Multicomponent Flash Algorithm for Mixtures Containing Polydisperse Polymers

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An algorithm called POLYMIX is introduced for flash calculations of multicomponent systems containing polydisperse polymers. The polydispersity of polymers is taken into account through the concept of pseudocomponents. In industrial practice, a relatively high number of pseudocomponents are often required to represent multimodal polymer molecular-weight distributions. The algorithm formulation is independent of use of specific segment-based polymer equations of state for computing thermodynamic properties of polymer mixtures. The algorithm further offers the advantage that the computing time for polymer flash calculations is independent of the number of pseudocomponents used to represent the polydisperse polymer. Applications to polymer mixtures containing polyethylene and polypropylene are presented.

Introduction

Most industrially produced polymers are mixtures of polymer components with varying chain length, chain chemical compositions, degrees of branching, and so on. In other words, polymers are polydisperse. This polydisperse nature of polymers has a strong effect on the phase behavior of mixtures containing polymers (Shultz and Flory, 1952; Koningveld and Staverman, 1968; Bonner et al., 1974; Folie, 1996; Bokis et al., 1999). For example, the molecular-weight distributions of polymers over different phases will be different from that of the feed polymer being flashed.

In executing polymer flash calculation, there are two different approaches to account for the molecular-weight distribution (MWD) of polydisperse polymers. One is to treat the distribution with continuous distribution functions (Kehlen and Raetzsch, 1980; Gualtieri et al., 1982; Raetzsch and Kehlen, 1983, 1985), such as Schulz−Flory distribution or Wesslau distribution, and to apply the functional theory to derive an expression for the chemical potential. Phoenix and Heidemann (1999) applied this approach to develop an algorithm for determining the cloud- and shadow-point curves of polydisperse polymer solutions. Another approach is to treat the distribution with a set of discrete pseudocomponents (Chen et al., 1993; Sadowski and Arlt, 1995; Folie, 1996; Behme et al., 1999; Cheluget et al., 2002; Jog and Chapman, 2002). For unimodal molecular-weight distribution curves, pseudocomponents are generated by matching the statistical moments of the distribution to those of the pseudocomponents to be determined (Tork et al., 1999) or by discretizing a continuous distribution function using Gaussian quadrature method (Cotterman et al., 1985, 1986; Cotterman and Prausnitz, 1985). These two methods, however, are limited to flash calculations with small numbers of pseudocomponents when detailed shape of a molecular-weight distribution is not important.

Many industrial polymerization processes involve multiple reactors in series or use multisite catalysts, resulting in polymers with bimodal or multimodal MWD curves (Hungenberg et al., 2001; Cheluget et al., 2002). Representation of these multimodal MWD curves with continuous distribution functions would be extremely cumbersome, if not impossible. In contrast, the pseudocomponent approach is preferred be-

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cause it provides a simple and flexible mechanism to represent these MWD curves with high fidelity when a large number of pseudocomponents (that is, on the order of hundreds) are used. In practice, the challenge with the pseudocomponent approach is to develop a computationally efficient and robust flash algorithm for polymer systems when a high number of pseudocomponents are required to faithfully represent the detailed shape of MWD curves, bimodal or multimodal.

In this work, we introduce a flash algorithm called POLYMIX that is designed to perform flash calculations for multicomponent systems containing polydisperse polymers. This algorithm has been successfully used in academia and in industry for a number of years (Behme et al., 1999; Tork et al., 1999; Wiesmet et al., 2000; Hungenberg et al., 2001; Cheluget et al., 2002). The POLYMIX algorithm is similar to the algorithm recently reported by Jog and Chapman (2002), although they only formulated their algorithm in terms of bubble-point calculations with the SAFT equation of state (EOS). In POLYMIX, the concept of pseudocomponents is applied to rigorously account for the polymer MWD curves in flash calculations. The MWD curve of the polydisperse polymer is divided into any number of discrete pseudocomponents, each representing a certain fraction of the molecular-weight distribution. Thus, all pseudocomponents together represent the polydisperse polymer. Each pseudocomponent is characterized by its molecular weight or degree of polymerization. Changes in MWD curves are expressed in terms of changes in mole fractions of pseudocomponents within the polydisperse polymer.

The POLYMIX algorithm formulation is independent of use of a specific segment-based polymer EOS for computing thermodynamic properties of the polymer mixture. Although many of the details are different, these segment-based polymer equations of state that were derived from statistical thermodynamics share a common formulation. That is, each pure component in the polymer mixture is characterized by three segment-based parameters: segment number, segment size or volume, and segment energy. Among the commonly used EOS are the original statistical associating fluid theory (SAFT) EOS (Chapman et al., 1988, 1990) and its numerous variations (for example, see Huang and Radosz, 1990, 1991; Gross and Sadowski, 2001, 2002), perturbed hard-sphere-chain (PHSC) EOS (Song et al., 1994, 1996), and Sanchez−Lacombe EOS (Sanchez and Lacombe, 1976, 1978; Koak and Heidemann, 1996). Furthermore, POLYMIX takes advantage of the fact that polymer mixture properties (such as pressure, compressibility factor, Helmholtz energy) can be calculated based on the number-average molecular weight of the polydisperse polymer. This is a result of segment-based polymer EOS in which all pseudocomponents and the polydisperse polymer share the same segment-based model parameters but with different molecular weight or degree of polymerization. Consequently, the derived natural logarithm of the fugacity coefficient of a pseudocomponent in the mixture is a linear function of its segment number and is independent of mole fractions of pseudocomponents representing the polydisperse polymer. This leads to a highly efficient flash algorithm as the computation time becomes independent of the number of pseudocomponents used to represent the polymer MWD curve. Therefore, POLYMIX achieves the computational efficiency required to perform flash calculations with polydisperse polymers when a large number of pseudocomponents are required to obtain a high-fidelity representation of MWD curves, bimodal or multimodal.

Theory

Segment number for polymers

Unlike "small molecule" components (solvents and monomers), polymer components can have different size (molecular weight). To account for the variation in polymer size, the most commonly used parameter is the segment number for polymers, r, which is linearly related to the polymer molecular weight, M, as follows

$$M = rM_{\text{seg}}. \tag{1}$$

Here M_{seg} is the molecular weight of the segment from which the polymer is composed. In segment-based polymer EOS, each pure component is usually characterized by three segment-based parameters (for examples, see Huang and Radosz, 1990, 1991; Song et al., 1994, 1996; Gross and Sadowski, 2001, 2002; Sanchez and Lacombe, 1976, 1978; Koak and Heidemann, 1996): segment number, r (number of single spheres per chain molecule), segment size, σ, or segment volume, ν, and segment-pair interaction energy, ϵ. If the segment size and energy parameters are the same for all segments of the same polymer, the segment number, r, turns out to be the only parameter that depends on the molecular weight of the polymer. Here one can relate the number-average molecular weight, M_n, of polydisperse polymers to the average segment number, $\bar{r}$

$$M_n = \bar{r}M_{\text{seg}}. \tag{2}$$

We will use the segment number instead of the molecular weight in characterizing the MWD in this article.

Pseudocomponents

For simplicity and convenience, consider a mixture of K components in which we define component p as a polydisperse polymer. We then divide component p into N pseudocomponents. The following quantities are introduced for this mixture:

- Mole fraction of components: x_i ($i = 1, 2, \ldots, K$).
- Mole fraction of pseudocomponents in the mixture: $x_{p,j}$ ($j = 1, 2, \ldots, N$).
- Mole fraction of pseudocomponents within component p: X_j ($j = 1,2, \ldots, N$).
- Segment number of pseudocomponents within component p: $r_{p,j}$ ($j = 1,2, \ldots, N$).
- Average segment number of pseudocomponents for component p: $\bar{r}_p$.

The following relations and summations hold for these quantities:

$$\sum_{i=1}^{K} x_i = 1 \tag{3}$$

$$x_p = \sum_{j=1}^{N} x_{p,j} \tag{4}$$

$$\sum_{j=1}^{N} X_j = 1 \tag{5}$$

$$\bar{r}_p = \sum_{j=1}^{N} X_j r_{p,j} \tag{6}$$

$$x_{p,j} = x_p X_j \quad j = 1,2,\ldots,N \tag{7}$$

$$x_p \bar{r}_p = \sum_{j=1}^{N} x_{p,j} r_{p,j}. \tag{8}$$

Mixture property calculations

Unlike the approaches by Phoenix and Heidemann (1999) and Jog and Chapman (2002), which include specific polymer equations of state in their derivations, we start with mixture property calculations from general thermodynamics so that the formulation of POLYMIX becomes independent of a specific polymer EOS. For a mixture containing N pseudocomponents, the compressibility factor can be expressed as

$$Z = Z\big(T,\rho,\{x_{p,j}\},\{r_{p,j}\},\ldots\big). \tag{9}$$

Here Z is the compressibility factor for the mixture, T is the temperature, and ρ is the molar density. In Eq. 9, $\{x_{p,j}\}$ and $\{r_{p,j}\}$ are vectors of mole fractions and segment numbers of pseudocomponents in the mixture, respectively, as defined in Eqs. 1, 4, 5 and 7. All other parameters and compositions for monodisperse components are not explicitly displayed in Eq. 9 because they are irrelevant to this discussion.

Since the segment size and energy parameters for all pseudocomponents of the polydisperse polymer are the same and the only differences among the pseudocomponents are their segment numbers, the compressibility factor for the mixture can be calculated using the mole fraction of the polydisperse polymer in the mixture and the average segment number of pseudocomponents for the polydisperse polymer in general. Therefore, we can rewrite Eq. 9 as follows

$$Z = Z\big(T,\rho,x_p,\bar{r}_p,\ldots\big), \tag{10}$$

where x_p is the mole fraction of the polydisperse polymer in the mixture and $\bar{r}_p$ is the average segment number of pseudocomponents for component p, as defined by Eqs. 4 and 6, respectively.

For polymer EOS, another useful mixture property is the molar residual Helmholtz energy, from which any other thermodynamic function can be derived. It is defined as

$$a^{\text{res}} = a - a^{\text{ig}}, \tag{11}$$

where a is the molar Helmholtz energy of the mixture and a^{ig} is the molar Helmholtz energy of a mixture of ideal gases at the same temperature, volume, and compositions. From thermodynamics, we can obtain

$$\frac{a^{\text{res}}}{RT} = \int_0^{\rho} (Z-1)\frac{d\rho}{\rho}, \tag{12}$$

where R is the gas constant. Using Eq. 10 for Z, a^{res} can also be calculated using the mole fraction of the polydisperse polymer in the mixture and the average segment number of pseudocomponents for the polydisperse polymer

$$a^{\text{res}} = a^{\text{res}}\big(T,\rho,x_p,\bar{r}_p,\ldots\big). \tag{13}$$

Fugacity coefficients of pseudocomponents

Once we know the molar residual Helmholtz energy of the mixture, we can calculate any other thermodynamic functions of interest. Here fugacity coefficients of pseudocomponents in the mixture are of particular interest, as they are needed in phase-equilibrium calculations. By standard thermodynamics, the natural logarithm of the fugacity coefficient of components in the mixture is calculated as

$$\ln \varphi_i = \frac{\mu_i^{\text{res}}}{RT} - \ln Z. \tag{14}$$

Equation 14 applies to both monodisperse components and pseudocomponents in the polymer mixture. The residual chemical potential, μ_i^{res}, is given by

$$\begin{aligned}\mu_i^{\text{res}} &= a^{\text{res}} + \rho\frac{\partial a^{\text{res}}}{\partial \rho} + \frac{\partial a^{\text{res}}}{\partial x_i} - \sum x_l\left(\frac{\partial a^{\text{res}}}{\partial x_l}\right) \\ &= a^{\text{res}} + RT(Z-1) + \frac{\partial a^{\text{res}}}{\partial x_i} - \sum x_l\left(\frac{\partial a^{\text{res}}}{\partial x_l}\right),\end{aligned} \tag{15}$$

where $\partial a^{\text{res}}/\partial x_i$ is a partial derivative that is always done to the mole fraction stated in the denominator, while all other mole fractions are considered constant. The summation term in Eq. 15 is over both monodisperse components and pseudocomponents

$$\sum x_l\left(\frac{\partial a^{\text{res}}}{\partial x_l}\right) = \sum_{i \neq p}^{K} x_i\left(\frac{\partial a^{\text{res}}}{\partial x_i}\right) + \sum_{j=1}^{N} x_{p,j}\left(\frac{\partial a^{\text{res}}}{\partial x_{p,j}}\right). \tag{16}$$

Therefore, we only need to calculate the derivative of the molar Helmholtz energy of the mixture with respect to the mole fraction of components in the mixture, and the calculations for monodisperse components are straightforward. Here we focus on how to calculate the derivatives for pseudocomponents in the mixture

$$\frac{\partial a^{\text{res}}}{\partial x_{p,j}} = \frac{\partial a^{\text{res}}}{\partial x_p}\frac{\partial x_p}{\partial x_{p,j}} + \frac{\partial a^{\text{res}}}{\partial \bar{r}_p}\frac{\partial \bar{r}_p}{\partial x_{p,j}}. \tag{17}$$

Using Eqs. 4 and 8, we can obtain

$$\frac{\partial x_p}{\partial x_{p,j}} = 1 \tag{18}$$

$$\frac{\partial \bar{r}_p}{\partial x_{p,j}} = \frac{r_{p,j}}{x_p} - \frac{\bar{r}_p}{x_p} \tag{19}$$

Therefore, we have

$$\frac{\partial a^{\text{res}}}{\partial x_{p,j}} = \frac{\partial a^{\text{res}}}{\partial x_p} - \frac{\bar{r}_p}{x_p}\frac{\partial a^{\text{res}}}{\partial \bar{r}_p} + \frac{r_{p,j}}{x_p}\frac{\partial a^{\text{res}}}{\partial \bar{r}_p} \tag{20}$$

$$\sum_{j=1}^{N} x_{p,j}\left(\frac{\partial a^{\text{res}}}{\partial x_{p,j}}\right) = \frac{\partial a^{\text{res}}}{\partial x_p}. \tag{21}$$

Equation 20 indicates that the derivative for pseudocomponents in the mixture depends on the segment numbers of pseudocomponents in the mixture, but is independent of the mole fractions of pseudocomponents within the polymer explicitly. Substituting Eq. 21 in Eq. 16, we obtain

$$\sum x_l\left(\frac{\partial a^{\text{res}}}{\partial x_l}\right) = \sum_{i \neq p}^{K} x_i\left(\frac{\partial a^{\text{res}}}{\partial x_i}\right) + x_p\frac{\partial a^{\text{res}}}{\partial x_p} = \sum_{i=1}^{K} x_i\left(\frac{\partial a^{\text{res}}}{\partial x_i}\right). \tag{22}$$

Applying Eqs. 20 and 22 in Eqs. 14 and 15, we can derive a general expression for the fugacity coefficients of pseudocomponents in the mixture

$$\ln \varphi_{p,j} = \ln \varphi_A(T,v,x_p,\bar{r}_p,\ldots) + r_{p,j}\ln \varphi_B(T,v,x_p,\bar{r}_p,\ldots) \qquad j=1,2,\ldots,N, \tag{23}$$

where

$$RT\ln \varphi_A = a^{\text{res}} + RT[(Z-1) - \ln Z] - \sum_{i=1}^{K} x_i\left(\frac{\partial a^{\text{res}}}{\partial x_i}\right) + \frac{\partial a^{\text{res}}}{\partial x_p} - \frac{\bar{r}_p}{x_p}\frac{\partial a^{\text{res}}}{\partial \bar{r}_p} \tag{24}$$

$$RT\ln \varphi_B = \frac{1}{x_p}\frac{\partial a^{\text{res}}}{\partial \bar{r}_p}. \tag{25}$$

Equations 23–25 show that the natural logarithm of the fugacity coefficient of a pseudocomponent in the mixture is a linear function of its segment number and is independent of mole fractions of pseudocomponents within the polymer. Also note that both ln φ_A and ln φ_B are the same for all pseudocomponents. As we will show in the next section for flash algorithm formulation, Eqs. 23–25 are the key equations that lead to a highly efficient flash algorithm as the computation time for polymer systems becomes independent of the number of pseudocomponents used to represent the polydisperse polymer.

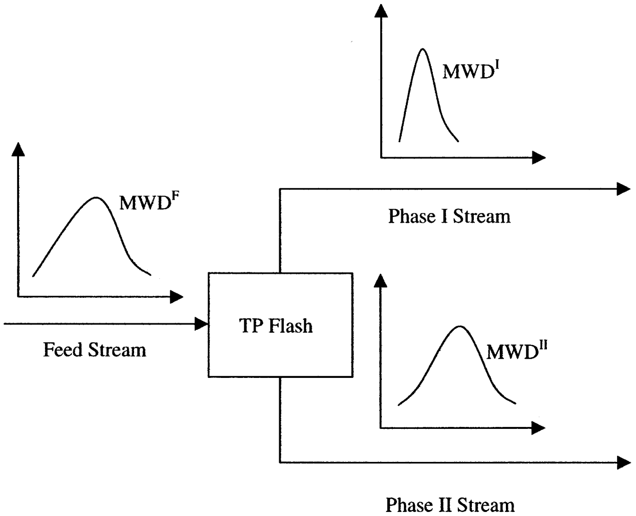

Figure 1. Two-phase TP flash for a mixture containing a polydisperse polymer.

It should be pointed out that similar conclusions from Eqs. 23–25 were also obtained by Phoenix and Heidemann (1999) and Jog and Chapman (2002) in their formulations for bubble-point calculations. However, unlike their approaches for a specific EOS model in each case, we arrive at a general conclusion that is independent of a specific segment-based polymer EOS.

TP Flash

In a two-phase temperature pressure (TP) flash calculation, temperature, pressure, and feed-stream compositions are defined. From a mathematical point of view, it is a problem of solving a system of coupled nonlinear equations derived from phase equilibrium conditions and mass balances. In the particular case of interest, in which one component is a polydisperse polymer, the flash calculation leads to a polymer MWD in each phase that is different from the polymer MWD of the feed stream, as shown in Figure 1. In this section, we derive all equations needed for the flash calculation from phase equilibrium conditions and mass balances.

Phase equilibrium and mass balance for monodisperse components

For a $(K-1+N)$ component system, the phase equilibrium conditions for the $K-1$ monodisperse components in the mixture are

$$0 = x_i^{\text{I}}\varphi_i^{\text{I}} - x_i^{\text{II}}\varphi_i^{\text{II}} \quad i=1,\ldots,K, \quad i \neq p, \tag{26}$$

where I and II denote phase 1 and 2, respectively, and φ_i is the fugacity coefficient of component i in the mixture.

Mass balances are also needed for flash calculations. The mass-balance component for all monodisperse components in the mixture can be written as

$$n_i^F = n_i^{\text{I}} + n_i^{\text{II}} \quad i=1,\ldots,K, \quad i \neq p, \tag{27}$$

where n_i^F is the molar flow rate of component i in the feedstream. By introducing the phase fraction, Eq. 27 can be rewritten as

$$x_i^F = \alpha^{\mathrm{I}} x_i^{\mathrm{I}} + \alpha^{\mathrm{II}} x_i^{\mathrm{II}} \quad i = 1, \ldots, K, \quad i \neq p, \tag{28}$$

where α^{I} and α^{II} are phase fractions

$$\alpha^{\mathrm{I}} = \frac{n^{\mathrm{I}}}{n^F}, \quad \alpha^{\mathrm{II}} = \frac{n^{\mathrm{II}}}{n^F}, \quad \alpha^{\mathrm{I}} + \alpha^{\mathrm{II}} = 1, \tag{29}$$

with n being the total molar flow rate

$$n = \sum_{i=1}^{K} n_i \tag{30}$$

In addition, the summation of mole fractions of all components in each phase is unity

$$\sum_{i=1}^{K} x_i^{\mathrm{I}} = 1 \tag{31}$$

$$\sum_{i=1}^{K} x_i^{\mathrm{II}} = 1. \tag{32}$$

Phase equilibrium and mass balance for pseudocomponents

Similarly, the equilibrium conditions for pseudocomponents in the mixture are given

$$0 = x_{p,j}^{\mathrm{I}} \varphi_{p,j}^{\mathrm{I}} - x_{p,j}^{\mathrm{II}} \varphi_{p,j}^{\mathrm{II}} \quad j = 1, 2, \ldots, N, \tag{33}$$

where $\varphi_{p,j}$ is the fugacity coefficient of pseudocomponent j in the mixture. Using Eq. 7, we can rewrite Eq. 33 as

$$0 = x_p^{\mathrm{I}} X_j^{\mathrm{I}} \varphi_{p,j}^{\mathrm{I}} - x_p^{\mathrm{II}} X_j^{\mathrm{II}} \varphi_{p,j}^{\mathrm{II}} \quad j = 1, 2, \ldots, N. \tag{34}$$

The same mass balance equation, Eq. 27, for monodisperse components can also apply to pseudocomponents, leading to

$$n_{p,j}^F = n_{p,j}^{\mathrm{I}} + n_{p,j}^{\mathrm{II}} \quad j = 1,2,\ldots,N, \tag{35}$$

where $n_{p,j}^F$ is the molar flow rate of pseudocomponent j in the feed stream. After some algebra, we can obtain

$$x_p^F X_j^F = \alpha^{\mathrm{I}} x_p^{\mathrm{I}} X_j^{\mathrm{I}} + \alpha^{\mathrm{II}} x_p^{\mathrm{II}} X_j^{\mathrm{II}} \quad j = 1,2,\ldots,N. \tag{36}$$

In addition, the summation of mole fractions of pseudocomponents in each phase is also unity

$$\sum_{j=1}^{N} X_j^{\mathrm{I}} = 1 \tag{37}$$

$$\sum_{j=1}^{N} X_j^{\mathrm{II}} = 1. \tag{38}$$

In principle, Eqs. 34 and 36–38 could all be used in the flash calculations. However, based on the results that fugacity coefficients of pseudocomponents are independent of their own mole fractions within the polydisperse polymer, as shown in Eqs. 23–25, we can reformulate Eqs. 34 and 36–38 by eliminating mole fractions of pseudocomponents (i.e., X_j) such that these mole fractions are not explicitly computed during the flash calculation. In other words, the flash calculation can be independent of the number of pseudocomponents used to represent the polydisperse polymer. The procedure can be easily done as follows:

First we rearrange Eq. 36 as

$$x_p^{\mathrm{I}} X_j^{\mathrm{I}} = \frac{x_p^F X_j^F - \alpha^{\mathrm{II}} x_p^{\mathrm{II}} X_j^{\mathrm{II}}}{\alpha^{\mathrm{I}}}, \tag{39}$$

and then introduce it into Eq. 34

$$\frac{x_p^F X_j^F - \alpha^{\mathrm{II}} x_p^{\mathrm{II}} X_j^{\mathrm{II}}}{\alpha^{\mathrm{I}}} \varphi_{p,j}^{\mathrm{I}} = x_p^{\mathrm{II}} X_j^{\mathrm{II}} \varphi_{p,j}^{\mathrm{II}}. \tag{40}$$

We now rearrange Eq. 40 for X_j^{II}

$$X_j^{\mathrm{II}} = \frac{x_p^F X_j^F}{x_j^{\mathrm{II}}} \left[\alpha^{\mathrm{II}} + \alpha^{\mathrm{I}} \frac{\varphi_{p,j}^{\mathrm{II}}}{\varphi_{p,j}^{\mathrm{I}}} \right]^{-1}, \tag{41}$$

and then applying the summation, Eq. 38, for phase II, we obtain

$$0 = 1 - \frac{x_p^F}{x_p^{\mathrm{II}}} \sum_{j=1}^{N} X_j^F \left[\alpha^{\mathrm{II}} + \alpha^{\mathrm{I}} \frac{\varphi_{p,j}^{\mathrm{II}}}{\varphi_{p,j}^{\mathrm{I}}} \right]^{-1}. \tag{42}$$

Similarly, if we apply the same procedure for phase I, we can obtain

$$0 = 1 - \frac{x_p^F}{x_p^{\mathrm{I}}} \sum_{j=1}^{N} X_j^F \left[\alpha^{\mathrm{I}} + \alpha^{\mathrm{II}} \frac{\varphi_{p,j}^{\mathrm{I}}}{\varphi_{p,j}^{\mathrm{II}}} \right]^{-1}. \tag{43}$$

If we multiply the segment number of pseudocomponent j on both sides in Eq. 41, then apply Eq. 6 for the average segment number of pseudocomponents, we can obtain the third equation

$$0 = \bar{r}_p^{\mathrm{II}} - \frac{x_p^F}{x_p^{\mathrm{II}}} \sum_{j=1}^{N} X_j^F r_{p,j} \left[\alpha^{\mathrm{II}} + \alpha^{\mathrm{I}} \frac{\varphi_{p,j}^{\mathrm{II}}}{\varphi_{p,j}^{\mathrm{I}}} \right]^{-1}. \tag{44}$$

Finally, if we multiply the segment number of pseudocomponent j on both sides in Eq. 36, then apply Eq. 6 for the average segment number of pseudocomponents, we can obtain the fourth equation

$$x_p^F \bar{r}_p^F = \alpha^{\mathrm{I}} x_p^{\mathrm{I}} \bar{r}_p^{\mathrm{I}} + \alpha^{\mathrm{II}} x_p^{\mathrm{II}} \bar{r}_p^{\mathrm{II}}. \tag{45}$$

Clearly, although the mole fractions of pseudocomponents in the feedstream (that is, X_j^F) do appear in Eqs. 42–45, they are known quantities; the mole fractions of pseudocomponents in two phases (that is, X_j^{I} and X_j^{II}) do not appear. What enter these four equations are the mole fraction and the average segment number of the polydisperse polymer in each phase. These four quantities will be part of calculated unknown variables in the flash calculations, independent of the number of pseudocomponents used to represent the polydisperse polymer, as shown in the next section.

Equations of the system matrix

For a two-phase TP flash calculation of a mixture containing one polydisperse polymer, there are the following $(4+2K)$ unknown variables to be considered:

- Mole fractions in phase I, $\{x_i^{\mathrm{I}}\}$.
- Mole fraction in phase II, $\{x_i^{\mathrm{II}}\}$.
- Average segment number of the polydisperse polymer in both phases, $\bar{r}_p^{\mathrm{I}}$ and $\bar{r}_p^{\mathrm{II}}$.
- Phase fractions in both phases, α^{I} and α^{II}.

The equations of system matrix used to solve for these unknown variables were already given in the preceding section; they are summarized here for convenience:

Mass balance of monodisperse components

$$x_i^F = \alpha^{\mathrm{I}} x_i^{\mathrm{I}} + \alpha^{\mathrm{II}} x_i^{\mathrm{II}} \quad i=1,\ldots,K, \quad i \neq p. \tag{46}$$

Summations of component mole fractions

$$\sum_{i=1}^{K} x_i^{\mathrm{I}} - \sum_{i=1}^{K} x_i^{\mathrm{II}} = 0. \tag{47}$$

Summation of phase fractions

$$\alpha^{\mathrm{I}} + \alpha^{\mathrm{II}} = 1. \tag{48}$$

Definition of average segment number in phase I with the mass balance:

$$x_p^F \bar{r}_p^F = \alpha^{\mathrm{I}} x_p^{\mathrm{I}} \bar{r}_p^{\mathrm{I}} + \alpha^{\mathrm{II}} x_p^{\mathrm{II}} \bar{r}_p^{\mathrm{II}}. \tag{49}$$

Isofugacity equations

$$0 = 1 - \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} \frac{\varphi_i^{\mathrm{I}}}{\varphi_i^{\mathrm{II}}} \quad i=1,\ldots,K, \quad i \neq p. \tag{50}$$

Summation of pseudocomponents in phase I

$$0 = 1 - \frac{x_p^F}{x_p^{\mathrm{I}}} \sum_{j=1}^{N} X_j^F \left[\alpha^{\mathrm{I}} + \alpha^{\mathrm{II}} \frac{\varphi_{p,j}^{\mathrm{I}}}{\varphi_{p,j}^{\mathrm{II}}} \right]^{-1}. \tag{51}$$

Summation of pseudocomponents in phase II

$$0 = 1 - \frac{x_p^F}{x_p^{\mathrm{II}}} \sum_{j=1}^{N} X_j^F \left[\alpha^{\mathrm{II}} + \alpha^{\mathrm{I}} \frac{\varphi_{p,j}^{\mathrm{II}}}{\varphi_{p,j}^{\mathrm{I}}} \right]^{-1}. \tag{52}$$

Definition of average segment number in phase II

$$0 = \bar{r}_p^{\mathrm{II}} - \frac{x_p^F}{x_p^{\mathrm{II}}} \sum_{j=1}^{N} X_j^F r_{p,j} \left[\alpha^{\mathrm{II}} + \alpha^{\mathrm{I}} \frac{\varphi_{p,j}^{\mathrm{II}}}{\varphi_{p,j}^{\mathrm{I}}} \right]^{-1}. \tag{53}$$

Obviously, the total number of equations available is also $(4+2K)$.

In principle, one could solve all these equations (Eqs. 46–53) in an iterative scheme. However, this would be more expensive from a computational point of view, because one would have to iterate for all $(4+2K)$ unknown variables. A scheme for decreasing the number of iterative variables can be derived by dividing Eqs. 46–53 into two types as follows.

Type I equations do not contain any fugacity coefficients, and therefore can be rearranged to calculate an unknown variable explicitly. Equations 46–49 all belong to this type. For instance, we can rearrange Eq. 49 to calculate the average segment number of pseudocomponents in phase I explicitly

$$\bar{r}_p^{\mathrm{I}} = \frac{\bar{r}_p^F x_p^F - \alpha^{\mathrm{II}} \bar{r}_p^{\mathrm{II}} x_p^{\mathrm{II}}}{\alpha^{\mathrm{I}} x_p^{\mathrm{I}}}. \tag{54}$$

Type II equations contain the fugacity coefficients of components, which appear as multiplying factors of mole fractions of components and phase fractions. Equations 50–53 all belong to this type. Type II equations cannot be rearranged to solve for an unknown variable (like mole fractions) explicitly. In other words, the unknown variables have to be solved in an iterative procedure.

Clearly, the number of variables that need to be iterated for solutions can be determined by equations of Type II, which is $(2+K)$, half of the total unknown variables. All other variables can be calculated from Type I equations along with the $(2+K)$ iterative variables. Type I equations are called *simultaneous explicit*, and Type II equations are called *simultaneous implicit*. The advantage of this approach lies in the reduction of the number of variables to iterate, and in the fact that it is easier to converge on the simpler simultaneous explicit equations as compared to solving all $(4+2K)$ equations simultaneously. Note that the mole fractions of pseudocomponents in each phase do not appear in any equation of the system matrix; therefore, the iterative procedure is independent of the number of pseudocomponents used to represent the polydisperse polymer. The mole fractions of pseudocomponents in both phases can be calculated after obtaining a converged solution as secondary output values. They can be calculated explicitly by rearranging Eqs. 34 and 36

$$X_j^{\mathrm{I}} = \frac{x_p^F X_j^F \varphi_{p,j}^{\mathrm{II}}}{x_p^{\mathrm{I}}\left[\alpha^{\mathrm{II}}\varphi_{p,j}^{\mathrm{I}} + \alpha^{\mathrm{I}}\varphi_{p,j}^{\mathrm{II}}\right]} \quad j = 1, 2, \ldots, N \tag{55}$$

$$X_j^{\mathrm{II}} = \frac{x_p^F X_j^F \varphi_{p,j}^{\mathrm{I}}}{x_p^{\mathrm{II}}\left[\alpha^{\mathrm{II}}\varphi_{p,j}^{\mathrm{I}} + \alpha^{\mathrm{I}}\varphi_{p,j}^{\mathrm{II}}\right]} \quad j = 1, 2, \ldots, N. \tag{56}$$

A final note on the formulation of iterative equations, for example, implicit equations (Eqs. 50–53), follows. Although this formulation is applicable to any system, it has been specifically designed to handle numerical complexities for mixtures containing polydisperse polymers. These complexities come from the fact that fugacity coefficients in polymer mixtures are strongly composition dependent. A conventional numerical procedure such as the Rachford–Rice (RR) algorithm is not applicable to such highly asymmetric systems, as already recognized by Chen et al. (1993) and Kosinski and Anderko (1996). Here we present POLYMIX as an efficient flash algorithm to solve the implicit equations (Eqs. 50–53) for polymer systems.

Initialization strategy

In general, in performing the two-phase TP flash calculation, there is no restriction or regulation on how to choose the half of unknown variables as iterative variables for the implicit equations, that is, Eqs. 50–53. Usually, the average segment number and phase fraction in one phase should be chosen as iterative variables and their values in another phase should be calculated. The remaining iterative variables should come from the mole fractions of components. Once the iterative variables are chosen, they need to be initialized. For systems where no polymers are involved, a standard initialization scheme can be used, for example, the feed condition is used to provide the starting values for the flash iteration; this is usually sufficient to solve the flash problem. In the case of polymer solutions, initialization is very critical, because the success of the flash algorithm depends heavily on the quality of the starting values.

The initialization procedure in POLYMIX starts with a binary mixture of a monodisperse polymer and the lightest solvent at the system temperature and pressure. If the polymer is polydisperse, the number average molecular weight (M_n) is calculated and used to represent the monodisperse polymer in the binary system. For this binary system, we solve the phase equilibrium conditions at the system temperature and pressure. If the considered binary system is homogeneous at the system temperature and pressure, we go to lower pressures until we reach the vapor–liquid two-phase region (later, such as in the ternary system, we try again to go to higher pressures until we reach the system pressure). The solutions of the monodisperse problem are taken as initial values for the calculations of the polydisperse polymer/solvent system by making the polymer distribution stepwise broader and broader until the polymer MWD in the cloud-point phase is equal to the input polymer MWD in the feed. Once we have the solution for the polydisperse polymer/solvent system we add the third component and then the fourth and so forth. At the end, the complete flash has been solved for the entire feed at the system temperature and pressure.

Molecular-weight distribution of the feedstream

In industrial practice, when one performs a flash calculation with POLYMIX, the MWD of the polydisperse polymer in the feed stream is known. For instance, in modeling polymer manufacturing processes involving single or multiple reactors, the polymer product MWDs are available from either plant measurements or process simulation models (Hungenberg et al., 2001; Cheluget et al., 2002).

However, complete experimental MWD of polydisperse polymer is rarely reported in the literature; only its number-average molecular weight and weight-average molecular-weight are commonly published. Therefore, a hypothetical analytical distribution function is usually assumed and used to generate pseudocomponents for the polydisperse polymer. In this work, for the purpose of illustrating the application of POLYMIX, the Schulz–Flory distribution function is used to generate the pseudocomponents. However, other well-known distribution functions (for example, the Wesslau distribution) can serve the same purpose. The Schulz–Flory distribution function, in terms of the mole fraction distribution, $x(M)$, is given by

$$x(M) = \left(\frac{\beta M}{M_0}\right)^{\beta} \frac{\beta}{M\Gamma(\beta+1)} \exp\left(-\frac{\beta M}{M_0}\right). \tag{57}$$

Here, Γ is the Gamma function, β and M_0 are two adjustable parameters, and they can be determined for a specific polydisperse polymer by its number-average molecular weight, M_n, and its weight average molecular weight, M_w, as follows

$$M_n = M_0 \tag{58}$$

$$M_w = M_0 \frac{\beta+1}{\beta}. \tag{59}$$

The mole fraction of pseudocomponent j, X_j, with molecular weight in the range M_{j-1} to M_j, is obtained as

$$X_j = \int_{M_{j-1}}^{M_j} x(M)\, dM. \tag{60}$$

The final complete MWD of pseudocomponents is readjusted by the following conditions

$$\sum_{j=1}^{N} X_j = 1 \tag{61}$$

$$\sum_{j=1}^{N} X_j M_j = M_n. \tag{62}$$

Table 1. Pure-Component Parameters of PC-SAFT Equation of State*

Substance	r/M	σ [Å]	ϵ/k
Polyethylene (PE)	0.0263	4.0217	252
Polypropylene (PP)	0.02305	4.1	217.0
Ethylene	0.056794	3.4450	176.47
Propane	0.045397	3.6184	208.11
Pentane	0.037279	3.7729	231.20
Hexane	0.035481	3.7983	236.77
n-Heptane	0.034762	3.8049	238.40
Cyclohexane	0.030070	3.8499	278.11

*These values are taken from the PhD thesis of Gross (2000).

Example flash calculations

We first apply POLYMIX to perform some TP flash calculations for a system containing polydisperse polyethylenes (PE). The PE is a model polydisperse polymer and does not mimic any specific polyethylene. It is characterized by a number-average molecular weight (M_n) of 8 kg/mol and a weight-average molecular weight (M_w) of 12 kg/mol. To illustrate, POLYMIX can efficiently deal with any number of pseudocomponents, and the polyethylene is represented by three sets of pseudocomponents, 10, 100, and 500, respectively, ranging from 100 to 100,000 in molecular weights. The feed stream consists of the polydisperse polyethylene and a number of hydrocarbon solvents (ethylene, propane, hexane, n-heptane, and cyclohexane) at temperature 473.15 K and pressure 10 MPa. The MWD (mole fractions) of the pseudocomponents in the feed-stream for PE is generated by the Schulz–Flory distribution function. All flash calculations were carried out using the PC-SAFT EOS (Gross, 2000). The PC-SAFT EOS pure-component parameters for all substances used in this article are taken directly from the PhD thesis of Gross (2000) and summarized in Table 1. The adjustable binary parameter, k_{12}, used in this work is either determined from experimental data or set to zero; the values are summarized in Table 2.

The computation time for all three sets of pseudocomponents (e.g., 10, 100, and 500) are about 1 s on a 400-MHz laptop. The time differences among the three cases are within 0.01 s. The results clearly indicate that the computation time by POLYMIX is essentially independent of the number of pseudocomponents to represent the polydisperse polyethylene. This flexibility allows POLYMIX to deal with many pseudocomponents, as required to represent the full polymer molecular distribution. The calculated MWDs of the polydisperse polyethylene over different phases for the set of 100 pseudocomponents are shown in Figure 2. The feed stream flashes into a solvent-rich phase that contains the PE lights and a polymer-rich phase that contains the PE heavies. In Figure 2, the solid curve represents the weight-fraction distributions of pseudocomponents for the feed stream as well as that of the heavy phase. The dash curve is the weight-fraction distribution for the light phase. The flash results indicate that only the low-end of the MWD is soluble in the light phase.

Table 2. Binary Parameters of PC-SAFT Equation of State

System	k_{12}
Polyethylene (PE)–ethylene	0.0436
Polyethylene (PE)–propane	0.0
Polyethylene (PE)–pentane	−0.001
Polyethylene (PE)–hexane	0.0
Polyethylene (PE)–n-heptane	0.0
Polyethylene (PE)–cyclohexane	0.0
Polypropylene (PP)–propane	0.025

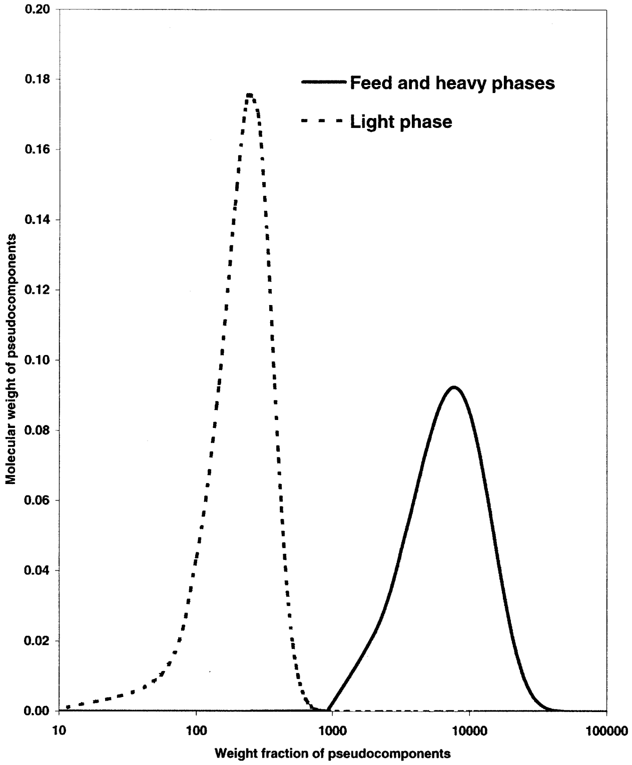

Figure 2. Flash results of polyethylene in hydrocarbon solvents at $T = 473.15$ K and $P = 10$ MPa.

The polydisperse polyethylene is characterized by a number-average molecular weight (M_n) of 8 kg/mol and a weight-average molecular weight (M_w) of 12 kg/mol.

Application to polyethylene solutions

It is well established that the phase behavior of polymer solutions is strongly affected by the molecular weight as well as the polydispersity of the polymer (de Loos et al., 1983). Unlike monodisperse mixtures, the phase behavior of polymer solutions is usually studied by measuring the cloud point, which is defined as the temperature or pressure at which the polymer solution indicates a formation of two-phase region. The locus of cloud points is called the cloud point curve. For each cloud point, a nonmeasurable incipient phase called the shadow point can be calculated by the phase equilibrium condition.

Figure 3 shows both the cloud-point curve and shadow-point curve for PE–ethylene systems at two supercritical temperatures of 403.15 K and 443.15 K for ethylene, respectively. The polydisperse polyethylene has a number-average molecular weight of 7.6 kg/mol and a weight-average molecular weight of 9.2 kg/mol. Since only the cloud-point curve is ac-

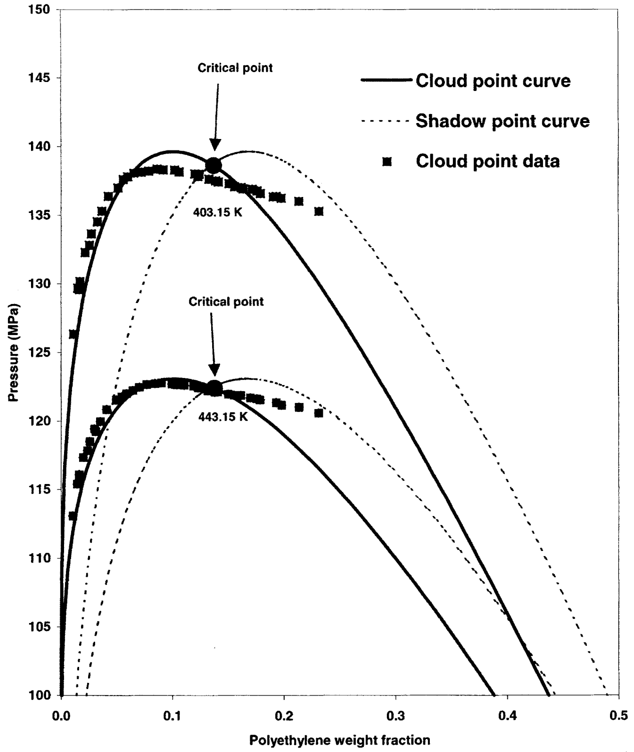

Figure 3. Phase equilibrium of polyethylene (PE)–ethylene systems at 403.1 K and 443.15 K.

PC-SAFT-calculated isotherms are compared with experimental cloud-point data of de Loos (1981) and de Loos et al. (1983).

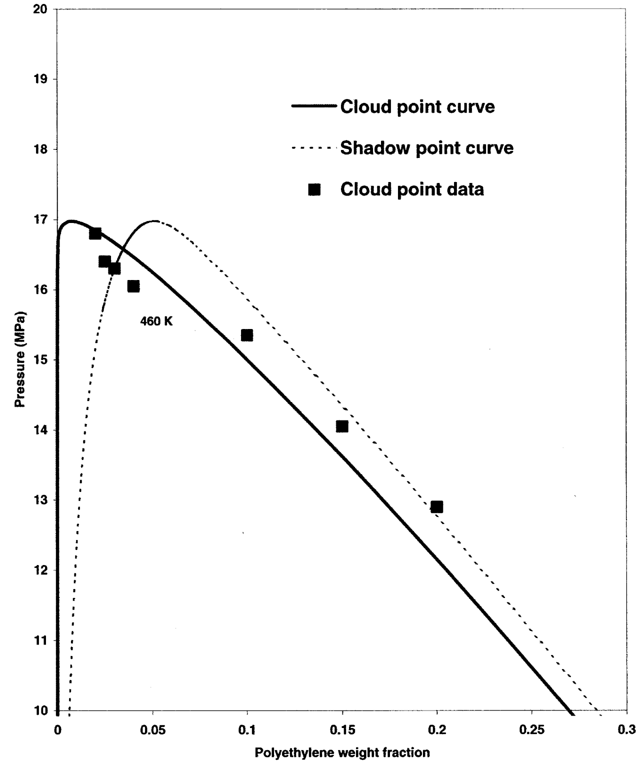

Figure 4. Liquid–liquid equilibrium of polyethylene–pentane at 460 K.

PC-SAFT-calculated isotherm is compared with experimental cloud-point data of Kiran et al. (1994).

cessible through measurements, the feed-stream distribution of the polymer component is assigned as the cloud-point phase in the flash calculation. Therefore, the cloud-point calculations are performed for a given MWD of PE. The MWD (mole fractions) of 500 pseudocomponents for the cloud-point phase of PE is generated by the Schulz–Flory distribution function. The shadow-point curve is determined by the flash calculation, and its MWD is calculated from Eq. 56, after the flash calculation is converged, and is generally different from that of the input cloud-point distribution.

We should point out that it is not always necessary to use as many as 500 pseudocomponents to represent the polydisperse polymer in phase equilibrium calculations. Nevertheless, as we just stated in the example flash calculation in the preceding section that the computation time by POLYMIX is essentially independent of number of pseudocomponents used, we keep using 500 pseudocomponents in the calculation.

In Figure 3, the calculated cloud-point curves are shown as solid curves and the calculated shadow-point curves are shown as dash-line curves. The most significant observation from this figure is that the critical point of the cloud-point curves at each temperature is not at the maximum of the cloud-point curve and is shifted to the position at high composition. As pointed out by de Loos et al. (1983), this shift is caused by the polydispersity of the polymer. In Figure 3, the calculated cloud-point curves are also compared with experimental cloud-point data from de Loos (1981) and de Loos et al. (1983). Only a single binary parameter, k_{12}, is adjusted, and a constant value ($k_{12} = 0.0436$) is sufficient for the correlation at both temperatures. The agreement is reasonable.

Figure 4 shows both the cloud-point curve and shadow-point curve of the PE–pentane systems at a subcritical temperature of 460 K for pentane, as opposed to the PE–ethylene systems shown in Figure 3. This example demonstrates that POLYMIX is applicable to both super- and subcritical regions of solvents at high-pressure conditions. The polymer (PE) has a number-average molecular weight of 19.4 kg/mol and a weight-average molecular weight of 131.4 kg/mol. The calculated cloud-point curve is compared with experimental cloud-point data from Kiran et al. (1994). A slight nonzero value ($k_{12} = -0.001$) is used for the correlation. As can be seen, the calculation results are in good agreement with experimental data.

Application to polypropylene solutions

Figure 5 shows the cloud-point curve correlation for polypropylene (PP)–propane systems. The flash calculation procedure is the same as that for the polyethylene solution systems shown in Figures 4 and 5. Namely, the MWD of the cloud-point phase is modeled using 500 pseudocomponents and the Schulz–Flory distribution function and the MWD of the shadow-point phase are calculated via Eq. 56. Note that the shadow-point curves are not shown in the figure. Only the direct comparison for the cloud points between calculations and experimental data are presented. The experimental

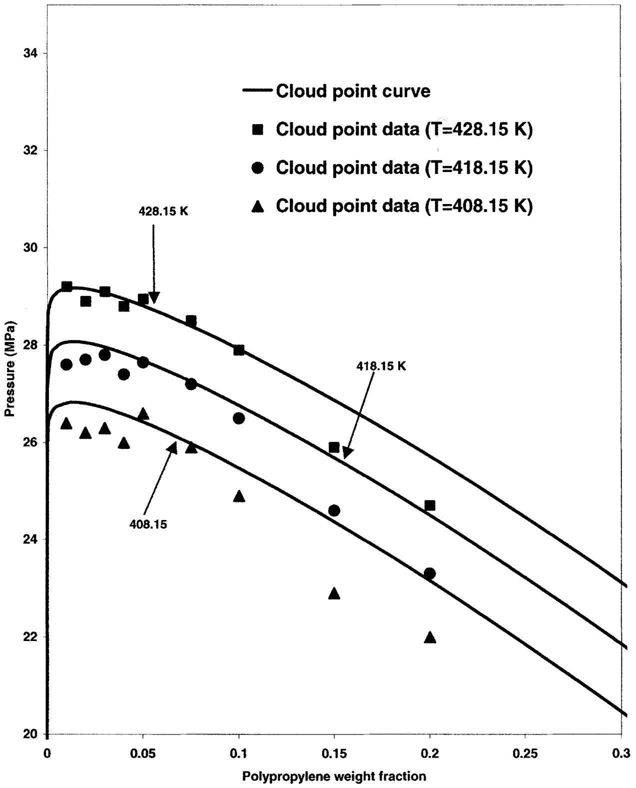

Figure 5. Liquid–liquid equilibria of polypropylene (PP)–propane at three temperatures.

PC-SAFT-calculated isotherms are compared with experimental cloud-point data of Whaley et al. (1997).

data were obtained by Whaley et al. (1997) for a weight-average molecular weight of $M_w = 290$ kg/mol and $M_w/M_n = 4.4$ of polypropylene. Similar to the earlier correlation on PE–ethylene systems, a single constant value of 0.025 for k_{12} is used for the correlation at all three temperatures. Again, the correlation results are in good agreement with the experimental data.

Conclusions

POLYMIX offers a computationally efficient algorithm for flash calculations of multicomponent systems containing polydisperse polymers. Incorporating the concept of pseudocomponents, the algorithm allows rigorous and generalized flash calculations with multimodal polymer MWD. The algorithm formulation is independent of the use of a specific segment-based polymer EOS for computing thermodynamic properties of the polymer mixture. Furthermore, it takes advantage of the fact that polymer mixture properties (such as pressure, compressibility factor, and Helmholtz energy) can be calculated based on the number-average molecular weight of the polydisperse polymer. This leads to a highly efficient and robust flash algorithm as the computation time for polymer flash calculations becomes independent of the number of pseudocomponents used to represent the polymer MWD curve.

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