant and simultaneously as a means to effectively control the physical and chemical properties of the reaction medium.

Although coupling reactions between epoxides and CO₂ have been under investigation since 1969 [1], little is known about the phase equilibrium thermodynamics of the systems involved. The majority of studies have focussed on catalyst performances based on overall batch yield and average turnover rates. Little attention is paid, however, to the effects of phase behaviour due to e.g. discrepancies between local and overall monomer and catalyst concentrations. As has been underlined by Beckman [2], phase behaviour plays a significant role for the accurate comparison of catalyst performance and analysis of reaction products in relation to initial pressure, temperature and composition. Another problem when using experimental data from batch-wise experiments is that catalyst activity and selectivity are likely not to be constant during the reaction period, which cannot be taken into account if no on-line data is available. Very recently, initial formation rates of polycarbonate and cyclic carbonate from in situ infrared spectroscopic measurements have been reported [3]. Because of high viscosities and pressures, few alternative methods are available. However, one reaction parameter, namely pressure, can be monitored relatively easy. In this paper it is shown that following the pressure decay during reaction provides an experimentally feasible and reliable method to monitor monomer conversion on-line.

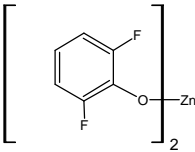
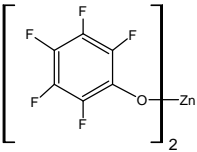
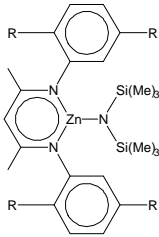
Furthermore, in order to exploit fully the potential of this novel process, it is imperative to study the phase behaviour both inside and outside the pressure and temperature range used for polycarbonate synthesis thus far. Knowledge of the phase behaviour will provide useful information for basic process development guidelines. Data on the performance of different

catalyst systems for the copolymerisation of cyclohexene-oxide (CHO) and CO₂ into poly(cyclohexene-carbonate) (PCHC) are briefly discussed. Additionally, experimental data regarding the thermodynamic phase equilibrium behaviour of the systems PCHC-CO₂, PCHC-CHO-CO₂ up to 200 °C and 4000 bar are presented. CHO-CO₂ vapour pressure isotherms have been measured and modelled up to 151 °C. The data are subsequently interpreted in terms of PCHC and CO₂ solubility in CHO and translated into basic process development guidelines.

Catalyst performance

For this work various transition-metal based catalyst systems are synthesised [4] and tested in batch-wise polymerisation runs. Yield, selectivity towards co- versus homopolymerisation, Mw and Mw/Mn of some of these systems are presented in Table 1. TOF's are calculated averages, based on overall reaction time.

Table 1: Performance of some catalyst systems

			
	1	2	3
Yield ¹ (g PCHC/g Zn)	742	198	392
TOF ¹ (h ⁻¹)	27	8.3	131
Selectivity ²	>99%	94%	>99%
Mw ³ (10 ³ g/mol)	355	235	24
Mw/Mn ³	13	13	1.3

Although these experiments provide highly valuable information for comparing catalyst performance and further development, as explained in the introduction, they need to be interpreted with care and additional information is necessary for a thorough comparison.

Phase behaviour

With the exception of amorphous fluoropolymers and polysiloxanes, CO₂ is a relatively poor solvent for polymers. Studies discussing the factors contributing to polymer-CO₂ phase behaviour generally agree that relatively subtle differences can have relatively large effects on phase behaviour [5]. As long as a fundamental lack of understanding persists, predictive modelling does not offer a reliable alternative to the experimental investigation of phase equilibrium behaviour.

For these experiments a high-pressure Cailletet tube (up to 200 bar) and a windowed autoclave (up to 4000 bar) are used to visually observe phase separation [6]. The experimental accuracy of the Cailletet experiments is within 0.05 °C, 0.05 bar and 0.1 wt%. The

¹ Calculations based on g PCHC per g of zinc and total batch-time

² CO₂ incorporation from H¹ NMR

³ From GPC using PS standard

experiments using the windowed autoclave have an experimental accuracy of 0.01 °C, 1 bar and 0.2 wt% (for PCHC 0.005 wt%). Type 3 catalyst system (Table 1) is used for the synthesis of PCHC with an Mw of 26 kg/mol and an Mw/Mn of 1.6. CHO is distilled from calcium hydride, CO₂ grade 4.5 is used as received from Messer-Griesheim.

Solubility of PCHC in CO₂

The solubility of PCHC in CO₂ is experimentally determined in the windowed autoclave up to pressures of 4000 bar and temperatures of 200 °C. The results of these experiments are shown in Figure 1.

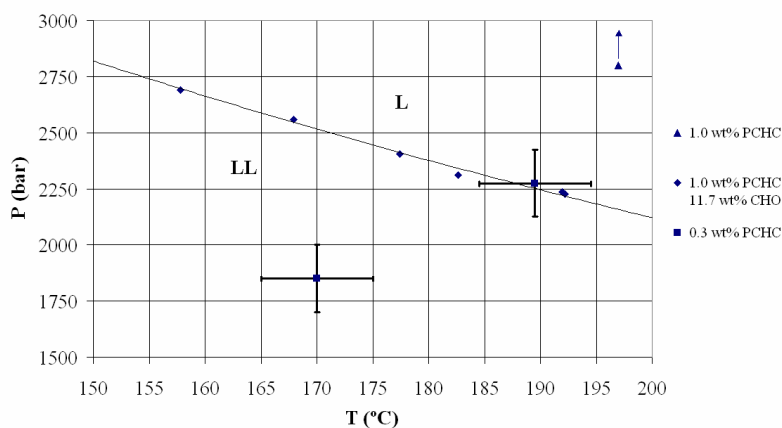


Figure 1: Solubility of PCHC in CO₂ and the co-solvent effect of CHO

The results indicate that, even at a temperature of 200 °C, the pressure that is required to dissolve 1 wt% of PCHC lies beyond the experimental range of the autoclave. Further experiments learn that lowering the polycarbonate concentration even to 0.5 wt% does not enable the formation of one single phase.

Secondly, the experiments demonstrate that 0.3 wt% of PCHC does dissolve in CO₂ at roughly 2000 bar and 170 °C and 2350 bar and 192 °C. For such a low concentration, however, the point of phase separation cannot be sharply indicated, because it is difficult to visually determine the exact location of the cloud point. Nevertheless, it seems reasonable to interpret these results as LCST-type phase behaviour in this region.

Finally, adding 11.7 wt% CHO to the 1 wt% PCHC in CO₂ mixture causes a dramatic increase in PCHC solubility and a change to UCST-type phase behaviour in the same region, both indicating that CHO has a profound influence on solubility. The curves in this and all following figures are arbitrary, unless specifically stated otherwise.

Solubility of CO₂ in CHO

Data on the binary system CHO-CO₂ are important for the interpretation of catalytic test results, as they provide information on local compositions and phase transitions occurring during polymerisations. These experiments do not take into account the effect of dissolved polymer on the phase equilibrium behaviour. This is the subject of the next paragraph. Data are measured using a high pressure Cailletet tube.

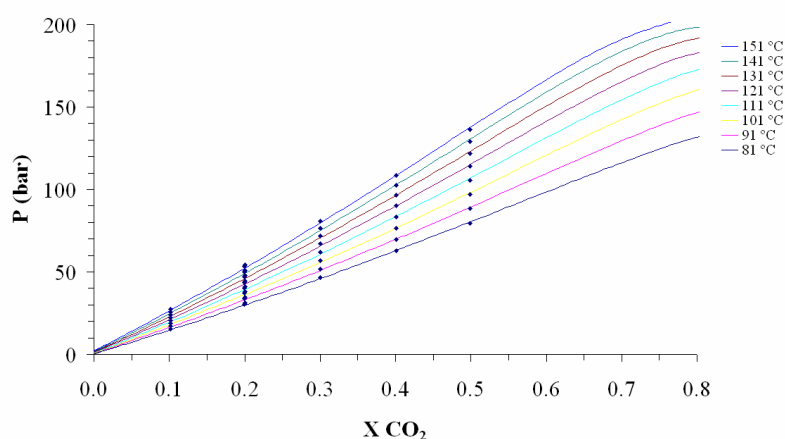


Figure 2: Measurements (•) and modelling (Peng-Robinson equation of state and van der Waals mixing rule) of CHO-CO₂ vapour pressure isotherms

In Figure 2 vapour pressures isotherms are plotted versus liquid phase composition. The experimental measurements are interpolations using the Peng-Robinson equation of state in combination with the van der Waals mixing rule. The critical point and acentric factor of CHO are estimated using the Joback method [7]. The binary interaction parameter correcting for the intermolecular attraction between CO₂ and CHO was fitted to the vapour pressure isotherms. The values of the fitted binary interaction parameters are plotted as a function of temperature in Figure 3. The binary interaction parameter correcting for hard sphere repulsion was set to zero.

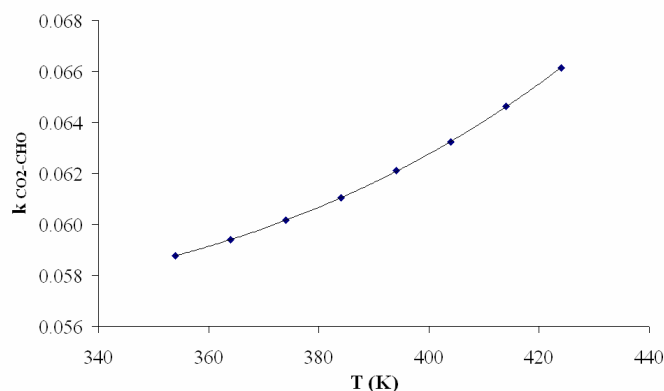


Figure 3: CHO-CO₂ binary interaction parameters from measured vapour pressure isotherms (Peng-Robinson equation of state and van der Waals mixing rule)

PCHC-CHO-CO₂

Considering the relatively low mutual solubility of PCHC and CO₂ (see Figure 1) a pronounced CO₂ anti-solvent effect can be expected in the ternary system PCHC-CHO-CO₂. Secondly, as noted in the previous section, the effect of PCHC on the vapour pressure of binary CHO-CO₂ mixtures is important, as it enables to interpret pressure and temperature in terms of composition of the reaction mixture and therefore provides information about the degree of polymerisation. The results are graphically represented in Figure 4. In none of these experiments polymer precipitation has been observed and the symbols in Figure 4 all indicate experimentally determined bubble points.

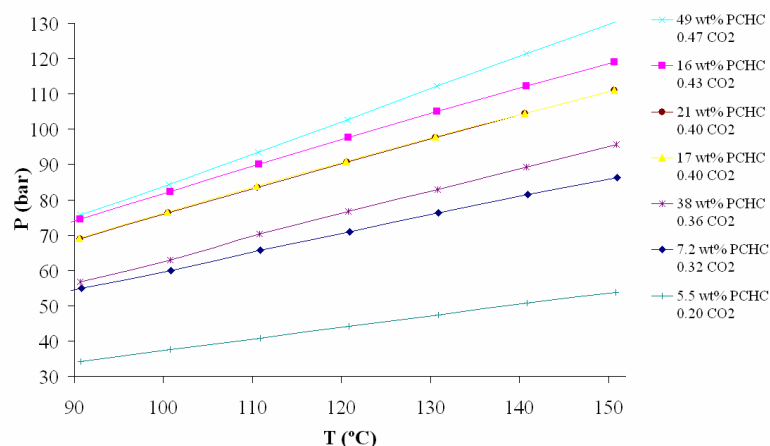


Figure 4: Experimentally determined vapour pressure isopleths of the PCHC-CHO-CO₂ ternary system

These results indicate that mixtures with a nearly equimolar CHO-CO₂ ratio can readily dissolve up to 50 wt% of PCHC, notwithstanding the anti-solvent character of CO₂. Due to the increasing viscosity no measurements can be performed using this experimental set-up. Additionally, the presence of PCHC does not contribute significantly to the vapour pressure of the mixture, which logically appears to be predominantly determined by the CHO-CO₂ ratio. In order to demonstrate this in more detail the 17 wt% and 21 wt% PCHC isopleths, both containing a mole fraction of 0.40 CO₂ (on a polymer free basis), are compared to the binary 0.40 CO₂ isopleth in Figure 5. To illustrate the effect of varying CHO-CO₂ ratio, two lines representing a mole fraction of 0.35 and 0.45 CO₂ are added. These are interpolations of experimentally determined points.

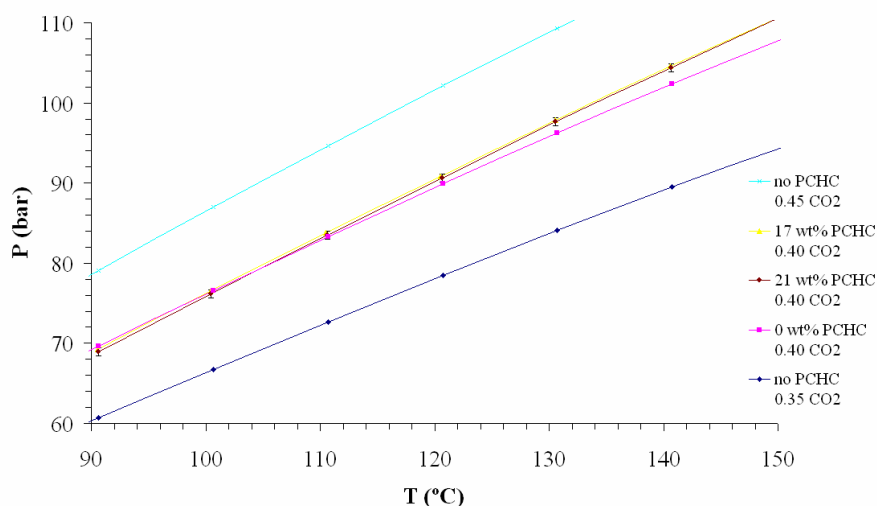


Figure 5: Vapour pressure curves for PCHC-CHO-CO₂ isopleths with the same CHO-CO₂ ratio. 0.35 and 0.45 are interpolations of experimentally determined vapour pressures

This figure emphasises the small effect of PCHC in the ternary PCHC-CHO-CO₂ systems on vapour pressure, relative to the effect of the CHO-CO₂ ratio. Inasmuch as there is a significant

difference, it clearly increases close to the binary critical point of CHO-CO₂. The higher vapour pressures, measured in the presence of polycarbonate can be indicative of more favourable interaction between PCHC and CHO than between PCHC and CO₂. In qualitative terms this means that PCHC and CO₂ compete for the total solubility capacity of CHO.

Figure 4 and 5 clearly demonstrate the dependence of system pressure on liquid phase composition. This suggests that monitoring the pressure decay of the reaction system is a feasible and relatively solid method to follow monomer conversion on-line.

Conclusion

Experiments up to 4000 bar and 200 °C have demonstrated the solubility of PCHC in CO₂ to be too low to be determined accurately. Nevertheless, CO₂ proved to dissolve 0.3 wt% of PCHC at 170 °C and 2000 bar and 192 °C and 2350 bar. Addition of 11.7 wt% CHO to CO₂ strongly increases PCHC solubility and causes the phase behaviour to develop from LCST to UCST-type behaviour. These results indicate CHO to be a highly efficient co-solvent for PCHC.

Up to pressures of 130 bar and 150 °C CO₂ does not act as an anti-solvent for PCHC in CHO solutions up to 49 wt% and CHO-CO₂ ratios of 1:1. Apparently, PCHC can be dissolved up to relatively high concentrations in equimolar CHO-CO₂ liquid mixtures. This again indicates CHO to be a highly efficient solvent for PCHC. In the same experimental range CHO-CO₂ vapour pressure isotherms have been successfully measured and modelled using the Peng-Robinson equation of state and van der Waals mixing rule.

The results suggest that conversion can be monitored on-line by observing the pressure decay of the reaction system as vapour pressure can be directly linked to composition, as long as certain obvious experimental restrictions are met. For this purpose additional experiments focussing on the thermodynamic phase equilibrium behaviour of this system as well as kinetic experiments will be performed in the near future, in order to clarify the effects of local composition, pressure and temperature on catalyst performance.

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