

POLYCARBONATES FROM SUPERCRITICAL CARBON DIOXIDE: PHASE EQUILIBRIA AND POLYMERISATION KINETICS

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Experimentally determined cloud-point pressures of poly(cyclohexene-carbonate) (PCHC) in supercritical carbon dioxide (scCO₂) are presented. The effects of polymer concentration, polymer molecular weight and cyclohexene oxide (CHO) are discussed for temperatures from 100 to 200°C and pressures up to 4000 bar. For the binary system CHO-CO₂ bubble points are shown and correlated using the Peng-Robinson equation of state. Bubble points are also presented for CHO-rich mixtures containing CO₂ and PCHC for temperatures up to 150°C and pressures up to 150 bar. This range covers the typical conditions for CHO-CO₂ copolymerisations. Moreover, these data constitute the basis for an effective method to observe reaction rates on-line via the development of vapour pressure during polymerisation. The basis for this method and the results obtained therewith are presented in this contribution.

INTRODUCTION

Supercritical CO₂ receives a lot of attention as a new or potential medium for polymer synthesis and processing. The most important reasons for this are that carbon dioxide is generally accepted to be environmentally benign and secondly because supercritical fluids possess a number of unique physical properties.

CO₂ plays another important role as an inexhaustible resource for carbon, which is interesting from both an environmental and an economical point of view. However, the use of CO₂ as an active reagent is limited due to its high chemical inertia, which is advantageous for process safety considerations. Fortunately, research into catalytic activation of CO₂ has led to a large number of such purposes for CO₂ [1]. An interesting example in this perspective is the development of catalysts for the copolymerisation of CO₂ and epoxides. This alternative route towards the synthesis of polycarbonates has been investigated since the late 1960's [2] and has provided us with a large amount of late transition metal catalyst systems [3].

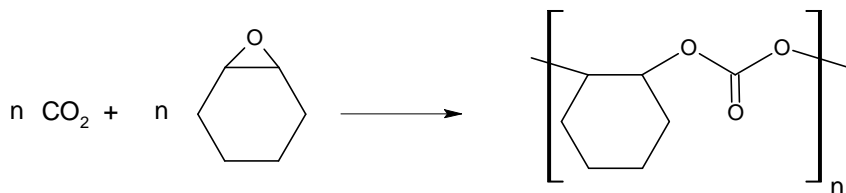


Figure 1: Model reaction for the co polymerisation of CO₂ and cyclohexene oxide (CHO)

In this study the use of CO₂ as an alternative monomer in a novel production route for polycarbonates is explored. It concerns a solvent-free process in which CO₂ is also used to effectively control the physical and chemical properties of the reaction medium. For this purpose the copolymerisation of CO₂ and cyclohexene oxide (CHO) into poly(cyclohexene carbonate) (PCHC) is studied as a model reaction (Figure 1).

Little is known, however, about the thermodynamic phase equilibrium behaviour of the model system. As the phase behaviour of polymer-SCF systems is relatively complex, predictive modelling does not provide an alternative to an experimental approach. In this work visually determined cloud points and bubble points are presented for the system PCHC-CHO-CO₂. The emphasis lies on the effect of polymer concentration, molecular weight and CHO concentration on the solubility of PCHC in CO₂ and the effect of composition on vapour pressure. These latter measurements are further used for the development of a method to observe reaction rates during polymerisation. This method enables to obtain essential data about the reaction kinetics of this model system.

EXPERIMENTAL

For all experiments CO₂ grade 4.5 from Messer-Griesheim was used. CHO was refluxed with calcium hydride under argon and subsequently distilled. PCHC samples were especially synthesized using a zinc β -diiminate complex as catalyst and have a maximum polydispersity of 1.2 and a weight average molecular weight of 12, 25 and 54 kg/mole, determined against polystyrene standards.

For the thermodynamic phase equilibrium measurements a static method with visual determination of cloud and bubble points is used. For this purpose a glass tube is filled with sample with an accurately controlled composition. Subsequently, a steel stirrer ball is added and the sample is sealed off with mercury. The tube is placed in a thermostated environment and the mercury is connected to a hydraulic pressure system and a dead weight gage. For the experiments in the 150-4000 bar pressure range a windowed autoclave is used [4].

PCHC SOLUBILITY IN SUPERCRITICAL CO₂

As for most polymers, the solubility of PCHC in supercritical CO₂ is extremely low; for example, 1 wt% of 25.000 g/mole PCHC cannot be dissolved at pressures and temperatures as high as 4000 bar and 200° C. Lowering the polymer concentration to 0.3 wt% makes dissolutions possible at these conditions, but hinders the accurate determination of the phase transitions. Addition of low concentrations of CHO to 1 wt% of PCHC in CO₂, however, significantly reduces the cloud-point pressures and enables an accurate determination of these transitions. In Figure 2 the results of some of the cloud-point measurements of 1 wt% PCHC in CO₂ with various concentrations of CHO are graphically presented. The curves denote the transitions from the two-phase region at low pressure to the single-phase region at higher pressures for 1 wt% of PCHC in CO₂ at different concentrations of CHO. These curves and those in all other figures are arbitrary, unless stated otherwise. Clearly, the addition of small amounts of CHO has a dramatic effect in the solubility of PCHC in CO₂. The slopes indicate that the transitions are mainly governed by enthalpic interactions, as they resemble UCST kind of behaviour. At higher concentrations of CHO a change in the direction of the PT-slope

is observed indicating a change in the nature of the phase transition. This indicates the transition from CO₂-rich to a CHO-rich regime.

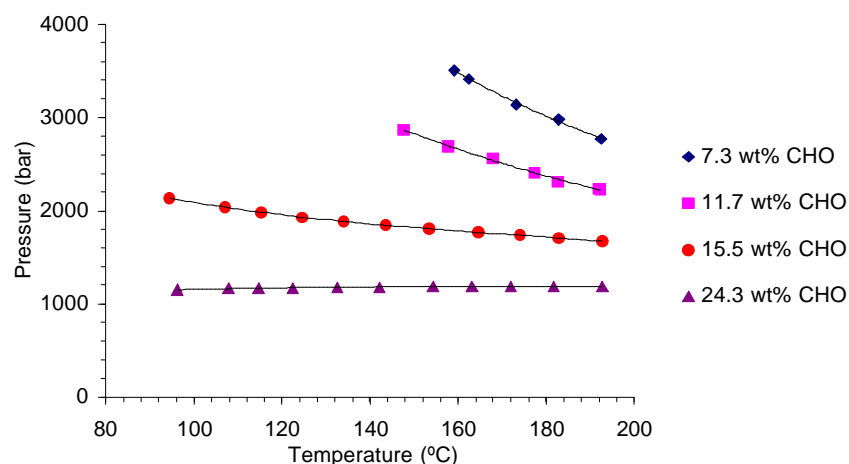


Figure 2: Effect of CHO concentration on the solubility pressure of 1 wt% of PCHC (25,000 g/mole) in scCO₂

In Figure 3 the effect of polymer molecular weight on the solubility pressure is graphically presented. As expected larger chains require higher pressures to be dissolved in CO₂ and this effect becomes less pronounced at higher molecular weights.

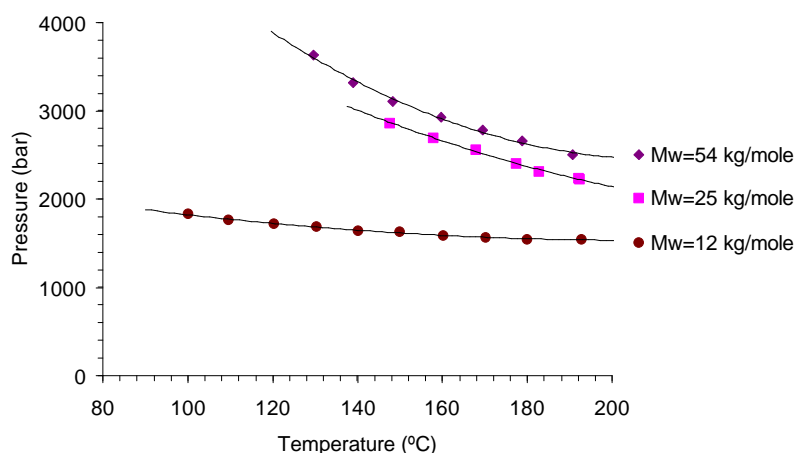


Figure 3: Effect of molecular weight on the solubility pressure of 1 wt% of PCHC in scCO₂ and 13 wt% CHO

VAPOUR PRESSURE OF CHO-CO₂ MIXTURES

In Figure 4 the results of the bubble point determinations in the CHO-CO₂ binary system are presented per isotherm. The experimentally determined values, represented by diamonds, are interpolated using the Peng-Robinson equation of state (Equation 1) and the Van der Waals mixing rules (Equations 2 and 3). The critical point (T_c and P_c) and acentric factor (ω) of CHO are estimated using the Joback method [5] (622 K, 43.3 bar and 0.276, respectively).

The binary interaction parameter (k_{ij}) correcting for the intermolecular attraction between CO₂ and CHO was optimised to fit the experimentally determined vapour pressures. The values of these temperature dependant binary interaction parameters are plotted as a function of temperature in Figure 5. The binary interaction parameter correcting for hard sphere repulsion (l_{ij}) was set to zero.

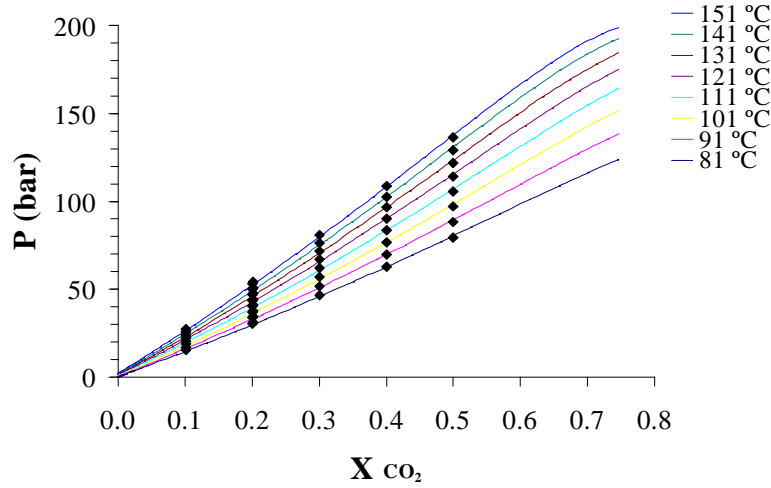


Figure 4: Measurements (•) and modelling (Peng-Robinson equation of state and Van der Waals mixing rules) of CO₂-CHO vapour pressure isotherms

$$P = \frac{RT}{v - b(T_c, P_c)} - \frac{a(T_c) \mathbf{a}(T_r, \mathbf{w})}{v^2 + 2b(T_c, P_c)v - b(T_c, P_c)^2} \quad \text{Equation (1)}$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad \text{Equation (2)}$$

$$b = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij}) \quad \text{Equation (3)}$$

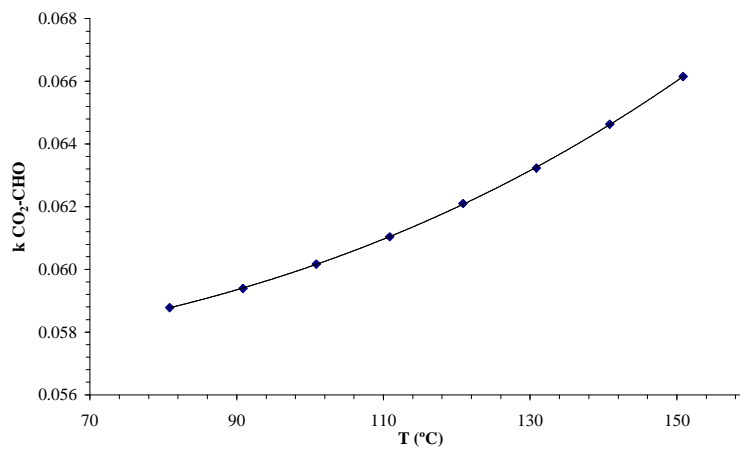


Figure 5: CO₂-CHO binary interaction parameters as a function of temperature (Peng-Robinson equation of state and Van der Waals mixing rule)

EFFECT OF PCHC ON THE VAPOUR PRESSURE OF CHO-CO₂ MIXTURES

When solutions of PCHC in CHO are pressurised with CO₂ polymer precipitation is not observed in spite of the anti-solvent effect of CO₂. Solutions containing up to 50 wt% PCHC are stable up to 150°C while CHO and CO₂ are present at an equimolar ratio. Due to the increasing viscosity no measurements can be performed using this experimental set-up at higher polymer concentrations or at lower temperatures. Instead of liquid to solid-liquid transitions liquid to vapour-liquid transitions are observed. These transitions are very similar to the behaviour observed in the CHO-CO₂ mixture. Figure 6 shows the relative effect of the PCHC concentration on vapour pressure in contrast to the effect of the CO₂-CHO ratio.

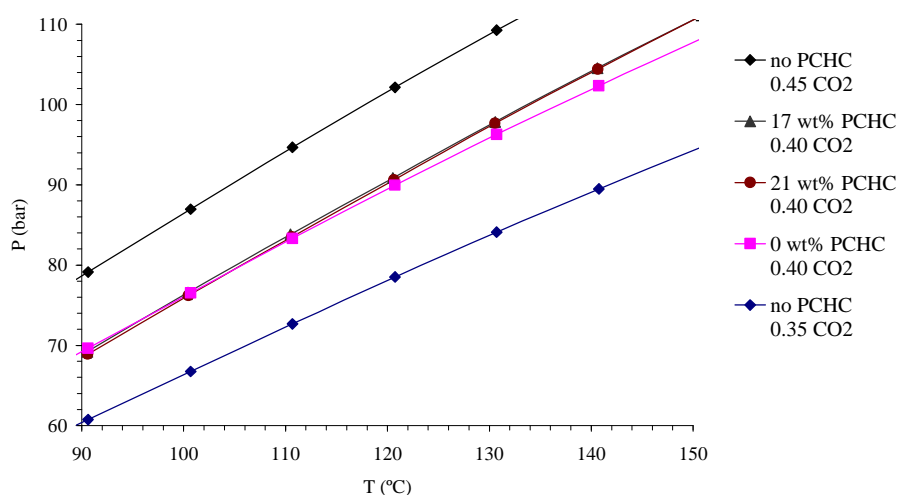


Figure 6: Effect of PCHC concentration on vapour pressure

In the middle of the graph three lines, of which 2 are practically on top of each other, indicate the vapour pressure of samples containing a mole fraction of 0.40 CO₂ (on a polymer free basis) each. The samples contain 0, 17 and 21 wt% PCHC, respectively. The lower and upper lines in Figure 5 represent the vapour pressure isopleths of polymer free samples with a mole fraction of CO₂ of 0.35 and 0.45. Clearly, the contribution of PCHC to the vapour pressure of the mixture is not significant compared to the effect of the CHO-CO₂ ratio. From these results it is concluded that the vapour pressure of liquid phase CO₂-CHO-PCHC ternary mixtures is predominantly determined by the CO₂-CHO ratio.

ON-LINE REACTION RATE DETERMINATION USING VAPOR PRESSURE

The conclusion that the CO₂-CHO ratio is the main factor determining vapour pressure means that vapour pressure can be readily interpreted in terms of the composition of the model system. Gibb's phase rule states that a system containing three components and two phases has three degrees of freedom as long as the requirements for thermodynamic phase equilibrium are met. This means that if temperature and pressure are fixed, the overall composition entirely determines the system. As in a batch process the composition of the system is determined by the initial composition, the stoichiometry of the reaction and conversion, vapour pressure can be linked to the composition of the liquid phase, as long as the system is at vapour-liquid equilibrium and the size of the vapour pressure is not significant. However, in order to do this the relationship between composition and vapour

pressure has to be available. As seen in the previous section, this relationship is mainly determined by the CHO-CO₂ ratio but polymer concentration and polymer molecular weight still have a small but significant effect. Therefore, a large number of mixtures have been prepared with compositions corresponding to compositions of samples taken from a virtual polymerisation reaction. In Figure 7 the experimentally determined vapour pressures of these mixtures are plotted versus composition, which is expressed in terms of initial concentration and monomer conversion. The initial mole fraction of CO₂ in these samples is 0.33 and PCHC has a molecular weight of 25.000 g/mole. Since, this has been done for a large range of compositions and temperatures, these data constitute the basis for an effective method to observe reaction rates during polymerisation.

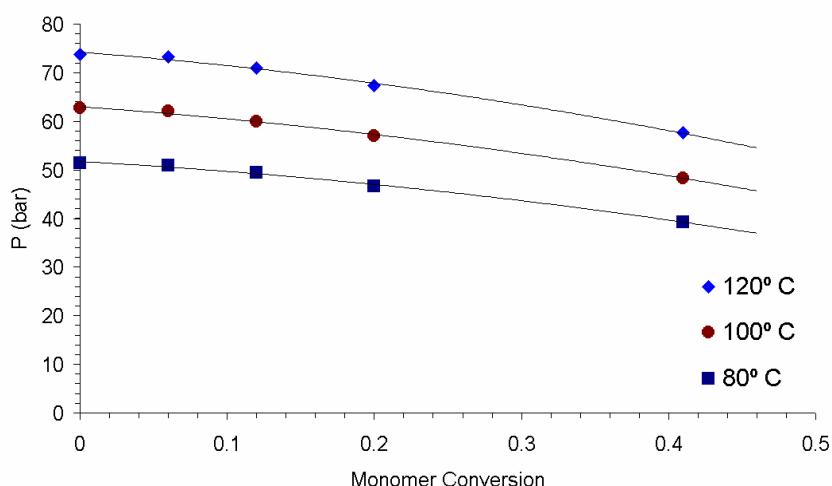


Figure 7: Vapour pressure as a function of monomer conversion, initial fraction of CO₂ is 0.33

CONCLUSIONS

Cloud-point pressures of PCHC in scCO₂ have been experimentally determined and presented at temperatures from 100 to 200° C and at pressures up to 4000 bar, including the effect of polymer concentration, polymer molecular weight and CHO concentration. For the system CHO-CO₂ bubble points have been determined and correlated using the Peng-Robinson equation of state. Bubble points have also been presented for CHO rich mixtures containing CO₂ and PCHC at temperatures up to 150° C and pressures up to 150 bar. Finally, these data have been partially used for the development of a method to observe reaction rates on-line via the vapour pressure during polymerisation.

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