Research note

Ternary Phase Diagram for Polymer/ Solvent/ Supercritical-CO$_2$ by Sanchez-Lacombe Model

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Abstract
Ternary phase diagrams for [polyethylene (Mw=420,000, Mw/Mn=2.6) / n-butane/ carbon dioxide], [polypropylene (Mw=290,000, Mw/Mn=1.32)/ n-pentane/carbon dioxide] and [polystyrene (Mw=187,000)/ cyclohexane/ carbon dioxide] have been generated using the Sanchez-Lacombe (SL) lattice-fluid model. The results show that at relatively low pressure, the ternary phase diagram has a L-L-V three-phase region bounded by two two-phase regions (L-V and L-L). At high pressure, L-L-V and L-V regions disappear and only the L-L region remains. With an increase of pressure this two-phase L-L region becomes smaller. This model can also predict transition LCST to UCST by increasing pressure. For polystyrene/ cyclohexane/ carbon dioxide mixture, the calculated results obtained using the SL-model are compared with the reported calculated results created by the perturbed hard-sphere chain model (PHSC) and the reported experimental data which indicate good agreement with both the calculated results by PHSC-model and experimental data.

Keywords: *high pressure, phase diagram, Sanchez-Lacombe (SL) model, polymer-solvent- SCF, ternary mixtures*

Introduction
Recently supercritical fluids (SCFs) have been applied in a variety of polymer processes including fractionations [1,2], particle formation [3], reactions [4,5], process involving polymer blends, and the new separation processes of polymer-solvent mixture using supercritical anti-solvents (SAS).
The SAS process is particularly interesting from a practical and theoretical point of view. In this separation technique, by addition of a supercritical gas (namely, anti-solvent), the lower critical solution temperature (LCST)

curve can be shifted to a lower temperature. Therefore in practice, this separation technique may be successfully applied when the high de-mixing temperatures in such separation processes cause large energy consumption and the consequent risk of polymer degradation. This technique can separate the polymer solution into a polymer-rich phase and a solvent-rich phase, which is almost polymer free.
Coen et al.[6] studied the gas anti-solvent method for fractionation of poly-methacrylate in acetone. They found this technique for a polymer with a broad molecular weight

distribution effective.

It is important to determine the phase behavior of polymer-solvent-gas systems for future supercritical anti-solvent (SAS) processses. Simpler forms of equation of state such as the cubic equations of state are not effective in describing these systems containing components with large differences in size and molecular interactions.

The lattice-fluid model was proposed by Sanchez and Lacombe [7,8] to describe thermodynamic properties of molecular fluids of arbitrary size, mainly polymer-solvent phase behavior. In this theory, the Sanchez and Lacombe equation of state (SL-EOS) has a simpler analytical form compared with other equations such as Kleintjens-Koninigsveld mean field lattice gas model [9], group-contribution lattice fluid (GCLF) equation of state [10,11], perturbed hard-sphere chain model (PHSC) [12-15] and the statistical associated fluid theory (SAFT) [16,18].

Xiong and Kiran [19,20] obtained the phase diagrams for ternary systems of [polyethylene / n-pentane / CO_2] by using the SL-EOS and in order to achieve a good correlation of the phase behavior, they fitted the binary interaction parameter for the polymer and the gas to the ternary data.

Gauter and Heidemann [21] used the SL-EOS to model cloud point isotherms of two binary systems of polyethylene (the first polyethylene has a mass average and number molar masses of 99,000 and 56,000 and the second polyethylene has a mass average and number molar masses of 8,800 and 7,600, respectively) in ethylene and one binary system of polyethylene (the polyethylene has mass average and number molar masses being 177,000 and 8,000) in n-hexane. They found good agreement with the experimental cloud point data. Trumpi et al.[22] measured the cloud point for a binary system of [linear low density polyethylene/ethylene]. They also modeled their experimental data with the SL-EOS. Hamedi et al.[11] extended the GCLF-

EOS to predict the density of pure polymers, VLE of vapors, supercritical gas solubility and the LLE of polymer-solvent systems. They proposed a new mixing rule for the calculation of the binary interaction parameters for the mixtures studied.

Horst et al.[17] measured the cloud-point curves for [polystyrene/cyclohexane/gas] and [polyethylene/cyclohexane/gas] systems to determine the influence of anti-solvent gases ethane, propane and nitrogen on the conditions for LCST-phase separation of these systems. They used the SAFT equation to correlate the phase equilibria of the [polymer/solvent] systems investigated and they used the results obtained for binary systems to predict qualitatively the phase behavior of the ternary system of [polymer/solvent/gas]. Their results showed that a quantitatively correct prediction of the influence of the addition of supercritical gases on the polymer-solvent phase behavior with SAFT is not possible.

Lora and McHugh [16] measured the cloud-point data for the system [poly-methyl methacrylate / CO_2 / methyl methacrylate (MMA)] in the temperature range of 20 to 170 $^{\circ}$C and pressures as high as 2,500bar. They used the SAFT equation to model their results. The SAFT model qualitatively indicated that the cloud-point curve pressure decreases with increasing MMA concentration.

Ndiaye et al.[18] investigated the phase behavior of two types of polypropylene (commercial Ziegler-Natta PP and a metallocenic PP) in n-butane in a high pressure variable-volume view cell. For these systems, they observed three types of phase equilibrium, vapor-liquid, liquid-liquid and vapor-liquid-liquid regions. They modeled the experimental data with the SAFT equation and showed a good agreement between the SAFT model and experimental data when a binary interaction parameter was employed to fit the experimental values.

In the present paper the SL-EOS is used to predict the phase behavior of [polyethylene/ n-butane/ CO2], [polypropylene / n-pentane / CO2] and [polystyrene / cyclohexane / CO_2] ternary mixtures over a wide range of temperatures and pressures. The results are presented in the form of ternary phase diagrams at different compositions and varying temperature and pressure.

Model

A detailed description of the Sanchez-Lacombe model can be found in the literature [7, 8]. Briefly, the basic equation of state for the model is given in the following form:

$$\bar{\rho}^2 + \bar{P} + \bar{T}[Ln(1-\bar{\rho}) + (1-\frac{1}{r})\bar{\rho}] = 0 \qquad (1)$$

where $\bar{P}, \bar{T}, \bar{\upsilon}$ and $\bar{\rho}$ are the reduced temperature, pressure, volume, and density, respectively, and are defined as

$$\bar{T} = T/T^*, \qquad T^* = \varepsilon^*/R \qquad (2)$$

$$\bar{P} = P/P^* , \qquad P^* = \varepsilon^*/v^* \qquad (3)$$

$$\bar{\rho} = \rho/\rho^* = 1/\bar{v} = V^*/V \qquad (4)$$

$$V^* = N(rv^*), \qquad \rho^* = M^*/(rv^*) \qquad (5)$$

where ε^* is the mer-mer interaction energy, v^* is the close-packed molar volume of a mer, M is the molecular weight, N is the number of molecules, r is the number of sites (mers) occupied in the lattice by a molecule,

and R is the universal gas constant. T^*, P^*, and ρ^* are respectively the characteristic temperature, pressure, and close-packed mass density and a pure component is completely characterized by three parameters T^*, P^*, and ρ^*.

For multi-component mixtures it is necessary to define mixing rules for ε^*_{mix}, v^*_{mix} and r^*_{mix} to calculate properties of a mixture. The mixing rule for the characteristic close-packed molar volume of a mer of the mixture v^*_{mix} is:

$$v^*_{mix} = \sum_{i=1} \sum_{j=1} \Phi_i \Phi_j v^*_{ij} \qquad (6)$$

where v^*_{ij} is given as:

$$v^*_{ij} = \frac{v^*_{ii} + v^*_{jj}}{2}(1 - \eta_{ij}) \qquad (7)$$

where η_{ij}, corrects for deviations from the arithmetic mean for the components i and j in the mixture. The volume fraction ϕ_i is defined as:

$$\Phi_i = \frac{m_i}{\rho_i^* v_i^*} \Big/ \sum_j \left(\frac{m_j}{\rho_j^* v_j^*} \right) \qquad (8)$$

where m_i is the mass fraction of component i in the mixture, and r_i^* and v_i^* are the characteristic mass density and close-packed molar volume of component i, respectively.

The mixing rule for the characteristic interaction energy for the mixture ε^*_{mix} is:

$$\varepsilon^{*}_{mix} = \frac{1}{v_{mix}} \sum_{i} \sum_{j} \Phi_{i} \Phi_{j} \varepsilon^{*}_{ij} v^{*}_{ij} \qquad (9)$$

$$\frac{1}{r_{mix}} = \sum_{j} \frac{\Phi_{j}}{r_{j}} \qquad (11)$$

$$\varepsilon^{*}_{ij} = (\varepsilon^{*}_{ii} \varepsilon^{*}_{jj})^{0.5} (1 - \delta_{ij}) \qquad (10)$$

where r_{i} represents the number of sites of molecule j occupies in the lattice.

For polymer-solvent calculations it is more convenient to derive a chemical potential rather than a fugacity coefficient. Applying these combining rules, the Sanchez-Lacombe treatment leads to the following general expression for the chemical potential of the ith component in a multi-component system:

where ε^{*}_{ii} and ε^{*}_{jj} are the characteristic mer-mer interaction energies for components i and j, and δ_{ij} is a mixture parameter that accounts for specific binary interactions between components i and j. The mixing rule for the number of sites occupied by a molecule of the mixture, r_{mix}, is given by:

$$\mu_{i} = RT\left[\ln \Phi_{i} + \left(1 - \frac{r_{i}}{r}\right)\right] + r_{i}\left\{ -\overline{\rho}\left[\frac{2}{v^{*}}\left(\sum_{j=1}^{c} \Phi_{j} v^{*}_{ij} \varepsilon^{*}_{ij} - \varepsilon^{*} \sum_{j=1}^{c} \Phi_{j} v^{*}_{ij} \right) + \varepsilon^{*} \right]\right.$$

$$\left. -\overline{\rho}\left[\frac{2}{v^{*}}\left(\sum_{j=1}^{c} \Phi_{j} v^{*}_{ij} \varepsilon^{*}_{ij} - \varepsilon^{*} \sum_{j=1}^{c} \Phi_{j} v^{*}_{ij} \right) + \varepsilon^{*} \right] + RT\overline{v}\left[(1-\overline{\rho})\ln(1-\overline{\rho}) + \frac{\overline{\rho}}{r_{i}}\ln \overline{\rho} \right] + P\overline{v}\left(2\sum_{j=1}^{c} \Phi_{j} v^{*}_{ij} - v^{*} \right) \right\} \qquad (12)$$

Result and Discusion

For the ternary mixtures of [polymer (1)/solvent (2)/SC-CO$_2$ (3)], the values of interaction parameters (δ_{23} and δ_{12}) for the binary pairs of [SC-CO$_2$ /solvent] and [polymer/solvent] mixtures are optimized firstly and then they are used directly in ternary mixtures without further adjustment. The interaction parameter δ_{13} for the binary pair [polymer/ SC-CO$_2$] is optimized by ternary data since experimental data for this binary pair is not available in the literature. The interaction parameters, δ_{ij}, are obtained using an optimization method. The method is

designed to obtain the minimum absolute average deviation between the calculated results and the experimental data (obtained from the references 15, 19 and 23). The characteristic parameters (P^{*}, T^{*}, ρ^{*}) for the SL-model are listed in Table 1. In Table 2, the optimized interaction parameters (δ_{ij}) are reported.

The phase diagrams for the ternary mixture of [polyethylene (Mw=420,000, Mw /Mn= 2.6)/ n-butane/carbon dioxide] are generated and shown in Figures 1 to 5. Figures 1 and 2 show the phase behavior of the mixture at 400 K.

In Figure 1 for the ternary system of [PE/n-butane/CO_2] at 3 MPa the L-L-V three-phase region is bounded by two two-phase regions (L-V and L-L) but for the same system as the pressure is increased to higher than 10 MPa which CO_2 is in supercritical condition (as shown in Figures 2 and 3) the L-V region disappears and the phase diagram consists of a one miscible liquid phase region and a two immiscible liquid phase region.

Table 1. Characteristic parameters from literature

	P^*(MPa)	T^*(K)	ρ^*(gcm^{-3})	Ref.
n - Pentane (C5)	310.1	441	0.755	13
n – Butane (C4)	322.0	403	0.736	8
Carbon dioxide (CO_2)	574.5	305	1.510	13
Cyclohexane	298.0	476	0.755	8
Polyethylene (PE)	359.0	521	0.895	13
Polypropylene (PP)	281.1	770.9	0.852	14
Polystyrene	353.0	735	1.105	8

Table 2. Optimized interaction parameters used in this study

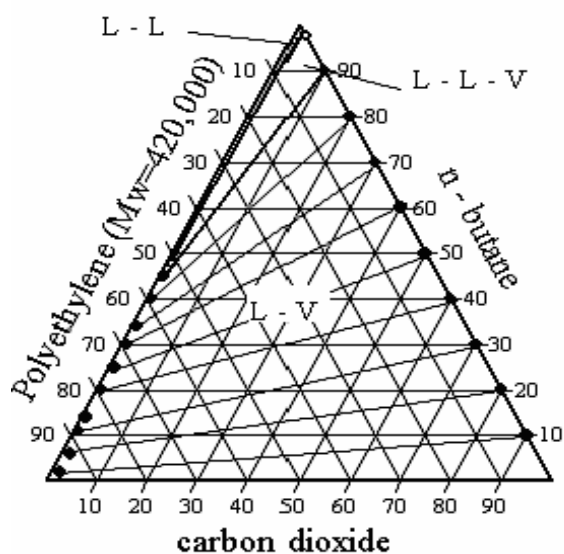| System	δ_{12}	δ_{23}	δ_{13}
PE (1)/n-butane (2)/CO2 (3)	0.0014	0.1370	0.0761
PP (1)/n- pentane (2)/CO2 (3)	0.0033	0.0100	0.0100
PS (1)/cyclohexane (2)/CO2 (3)	0.0172	0.0100	0.0400

Figure 1. Phase diagrams for PE/n-butane/ CO2 system at 400K and 3 MPa .[19]
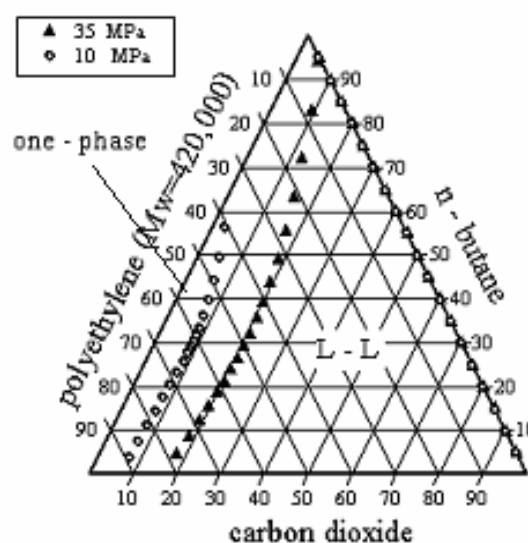

Figure 2. Comparison of phase diagrams of PE/n-butane/CO2 system at 10 and 35 MPa. *T*= 400K [19]
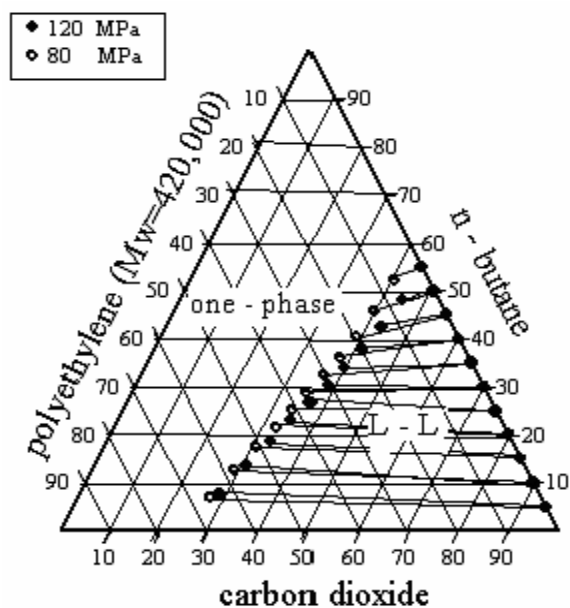
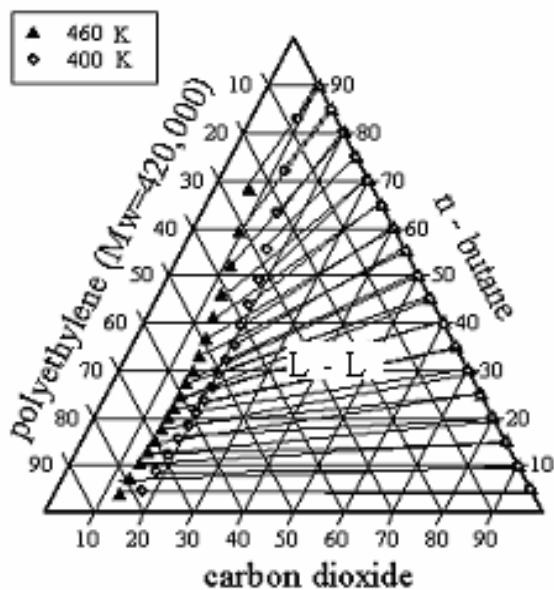**Figure 3.** Phase diagrams for PE/n-butane/CO2 system at 400K at 80 and 120 MPa [19]

Figure 4. Comparison of phase diagrams of PE/n-butane/CO2 system at 400K and 460 and *P*=30 MPa [19]
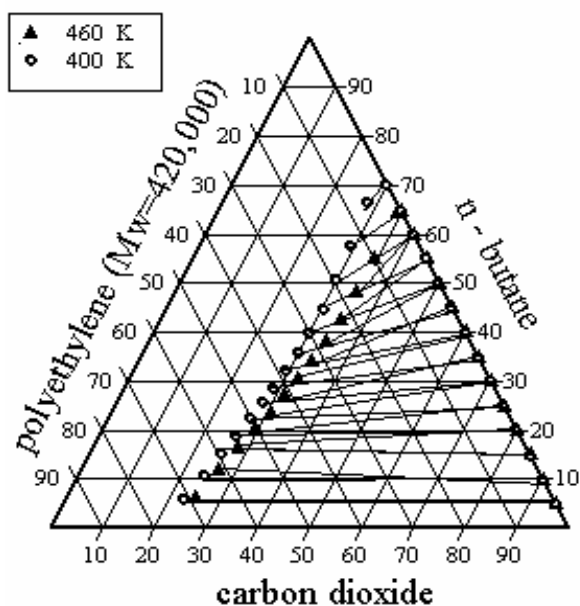

Figure 5. Comparison of phase diagrams of PE/n-butane/CO2 system at 400K and 460K. *P*=100 MPa [19]

Analysis of the systemic behavior at the same pressure but different temperatures indicates an interesting effect of temperature. For example, Figures 4 and 5 show the comparisons of the phase diagrams at two temperatures (400 and 460K) at 30 and 100 MPa pressures (In these conditions CO_2 is in supercritical condition, SC-CO_2). As shown in Figure 4, at 30MPa, as the temperature increases a shrinking in the one-phase region is observed. As a result a point in the one-phase region at 400 K may fall into a two-phase region at higher temperature, i.e. at 460 K. This means that a ternary mixture of specific composition may undergo phase separation upon increasing the temperature. This is the well known behavior termed as LCST (lower critical solution temperature).

As the pressure is increased to even higher values (100 MPa, Figure 5), the one-phase region begins to shrink, but now with decreasing temperature and the system undergoes a phase separation upon a decrease in temperature. This type of behavior is known as UCST (upper critical solution temperature). Thus, with increasing pressure (which accompanies an increase in the carbon dioxide content in the mixtures wherein CO_2 is in supercritical condition), a transition from LCST to UCST type behavior takes place. This transition was also reported by Xiong and Kiran [20] for [polyethylene/n-pentane/ carbon dioxide] mixture.

Similar calculations are done for [polypropylene (Mw = 290,000, Mw / Mn=1.32) / n-pentane / carbon dioxide] as shown in Figures 6 to 9. Figure 6 for this system is at 400 K and 2 MPa (in which CO_2 is in sub-critical condition) and consists of three regions of L-L, L-V and L-L-V. In Figure 7 for the same system as the pressure is increased to higher than 20 MPa in which CO_2 is in supercritical condition, the L-V region disappears and the phase diagram consists of a one miscible liquid phase region and a two immiscible liquid phase region. In this figure when the pressure increases, two
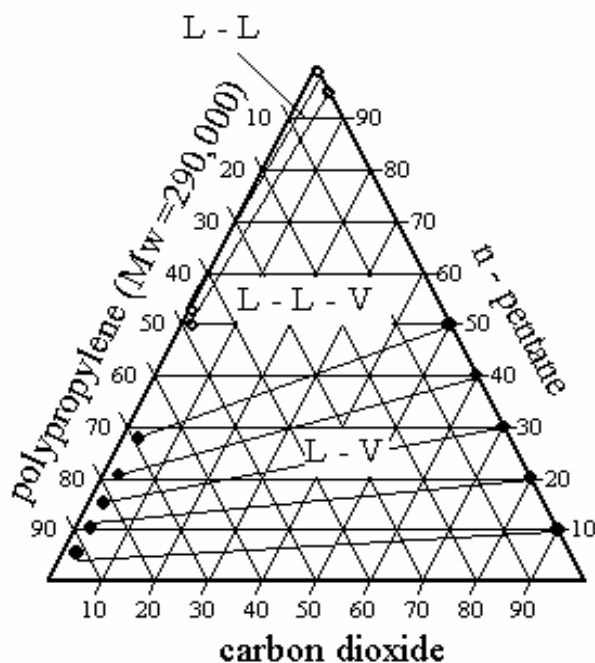
phase L-L region shrinks.

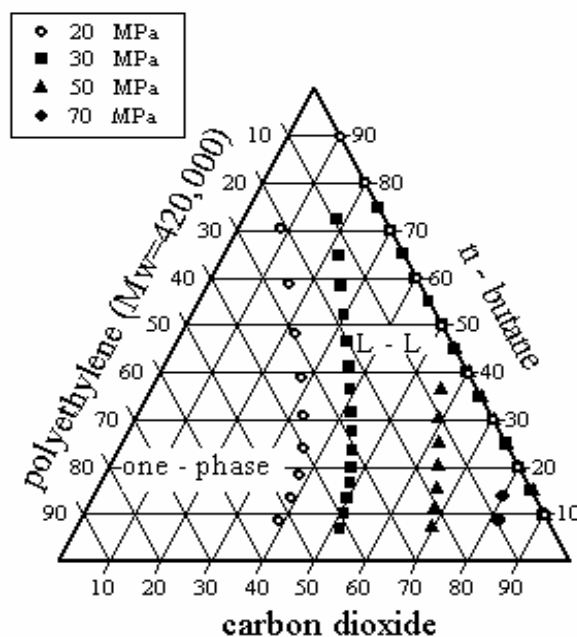**Figure 6.** Phase diagrams for PP/n-pantane/CO2 system at 400K and 2 MPa [23]

Figure 7. Comparison of phase diagrams of PP/n-pantane/CO2 system at 20, 30, 50 and 70 MPa. *T*=400K [23]

Figures 8 and 9 are at two temperatures 400 K and 460 K but at 20 MPa and 50 MPa. These figures are same as Figures 4 and 5, and show the effect of pressure on LCST and UCST.
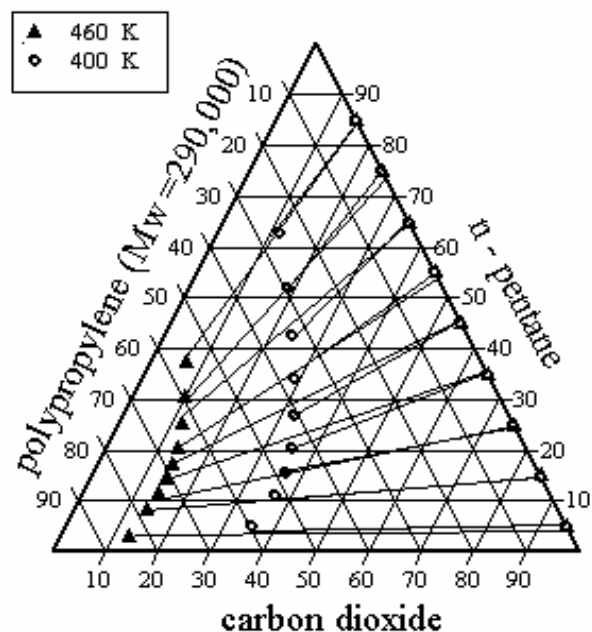

Figure 8. Comparison of phase diagrams of PP/n-pantane/CO2 system at 400K and 460K. *P*=20 MPa [23]
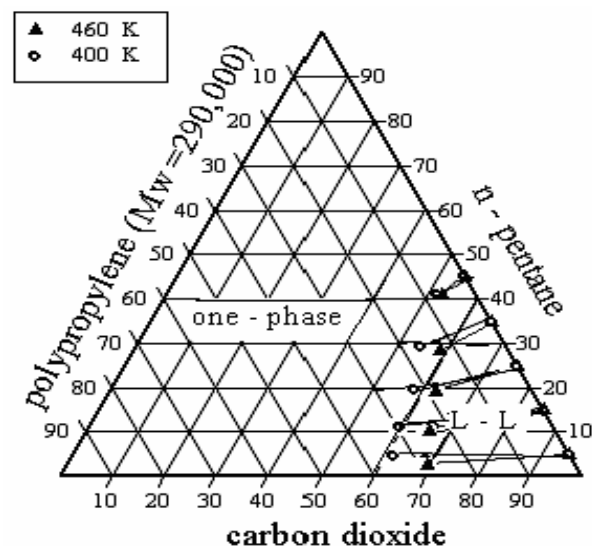

Figure 9. Comparison of phase diagrams of PP/n-pantane/CO2 system at 400K and 460K. *P*=50 MPa [23]

Figure 10 compares the reported experimental data [15] (circle) for the [polystyrene (Mw=187,000)/cyclohexane/carbon dioxide] mixture at 443 K and 10.1 MPa with calculated results obtained through the SL-model. This phase diagram was also generated by Favari et. al. [15] (as shown in Figure 10 (dashed lines)) using the perturbed hard-sphere chain (PHSC) model (solid lines). This figure shows good agreement between our results obtained by the SL-model with both Favari et. al. results obtained the PHSC-model and the experimental data.
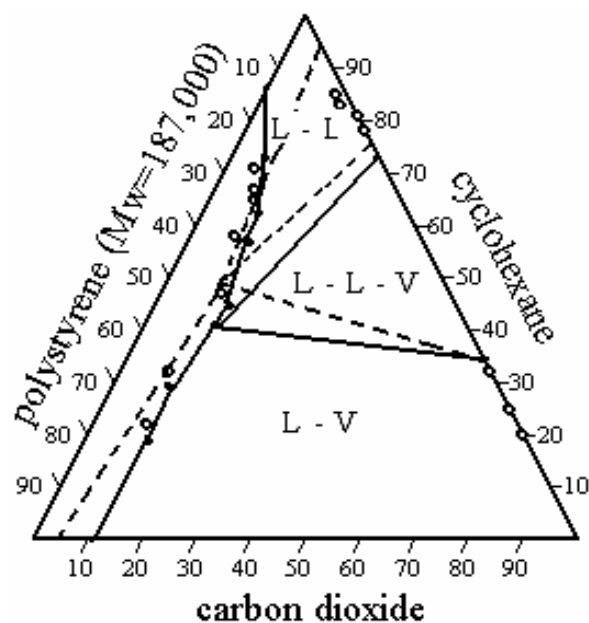

Figure 10. Comparison of experimental data [18] (circle) for polystyrene/cyclohexane/CO_2 system at 443 K and 10.1 MPa with calculations obtained with the SL model(solid lines) and PHSC model(dashed lines) [15]

Conclusion

It is concluded that the SL-model can be used to obtain a phase diagram over a wide range of temperatures, pressures and compositions for the system of [polymer/solvent/carbon dioxide]. This model can also predict qualitatively the transition from LCST to

UCST upon increasing pressure. The SL-model calculation has the added advantage over the PHSC-model, since the PHSC model needs complicated and more time consuming calculations to obtain the phase behavior for the systems studied in this work.

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