Thermodynamic Model for Branched Polyolefins Using the PC-SAFT Equation of State

Aleksandra Dominik and Walter G. Chapman*

Department of Chemical and Biomolecular Engineering, Rice University, 6100 S. Main, Houston, Texas 77005

Received August 15, 2005; Revised Manuscript Received October 14, 2005

ABSTRACT: This article presents a simple thermodynamic model for branched polyolefin systems in the framework of the PC-SAFT equation of state. The physical properties of the polymeric material can be tailored to a customer's specific needs by the choice of the α-olefin comonomer and the adjustment of its content in the chain. The model efficiently captures the effect of chain branching, comonomer type, and branching density on the phase behavior of polyolefin solutions. Since few adjustable parameters are required, it can be applied to systems for which little experimental data is available. The model parameters follow sensible trends, demonstrating its robustness for extrapolations and parameter prediction. Finally, the simple formulation facilitates its incorporation into commercial software for phase equilibria calculations.

1. Introduction

The physical properties of polyethylene resins and plastics are determined by the architecture of the polymer chain. Low-density polyethylene (LDPE) is manufactured by free radical polymerization; it consists of branchy molecules differing in branch size and branch density. LDPE chains are not able to pack closely because of the branching; this results in lower density and tensile strength and higher malleability of the material. High-density polyethylene (HDPE) is synthesized in the presence of a catalyst, which ensures the linearity of the polymer and thus a high density and strength of the material. Finally, linear low-density polyethylene (LLDPE) is the result of a copolymerization of ethylene with a higher α-olefin (e.g., 1-butene or 1-hexene) in the presence of a metallocene catalyst, which enables control over the short chain branching distribution and molecular weight distribution of the polymer. Consequently, the properties of the resulting material can be tuned to the customer's specific needs.

The structure of the chain is a determinant factor for the phase behavior of polymer solutions. Spahl and Luft reported that the cloud point pressures decreased with increasing branchiness of LDPE in ethylene.[1] De Loos et al. found that the phase boundary of a branched polyethylene (PE) in ethylene is situated at significantly lower pressures than the phase boundary of a linear PE in ethylene.[2] The position of the phase boundary depends on the branch length and branch density. Han et al. studied the phase behavior of branched polyolefins in propane and found that the cloud point pressure decreases with increasing branch length.[3] Whaley et al. reported that the cloud point pressure decreases with increasing 1-octene content for a system consisting of poly(ethylene-*co*-1-octene) in propane.[4] A predictive thermodynamic model for branched polyolefins should capture the effect of branch length and branch density on the phase behavior. Banaszak et al.[5] and later Gross et al.[6] proposed modeling concepts in which the branch length and branch density of the poly(ethylene-*co*-α-olefin) copolymers are explicitly taken into account. Banaszak and co-workers developed a model for branched polyolefins in the framework of the SAFT equation of state, which included the dispersion contribution developed by Chen and Kreglewski.[7] Gross et al. developed a model for copolymer systems based on the perturbed-chain SAFT (PC-SAFT) equation of state.[8] Other contributions in this field are due to Song et al.[9] and Hasch et al.[10]

The objective of this work is to develop a simple and effective modeling concept for branched polyolefins. The model should explicitly take into account the branch length and branch density of the copolymer. Additionally, the model must be simple enough to allow accurate parameter estimation from the limited number of experimental data sets for poly(ethylene-*co*-α-olefin) solutions. Finally, the model parameters should follow consistent trends, thus being transferable to other polymer/solvent systems. The PC-SAFT equation of state is chosen as the underlying thermodynamic model, since it proved accurate for modeling high-pressure phase equilibria of polymer solutions.[6,13] We briefly present the essential equations and the parameters pertaining to the PC-SAFT equation of state in the next section of this article. In a subsequent section, we describe the key features of the modeling concepts due to Banaszak et al.[5] and Gross et al.[6] and motivate the need for a new model for branched polyolefins. We then describe the proposed methodology for modeling branched polyolefin copolymers. This is followed by a parametrization of the model for various LLDPE types and a comparison of our results with results obtained by Gross et al.[6] We end with a discussion highlighting the key advantages of our model vis-à-vis the existing approaches.

2. PC-SAFT Equation of State

The underlying thermodynamic model for this concept is the PC-SAFT equation of state proposed by Gross and Sadowski. The objective of this section is to present the reader with the essential information about the equation of state as well as define the parameters of the model. Detailed information about the equation of state

* To whom correspondence should be addressed: Tel (1)-713.348.4900; Fax (1)713.348.5478; e-mail wgchap@rice.edu.

10.1021/ma0517953 CCC: $30.25
Published on Web 11/10/2005

can be found in its author's original publication.[8]

The molar residual Helmholtz free energy for nonassociating, nonpolar components is given in terms of a perturbation expansion:

$$a^{\text{res}} = a^{\text{hs}} + a^{\text{chain}} + a^{\text{disp}} \tag{1}$$

where a^{res} is the free energy residual to an ideal gas at the same temperature and density as the fluid of interest. The hard-sphere contribution (a^{hs}) is due to Carnahan and Starling,[14] and the chain term was developed by Chapman and co-workers[15,16] on the basis of Wertheim's thermodynamic perturbation theory of first order. The expression for the dispersion contribution (a^{disp}) was developed by Gross and Sadowski, who proposed the PC-SAFT equation of state.[8] The molecular model underlying PC-SAFT was initially developed for chain molecules comprising spherical segments of the same type. Since the focus of this work is on copolymers, the equation of state must be applicable to heterosegmented chains. The theoretical framework for extending SAFT-type equations of state to heterosegmented molecules was first developed for trimers by Amos and Jackson[17] and then extended by Shukla and Chapman[18] and Banaszak et al.[5] to heterosegmented chains. A summary of the equations for calculating thermodynamic properties of heterosegmented chains using the PC-SAFT model can be found in a recent publication by Gross et al.[6]

Each segment type in the system is characterized by three pure component parameters: the number of segments of type i in a chain (m_i), the segment diameter σ_i, and the segment dispersion energy ϵ_i/k, where i runs over all the segment types of the system. A system comprising a copolymer of the type poly(α-*co*-β) and a solvent (S) will be modeled using the three pure component parameters of α, β, and S. Additionally, three binary interaction parameters (k_{ij}) may be required to model the system, since the Lorentz−Berthelot mixing rules are used for the unlike pair interactions.

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}(1 - k_{ij}) \tag{2}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{3}$$

Two of these binary interaction parameters describe the interactions between each segment type in the copolymer chain and the solvent ($k_{S-\alpha}$ and $k_{S-\beta}$). The third interaction parameter ($k_{\alpha-\beta}$) may be used to correct the cross-dispersive interactions between the different segment types in the copolymer. The values of all the model parameters for a given copolymer depend on the choice of the modeling concept.

3. New Modeling Concept for Poly(ethylene-*co*-α-olefins)

The focus of this work was to develop an efficient methodology for modeling LLDPE in the framework of the PC-SAFT equation of state. Currently available in the framework of the SAFT equation of state are two models applicable to LLDPE. The first model was developed by Banaszak et al.[5] in the framework of the SAFT version due to Huang and Radosz.[7,19] The basic concept of the model was to distinguish two types of segments in the polymer chain: a backbone segment and a branch segment. The relative amount of branch and backbone segments is known because it is proportional to the mass fraction of comonomer in the polymer chain. In their earlier publications, Radosz and coworkers chose to assign the same values of the segment number and segment diameter parameters to all the segments in the chain; the two segment types differed by the dispersion energy parameter as well as by the value of their binary interaction parameter with the solvent.[3,5,20] In their later work, the authors of the model chose to assign to the branch segments the parameters of the corresponding alkane[21−23] (e.g., in the case of poly(ethylene-*co*-1-octene) the hexyl branch will be described by the parameters of *n*-hexane). The binary interaction parameters are adjusted to experimental cloud-point data. This method has the advantage of requiring few parameters to be adjusted to polymer phase behavior. The binary interaction parameters are temperature-dependent, however, and they do not follow consistent trends, which makes parameter prediction difficult. Moreover, the validity of the model over the whole range of comonomer incorporation (between pure polyethylene and pure polypropylene, for example) has not been demonstrated.

Another modeling concept for copolymers was proposed by Gross et al.[6] in the framework of the PC-SAFT equation of state. The authors also distinguish two segment types in the chain; their copolymer concept is based on the idea that there are as many segment types as there are monomer types in the copolymer chain. If the copolymer is of type "poly(α-*co*-β)", the segments of type α and β will have their own PC-SAFT pure component parameters, regressed from densities and phase equilibrium data of polyα and polyβ homopolymers, respectively. Three binary interaction parameters are needed in this model. The binary interaction parameters between the different segment types in the chain and the solvent are regressed from homopolymer phase equilibrium data. The interaction parameter between the different segment types in the copolymer is obtained by matching the copolymer phase equilibrium data. The model provides a satisfactory description of the phase behavior over the whole range of comonomer incorporation, but the polymer and copolymer densities are not accurately predicted. Another drawback of this model is that in order to describe a copolymer the parameters should be regressed from experimental data for the corresponding homopolymers. Such data are not readily available for polymers such as poly(1-hexene) or poly(1-octene). The parameters for the comonomer (1-hexene or 1-octene) could in principle be regressed to copolymer data, but with such a large number of parameters to be obtained from copolymer data, uniqueness of the parameter set and correct homopolymer limits are not ensured. More importantly, the pure component parameters for poly(ethylene-*co*-α-olefins) do not follow a sensible trend from one species to the other, which makes extrapolations to other types of polyolefins difficult.

Experimental results lead to the conclusion that branches on the polymer chain lower the cloud point pressure of the polymer solution (see de Loos et al.[2]). A parametric study of the PC-SAFT model reveals that the parameter controlling the position of the phase boundary is the dispersion energy of the segments. On the basis of these observations, we propose a new, simpler concept for modeling branched polyolefins such as LLDPE. Our model still distinguishes two types of

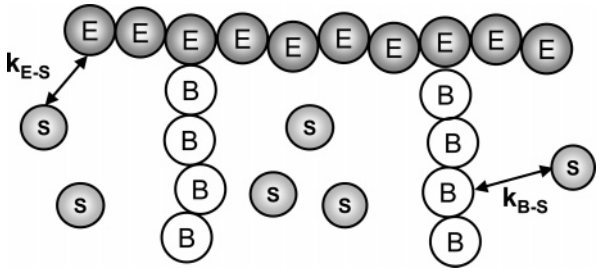

Figure 1. Representation of branched polyolefins in the framework of the proposed modeling concept.

segments in the copolymer chain: the backbone segments (E) and the branch segments (B), as shown in Figure 1. All backbone segments are assigned the PC-SAFT pure component parameters of the linear HDPE published by Tumakaka et al.[13] The branch segments are assigned the pure component chain length and segment diameter parameters of HDPE. This parametrization is consistent with the fact that the chemical nature of both branch and backbone segments is the same. The dispersion energy parameter of the branch segments is to be adjusted to experimental phase behavior data for polyolefins, along with the binary interaction parameter between the branch segments and the solvent. All the binary interaction parameters between backbone segments and various solvents are assigned the values of binary interaction parameters between HDPE and solvents, previously published by Tumakaka et al.[13] and Gross et al.[6] The relative fractions of segments in the backbone and in the branches can be easily calculated from the comonomer incorporation, which is a known copolymer property. As for the bonds between segments, three types of bonds could in principle be considered: bonds between segments in the backbone (E−E), bonds between segments in the branches (B−B), and finally backbone−branch bonds (E−B). The way in which the different segments are bonded has an impact on the value of the chain contribution to the free energy (see eq 1) only if the segment diameters are different. In our model, all segments have the same temperature-independent diameter; segments differ in value of the dispersion energy parameter ϵ_α/k. Considering the fact that an effective hard-sphere diameter is calculated from

$$d_\alpha = \sigma_\alpha\left(1 - \exp\left(-3\,\frac{\epsilon_\alpha}{kT}\right)\right) \tag{4}$$

the temperature-dependent diameters of the segments will be slightly different. The small difference between the temperature-dependent segment diameters has very little effect on the final values of the thermodynamic properties. Consequently, we adopt the simple assumptions for the segment arrangement in the chain, following Gross et al.[6]

- If the number of segments of type α is greater than the number of segments of type β, then all segments of type β are bonded to segments of type α. No bonds between segments of type β are considered, and the remaining segments of type α are bonded to one another.
- In the case when the number of segments of type α is equal to the number of segments of type β, a strictly alternating sequence of segments is considered.

Note that, in the framework of the first-order thermodynamic perturbation theory (TPT1) on which the SAFT equation of state is based, the Helmholtz free energy due to chain formation depends only on the number of segments forming the molecules, but not on the actual arrangement of the segments. Within TPT1, all bonds are formed independently of one another; the theory does not contain structural information beyond the radial pair correlation function. Extensions of Wertheim's second-order perturbation theory (TPT2), which accounts explicitly for the correlation between three consecutive beads through the three body distribution function, can provide a more accurate description of the chain connectivity[18,35,36] at the expense of the simplicity of the TPT1 framework. In the copolymer concept proposed in this work, chain branching is taken into account through the parametrization, while the assumptions regarding the bonding between segments remain simple.

The number of parameters needed to model a copolymer of type poly(ethylene-*co*-α-olefin) is reduced by 2, compared to the copolymer concept proposed by Gross et al.[6] This enables us to model copolymers for which a very limited amount of experimental data is available. Moreover, the limits of pure polyα and polyβ are also ensured. In fact, the branched polyolefin homopolymers such as polypropylene or poly(1-butene) are modeled as copolymers comprising two types of segments: backbone and branch segments. The dispersion energy parameter for the branch in the poly(ethylene-*co*-propylene) copolymer, for example, as well as the binary interaction parameter between the branch segments and the solvent, can be regressed to experimental data for polypropylene.

The proposed model for branched polyolefins is consistent with their chemical structure, as previously mentioned, as well as with the experimental observations regarding their phase behavior.

4. Results

This section summarizes the results obtained for the densities as well as for the phase equilibria of polymer and copolymer systems. The regression method employed to obtain polymer parameters was identical to the method described by Tumakaka et al.[13] Every parameter set was obtained by simultaneously fitting liquid density data and one single polymer/solvent cloud-point curve. As previously mentioned, the parameters obtained by Tumakaka et al. for HDPE, as well as the binary interaction parameters between HDPE and the considered solvents, were not refitted. Consequently, following the reasoning described in the previous section of this article, only one pure component parameter—the dispersion energy ϵ/k of the branch segments—is to be adjusted in order to model a branched polymer or copolymer. The regressed polymer parameters are given in Table 1. Additionally, the interaction parameter between the solvent and the branch segment must also be regressed. These binary interaction parameters are summarized in Table 2. The study revealed that the additional interaction parameter which corrects the cross-dispersive energy between different segment types in the polymer chain was not necessary to get good representation of the phase behavior; this cross-interaction parameter will therefore be set to zero in this work. The characteristics of the polymers considered in this study are summarized in Table 3.

4.1. Branched Polyolefin Homopolymers. Both polypropylene (PP) and poly(1-butene) (PB) were mod-

Table 1. Pure Component Parameters for the Polyolefins Considered in the Study

branch	ϵ/k [K]	m/M_w [mol/]g	σ [Å]	AAD% ρ^a	P range [bar]	binary system	ref
methyl	152	0.0263	4.0217	3.17 (5.5)	1−981	PP−pentane	27
ethyl	190	0.0263	4.0217	6.77[b] (30)	1−981	PB−1-butene	28
butyl	196	0.0263	4.0217	n/a	n/a	PEH_{35}−propane[c]	29
hexyl	225	0.0263	4.0217	2.38[d]	1−2000	PEO_{39}−ethylene[c]	22
HDPE[e]	252	0.0263	4.0217	1.62	1−1000	HDPE−ethylene	30

[a] In parentheses are the average absolute deviations obtained when the parameters of Gross and Sadowski are used for the homopolymers.[33] [b] The predicted densities of PB homopolymer were compared to experimental data from Zoller.[31] Only the viscosity average molecular weight M_v was available for this polymer, which explains the high deviation of the model predictions from the data. Excellent agreement with experimental data is obtained for PEB with up to 88% of 1-butene in the chain (see Figure 6). [c] The parameters are always obtained from the data set for the copolymer with the highest branching density available. [d] The density predictions were compared to experimental data for a PEO containing 64 wt % 1-octene in the chain.[32] [e] Parameters for HDPE were obtained by Gross and Sadowski.[33]

Table 2. Values of the Binary Interaction Parameters for All Considered Polymer Segment Types with Different Solvents

segment type	solvent	k_{ij}	ref
HDPE backbone	ethylene	0.0404[a]	
	propane	0.0206[a]	
	propylene	0.029[a]	
	1-butene	0.001[a]	
	1-hexene	0.004[a]	
	n-hexane	0.0055[a]	
	n-heptane	0	26
	n-octane	0	26
methyl branch	propylene	0.022	24
	propane	0.02	4
	1-butene	0.003	24
	1-hexene	0	24
ethyl branch	propane	0.013	25
	1-butene	0.023	28
butyl branch	ethylene	0.041	29
	propane	0.0105	29
hexyl branch	ethylene	0.029	22
	propane	−0.018	21
	n-hexane	0	26
	n-heptane	0	26
	n-octane	0	26

[a] Values of binary interaction parameters regressed by Gross et al.[6,33]

eled by Tumakaka et al.[13] as homopolymers comprising one segment type. The results obtained by these authors for the phase behavior of the polymers were satisfactory, but the polymer density predicted by PC-SAFT was not in good agreement with the experimental polymer density, especially for poly(1-butene). The description of the phase behavior of PP and PB with the new model is satisfactory; the results from our model for the system PP in propane are compared to results obtained by Gross in Figure 2. The polymer is polydisperse (M_w/M_n = 4.4); it was modeled using three pseudocomponents, as suggested by Gross and Sadowski.[33] The representation of the density of PP and PB is improved (see Table 1). The densities of PB are predicted with a 6.77% average deviation over the whole range of temperatures and pressures, as opposed to about 30% with the modeling concept proposed by Gross et al.[6]

A closer look at the results presented in Figure 2 reveals that the predictions of the model deteriorate when polymer concentration exceeds 15 wt %. The two-phase domain predicted by the equation of state is narrower than experimental data suggest; the predicted cloud point pressure at polymer concentrations greater than 15 wt % is lower than the value of the cloud point

Table 3. Characteristics of the Copolymers Considered in This Study

system	polymer M_w [kg/mol]	M_w/M_n	co-monomer	wt % comonomer	ref
PP−propane	290	4.4	n/a	n/a	4
PB−1-butene	99	4.74	n/a	n/a	28
PEP−1-butene	0.709	1.01	propylene	60.0	24
	5.9	1.08		60.0	
	26	1.03		60.0	
	96.4	1.1		60.0	
PEB−propane	120	<1.1	1-butene	0.0	25
	62	<1.1		8.0	
	96	<1.1		32.0	
	85	<1.1		52.0	
	91	<1.1		88.0	
	90	<1.1		97.0	
PEH−ethylene	80	1.52	1-hexene	10.6	21
	129	2.14		16.1	
	103	2.15		35.0	
PEH−propane	80	1.52	1-hexene	10.6	22
	103	2.15		35.0	
PEO−ethylene	32	1.11	1-octene	0.0	21
	83	1.62		13.9	
	115	2.1		25.8	
	26	2.3		36.5	
	154	2.0		38.7	
PEO−*n*-hexane	124	3.75	1-octene	13.0[a]	26
PEO−*n*-heptane	124	3.76	1-octene	13.0[a]	26
PEO−*n*-octane	124	3.76	1-octene	13.0[a]	26

[a] The comonomer content for PEO was not reported by the authors. Since all other PEO copolymers studied by de Loos et al.[26] had an 1-octene content of ca. 13 wt %, the comonomer content of the PEO considered in the present study was set to 13 wt %.

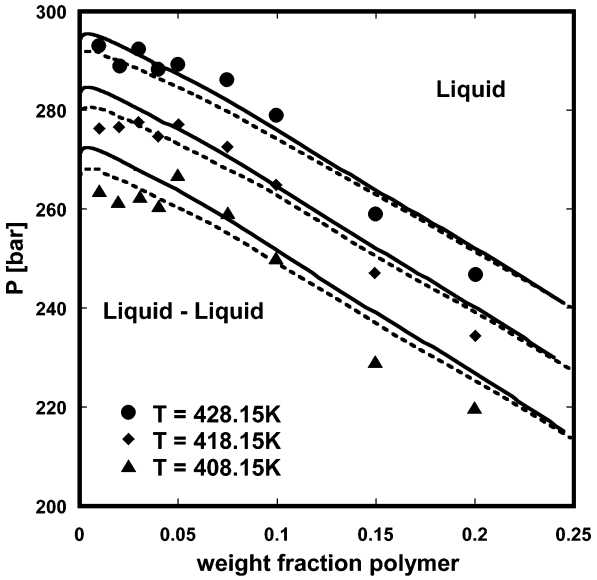

Figure 2. Liquid−liquid equilibria of polypropylene in propane. Symbols are experimental results from Whaley et al.;[4] solid lines are PC-SAFT predictions using the modeling concept proposed in this work. The results obtained by Gross and Sadowski[33] for this system are shown for comparison (dashed lines). The polydisperse polymer was modeled using the same three pseudocomponents as in Gross and Sadowski.[33]

pressure determined experimentally. This systematically observed behavior of the PC-SAFT equation of state was already visible for HDPE systems (see Tumakaka et al.[13]). The parameters of HDPE are used in the modeling of all polyolefins with our method, since they describe the backbone segments of the polymer. This reflects on the results obtained for PP and PB at high polymer concentration. The broadness of the demixing region predicted by PC-SAFT is controlled by the chain length parameter of the polymer. When the value of the chain length parameter of the polymer is decreased, the two-phase region becomes broader, and

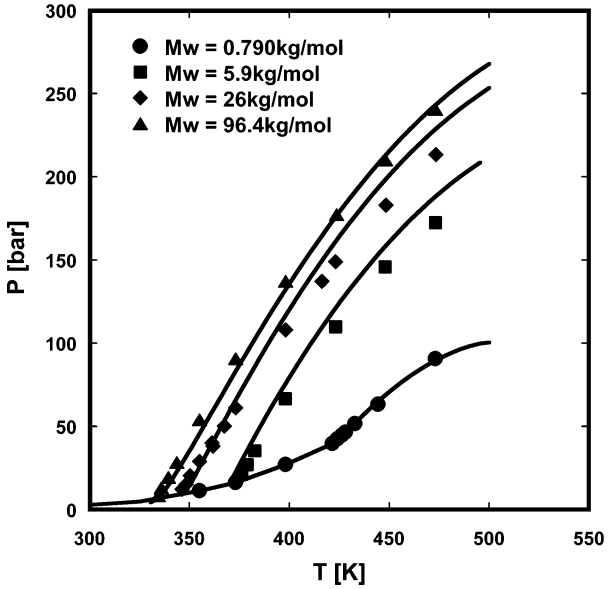

Figure 3. Liquid−liquid cloud point curves for PEP in 1-butene. Symbols are experimental results from Chen et al.;[24] lines are results from PC-SAFT using the modeling concept proposed in this work. The weight fraction of propylene in the copolymer is 0.6, and the weight fraction of PEP in solution is 0.15. The copolymer was modeled as monodisperse.

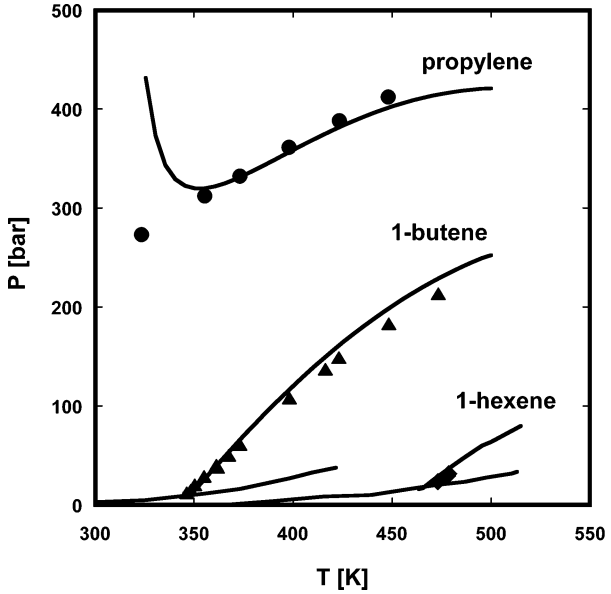

Figure 4. Liquid−liquid cloud point curves for PEP in various solvents. Symbols are experimental results from Chen et al.;[24] lines are results from PC-SAFT using the modeling concept proposed in this work. The weight fraction of propylene in the copolymer is 0.6, and the weight fraction of PEP in solution is 0.15. The copolymer was modeled as monodisperse.

the absolute value of the slope of the pressure−composition phase boundary at high polymer concentrations is reduced. Polymer densities must be taken into account during the regression of polymer parameters, and they must be predicted with reasonable accuracy, just as they are represented correctly for short chain molecules and oligomers.[8,33] Therefore, the difficulties encountered while simultaneously modeling polymer PVT properties and phase behavior of polymer solutions are an indication that other factors, such as polymer conformation, should be taken into account in order to quantitatively describe the phase behavior of polymer systems over the whole range of polymer concentrations.

4.2. Poly(ethylene-*co*-α-olefins). The parameters determined for the methyl and ethyl branches in PP and PB, respectively, are now used to model poly(ethylene-*co*-propylene) (PEP) and poly(ethylene-*co*-1-butene) (PEB). The number of branch and backbone segments is calculated from the copolymer (propylene or 1-butene) incorporation in the copolymer chain.

4.2.1. Poly(ethylene-*co*-propylene). The results obtained for PEP solutions in 1-butene are compared to experimental data from Chen et al.[24] in Figure 3. The only unknown binary interaction parameter for this system—k_{ij} between methyl branches and 1-butene—was regressed to phase behavior data for the heaviest copolymer in this data set. Results for PEP in various α-olefin solvents are shown in Figure 4. The model predicts a U-LCST (merging of the lower and upper critical solution temperature boundaries) for PEP in propylene, whereas the data do not show evidence of a U-LCST behavior. This problem was also observed by Tumakaka et al.,[13] which indicates that this sharp increase in pressure at low temperatures predicted by PC-SAFT is indeed an intrinsic problem of the equation of state and not of its parametrization.

4.2.2. Poly(ethylene-*co*-1-butene). The PC-SAFT predictions for PEB in propane are shown in Figure 5. The k_{ij} between ethyl branches of PEB and propane was determined from the data for PEB containing 97 wt %

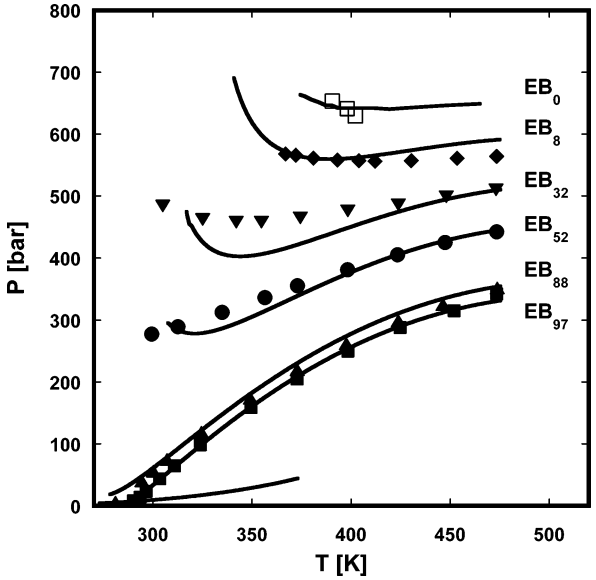

Figure 5. Liquid−liquid cloud point curves for PEB in propane. Symbols are experimental results from Chen et al.;[25] lines are results from PC-SAFT using the modeling concept proposed in this work. The weight fraction of PEB in solution is 0.053. The copolymer was modeled as monodisperse. The subscripts denote the 1-butene content in wt %.

1-butene units. The agreement between the model predictions and the experimental data of Chen et al.[25] is satisfactory. A significant improvement compared with the method of Gross et al.[6] is observed for the densities of PEB with the proposed methodology for modeling of branched polyolefins (see Figure 6). The densities of PB were not accurately predicted when PB was modeled using the copolymer concept developed by Gross et al.;[6] this discrepancy between experimental and predicted densities of PB strongly reflected on the quality of the predictions of the copolymer densities, as shown in Figure 6. The results obtained for both the phase behavior and the densities of PEB illustrate the

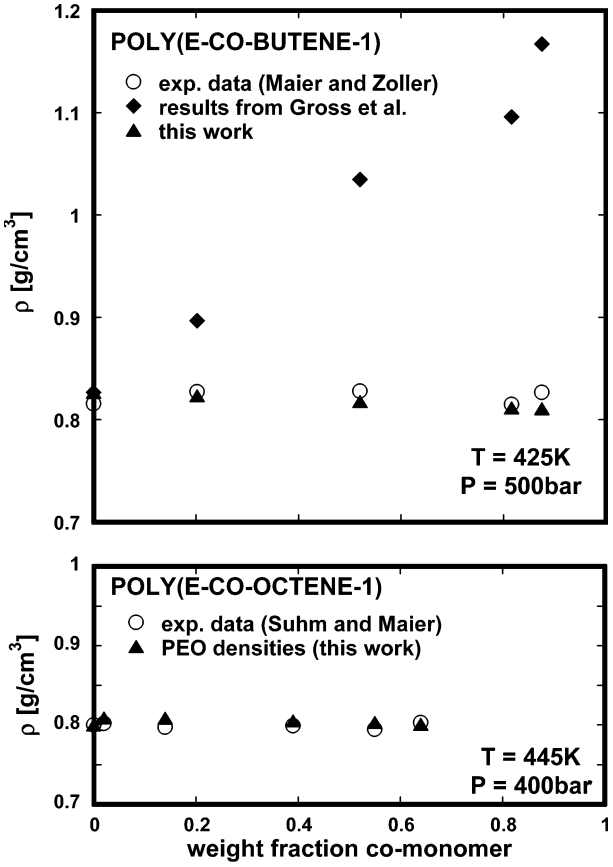

Figure 6. Densities of PEB and PEO copolymers vs the weight fraction of 1-butene and 1-octene in the polymer chain.

validity of the proposed modeling concept over the whole range of comonomer content.

4.3. Poly(ethylene-*co*-1-hexene) and Poly(ethylene-*co*-1-octene). The modeling concept proposed in this work was initially developed for modeling of poly(ethylene-*co*-1-hexene) (PEH) and of poly(ethylene-*co*-1-octene) (PEO). These two copolymers are of great industrial interest; they are the two most widely produced types of LLDPE. Modeling of PEH and PEO with the approach proposed by Gross et al.[6] was difficult, however, because there is currently no data for poly(1-hexene) (PH) or poly(1-octene) (PO) in the literature. The very limited amount of copolymer data for both PEH and PEO called for a simpler model for these systems.

Results for PEH in ethylene and propane are presented in Figure 7. The agreement of the model predictions with experimental data is satisfactory. The value of the branch segment dispersion energy parameter for the butyl branch was regressed to data for PEH in ethylene, together with the k_{ij} parameter between the butyl branch and the solvent. One temperature-independent k_{ij} was adjusted to match the cloud-point curves of PEH in propane. The model captures the phase behavior of PEH with as much as 35 wt % of 1-hexene, which is the highest 1-hexene content in the chain for which experimental data are available. It is worth mentioning that the industrially produced LLDPE from ethylene and 1-hexene commonly contains between 10 and 15 wt % 1-hexene. Unfortunately, we found no PVT data available for this copolymer; the validation of PEH parameters by comparison of the EOS predictions to experimental PVT data was not possible.

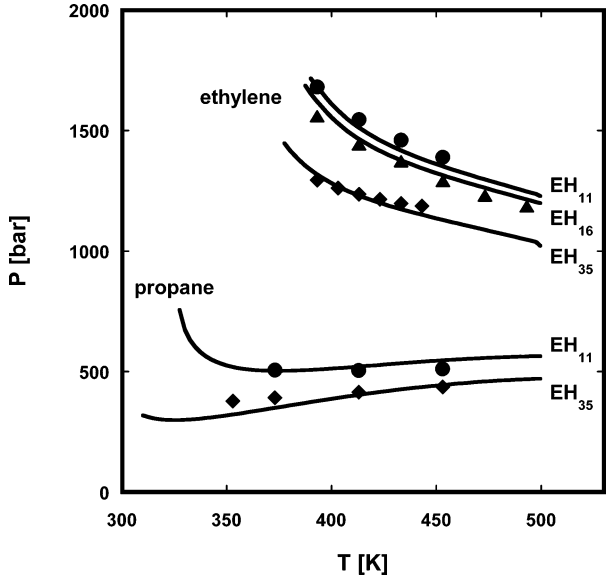

Figure 7. Liquid−liquid cloud point curves for PEH in ethylene and propane. Symbols are experimental results from Chan et al.;[21,22] lines are results from PC-SAFT using the modeling concept proposed in this work. The weight fraction of PEH in solution is 0.15. The subscripts denote the 1-hexene content in wt %.

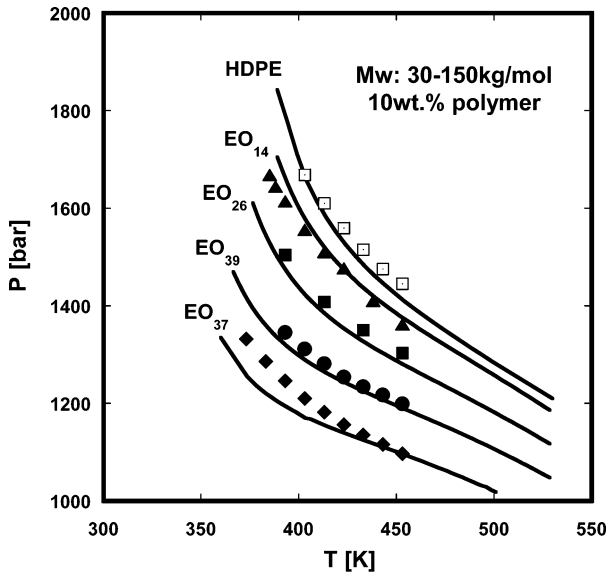

Figure 8. Liquid−liquid cloud point curves for PEO in ethylene. Symbols are experimental results from Chan et al.;[21] lines are results from PC-SAFT using the modeling concept proposed in this work. The weight fraction of PEH in solution is 0.10. The subscripts denote the 1-octene content in wt %.

Finally, the phase behavior of PEO in various solvents was modeled with PC-SAFT, using the new modeling concept. The results for PEO in ethylene are presented in Figure 8. The value of the branch segment dispersion energy for the hexyl branch was regressed to experimental data for PEO in ethylene; the 1-octene content in the copolymer was 39 wt %, which is the highest 1-octene content for which phase behavior data are currently available. The PVT properties of PEO were compared to experimental PVT properties of a copolymer containing 64 wt % 1-octene (see Table 5). The model parameters are transferable to other systems, as shown in Figure 9. The experimental data shown in Figure 9 were originally published by de Loos et al.;[26] the 1-octene content for this copolymer was not speci-

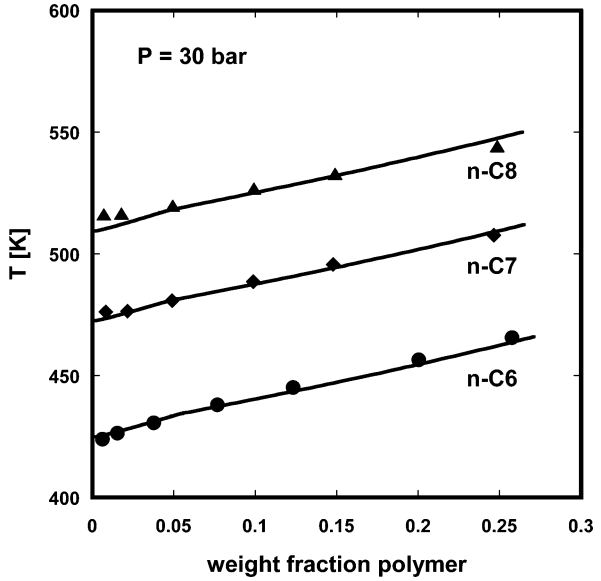

Figure 9. Liquid−liquid cloud point curves for PEO in *n*-alkanes. Symbols are experimental results from de Loos et al.;[26] lines are results from PC-SAFT using the modeling concept proposed in this work. The polydisperse copolymer was modeled using a 10-pseudocomponent logarithmic normal molecular weight distribution as in Jog et al.[34]

fied, however. It was assumed that the PEO contained 13 wt % 1-octene, just as the other ethylene−1-octene copolymers studied by de Loos et al.[26] The copolymer is polydisperse ($M_w/M_n = 3.76$); it was modeled using 10 pseudocomponents of a logarithmic normal distribution, as suggested by Jog et al.[34] The decrease of the cloud-point pressure appears to be nonmonotonic with the comonomer content for PEO, as shown in Figure 8. Whereas the comonomer incorporation controls the position of the phase boundary for copolymers having similar values of their molecular weight, as illustrated by the example of PEB (see Figure 5), it is not the case when the molecular weights are significantly different. PEO_{37} is about 6 times lighter than PEO_{39}; the former is consequently miscible with the solvent at lower pressures than the latter. A nonmonotonic dependence of the demixing pressures on comonomer content was observed for poly(E-*co*-methyl acrylate)[11] and poly(E-*co*-vinyl acetate).[12] This inversion was attributed by Hasch et al.[11] to specific multipolar interactions between the polar methyl acrylate and vinyl acetate units and the solvent. The dispersive interactions between the branched polyolefins and the solvent are not expected to produce this effect.

4.4. Discussion. The sensible representation of branched polyolefins in the framework of the model is corroborated by the consistent, monotonic parameter trend obtained for the branch segments. A relatively small number of solvents studied experimentally makes a study of the trends for the binary interaction parameters premature (see Table 2). We can anticipate, however, that the k_{ij} trends will be consistent and valid for extrapolations to other solvents, considering the sensible trend obtained for the dispersion energy parameter. The high sensitivity of the model to the values of the binary interaction parameters demands that correlations used to predict k_{ij} values be obtained after a study of a larger number of systems.

5. Conclusions

The modeling concept for branched polyolefins proposed in this work accurately describes the phase behavior of the considered copolymers over the whole range of comonomer content. Remarkably, the PVT properties of the copolymers are also predicted correctly; this was not possible with other currently available models for branched polyolefins. It corroborates the physical meaningfulness of the proposed representation of branched polyolefins. The parameters obtained for the copolymers are transferable to other solvents, and they follow a sensible trend. More importantly, the model's simple formulation and small number of adjustable parameters render it easily applicable to systems for which few experimental data sets are available. This key feature of the model makes possible the modeling of a wide range of systems of industrial interest.

Acknowledgment. The authors thank the Consortium of Complex Fluids for financial support.

References and Notes

(1) Spahl, R.; Luft, G. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 621−624.
(2) de Loos, T. W.; Poot, W.; Lichtenthaler, R. *J. Supercrit. Fluids* **1995**, *8*, 282−286.
(3) Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling, L. H. *Macromolecules* **1998**, *31*, 2533−2538.
(4) Whaley, P. D.; Winter, H. H.; Ehrlich, P. *Macromolecules* **1997**, *30*, 4882−4886.
(5) Banaszak, M.; Chen, C. K.; Radosz, M. *Macromolecules* **1996**, *29*, 6481−6486.
(6) Gross, J.; Spuhl, O.; Tumakaka, F.; Sadowski, G. *Ind. Eng. Chem. Res.* **2003**, *42*, 1266−1274.
(7) Huang, S.; Radosz, M. *Ind. Eng. Chem. Res.* **1991**, *29*, 2284−2294.
(8) Gross, J.; Sadowski, G. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244−1260.
(9) Song, Y.; Hino, T.; Lambert, S. M.; Prausnitz, J. M. *Fluid Phase Equilib.* **1996**, *117*, 69.
(10) Hasch, B. M.; Lee, S.-H.; McHugh, M. A. *J. Appl. Polym. Sci.* **1994**, *59*, 1107.
(11) Hasch, B. M.; Meilchen, M. A.; Lee, S.-H.; McHugh, M. A. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1365.
(12) Beyer, C.; Oellrich, L. R.; McHugh, M. A. *Chem. Ing. Technol.* **1992**, *71*, 1306.
(13) Tumakaka, F.; Gross, J.; Sadowski, G. *Fluid Phase Equilib.* **2002**, *194−197*, 541−551.
(14) Carnahan, N.; Starling, K. *J. Chem. Phys.* **1969**, *51*, 635−636.
(15) Chapman, W. G.; Gubbins, K. E.; Jackson, G. *Mol. Phys.* **1988**, *65*, 1057−1079.
(16) Chapman, W.; Gubbins, K. E.; Jackson, G.; Radosz, M. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709−1721.
(17) Amos, M.; Jackson, G. *Mol. Phys.* **1991**, *74*, 191−210.
(18) Shukla, K.; Chapman, W. G. *Mol. Phys.* **1997**, *91*, 1075−1081.
(19) Huang, S.; Radosz, M. *Ind. Eng. Chem. Res.* **1991**, *30*, 2284−2294.
(20) Pan, C.; Radosz, M. *Ind. Eng. Chem. Res.* **1998**, *37*, 3169−3179.
(21) Chan, K.; Adidharma, H.; Radosz, M. *Ind. Eng. Chem. Res.* **2000**, *39*, 3069−3075.
(22) Chan, K.; Adidharma, H.; Radosz, M. *Ind. Eng. Chem. Res.* **2000**, *39*, 4370−4375.
(23) Chan, K.; Adidharma, H.; Radosz, M. *Ind. Eng. Chem. Res.* **1999**, *38*, 2842−2848.
(24) Chen, S.-J.; Economou, I.; Radosz, M. *Macromolecules* **1992**, *25*, 3089−3096.
(25) Chen, S.-J.; Banaszak, M.; Radosz, M. *Macromolecules* **1995**, *258*, 1812−1817.
(26) de Loos, T. W.; de Graaf, L.; de Swaan Arons, J. *Fluid Phase Equilib.* **1996**, *117*, 40−47.
(27) Martin, T.; Lateef, A.; Roberts, C. *Fluid Phase Equilib.* **1999**, *154*, 241−259.
(28) Koak, N.; Visser, R.; de Loos, T. W. *Fluid Phase Equilib.* **1999**, *158−160*, 835−846.
(29) Chan, A.; Radosz, M. *Macromolecules* **2000**, *33*, 6800−6807.

(30) de Loos, T. W.; Poot, W.; Diepen, A. *Macromolecules* **1983**, *16*, 111−117.
(31) Zoller, P. *J. Appl. Polym. Sci.* **1979**, *23*, 1057−1061.
(32) Suhm, J.; Maier, R.-D.; Kressler, J.; Mulhaupt, R. *Acta Polym.* **1998**, *49*, 80−87.
(33) Gross, J.; Sadowski, G. *Ind. Eng. Chem. Res.* **2002**, *41*, 1084−1093.
(34) Jog, P. K.; Chapman, W. G.; Gupta, S.; Swindoll, R. *Ind. Eng. Chem. Res.* **2002**, *41*, 887−891.
(35) Blas, F. J.; Vega, L. F. *J. Chem. Phys.* **2001**, *115*, 3906−3915.
(36) Phan, S.; Kierlik, E.; Rosinberg, M. L.; Yu, H.; Stell, G. *J. Chem. Phys.* **1993**, *99*, 5326−5335.

MA0517953