

# Novel Method for Estimating Pure-Component Parameters for Polymers: Application to the PC-SAFT Equation of State

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In this work, we develop a method for estimating pure-component parameters for polymers for the PC-SAFT equation of state. Our method is based on pure-polymer *PVT* data and extrapolating equations that relate the polymer parameters to those of the corresponding monomer. The obtained parameters are thus unique for each polymer and do not depend on any mixture data. The new pure-component parameters are used as input in the simplified PC-SAFT equation of state, to evaluate both the parameters and the equation of state for a variety of binary polymer mixtures exhibiting both vapor–liquid and liquid–liquid phase equilibria. In most of the systems studied, very satisfactory results are obtained. Vapor–liquid and upper critical solution temperatures in liquid–liquid equilibria are accurately correlated with small values of the interaction parameter.

## 1. Introduction

The SAFT equation of state, developed in the early 1990s, is a noncubic, segment-based equation of state that was designed specifically to deal with systems containing polymers and associating fluids. Reviews of SAFT and its applications have appeared recently.<sup>1,2</sup> A number of modifications of SAFT have appeared in the past 12 years, including SAFT-VR<sup>3</sup> and, more recently, PC-SAFT,<sup>4</sup> a simplification of which was developed in this group<sup>5,6</sup> and is employed in this work. The original version of PC-SAFT was proposed by Gross, Sadowski, and co-workers,<sup>4,7–11</sup> and more details can be found in their works. The main equations of the simplified PC-SAFT are presented in the Appendix.

Some applications of the original and simplified PC-SAFT to the vapor–liquid equilibria (VLE)<sup>4,6–8</sup> and liquid–liquid equilibria (LLE)<sup>7–9</sup> of polymer mixtures, copolymer mixtures,<sup>10</sup> and polymer blends<sup>12</sup> have also recently appeared, with quite promising results. One limitation, however, in the application of SAFT-family models to polymers is the availability of pure-component parameters for the polymer. Pure-component parameters for PC-SAFT are available for very few polymers.<sup>7,10,13</sup> Furthermore, there is no established, general method for obtaining them. Gross and Sadowski<sup>7</sup> obtained pure-component polymer parameters by simultaneous fitting four parameters—the three pure-component parameters and a binary interaction parameter—to pure-polymer liquid-density and binary phase equilibrium data for a single polymer–solvent system. The polymer parameters determined in this way are then fixed and can then be used to predict phase behavior in other mixtures.

In this work, we investigate several methodologies for obtaining pure-component polymer parameters for PC-SAFT. We evaluate methods on the basis of simultaneous parameter-fitting to pure-polymer *PVT* data and binary polymer–solvent phase equilibrium data,

and we propose a new methodology whereby the values of the polymer parameters are calculated from extrapolations of monomer parameters. The proposed method does not make use of mixture data.

A discussion of the proposed method and its implementation follows, together with results for a variety of different polymer–solvent mixtures displaying different types of phase behavior.

## 2. Estimation Methods for Polymer PC-SAFT Parameters

**2.1. Estimation Methods Using Binary Data.** In accordance with the molecular model underlying the simplified and original PC-SAFT equations of state, a set of three pure-component parameters is required for nonassociating compounds, namely, the segment diameter,  $\sigma$ ; the segment number,  $m$ ; and the segment energy,  $\epsilon$ . For low-molecular-weight compounds, these parameters are typically obtained by simultaneously regressing saturated liquid-density and vapor-pressure data. Unfortunately, this is not possible for polymers, as such vapor-pressure data do not exist. If the pure-component parameters are adjusted only to liquid-density data, they can acquire unexpected values that lead to unsatisfactory descriptions of phase equilibrium in polymer mixtures.<sup>7</sup>

To overcome this problem, Gross and Sadowski<sup>7</sup> included in the regression of the polymer parameters both pure-polymer *PVT* data and experimental LLE data for a single binary system for which such data were available. In this way, four parameters (three polymer parameters plus an interaction parameter for the binary system) are simultaneously regressed.

This method has led to successful LLE<sup>7</sup> and VLE<sup>6</sup> correlations for a variety of polymer–solvent systems. Nevertheless, we have observed that the pure-component polymer parameters obtained in this way are not unique for each polymer, but rather depend on the binary system chosen for the regression as well as the type (VLE/LLE) of experimental phase equilibrium data used.

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**Table 1. Values of PC-SAFT Parameters and Average Absolute Deviations between Calculated and Experimental Liquid Densities of Polystyrene for the Five Different Methods Evaluated for the Regression of Pure-Component Parameters for Polymers<sup>a</sup>**

method of pure-polymer parameter regression	<i>m</i> /MW	$\sigma$ (Å)	$\epsilon/k$ (K)	AAD (% $\rho$ )
1. PVT + single binary LLE	0.0190	4.107	267.00	5.1
2. PVT + single binary VLE	0.0242	3.939	366.43	0.3
3. PVT + single binary VLE excluding $k_{ij}$	0.0214	4.061	312.06	0.9
4. PVT + all binary VLE	0.0364	3.354	277.92	0.4
5. PVT + all binary VLE excluding $k_{ij}$	0.0390	3.243	243.81	0.8

<sup>a</sup> Temperature range = 390–470 K, pressure range = 1–1000 bar.

To demonstrate this problem, we compared the pure-component parameters of polystyrene (PS) regressed from pure-polymer PVT data and binary phase equilibrium data in five different ways. The five data sets and regression methods used are listed below, with references pertaining to the experimental VLE data sets: a single binary LLE data set for the system PS–cyclohexane (parameters from Gross and Sadowski<sup>7</sup>); a single binary VLE data set for the system PS–cyclohexane;<sup>14</sup> a single binary VLE data set for the system PS–cyclohexane, with the binary interaction parameter excluded from the regression;<sup>14</sup> a large number of binary VLE data sets for PS with acetone,<sup>15</sup> benzene,<sup>16,17</sup> toluene,<sup>18,19</sup> carbon tetrachloride,<sup>16</sup> chloroform,<sup>15</sup> methyl ethyl ketone (MEK),<sup>18,20</sup> propyl acetate,<sup>15</sup> nonane,<sup>21</sup> and cyclohexane;<sup>14</sup> and the same number of binary VLE data sets as above, with the binary interaction parameter excluded from the regression.

The results are summarized in Table 1, where it can be seen that the values of all the parameters depend to a great extent on the type and number of the binary data sets used in combination with the pure-polymer PVT data. The effect of the polymer parameters on the LLE of PS with acetone and cyclohexane was also evaluated. These results are discussed in the next section.

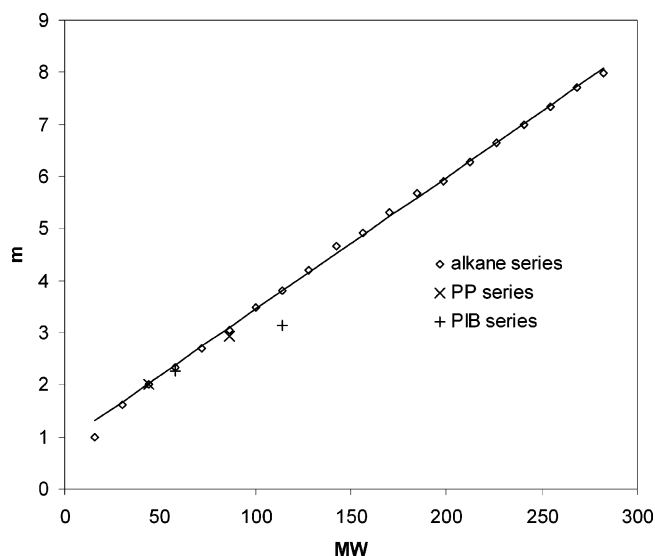
**2.2. Novel Estimation Method Using Pure-Component Data.** Our aim is to develop a method that will yield unique pure-component polymer parameters that also give good results when used to describe phase equilibria in polymer mixtures. The basic principle behind this method is to extrapolate from the parameters of similar, lower-molecular-weight compounds. This approach has been tried before for polyethylene (based on parameters of the alkane series<sup>22</sup>). Because the alkane series is so well characterized, this seems to be a suitable starting point.

A similar approach was also proposed by Huang and Radosz,<sup>23</sup> who presented extrapolation equations for the three pure-component parameters of SAFT (namely  $m$ ,  $v^\infty$  and  $v^0$ ) for many homologous series and molecular weights up to 300. Huang and Radosz observed that: "The segment number  $m$  increases with increasing molar mass within each homologous series practically linearly."

Similarly, it was noted previously<sup>5</sup> that the following combinations of the pure-component parameters for alkanes are linear functions of molecular weight (MW)

$$m = 0.02537\text{MW} + 0.9081 \quad (1)$$

$$m\epsilon/k = 6.918\text{MW} + 127.3 \quad (2)$$



**Figure 1.**  $m$  vs molecular weight for the alkane, PP, and PIB series. Points are PC-SAFT parameters reported by Gross and Sadowski;<sup>4</sup> the line is a linear fit to the alkane series, excluding methane, described by eqs 1 and 2.

It might be mentioned that this trend has also been observed for SAFT-VR,<sup>24</sup> which suggests that our approach is not solely applicable to PC-SAFT but might also be suitable for other SAFT-family models, as well as other segment-based models for polymers. Equations 1 and 2 were obtained by plotting  $m$  and  $m\epsilon/k$  against MW for linear alkanes from ethane to eicosane. Although the functional form of eqs 1 and 2 can only be verified against the alkane series, it seems reasonable to assume that it holds for all polymers. We generalize these equations as follows

$$m = A_m\text{MW} + B_m \quad (3)$$

$$m\epsilon/k = A_\epsilon\text{MW} + B_\epsilon \quad (4)$$

Now, to find the four constants  $A_m$ ,  $B_m$ ,  $A_\epsilon$ , and  $B_\epsilon$ , we need four equations, i.e., both parameters  $m$  and  $\epsilon$  for at least two compounds in the series. However, finding properties even for a polymer dimer is problematic. For example, although saturated liquid-density and vapor-pressure data have been reported for ethyl benzene (the monomer of polystyrene), virtually no physical property data are available for the dimer (1,3-diphenylbutane).

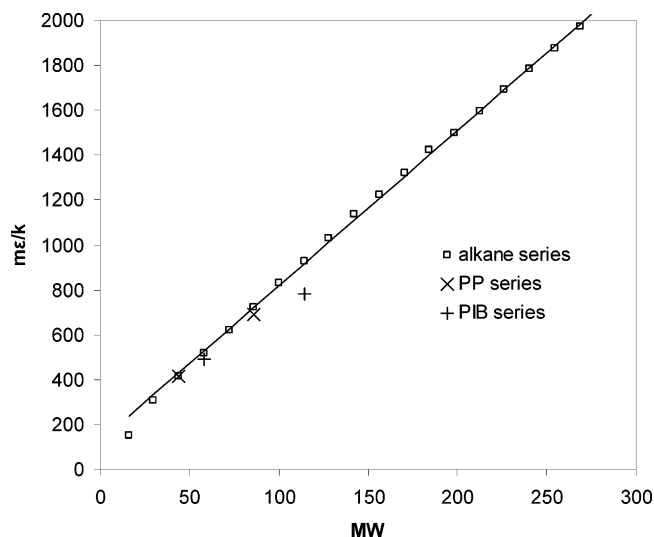
We now make the further assumption that, in the limit of zero molecular weight, polymers become indistinguishable. As can be seen in Figures 1 and 2, this is a good approximation for the polypropylene (PP) and polyisobutylene (PIB) series, for which information for both the monomer and the dimer of each series is available.

Thus, we assume that the constants  $B_m$  and  $B_\epsilon$  are universal and can be determined from any homologous series. Using the alkane series (eqs 1 and 2) and setting MW to 0, we have

$$B_m = 0.9081 \quad (5)$$

$$B_\epsilon = 127.3 \quad (6)$$

Now, the constants  $A_m$  and  $A_\epsilon$  can be determined for each polymer using eqs 3 and 4 and the values of the parameters  $m$  and  $\epsilon$  for the monomer. Dividing eqs 3 and 4 by molecular weight and considering the limit of



**Figure 2.**  $m\epsilon/k$  vs molecular weight for the alkane, PP, and PIB series. Points are PC-SAFT parameters reported by Gross and Sadowski;<sup>4</sup> the line is a linear fit to the alkane series, excluding methane, described by eqs 1 and 2.

**Table 2.** Corresponding Monomer and Values of the  $A_m$  and  $A_\epsilon$  Parameters of Eqs 3 and 4 for the Studied Polymers

polymer	corresponding monomer	$A_m$	$A_\epsilon$
PS	ethylbenzene	0.0205	7.1370
PIB	isobutane	0.02330	6.2351
PP	propane	0.0248	6.5615
PVAc	ethyl acetate	0.0299	7.8219
PE	ethane	0.0254 <sup>a</sup>	6.918 <sup>a</sup>
PMMA	methylisobutyrate	0.0270	7.1443
PBMA	isobutylisobutyrate <sup>b</sup>	0.0241	6.3798
BR	2-butene	0.0263	7.3473
PMA	methylpropionate	0.0292	7.8337
PB	butane	0.0245	6.7506

<sup>a</sup> From the original extrapolation eqs 1 and 2 that are based on the *n*-alkane series from  $C_2$  to  $C_{20}$ . <sup>b</sup> Isomer, because vapor-pressure and liquid-density data of butylisobutyrate are not available.

high molecular weight (as in the case of a typical polymer), we obtain

$$\frac{m}{MW} = A_m \quad (7)$$

$$\frac{\epsilon}{k} = \frac{A_\epsilon}{A_m} \quad (8)$$

These simple expressions give the chain length and energy parameters, respectively, of the polymer. We consider the first member of the series of a given polymer to be the saturated monomer of the repeating unit, e.g., ethylbenzene for PS, isobutane for PIB, etc. (see Table 2). The last step of this method for obtaining pure-component polymer parameters is to fit the value of the remaining parameter (the size parameter,  $\sigma$ ) to the pure-polymer *PVT* data over a wide range of temperatures and pressures.

We followed the above procedure for a variety of polymers, and the results are summarized in Table 3. Our polymer database includes polymers for which PC-SAFT parameters have already been published, as well as polymers for which parameters are reported here for the first time. In some cases, this required that parameters for monomers for which no PC-SAFT parameters

**Table 3.** PC-SAFT Parameters<sup>a</sup> and Average Absolute Deviations between Calculated and Experimental Liquid Densities of the Studied Polymers

polymer	$m/MW$	$\sigma$ (Å)	$\epsilon/k$ (K)	$T_{range}$ (K)	$P_{range}$ (bar)	AAD (% $\rho$ )
PS	0.0205	4.152	348.2	390–470	1–1000	0.6
PIB	0.0233	4.117	267.6	325–385	1–1000	1.4
PP	0.0248	4.132	264.6	445–565	1–1000	1.1
PVAc	0.0299	3.463	261.6	310–370	1–800	0.4
PE	0.0254	4.107	272.4	410–470	1–1000	1.0
PMMA	0.0270	3.553	264.6	390–430	1–1000	1.0
PBMA	0.0241	3.884	264.7	310–470	1–1000	1.0
BR	0.0263	4.008	279.4	275–325	1–1000	1.0
PMA	0.0292	3.511	268.3	310–490	1–1000	0.5
PB	0.0245	4.144	275.5	410–510	1–1000	0.9

<sup>a</sup> Parameters obtained using the new pure-component extrapolation method.

had previously been available in the literature be obtained.<sup>4</sup> Table 4 lists the PC-SAFT pure-component parameters for these new monomers. These solvent parameters were obtained in the usual way (from experimental liquid-density and vapor-pressure data extracted from the DIPPR correlations<sup>25</sup>).

The new polymer parameters were evaluated for a variety of polymer–solvent systems exhibiting LLE, some displaying both upper and lower critical solution temperatures, as well as one VLE system [poly(vinyl acetate) (PVAc), for which LLE experimental data were not available]. The results are discussed below.

### 3. Results and Discussion

Figures 3–6 show results for the simplified PC-SAFT using polymer pure-component parameters obtained from mixture data. Figures 3 and 4 show LLE for the system PS–acetone. In Figure 3, the polymer parameters are from method 1 (the original parameters from Gross and Sadowski<sup>4</sup>). In Figure 4, the polymer parameters are obtained by method 4.

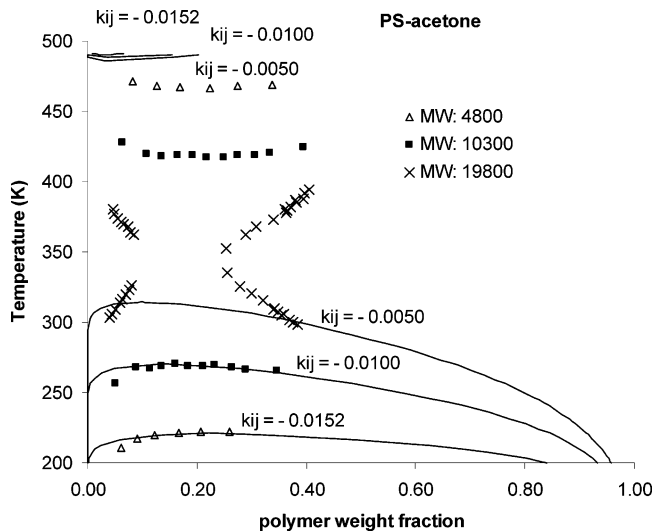
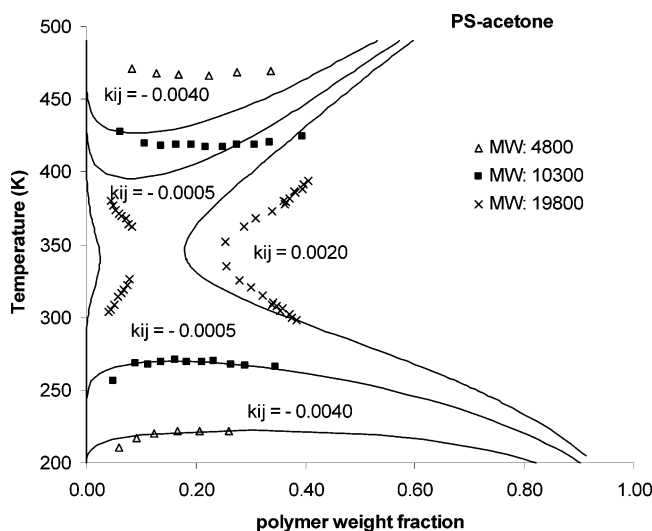
The correlations shown in Figure 3 give a good representation of the UCST curve at the two lower molecular weights when different binary interaction parameters are used, but the molecular-weight sensitivity exhibited experimentally cannot be explained. In particular, the calculated LCST curves are almost independent of the molecular weight. For the same reason, it is not possible to obtain the experimentally observed hourglass behavior for the highest molecular weight.

Figure 4 shows the same system, but with the polymer parameters obtained using method 4 (regression including all three parameters for PS and the interaction parameters for all binary pairs). The LLE diagram is now correlated much more successfully. The LCST curves now exhibit high sensitivity to the molecular weight and eventually merge with the UCST curve at the highest molecular weight, with the narrowing of the hourglass falling in the correct temperature range.

We now consider the same sets of polymer parameters with the solvent cyclohexane. Figure 5 shows that the original parameters for PS (obtained according to method 1, i.e., the same parameters as used in Figure 1) correlate quite satisfactorily both UCST and LCST with the same interaction parameter for all three molecular weights. This is not surprising, given that experimental data for the system PS–cyclohexane were used to obtain the pure-component parameters for PS. On the other hand, Figure 6 shows that, with the parameters obtained according to method 4 (which were so successful

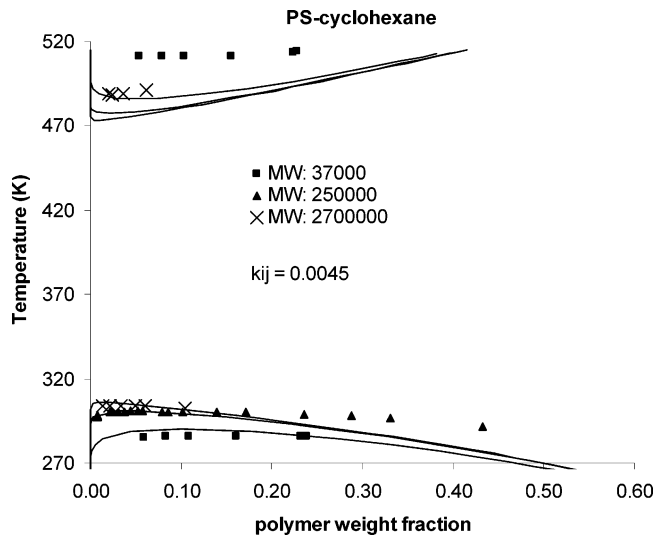
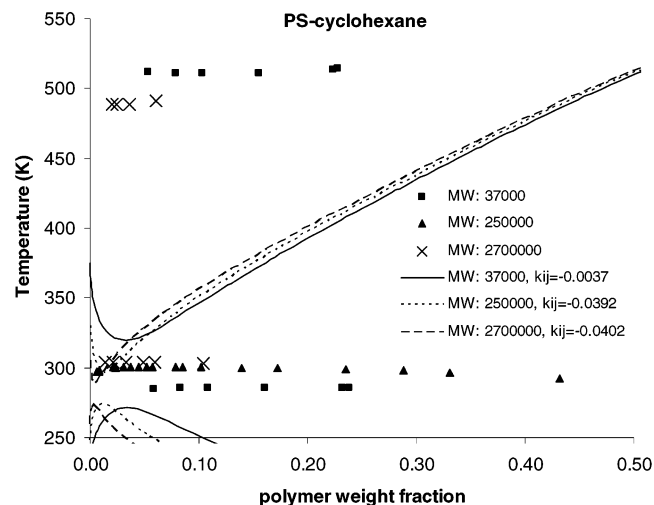
**Table 4. PC-SAFT Pure-Component Parameters and Average Absolute Deviations between Calculated and Experimental Liquid Densities and Vapor Pressures of Solvents Used in this Study for Which Parameters Were Not Already Available**

solvent	MW	$m$	$\sigma$ (Å)	$\epsilon/k$ (K)	$T_{\text{range}}$ (K)	AAD (%) ( $V_L/P^{\text{sat}}$ )
methylisobutyrate	102.133	3.6605	3.444	234.109	220–510	0.6/0.8
isobutylisobutyrate	144.214	4.3798	3.7321	239.135	250–560	1.1/1.6
2-butene	56.107	2.3842	3.5640	226.296	150–390	0.4/0.7
heptanone	114.188	3.7965	3.6415	259.346	300–550	1.0/1.3
2,2,4-trimethylpentane	114.231	3.1366	4.0875	249.987	270–510	0.1/0.1

**Figure 3.** Liquid-liquid equilibrium for the system PS-acetone. Experimental data are from Siow et al.<sup>26</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained according to method 1 (Table 1). The LCSTs are highly insensitive to the molecular weight, in disagreement with the experimental data, and further, the model is incapable of providing the hourglass behavior for MW = 19 800.**Figure 4.** Liquid-liquid equilibrium for the system PS-acetone. Experimental data are from Siow et al.<sup>26</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained according to method 4 (Table 1). The MW sensitivity of the LCSTs is now much closer to that indicated by the experimental data, and the model correctly provides the hourglass behavior at MW = 19 800.

in the PS-acetone system of Figure 2), the flatness of the curves and the good correlation of the LCST are lost.

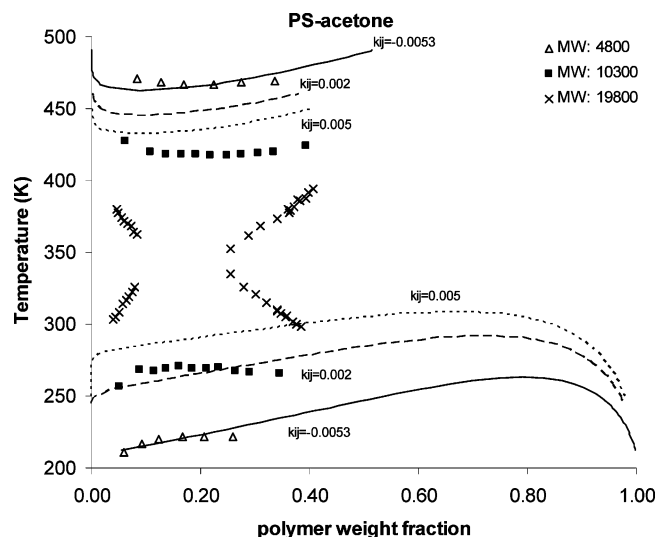
None of the parameter sets obtained from mixture data (methods 1–5) are capable of simultaneously correlating the PS-acetone and PS-cyclohexane binary LLE diagrams. Parameters that give the experimentally

**Figure 5.** Liquid-liquid equilibrium for the system PS-cyclohexane. Experimental data are from Saeki et al.<sup>27</sup> (MW = 37 000 and 2 700 000) and Shultz et al.<sup>28</sup> (MW = 250 000). Lines are simplified PC-SAFT correlations with PS parameters obtained according to method 1 (Table 1).**Figure 6.** Liquid-liquid equilibrium for the system PS-cyclohexane. Experimental data are from Saeki et al.<sup>27</sup> (MW = 37 000 and 2 700 000) and Shultz et al.<sup>28</sup> (MW = 250 000). Lines are simplified PC-SAFT correlations with PS parameters obtained according to method 4 (Table 1).

indicated hourglass behavior for PS-acetone at high PS molecular weight fail in representing the flatness of the PS-cyclohexane phase diagrams and vice versa.

We now consider the performance of parameters obtained using only pure-component data, as discussed in section 2.2 above. Parameters for a number of polymers obtained in this way are listed in Table 3. The new approach provides sets of pure-component polymer parameters that yield satisfactory results and combine the following advantages:





**Figure 7.** Liquid-liquid equilibrium for the system PS-acetone. Experimental data are from Siow et al.<sup>26</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained according to the proposed novel method (Table 3).

(1) Both  $m$  and  $\epsilon$  are based on extrapolation equations, equations that are different for each homologous series. All that is required are the PC-SAFT parameters of the monomer (the first component of the series), which are either already available or easily regressed from readily available vapor pressures and liquid densities, e.g., generated from the DIPPR correlations.<sup>25</sup>

The energy parameter for the polymer is always higher than that for the corresponding monomer. This is the expected physical behavior. The segments in the polymer are larger than those of the monomer, so there are consequently fewer segments in the polymer per unit of molecular weight. This means that each segment carries more of the polymer's interaction energy.

The average percent absolute deviations between calculated and experimental liquid densities are very low.

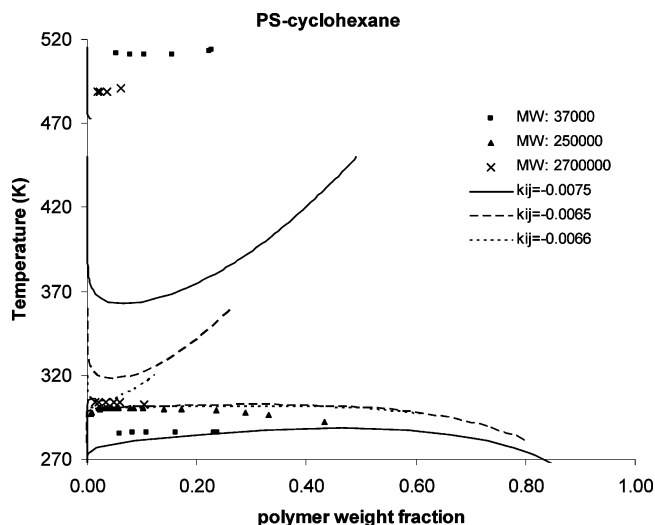
The segment parameter,  $\sigma$ , has a value of around 4.1 Å for many of the studied polymers (apart from PVAc, PMA, PMMA, and PBMA, because of the high  $m$  values), which has been shown to give good results for polymers.<sup>7</sup>

The performance of simplified PC-SAFT using the pure-component polymer parameters estimated with the procedure discussed above was tested against binary polymer-solvent mixtures exhibiting LLE and VLE phase behavior. The results are shown in Figures 7–18.

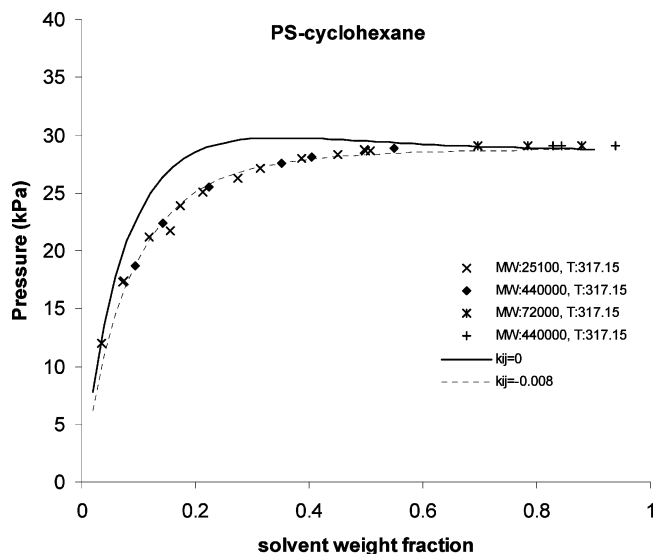
Figures 7 and 8 show the same PS systems as above, this time with PS parameters obtained according to the method we proposed here. Figure 7 shows the PS-acetone solution, for which the correlation with simplified PC-SAFT is similar to that shown in Figure 3 (that is, with PS parameters obtained according to method 1). Still, the hourglass behavior cannot be captured, even though the model now shows a MW sensitivity. The UCST is satisfactorily correlated with low values for the interaction parameter.

Figure 8 shows the PS-cyclohexane solution, for which the UCST is well described, although—unlike as shown in Figure 5—slightly different values for the optimum interaction parameter are now necessary.

Figure 9 shows the vapor-liquid equilibrium for the system PS-cyclohexane. Simplified PC-SAFT slightly



**Figure 8.** Liquid-liquid equilibrium for the system PS-cyclohexane. Experimental data are from Saeki et al.<sup>27</sup> (MW = 37 000 and 2 700 000) and Shultz et al.<sup>28</sup> (MW = 250 000). Lines are simplified PC-SAFT correlations with PS parameters obtained according to the proposed novel method (Table 3).



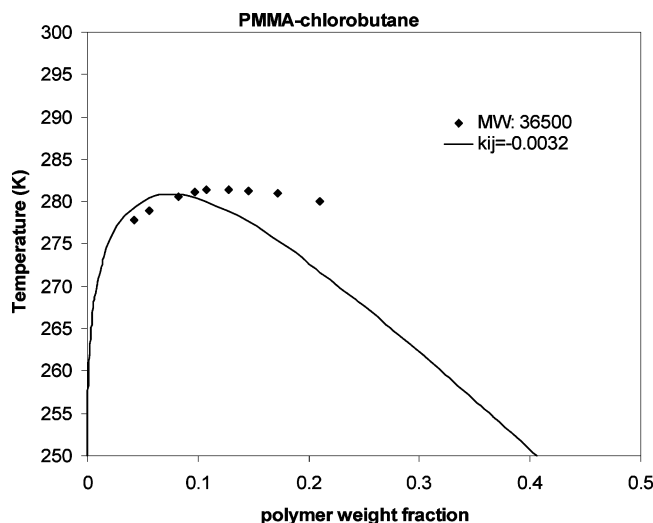
**Figure 9.** Vapor-liquid equilibrium for the system PS-cyclohexane. Experimental data are from Krigbaum et al.<sup>29</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained according to the proposed novel method (Table 3).

underpredicts the temperature of the liquid split, but it provides an excellent correlation with a low, negative interaction parameter.

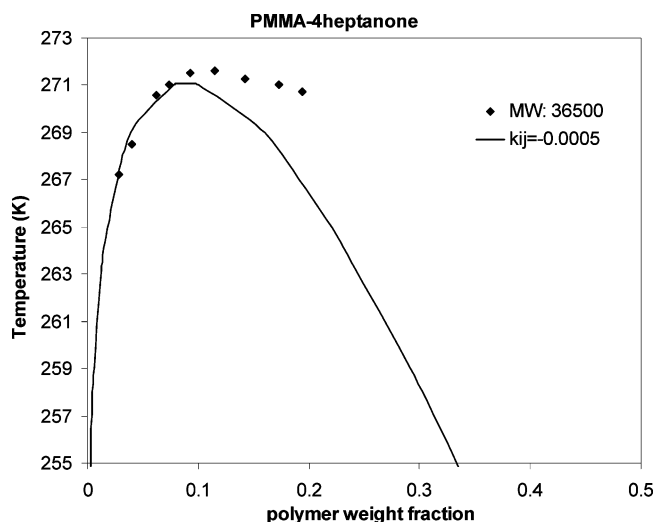
Figures 10 and 11 show two different PMMA solutions with chlorobutane and 4-heptanone, respectively, that display upper critical solution temperature behavior. Both systems are satisfactorily correlated with quite small, negative interaction parameters. However, in both cases, the flatness of the experimental data toward the higher polymer weight fractions cannot be accurately described.

The same behavior is shown in Figure 12 for two binary solutions of PBMA with pentane and octane. Both systems display upper critical solution temperature behavior and are very well correlated with small values of the interaction parameters.

Figure 13 shows results for the system PP-diethyl ether, which displays lower critical solution temperature behavior, at two different molecular weights of the



**Figure 10.** Liquid-liquid equilibrium for the system PMMA (MW = 36 500)-chlorobutane. Experimental data are from Wolf et al.<sup>30</sup> The line is a simplified PC-SAFT correlation with  $k_{ij} = -0.0032$ . This system displays upper critical solution temperature (UCST) behavior.



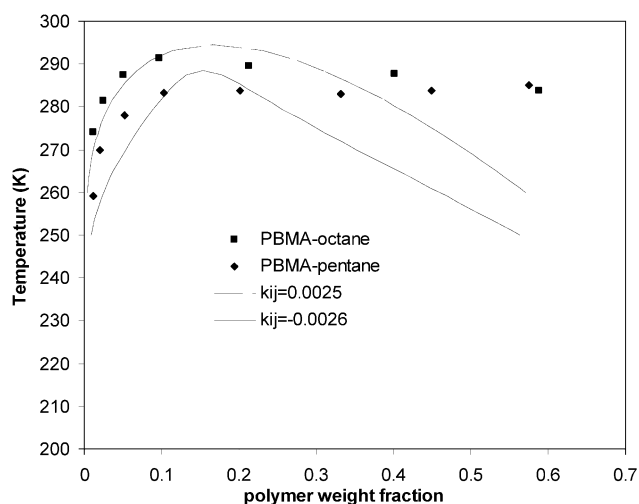
**Figure 11.** Liquid-liquid equilibrium for the system PMMA (MW = 36 500)-4-heptanone. Experimental data are from Wolf et al.<sup>30</sup> The line is a simplified PC-SAFT correlation with  $k_{ij} = -0.0005$ . This system displays upper critical solution temperature (UCST) behavior.

polymer. The prediction and correlation with simplified PC-SAFT is very good at the higher molecular weight of the polymer but less so at the lower one.

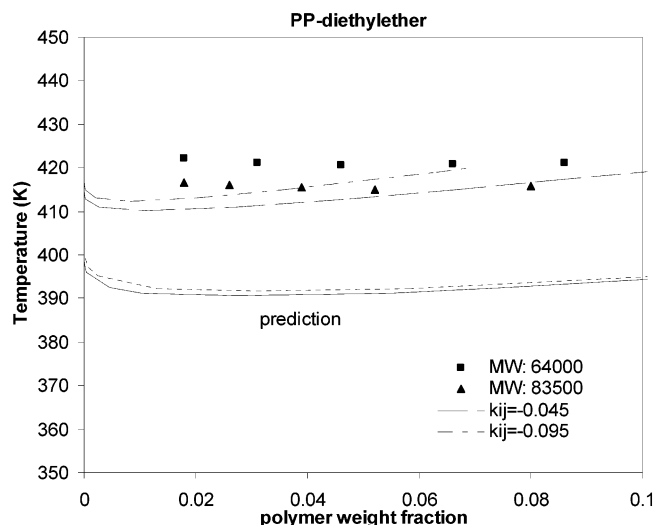
Figure 14 shows the nearly athermal PIB-octane system, which also displays lower critical solution temperature behavior and is very well predicted ( $k_{ij} = 0$ ) and correlated with simplified PC-SAFT.

Figure 15 shows a more complicated phase diagram, where the butadiene rubber (polybutadiene, BR) solution in hexane displays both upper and lower phase splits, as well as hourglass behavior for the highest molecular weight of BR. Unfortunately, even though the correlation of the UCST is possible with a single interaction parameter for the three lower molecular weights, the LCST is only qualitatively described, and the hourglass behavior cannot be correlated at all.

Results for the system BR-2-methylhexane, which exhibits both upper and lower critical solution behavior, are shown in Figure 16. The correlated curve successfully matches the experimental UCST data with



**Figure 12.** Liquid-liquid equilibrium for the systems PBMA-pentane and PBMA-octane. Experimental data are from Saraiva et al.<sup>31</sup> Lines are simplified PC-SAFT correlations with  $k_{ij} = -0.0026$  (PBMA-pentane) and  $k_{ij} = 0.0025$  (PBMA-octane). The molecular weight of PBMA is 11 600. These systems display upper critical solution temperature (UCST) behavior.

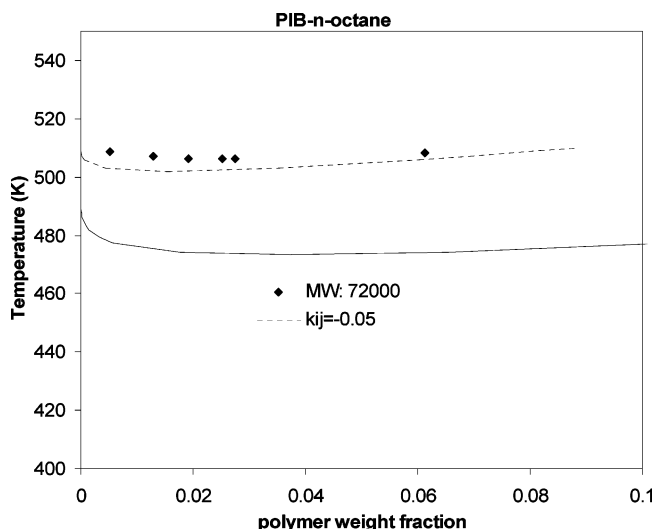


**Figure 13.** Liquid-liquid equilibrium for the system PP-diethyl ether. Experimental data are from Cowie et al.<sup>32</sup> Lines are simplified PC-SAFT predictions and correlations with  $k_{ij} = -0.045$  (MW = 83 500) and  $k_{ij} = -0.095$  (MW = 64 000). This system displays lower critical solution temperature (LCST) behavior.

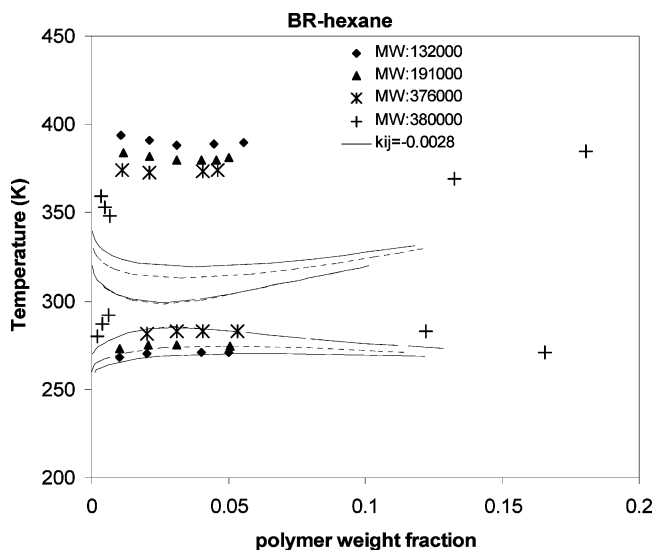
a small negative binary interaction parameter, but it greatly underestimates the LCST. As has been observed and discussed previously,<sup>9</sup> generally, the LCST behavior is rather insensitive to the binary interaction parameter. This is because LCST behavior is usually observed at elevated temperatures, where the effect of the energy parameters is not as marked. Because  $k_{ij}$  is a correction to the cross-energy parameter  $\epsilon_{ij}$ , changing the  $k_{ij}$  value generally has only a marginal effect. However, if a binary interaction parameter  $I_{ij}$  is applied in the calculation of the cross-segment parameter

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2}(1 - I_{ij}) \quad (9)$$

as shown in the same figure by the dashed line, then the LCST curve can be successfully fitted as well,



**Figure 14.** Liquid-liquid equilibrium for the system PIB (MW = 72 000)-*n*-octane. Experimental data are from Liddell et al.<sup>33</sup> Lines are a simplified PC-SAFT prediction and correlation with  $k_{ij} = -0.05$ . This system displays lower critical solution temperature (LCST) behavior.

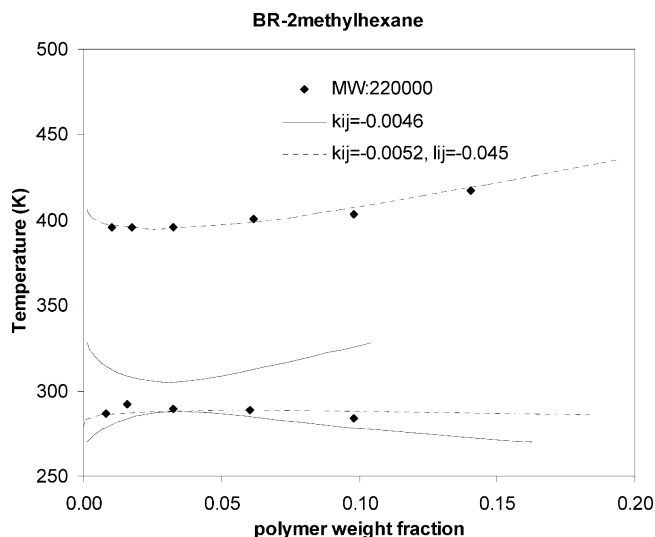


**Figure 15.** Liquid-liquid equilibrium for the system BR-hexane. Experimental data are from Delmas et al.<sup>34</sup> Lines are simplified PC-SAFT correlations with  $k_{ij} = -0.0028$ , the same for all three molecular weights (132 000, 191 000, and 376 000). This system displays both upper and lower critical solution temperature behavior.

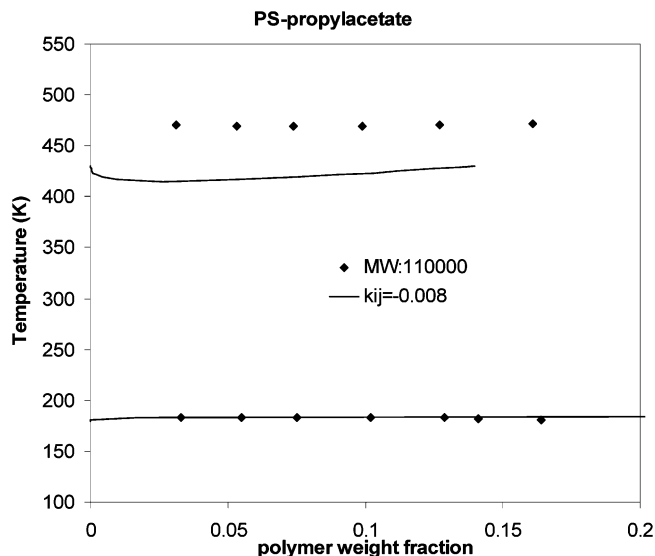
without considerably affecting the fit of the UCST (the value of  $k_{ij}$  has to change from  $-0.0046$  to  $-0.0052$ ).

On the other hand, for the system PS-propyl acetate shown in Figure 17, the simplified PC-SAFT correlates both the UCST and LCST with great accuracy, using the same binary interaction parameter.

Finally, in Figure 18, the vapor-liquid phase diagram for the system PVAc-2-methyl-1-propanol is presented at three different temperatures. Pure-component parameters for the solvent are taken from the literature.<sup>6</sup> A comparison with experimental VLE data was chosen in this case for the evaluation of the PVAc parameters, as LLE data for this polymer are not available. This system is very well predicted by simplified PC-SAFT at all three temperatures. Deviations increase, however, as the temperature increases. In general, comparisons with LLE data provide a much stricter test of a model than comparisons with VLE data.



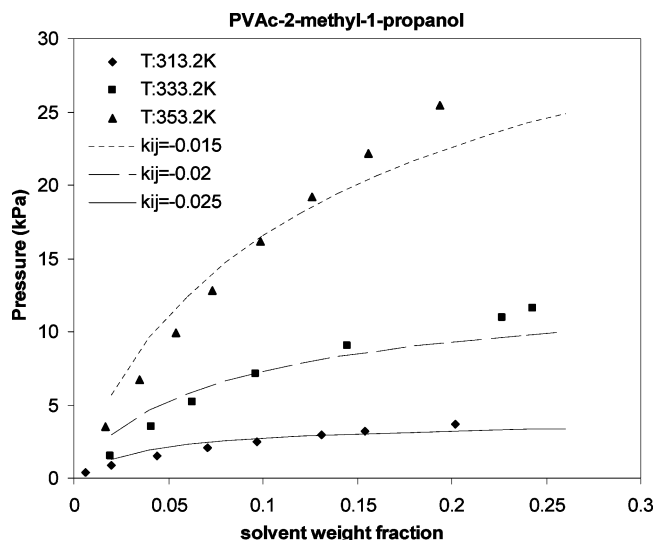
**Figure 16.** Liquid-liquid equilibrium for the system BR (MW = 220 000)-2-methylhexane. Experimental data are from Delmas et al.<sup>34</sup> Solid lines are simplified PC-SAFT correlations with  $k_{ij} = -0.0046$ . Dashed lines are simplified PC-SAFT correlations with  $k_{ij} = -0.0052$  and  $l_{ij} = -0.045$ . This system displays both upper and lower critical solution temperature behavior.



**Figure 17.** Liquid-liquid equilibrium for the system PS (MW = 110 000)-propyl acetate. Experimental data are from Saeki et al.<sup>35</sup> Lines are simplified PC-SAFT correlations with  $k_{ij} = -0.008$ . This system displays both upper and lower critical solution temperature behavior.

#### 4. Conclusions

In this work, we have evaluated a number of different methods for obtaining pure-component polymer parameters from mixture data and pure-polymer liquid-density data. We have found that these methods do not lead to a unique set of polymer parameters, but rather depend greatly on the number and type of selected binary data used in the regression. On the basis of this observation, we have directed our efforts toward developing a procedure that is dependent only on pure-polymer *PVT* data and extrapolation equations that relate the parameters of the monomer to those of the polymer for each homologous series. This novel method is easy to implement, even in cases of relatively complex polymers. We have obtained parameters for a number of polymers of varying complexity. Using these param-



**Figure 18.** Vapor–liquid equilibrium for the system PVAc (MW = 110 000)–2-methyl-1-propanol. Experimental data are from Wibawa et al.<sup>36</sup> Lines are simplified PC-SAFT correlations at three different temperatures with  $k_{ij} = -0.025$  ( $T = 313$  K),  $k_{ij} = -0.020$  ( $T = 333$  K), and  $k_{ij} = -0.015$  ( $T = 353$  K).

eters, simplified PC-SAFT can successfully describe vapor–liquid and liquid–liquid equilibria for a wide variety of binary polymer–solvent mixtures.

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### Nomenclature

#### Abbreviations

AAD = average absolute deviation  
BR = butadiene rubber (polybutadiene)  
EoS = equation of state  
LCST = lower critical solution temperature  
LLE = liquid–liquid equilibrium  
MEK = methyl ethyl ketone  
MW = molecular weight, g/mol  
PBMA = poly(butyl methacrylate)  
PC-SAFT = perturbed-chain statistical associating fluid theory  
PE = polyethylene  
PIB = polyisobutylene  
PMA = poly(methyl acrylate)  
PMMA = poly(methyl methacrylate)  
PP = polypropylene  
PS = polystyrene  
PVAc = poly(vinyl acetate)  
PVT = pressure–volume–temperature  
SAFT = statistical associating fluid theory  
UCST = upper critical solution temperature  
VLE = vapor–liquid equilibrium

#### Symbols

$k$  = Boltzmann constant, J/K  
 $m$  = segment number  
 $P$  = pressure, bar/atm  
 $T$  = temperature, °C/K  
 $v^\infty$  = temperature-independent segment volume, mL/mol of segments  
 $u^0/k$  = temperature-independent dispersion energy of interactions between segments, K

#### Greek Symbols

$\epsilon$  = (energy parameter) depth of the dispersion potential, J  
 $\rho$  = liquid density, g/cm<sup>3</sup>  
 $\sigma$  = (size parameter) segment diameter, Å

#### Subscripts

$i, j$  = component  $i, j$

### Appendix. Equations of Simplified PC-SAFT

The equation of state employed here is the simplified version of PC-SAFT developed by von Solms et al.<sup>5</sup> Our starting point is the reduced Helmholtz energy for a mixture of associating molecules

$$\tilde{a} \equiv \frac{A}{NkT} = \tilde{a}^{\text{id}} + \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{assoc}} \quad (\text{A1})$$

where  $\tilde{a}^{\text{id}}$  is the ideal gas contribution,  $\tilde{a}^{\text{hc}}$  is the contribution of the hard-sphere chain reference system,  $\tilde{a}^{\text{disp}}$  is the dispersion contribution arising from the square-well attractive potential, and  $\tilde{a}^{\text{assoc}}$  is the contribution due to association. The expressions for the contributions from the ideal gas ( $\tilde{a}^{\text{id}}$ ) and dispersion ( $\tilde{a}^{\text{disp}}$ ) are identical to those of Gross and Sadowski,<sup>4</sup> and the reader is referred to their paper for more detail. The contribution to the hard-chain term is made up of two contributions: the hard-sphere term and the chain term

$$\tilde{a}^{\text{hc}} = \bar{m}\tilde{a}^{\text{hs}} - \sum_i x_i(m_i - 1) \ln g^{\text{hs}} \quad (\text{A2})$$

where  $\bar{m}$  is a mean segment length defined simply as  $\bar{m} = \sum_i x_i m_i$  and the hard-sphere term is given by

$$\tilde{a}^{\text{hs}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (\text{A3})$$

Here,  $x_i$  is the mole fraction of component  $i$ . The radial distribution function at contact is

$$g^{\text{hs}}(d^+) = \frac{1 - \eta/2}{(1 - \eta)^3} \quad (\text{A4})$$

The volume fractions  $\eta = \pi\rho\bar{m}d^3/6$  are based on the diameter of an equivalent one-component mixture

$$d = \left( \frac{\sum_i x_i m_i d_i^3}{\sum_i x_i m_i} \right)^{1/3} \quad (\text{A5})$$

where the individual  $d_i$  variables are temperature-dependent segment diameters

$$d_i = \sigma_i \left[ 1 - 0.12 \exp\left(-\frac{3\epsilon_i}{kT}\right) \right] \quad (\text{A6})$$

Thus, it is assumed that all of the segments in the mixture have a mean diameter  $d$ , which gives a mixture volume fraction identical to that of the actual mixture.

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