Determination of melting point of polycaprolactones under carbon dioxide pressure

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Solid-Liquid-Gas equilibrium of poly-(ε-caprolactone) – carbon dioxide systems at high pressure has been determined by visual determination of the first melting point using a static apparatus. Measurements have been performed with poly-(ε-caprolactones) of three different molecular weights: 4000 g/mol, 10000 g/mol and 25000 g/mol. The determined SLG equilibrium lines show a temperature maximum at low pressures (0.5 Pa < P < 1.6 MPa) and a temperature minimum at moderate pressures (8 MPa < P < 10 MPa). The maximum reduction of melting temperature ranges from 12.5 K to 16.0 K depending on the molecular weight of the polymer. A thermodynamic model based on the PC-SAFT equation of state has been developed to describe experimental data.

1. Introduction

Controlled release formulations are often prepared by encapsulation of the active compound in a natural or biodegradable polymer. Polymeric nanocarriers can show several desirable properties including controlled release of the active compound, long longevity in the body or even specific targeting to certain disease sites [1]. Polyesters such as poly (lactic acid) (PLA) or poly (glycolic acid) (PLG) have been widely employed to prepare carriers for controlled release of drugs and proteins. These polymers degrade by bulk hydrolysis of ester bonds, and their rate of degradation depends on several parameters such as chemical structure, crystallinity, hydrophobicity and molecular weight [2]. The successful use of these polymers in pharmaceutical applications has led to the evaluation of other aliphatic polyesters such as poly (ε-caprolactone) (PCL).

Poly(ε-caprolactone) is a synthetic biocompatible semi-crystalline polymer. PCL exhibits a low glass transition temperature (from -60 ºC to -10 ºC, depending on its molecular weight) which imparts a rubbery characteristic to the material, which results in high permeability. This property has been exploited for delivery of low molecular weight drugs such as steroids and vaccines [3]. It has been also used as platform for high molecular weight substances as for example proteins where protection against degradation provided by PCL has been proved to be better than the protection achieved with other polyesters [4, 5].

Precipitation processes based on the use of supercritical fluids, and in particular of supercritical carbon dioxide have been successfully applied to produce polymeric carriers. Different techniques have been developed, including Rapid Expansion of Supercritical Solutions (RESS), Supercritical Anti Solvent (SAS) and Particles from Gas Saturated Solutions (PGSS), which present significant advantages over other precipitation techniques including the possibility to process the material in an inert and non-toxic medium and an enhanced control over particle size.
and morphology [6]. In order to design these processes and optimize the operating conditions a
detailed knowledge of the phase behavior of polymer + supercritical fluid mixtures is required.

It is well known that supercritical carbon dioxide interacts with polymers acting as a
plasticizing and swelling agent, and reduces significantly the glass transition and melting
temperatures of the polymer [7]. Knowledge of Solid-Liquid-Gas (SLG) phase behavior of
polymer + CO$_2$ mixtures is therefore very important for developing formulation processes
because it determines the conditions in which solid particles can actually be produced, as well as
near-melting conditions which may be favorable for impregnation processes.

In Table 1, experimental data of melting temperature under carbon dioxide pressure of different
compounds are shown. In the case of polyethylene glycol (PEG) [8], it can be seen that the
maximum reduction of the melting temperature is 16, 15 and 13K for PEG 1500, 4000 and
35000, respectively. The largest melting point depression is 55K in the case of poly ($\varepsilon$)-lactic acid
(PLLA) [9]. Comparing to naphthalene, the maximum reduction of the melting temperature is
20.6K when the experiment is carried out by freezing method.

The most common method used for the determination of the melting point under carbon
dioxide pressure is the capillary method using a high pressure optical cell with sapphire windows.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tm (K)</th>
<th>Pressure range (MPa)</th>
<th>Minimum Tm (K)</th>
<th>P at minimum Tm (MPa)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 1500 [8]</td>
<td>318.0</td>
<td>0.1 – 23.65</td>
<td>302.0</td>
<td>6.95</td>
<td>Capillary method. High pressure optical cell</td>
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<td>PEG 4000 [8]</td>
<td>330.0</td>
<td>0.1 – 22.23</td>
<td>315.0</td>
<td>9.40</td>
<td>Capillary method. High pressure optical cell</td>
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<tr>
<td>PEG 35000 [8]</td>
<td>334.0</td>
<td>0.1 – 24.13</td>
<td>321.0</td>
<td>10.73</td>
<td>Capillary method. High pressure optical cell</td>
</tr>
<tr>
<td>PCL 4000 [9]</td>
<td>332.0</td>
<td>0.1 – 27.6</td>
<td>307.2</td>
<td>8.80</td>
<td>Constant volume view cell</td>
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<td>PBS [9]</td>
<td>388.0</td>
<td>0.1 – 20.76</td>
<td>373.9</td>
<td>14.50</td>
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</tr>
<tr>
<td>PEA [9]</td>
<td>328.0</td>
<td>-</td>
<td>306.2</td>
<td>27.60</td>
<td>Variable volume view cell</td>
</tr>
<tr>
<td>PLLA [9]</td>
<td>448.0</td>
<td>-</td>
<td>393.2</td>
<td>27.60</td>
<td>Variable volume view cell</td>
</tr>
<tr>
<td>PVDF homopolymer</td>
<td>431.0</td>
<td>-</td>
<td>409.0</td>
<td>47.60</td>
<td>LVDT (Linear Variable Displacement Transformer)</td>
</tr>
<tr>
<td>PVDF copolymer</td>
<td>405.0</td>
<td>-</td>
<td>379.0</td>
<td>55.20</td>
<td>LVDT (Linear Variable Displacement Transformer)</td>
</tr>
</tbody>
</table>
### Table 1. Continuation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tm (K)</th>
<th>Pressure range (MPa)</th>
<th>Minimum Tm (K)</th>
<th>P at minimum Tm (MPa)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcone [11]</td>
<td>329.8</td>
<td>0 – 20.0</td>
<td>312.3</td>
<td>10.45</td>
<td>Capillary method. High pressure cell</td>
</tr>
<tr>
<td>Precirol® ATO5 [12]</td>
<td>336.2</td>
<td>0 – 30.0</td>
<td>323.3</td>
<td>15.15</td>
<td>Capillary method. High pressure cell</td>
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<tr>
<td>Compritol® 888ATO [12]</td>
<td>345.7</td>
<td>0 – 30.0</td>
<td>340.0</td>
<td>19.40</td>
<td>Capillary method. High pressure cell</td>
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<tr>
<td>Gelucire® 43-01 [12]</td>
<td>321.5</td>
<td>0 – 30.0</td>
<td>308.4</td>
<td>19.80</td>
<td>Capillary method. High pressure cell</td>
</tr>
<tr>
<td>Naphthalene [13]</td>
<td>353.7</td>
<td>0.1 – 20.0</td>
<td>333.4</td>
<td>12.40</td>
<td>Freezing method</td>
</tr>
<tr>
<td>Naphthalene [13]</td>
<td>353.4</td>
<td>0.1 – 20.0</td>
<td>332.8</td>
<td>17.50</td>
<td>Capillary method. High pressure view cell</td>
</tr>
<tr>
<td>Biphenyl [13]</td>
<td>341.3</td>
<td>0.1 – 19.8</td>
<td>321.4</td>
<td>10.40</td>
<td>Freezing method</td>
</tr>
<tr>
<td>Ethyl-o-vanillin [13]</td>
<td>338.9</td>
<td>0.1 – 29.5</td>
<td>314.4</td>
<td>19.60</td>
<td>Capillary method. High pressure view cell</td>
</tr>
<tr>
<td>Vanillin [13]</td>
<td>353.8</td>
<td>0.1 – 19.7</td>
<td>343.7</td>
<td>13.30</td>
<td>Freezing method</td>
</tr>
<tr>
<td>Ethyl-o-vanillin [13]</td>
<td>338.4</td>
<td>0.1 – 19.8</td>
<td>314.6</td>
<td>15.15</td>
<td>Freezing method</td>
</tr>
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Several articles deal with the determination of the phase behavior of PCL + CO\(_2\) mixtures. Cotugno et al. [14] reported the solubility of near-critical CO\(_2\) in PCL (molecular weight: 80000 g/mol, melting temperature: 58°C) at high temperature (from 70 to 85°C). Domingo et al. [15] measured the solubility of a polymer blend (PMMA/PCL) in supercritical CO\(_2\) without and with cosolvents (acetone, dichloromethane and ethanol). Rodríguez-Rojo et al. [16] determined the solubility of PCL with average molecular weight 1000 g/mol in CO\(_2\) using ethanol as co-solvent. Leeke et al. [17] measured the solubility of supercritical CO\(_2\) in the polymer in the temperature range from 40 to 60°C with pressures up to 20 MPa. Lian et al. [9] determined the SLG phase behavior of PCL with average mol weight 4000 g/mol with CO\(_2\).

In this work the SLG phase behavior of PCL and CO\(_2\) at high pressure (P = 0.1 MPa to 25 MPa) is reported. Measurements have been carried out using PCL with three different molecular
weights: 4000 g/mol, 10000 g/mol and 25000 g/mol. Furthermore, a thermodynamic model of the phase behavior of CO$_2$ + PCL mixtures based on the PC-SAFT equation of state [18] is presented.

### 2. Materials and methods

#### 2.1 Materials

Carbon dioxide (purity: 99.5%) was provided by S. E. Carburos Metálicos S. A. (Spain). Poly-(ε-caprolactones) were kindly supplied by Solvay Caprolactones (Solvay Interox Ltd, United Kingdom). Three different commercial poly-(ε-caprolactones) were used: CAPA® 2043D, CAPA® 6100 and CAPA® 6250. Physical properties of PCLs used in this work are summarized in Table 2. All products were used as received.

#### Table 2. Physical properties of poly-(ε-caprolactones) used in this work. Data provided by the supplier.

<table>
<thead>
<tr>
<th>PCL</th>
<th>MW (g/mol)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPA® 2403D</td>
<td>4000</td>
<td>50 – 60</td>
</tr>
<tr>
<td>CAPA® 6100</td>
<td>10000</td>
<td>58 – 60</td>
</tr>
<tr>
<td>CAPA® 6250</td>
<td>25000</td>
<td>60 – 70</td>
</tr>
</tbody>
</table>

#### 2.2 Equipment

A schematic diagram of the equipment used for melting point determinations is shown in Figure 1. The main part of the equipment is an optical cell (SITEC 740.2120) with an inner volume of 25 mL. Maximum operating conditions inside the cell are P = 50 MPa and T = 473 K. The cell has two opposite sapphire windows. Through one of them a cold light lamp is situated to allow the visualization of the different processes taking place inside the cell aided by a CCD camcorder (Eurotechnica Ingenieurbüro GMBH) connected to a personal computer. Internal temperature of the cell is controlled by a PID temperature controller (OMRON E5GN) acting over an electrical jacket and measuring the temperature with a J type thermocouple (SITEC 770.5131-22, accuracy 0.1 K). Pressure is measured with a membrane pressure meter (DESIN TPR-18/V2, accuracy 0.01 MPa). The system also has a manual pressure generator (SITEC 750.1060) which adjusted the system volume and a diaphragm pump (Dosapro).
In Figure 2, it is shown a picture of the equipment used for melting point determinations. In the center of the picture, it can be seen the optical cell with two opposite sapphire windows. On the left side, there is a cold light lamp and on the right side there is a camcorder which allows the visualization of the processes which take place inside the optical cell due to the fact the camcorder is connected to the computer. It can also be seen that the optical cell is connected to a mobile piston.

**2.3 Method**

The melting point of PCL with CO\textsubscript{2} at high pressure was measured by visually determining the temperature at which melting started at a certain fixed pressure, according to the first melting point method [9]. For doing so, a small amount of PCL was put in a glass vial and introduced in the optical cell. Afterwards the cell was flushed with CO\textsubscript{2} to remove air, and the cell was filled with CO\textsubscript{2} and pressurized up to desired operating pressure by using the diaphragm pump. Then the cell was gradually heated with the electrical jacket until melting of the PCL sample was
observed with the CCD camcorder. During the heating process, pressure was maintained constant within $\pm 0.1$ MPa by manipulation of the manual pressure generator. Preliminary experiments showed that melting temperatures visually determined with this method were reproducible within $\pm 0.5$ K.

In figure 3 it is shown a picture of CAPA® 6100 sample before starting the experiment at 5.18 MPa and just in the moment in which the sample starts to melt (328K).

![Figure 3. CAPA® 6100 sample a) before starting the experiment, b) CAPA® 6100 melting point (328K) at 5.18 MPa](image)

### 3. Thermodynamic model

The PC-SAFT Equation of State considers molecules to be constituted by chains of freely jointed spherical segments. This equation was developed in terms of the residual Helmholtz free energy $a_{res}$, which can be calculated as the sum of three contributions, as presented in Eq. (1):

$$a_{res} = a_{hc} + a_{disp} + a_{ass}$$

In this equation, $a_{hc}$ accounts for the repulsion of the chain-like molecule, using the hard-chain expression derived by Chapman et al. [19], $a_{disp}$ accounts for the dispersion forces due to attraction between temporarily induced dipoles, and $a_{ass}$ accounts for the association between molecules, described by the association term of the original SAFT Equation of State [20]. Full details about the calculation of these contributions to the residual Helmholtz energy were provided by Gross and Sadowski [18] and by Chapman et al. [19].

Within this framework, non-associating molecules are described by three parameters: the number of segments per chain $m$, the segment diameter $\sigma$, and the depth of the pair potential $\varepsilon/k_B$.

Conventional mixing rules can be used for the parameters $\sigma$ and $\varepsilon/k_B$:

$$\sigma_j = \frac{1}{2}(\sigma_i + \sigma_j)$$

$$\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{0.5} \cdot (1 - k_{ij})$$

Where $\varepsilon$, $k_0$, and $k_{ij}$ is the depth of the dispersion potential, Boltzmann’s constant and binary interaction parameter, respectively.

For calculation of SLG equilibria, this equation of state has to be applied to solve the condition of equality of fugacity in each phase:
As most equations of state, PC-SAFT can only be used to calculate the fugacity of fluid phases, and not of solid phases. As an approximation, the fugacity of the solid phase can be calculated as a function of the fugacity of a reference, sub cooled liquid $f_{SCL}^i$ with the following equation, which is strictly valid in the triple point of the substance [21]:

$$f_i(s, p) = f_i^{SCL}(T, p) \cdot \exp \left[ \frac{v_2^S - v_2^{SCL}}{RT} (p - p^0) + \frac{\Delta h^{fus}}{RT^0} \left( 1 - \frac{T^0}{T} \right) \right]$$

where $T^0$ and $\Delta h^{fus}$ are the melting temperature and heat of fusion of the PCL at the triple point pressure $p^0$ which can be approximated with good accuracy by the corresponding values at normal conditions. $v_2^S$ and $v_2^{SCL}$ are the molar volumes of the solid and sub-cooled liquid of the polymer, respectively.

4. Results and Discussion

Experimental results obtained in this work are presented in Figures 4, 5 and 6. It can be seen that the melting point curves obtained with the three investigated PCLs have a similar shape: at low pressures, there is a certain increase of melting temperature when pressure is increased. In the case of CAPA® 2403D melting temperature increases as much as 3.5 K, while in the case of the other two PCLs the extent of this increase is of 1 K. For CAPA® 2043D, the maximum melting temperature is observed at 1.6 MPa. In the case of CAPA® 6100 and CAPA® 6250, this temperature is observed at 0.8 and 0.5 MPa, respectively. In the pressure range 1 MPa < $p$ < 8 MPa melting temperature strongly decreases with pressures with a nearly linear variation. At higher pressures melting temperature either shows no variation or increases slightly when pressure is increased. The maximum melting temperature depression is 12.5 K in the case of CAPA® 2403D, 15.5 K in the case of CAPA® 6100 and 16.0 K in the case of CAPA® 6250.

Lian et al. [9] also determined the SLG phase equilibria of a poly-(ε-caprolactone) with average molecular weight of 4000 g/mol, equivalent to that of CAPA® 2043D. For comparison purposes, in Figure 4 the results of these authors are represented together with results obtained in this work. It can be seen that the results of Lian et al. present the same shape of data obtained in this work. Both data sets report the same melting temperature at ambient conditions (327 K), a similar maximum melting temperature ($T = 330.5$ K at $p = 1.6$ MPa in this work, and $T = 332.2$ K at $p = 0.7$ MPa in the data set of Lian et al.), and the slope of the $T$ vs. $p$ curve in the region of moderate pressures (1 MPa – 8 MPa) is also similar in both data sets. However, significant differences can be observed between the two data sets in the region of high pressure, because Lian et al. observed a minimum melting temperature of about 310 K, which is 4.5 K lower than that observed in this work. It is worth mentioning that the PCLs used in the two works were obtained from different suppliers: Solvay Polycaprolactones in this work and Dow Chemicals in the work of Lian et al. It is therefore possible that these products have differences in properties such as the exact value of the mean molecular weight or the polydispersity index which justify the observed differences in the melting behavior.
Figure 4. SLG equilibrium of PCL – CO$_2$ systems: results with PCL with molecular weight 4 000 g/mol (CAPA® 2403D). Symbols: (○) Experimental results. (□) Literature data [9]). Continuous line: model results.

Figure 5. SLG equilibrium of PCL – CO$_2$ systems: results with PCL with molecular weight 10 000 g/mol (CAPA® 6100). Symbols: Experimental results. Continuous line: model results.

Figure 6. SLG equilibrium of PCL – CO$_2$ systems: results with PCL with molecular weight 25 000 g/mol (CAPA® 6250). Symbols: Experimental results. Continuous line: model results.
In Figure 7, it is shown a DSC analysis of two samples of CAPA® 6100 at different conditions. In Figures 7a and 7b, it is shown a DSC analysis at 10.0 MPa and at 15.0 MPa, respectively. It can be seen that the results obtained are independent of the conditions of pressure and temperature in which the polymer is melted. It is obtained practically the same DSC analysis for different conditions of pressure and temperature.

![Figure 7. DSC analysis of different samples of CAPA® 6100 a) at 10.0 MPa b) at 15.0 MPa.](image)

A similar shape of the SLG equilibrium lines with maximum and minimum melting temperatures was observed by Weidner et al. for the system carbon dioxide + polyethylene glycol [8]. The minimum melting temperature phenomenon can be easily explained by considering the balanced effects of the dissolution of CO$_2$ into the polymer, which tends to reduce the melting temperature, and hydrostatic pressure, which tends to increase this temperature. Indeed, the solubility of CO$_2$ in most molten polymers can be very high and at moderate pressures it increases rapidly and almost linearly when pressure is increased, while over a certain pressure the solubility of CO$_2$ increases by a very small extent even if large pressure increases are applied, resulting in an almost vertical $P$ vs. $x_{CO2}$ equilibrium line [17]. Therefore it can be argued that at moderate pressures the effect of CO$_2$ solubilization prevails and hence the important reduction of melting temperature in this pressure range, while at high pressures the solubility of CO$_2$ in the molten polymer increases by a small extent when pressure is increased and therefore the hydrostatic pressure effect prevails. However, the maximum melting temperature phenomenon cannot be easily explained by thermodynamic considerations. In a detailed thermodynamic analysis, de Loos [22] concluded that in a binary system such behavior is possible only if the solubility of CO$_2$ in the solid phase is higher than in the liquid phase. Nevertheless de Loos pointed out that such behavior is very rare, as in most cases a negligible solubility of CO$_2$ in the solid is expected at low pressures.

On the other hand, Lian et al. [9], who also observed a maximum melting temperature in CO$_2$ + PCL systems, attributed this phenomenon to lamellar thickening of PCL due to the enhanced polymer-chain mobility in the CO$_2$-exposed amorphous regions. This explanation was based on the experimental observations of Siheh and Yang [23], who observed this phenomenon in PCL exposed to CO$_2$ at high pressure by application of Differential Scanning Calorimetry (DSC) and Small-Angle X-ray Scattering (SAXS). However, it must be pointed out that according to Siheh and Yang [23], these modifications in the crystalline structure of PCL only took place when the
polymer was exposed to CO$_2$ at moderately high pressures (P > 3.6 MPa). A similar behavior has been observed with other polymers: López-Periago et al. [24] found that CO$_2$ could cause a solvent-induced crystallization in poly lactic acid exposed to CO$_2$ at temperatures below the glass transition temperature. This crystallization resulted in an increase of the melting temperature and melting enthalpy, but high CO$_2$ pressure was required (10 MPa < P < 20 MPa).

Another possible explanation of the maximum melting temperature phenomenon arises from the fact that it has only been observed with polymers (e.g. PEG by Weidner et al. [8] or PCL by Lian et al. [9] and in this work). Indeed, SLG measurements with other substances such as tristearin, tripalmitin [22], tetradecanid acid, hexadecanoic acid or 1-hexadecanol [25] do not show a temperature maximum. It is possible that the maximum melting point phenomenon is a consequence of PCL + CO$_2$ mixtures not being binary systems due to the polydispersity of the polymer. CO$_2$ may be able to selectively extract low molecular weight oligomers from the polymer which act as plasticizing agents, thus causing an increase in the melting point.

A thermodynamic model of the phase equilibrium of (PCL + CO$_2$) mixtures based on the PC-SAFT EoS [18] has been developed in this work. Pure component parameters required by this model are presented in Table 3. The parameters of CO$_2$ have been taken from the literature [18] while the parameters of PCL have been estimated with the group contribution method developed by Tihic et al. [26]. As shown in this table, parameter $m$ of PCL depends on the molecular weight of the polymer, which enables using this set of parameters with PCLs of different molecular weights.

As previously described, in order to apply the PC-SAFT EoS to mixtures the binary interaction parameter must be calculated. The interaction parameter between CO$_2$ and PCL has been calculated by correlation of vapor-liquid equilibrium data reported by Cotugno et al. [14] in the temperature range 343 K < T < 358 K. The correlation has been performed by minimization of the Average Absolute Pressure Deviation AAPD between experimental and calculated bubble point pressures, according to the objective function presented in Eq. (6). With this procedure, the following expression has been obtained for the binary interaction coefficient between CO$_2$ and PCL: $k_{12} = 177.966/T - 0.4558$. With this parameterization, the maximum deviation between experimental LV bubble point pressures and PC-SAFT calculations is AAPD = 6.8%.

$$AAPD = \frac{100}{n_{exp}} \sum_{i} \frac{|p_{i,calc} - p_{i,exp}|}{p_{i,exp}}$$  \hspace{1cm} (6)

Density and heat of fusion data of PCLs required for SLG equilibrium calculations with Eq. (5) were taken from the literature [14, 22] and are listed in Table 3. Results of equilibrium calculations with the PC-SAFT equation are shown in Figures 4, 5 and 6 together with experimental results. It can be seen that the model correctly describes the decrease of melting temperature with increasing pressure in the region of moderate pressures (P < 10 MPa). It can be therefore used to estimate the melting temperature of PCLs of different molecular weights in this pressure range, which is of interest for several supercritical precipitation techniques such as SAS or PGSS. However, the model fails to predict the minimum melting point temperature and the increase of melting point with pressure at high pressures. This is probably due to the simplicity of the model used to represent the solid phase (Eq. 5). A similar limitation of this model was found in the modeling of SLG equilibrium of the system polyethylene glycol + CO$_2$[27].
Table 3. PC-SAFT EoS pure component properties considered in this work.

<table>
<thead>
<tr>
<th></th>
<th>m (-)</th>
<th>σ (Å)</th>
<th>ϵ/k_b (K)</th>
<th>ρ (Kg/m^3)</th>
<th>ΔH_fus (J/g)</th>
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<tbody>
<tr>
<td>CO₂</td>
<td>2.0729</td>
<td>2.7852</td>
<td>169.21</td>
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<td></td>
</tr>
<tr>
<td>PCL</td>
<td>0.0396·MW</td>
<td>3.3908</td>
<td>235.67</td>
<td>1140</td>
<td>76.9</td>
</tr>
</tbody>
</table>

5. Conclusions

The solid-liquid-gas equilibrium in poly-(ε-caprolactone) + CO₂ systems has been determined. Measurements have been carried out with PCLs of three different molecular weights: 4000 g/mol, 10000 g/mol and 25000 g/mol. The experimentally determined SLG equilibrium curves show both a temperature maximum at low pressures (0.5 MPa < P < 1.6 MPa) and a temperature minimum at moderate pressures (8 MPa < P < 10 MPa). The maximum reduction in melting temperature is 12.5 K in the case of PCL 4000 g/mol, 15.5 K in the case PCL 10000 g/mol and 16.0 K in the case of PCL 25000 g/mol.

A thermodynamic model based on the PC-SAFT equation of state has been developed to describe experimental data. The model correctly predicts the solubility of CO₂ in the molten polymer as well as the melting temperature at pressures below the pressure of the minimum melting temperature, but it is not able to describe the variation of melting temperature at higher pressures.

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References


