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# Copolymer SAFT Equation of State. Thermodynamic Perturbation Theory Extended to Heterobonded Chains

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**ABSTRACT:** Thermodynamic perturbation theory of the first order (TPT1) is extended to heterobonded chains, such as heteronuclear and branched copolymers. The TPT1 formalism provides the basis for a copolymer equation of state. This new copolymer equation of state, referred to as Copolymer SAFT (Statistical Associating Fluid Theory), explicitly accounts for the effects of chain heterogeneity and microstructure. In order to illustrate potential future applications, Copolymer SAFT is used to calculate high-pressure cloud points in real polymer solutions of supercritical propane + poly(ethylene-*co*-butene).

## Introduction

Theoretical equations of state (EOS) for model chain molecules, usually composed of freely-jointed tangent segments interacting via a spherically symmetric potential, are commonly used as prototypes of the engineering EOS models of real polymer systems.

Theory of the hard-core homonuclear linear chains has been worked out analytically by many workers. For example, Wertheim<sup>1</sup> developed the thermodynamic perturbation theory of the first order (TPT1) which gives an analytical EOS for hard-core homonuclear chain molecules, as shown by Chapman et al.<sup>2</sup> Chiew<sup>3</sup> was also able to obtain analytically both thermodynamic and structural properties of hard-core homonuclear chain molecules using the Percus–Yevick approximation. Similarly, the theories of Schweizer and Curro<sup>4</sup> and Dickman and Hall<sup>5</sup> capture thermodynamics of the hard-core homonuclear chain molecules.

There were also attempts to go beyond the hard-core homonuclear linear chains. First, there were attempts to go beyond the hard-core potential for homonuclear chain molecules. Examples are extensions of TPT1 to a sticky potential and square-well potential,<sup>6</sup> extensions of TPT1 to a Lennard-Jones (LJ) potential,<sup>7</sup> and extensions of the generalized Flory dimer (GFD) theory (by Yethitraj and Hall<sup>8</sup>) to a square-well potential. Second, there were attempts to go beyond the homonuclear architecture for hard-core chains. Examples are extensions of TPT1 to copolymers,<sup>9,10</sup> and to rings<sup>11</sup> and extensions of Chiew's PY theory to copolymers.<sup>10,12</sup>

The main objective of this work is to derive, and apply to a real system, a thermodynamic TPT1 formalism for heterobonded chain molecules composed of different types of segments interacting via spherically symmetric potentials, but not necessarily hard-core potentials. Per analogy to the previous work, we will refer to practical models derived on the basis of TPT1 as the Statistical Associating Fluid Theory (SAFT for short). SAFT applicable to heterobonded chains will be referred to as

Copolymer SAFT. An example of a specific version of Copolymer SAFT, with a LJ reference, has recently been demonstrated to be a good approximation for calculating the thermodynamic properties of mixtures of heterobonded LJ chains, on the basis of molecular dynamics data obtained by Peczak et al.<sup>13</sup> In this work, we build on a more advanced and practical version of SAFT that was proposed by Huang and Radosz<sup>14,15</sup> and applied to many real systems.

## Theory

We calculate the Helmholtz energy for a mixture of  $r$  types of chains. The chain of type  $i$  ( $i = 1, 2, \dots, r$ ) consists of  $m_i$  segments which can be the same (e.g. Chapman et al.<sup>2</sup>) or different (as in this paper). In general, therefore, we can have as many as  $\sum_{i=1}^r m_i$  types of segments. Conceptually, the chains are formed by *associating* segments, reminiscent of the Wertheim associating molecules, which are allowed to reach the limit of total association, that is the limit of covalently bonded chains; each pair of associating sites forms one covalent bond in the limit of total association. We note that the terminal segments will have a single associating site. A simplified illustration of this association process is that of a collection of initially nonbonded segments, with one or two associating sites, that are allowed to bond with a variable strength, and hence with a variable degree of association, and eventually to reach the state of complete bonding (complete polymerization). Before such a state is reached, there will be a fraction of the bonds that have already been formed and a fraction of the bonds that are to be formed (this fraction becomes zero in the limit of complete bonding). We will label bonds (either formed or to-be-formed) on chain  $i$  with letter  $j$ , where  $j = 1, 2, \dots, m_i - 1$ . Furthermore we will denote the number fraction of the to-be-formed  $j$ -bonds on chain  $i$  by  $x_j^i$  and the fraction of the formed  $j$ -bonds on chain  $i$  by  $b_j^i$ . Since a bond can be either formed or to-be-formed, for each chain  $i$ , we have

$$x_j^i + b_j^i = 1 \quad (1)$$

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The change in the Helmholtz energy in going from nonbonded, nonassociating segment fluid to "associating" segment fluid (segments will form chains), on the basis of Wertheim's TPT1, is given<sup>2</sup> by

$$\frac{A - A_R}{k_B TV} = 2 \sum_{i=1}^r \rho_c^i \left\{ \sum_{j=1}^{m_i-1} \left( \ln x_j^i - \frac{x_j^i}{2} \right) + \text{constant} \right\} \quad (2)$$

where  $\rho_c^i$  is the total number density of chain  $i$ ,  $V$  is the total volume,  $T$  is the temperature,  $k_B$  is Boltzmann's constant,  $A_R$  is the Helmholtz energy of the reference (nonbonded segment) fluid, and  $x_j^i$  is obtained in the same way as in ref 2; for a specific case of the chain-forming association only,  $x_j^i$  becomes

$$x_j^i = [1 + \rho_c^i x_j^i \Delta_j^i]^{-1} \quad (3)$$

where

$$\Delta_j^i = \int g_j^i(\mathbf{r}) f_j^i(\mathbf{r}) d\mathbf{r} \quad (4)$$

is a measure of the bond strength for bond  $j$  on chain  $i$ ,  $f_j^i(\mathbf{r})$  is the Mayer  $f$ -function of the association potential,  $\phi_j^i(\mathbf{r})$  (e.g., as defined in ref 2), between the segments that will form bond  $j$  on the chain  $i$ ,

$$f_j^i(\mathbf{r}) = \exp\left(\frac{-\phi_j^i(\mathbf{r})}{k_B T}\right) - 1 \quad (5)$$

and  $g_j^i(\mathbf{r})$  is the reference (segment) pair correlation function between the nonbonded segments (that will form bond  $j$  on the chain  $i$ ). Let us stress the point that  $\phi_j^i(\mathbf{r})$  is the site-site property whereas  $g_j^i(\mathbf{r})$  is the reference-fluid (nonbonded) property. Subsequently, we label the reference-fluid properties with subscript  $R$  when we want to distinguish them from the chain properties.

Pressure is calculated from the following general thermodynamic relation<sup>2</sup>

$$P = -\frac{\partial A}{\partial V} = \rho_s \frac{\partial A}{\partial \rho_s} \frac{1}{V} = \rho_s \frac{\partial}{\partial \rho_s} \left( \frac{A}{V} \right) - \frac{A}{V} \quad (6)$$

$$\rho_s \frac{\partial \rho_c^i}{\partial \rho_s} = \rho_c^i \quad (7)$$

where  $\rho_s$  is the total segment number density and the partial derivatives in eqs 6 and 7 are taken at constant temperature. Substituting (6) and (7) into (2) and differentiating eq 2 (see Appendix, eq A3), with  $P_R$  being the reference-fluid pressure, we obtain

$$\frac{P - P_R}{k_B T \rho_s} = \frac{\partial}{\partial \rho_s} \left( \frac{A - A_R}{k_B TV} \right) - \frac{A - A_R}{\rho_s k_B TV} = 2 \sum_{i=1}^r \rho_c^i \sum_{j=1}^{m_i-1} \frac{\partial x_j^i}{\partial \rho_s} \left( \frac{1}{x_j^i} - \frac{1}{2} \right) \quad (8)$$

After differentiating both sides of the mass-action eq 3 (see Appendix, (A3)), we obtain

$$\frac{\partial x_j^i}{\partial \rho_s} \left( \frac{1}{x_j^i} - \frac{1}{2} \right) = -\frac{1}{2} (x_j^i)^2 \left[ \frac{\rho_c^i}{\rho_s} \Delta_j^i + \rho_c^i \frac{\partial \Delta_j^i}{\partial \rho_s} \right] = -\frac{1}{2} \frac{(x_j^i)^2 \Delta_j^i \rho_c^i}{\rho_s} \left[ 1 + \rho_s \frac{\partial}{\partial \rho_s} \ln \Delta_j^i \right] \quad (9)$$

which, after substituting  $\Delta_j^i$  from eq A2, is equivalent to

$$\frac{\partial x_j^i}{\partial \rho_s} \left( \frac{1}{x_j^i} - \frac{1}{2} \right) = -\frac{1}{2} \frac{1 - x_j^i}{\rho_s} \left[ 1 + \rho_s \frac{\partial}{\partial \rho_s} \ln \Delta_j^i \right] \quad (10)$$

After substituting eq 10 into the equation for pressure (8), we obtain

$$\frac{P - P_R}{k_B T \rho_s} = - \sum_{i=1}^r \rho_c^i \sum_{j=1}^{m_i-1} \frac{1 - x_j^i}{\rho_s} \left[ 1 + \rho_s \frac{\partial}{\partial \rho_s} \ln \Delta_j^i \right] \quad (11)$$

In order to estimate the partial derivative in eq 11, we will approximate the association potential as a square-well potential. In the limit of total association (all  $j$ -bonds are formed), i.e.  $x_j^i \rightarrow 0$ , such a potential becomes very narrow and very deep around the bond length. As a result, and this is explained in ref 16,  $\Delta_j^i \propto g_j^i(L_j^i)$ , where  $L_j^i$  is the length of bond  $j$  on chain  $i$ . Applying this approximation to estimate the partial derivative in eq 11, we obtain a generalization of Malakhov and Brun's result<sup>10</sup> to an arbitrary spherically symmetric potential,

$$\frac{P - P_R}{k_B T \rho} = - \sum_{i=1}^r \sum_{j=1}^{m_i-1} \frac{\rho_c^i}{\rho} \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_j^i(L_j^i) \right] \quad (12)$$

or, equivalently, in terms of mole fractions,

$$\frac{P - P_R}{k_B T \rho} = - \sum_{i=1}^r \sum_{j=1}^{m_i-1} X_i \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_j^i(L_j^i) \right] \quad (13)$$

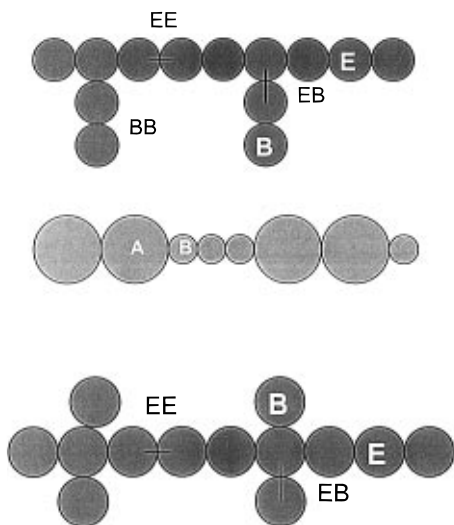
where  $X_i = \rho_c^i / \rho$  is the mole fraction of component (chain)  $i$ , and  $\rho = \rho_s / \sum_{i=1}^r X_i m_i$  is the total chain number density. Equation 13 can also be expressed in terms of the bond fractions, as it is shown in the Appendix, (A1):

$$\frac{P - P_R}{k_B T \rho} = \sum_{i=1}^r X_i (1 - m_i) \left[ 1 + \sum_{k=1}^{B_i} B_i^{k_i} \rho \frac{\partial}{\partial \rho} \ln g_i^{k_i}(L_i^{k_i}) \right] \quad (14)$$

where  $B_i^{k_i} = n_i^{k_i} / (m_i - 1)$  is the number fraction of bonds of type  $k_i$  in chain  $i$ ,  $n_i^{k_i}$  is the number of bonds of type  $k_i$  in chain  $i$ ,  $g_i^{k_i}(L_i^{k_i})$  is the pair correlation function corresponding to bond of type  $k_i$ , and  $B_i$  is the number of types of bonds in chain  $i$ . For a special case of identical segments on chain  $i$ , eq 14 becomes

$$\frac{P - P_R}{k_B T \rho} = \sum_{i=1}^r (1 - m_i) X_i \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g^i(L^i) \right] \quad (15)$$

which is the same as the expression for a mixture of homonuclear (homopolymer) chains derived by Chap-



**Figure 1.** (a) Branched copolymer, (b) linear copolymer, and (c) branched copolymer.

man et al.,<sup>2</sup> where all the segments and bonds are the same on a given chain.

When expressed in terms of the compressibility factor,  $Z$ , eq 14 becomes

$$Z = \sum_{i=1}^r (X_i m_i) Z_R + \sum_{i=1}^r X_i (1 - m_i) \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln \bar{g}^i \right] \quad (16)$$

where,  $Z = P/(k_B T \rho)$ ,  $Z_R = P_R/(k_B T \rho_s)$ , and  $\bar{g}^i$  is given by

$$\bar{g}^i = \prod_{k=1}^{B_i} g_i^{k_i} (L_i^{k_i})^{B_i^{k_i}} \quad (17)$$

The corresponding residual Helmholtz energy, therefore, can be expressed as

$$\frac{A^{res}}{N k_B T} = \int_0^\rho \frac{(Z - 1)}{\tilde{\rho}} d\tilde{\rho} = \frac{A_R^{res}}{N_s k_B T} \sum_{i=1}^r X_i m_i + \sum_{i=1}^r X_i (1 - m_i) \ln \bar{g}^i \quad (18)$$

and the corresponding molar Helmholtz energy,  $a^{res}$ , can be expressed as

$$\frac{a^{res}}{RT} = \frac{a_R^{res}}{RT} \sum_{i=1}^r X_i m_i + \sum_{i=1}^r X_i (1 - m_i) \ln \bar{g}^i \quad (19)$$

where  $R$  is the gas constant and  $a_R^{res}$  is the reference-fluid segmental Helmholtz energy (per mole of segments).

Our  $r$  chains are composed of  $M$  types of segments (e.g. labeled  $E$ ,  $B$ , and  $A$  in Figure 1); the types of segments are counted with index  $\alpha$ , where  $\alpha = 1, \dots, M$ . The mole fraction of the type- $\alpha$  segments, therefore, is

$$x_\alpha = \frac{\sum_{i=1}^r \gamma_\alpha^i m_i X_i}{\sum_{i=1}^r m_i X_i} \quad (20)$$

where  $\gamma_\alpha^i$  is the number fraction of the type- $\alpha$  segment in chain  $i$ .

In order to calculate the phase equilibria of chain mixtures, we will also need the fugacity coefficients,  $\varphi_i$ , which are calculated as follows:

$$\ln \varphi_i = \tilde{a} + \left[ \frac{\partial \tilde{a}}{\partial X_i} \right]_{\rho, T, X_{k \neq i}} - \sum_j X_j \left[ \frac{\partial \tilde{a}}{\partial X_j} \right]_{\rho, T, X_{k \neq j}} + (Z - 1) - \ln Z \quad (21)$$

where,  $\tilde{a} = a^{res}/RT$ , and similarly  $\tilde{a}_R = a_R^{res}/RT$ .

We will also need the mole-fraction derivatives, which are given below:

$$\frac{\partial \tilde{a}}{\partial X_i} = \frac{\partial \tilde{a}_R}{\partial X_i} \sum_{j=1}^r X_j m_j + \tilde{a}_R m_i + (1 - m_i) \ln \bar{g}^i + \sum_{j=1}^r X_j (1 - m_j) \frac{\partial \ln \bar{g}^j}{\partial X_i} \quad (22)$$

where

$$\frac{\partial \tilde{a}_R}{\partial X_i} = \sum_{\alpha=1}^M \frac{\partial \tilde{a}_R}{\partial x_\alpha} \frac{\partial x_\alpha}{\partial X_i}$$

and

$$\frac{\partial \ln \bar{g}^j}{\partial X_j} = \sum_{\alpha=1}^M \frac{\partial \ln \bar{g}^j}{\partial x_\alpha} \frac{\partial x_\alpha}{\partial X_j} \quad (23)$$

$$\frac{\partial \ln \bar{g}^j}{\partial x_\alpha} = \sum_{k=1}^{B_j} B_j^{k_j} \frac{\partial \ln g^{k_j}(L^{k_j})}{\partial x_\alpha} \quad (24)$$

where  $\partial \ln g^{k_j}(L^{k_j})/\partial x_\alpha$  and  $\partial \tilde{a}_R/\partial x_\alpha$  are the segment properties which, for hard spheres, can be found in refs 13 and 14; the  $\partial x_\alpha/\partial X_i$  derivative can be found in the Appendix, (A4).

### Examples of Bond Fractions for Model Copolymers

Our new working equation for the chain term accounts for the chain heterogeneity in general, and branching in particular, through the variable fraction of different bonds in eq 14. In other words, changes in the extent and type of branching are reflected by, and hence captured by, the changes in the bond fractions. This is illustrated with three examples of model copolymers schematically shown in Figure 1a–c.

The first case, shown in Figure 1a, is that of a branched copolymer resembling poly(ethylene-*co*-butene), hence referred to as EB:

$$m_1 = 13$$

$$k_1 = EE, BB, EB \quad (25)$$

$$B_1^{EE} = 8/12 \quad B_1^{BB} = 2/12 \quad B_1^{EB} = 2/12$$

The second case, shown in Figure 1b, is that of a linear heterosegmented copolymer composed of two types of segments,  $\alpha = A, B$ :

$$m_1 = 8$$

$$k_1 = AA, BB, AB \quad (26)$$

$$B_1^{AA} = 2/7 \quad B_1^{BB} = 2/7 \quad B_1^{AB} = 3/7$$

**Table 1. Properties of Poly(ethylene-*co*-butene) with Varying Branch Density (Number of Ethyl Branches per 100 Ethyl Units in the Backbone)**

polymer	branch density	backbone segment fraction, $\gamma_E$	branch segment fraction, $\gamma_B$	mol wt, MW
EB1	0	1.0	0.0	119 600
EB2	4	0.962	0.038	62 000
EB3	19	0.840	0.160	96 300
EB4	35	0.741	0.259	84 700
EB5	79	0.559	0.441	91 000
EB6	94	0.515	0.485	90 000

<sup>a</sup> Branch density is determined from proton NMR on pure polymer samples.  $\gamma_E$  and  $\gamma_B$  are the number fractions of segments in the backbone (E) and branches (B), respectively (we omit the superscript because there is only one polymer in the system). Hence, if BD = branch density,  $\gamma_B = \text{BD}/(100 + \text{BD})$  and  $\gamma_E = 1 - \gamma_B$ .

The third case, shown in Figure 1c, is that of a branched polymer with pairs of single-segment branches attached symmetrically to the same backbone segment (if the branch pairs are attached regularly to every other backbone segment, we will have the limiting case of polyisobutylene):

$$m_1 = 13$$

$$k_1 = EE, BB, EB \quad (27)$$

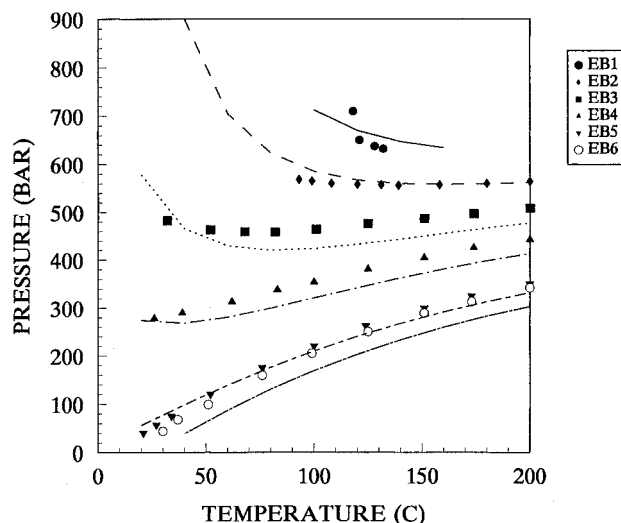
$$B_1^{EE} = 8/12 \quad B_1^{BB} = 0 \quad B_1^{EB} = 4/12$$

The hard-sphere structural and thermodynamic properties can be found in refs 14 and 15, and the Lennard-Jones-sphere structural and thermodynamic properties can be found in ref 18.

### Application to Real Copolymer Fluids

We apply this copolymer theory to real copolymer systems, such as binary solutions of ethylene-butene copolymers (EB) in propane. These EB copolymers, in the real experiments approximated by hydrogenated polybutadiene, are composed of a linear polyethylene-like backbone and ethyl side branches, as shown in Figure 1a. Thus, each branch has one branch-backbone (EB) bond and one branch-branch (BB) bond. The properties of the real EB copolymers used in the experiments<sup>17</sup> are shown in Table 1. These copolymers are listed in the order of increasing degree of branching, that is, increasing branch density or branch segment fraction, and decreasing backbone segment fraction. For example, EB1 polymer is a nearly linear polymer with no branches and thus it approximates a linear polyethylene. However, at the other extreme, the polymer EB6 has almost 50% of the total carbon atoms located in branches and thus it approximates poly(butene-1).

The experimental cloud points (binodal phase transitions) obtained by Chen et al.<sup>17</sup> are shown in Figure 2 for polymers of similar molecular weights. As these experimental results indicate, at constant temperature the cloud point pressure decreases as the degree of polymer branching increases. For example, the cloud point pressure drops from 480 to 100 bars at 50 °C as the branch segment fraction increases from 16 to 48.5% in going from EB3 to EB6. Also, the increasing degree of branching qualitatively changes the phase behavior of these polymer solutions. As shown in Figure 2, the EB/propane phase behavior is of the U-LCST type when the degree of polymer branching is low, and becomes of the LCST type when the degree of polymer branching is high.

**Figure 2.** Cloud point pressure as a function of temperature estimated from Copolymer SAFT. Points represent experimental data taken by Chen et al.<sup>17</sup> for ~5 wt % solutions of EB in propane.**Table 2. SAFT Parameters for Propane and EB (E = Backbone, B = Branch)**

N	<i>m</i>	$\nu^{00}$ , mL/mol	$(u/k)_E$ , K	$(u/k)_B$ , K
propane	2.696	13.457	193.03	
EB1	5980	12.0	210.0	
EB2	2893	12.0	210.0	160.0
EB3	4815	12.0	210.0	160.0
EB4	3952	12.0	210.0	160.0
EB5	4246	12.0	210.0	160.0
EB6	4199	12.0	210.0	160.0

The original version of the Statistical Associating Fluid Theory (SAFT) EOS<sup>2,14,15</sup> can correlate such data as those shown in Figure 2<sup>17</sup> but it treats the molecules as effective homopolymers, that is chains of equisized segments which are connected in a head-to-tail fashion. The differences in structure are implicitly accounted for by effective segment parameters that are adjustable to reflect changes in structure. By contrast, Copolymer SAFT can explicitly account for the geometrical differences caused by different degrees of branching, with constant values of segment parameters. We want to test Copolymer SAFT on the data presented in Figure 2.

For this purpose, we use the original SAFT,<sup>14,15</sup> except we replace its chain term developed in this work (eqs 14, 16, 19).<sup>19</sup> This means that all the SAFT parameters defined in refs 14 and 15 are also used in this work; the segment number, *m*, segment volume,  $\nu^{00}$ , and segment energy,  $u/k$ . These parameters, given in Table 2, are not fitted but estimated using an empirical formula developed by Huang and Radosz<sup>14</sup> for the alkane series. In addition to these three pure-component parameters, each component is characterized in terms of the number bond fractions that are not fitted either but estimated on the basis of the known molecular structure, for example, on the basis of the NMR-derived branch density and number segment fractions for branched polyolefins. The number segment fractions are given in Table 1.

The only parameter that is determined by fitting SAFT to the experimental data of EB1/propane is a binary interaction parameter,  $k_{ij}$ . This is because our EB1 is equivalent to a straight-chain polyethylene and SAFT has been shown to be accurate in correlating PE/alkane system by Chen et al.<sup>20</sup> The  $k_{ij}$  value is found

to be 0.022. This value will be constant for the interactions in all the systems; we assume  $k_{b-s}$  (backbone/solvent) =  $k_{br-s}$  (branch/solvent) = 0.022 even though the Copolymer SAFT approach allows for different  $k_{ij}$ 's for the backbone/solvent and branch/solvent interactions. The numerical approach to the cloud point calculations discussed here is a specialized version of the block algebra simultaneous (BAS) flash algorithm proposed by Chen et al.<sup>20</sup> for flash calculations in macromolecular solutions.

In general, there are two approaches to estimating the residual free energy contributions due to the backbone-segment interactions and due to the branch-segment interactions. The first approach is to assume the same segment energy for both backbone and branch segments but to allow for different interaction parameters with the solvent. The second approach is to assume a constant interaction parameter, as we do in this work, but to allow for different, but constant, backbone and branch segment energies. We estimate the effective segment energy for the ethylene branches to be 160. This value is used for all our EB/propane systems.

Figure 2 shows the Copolymer SAFT predictions as curves, except for the solid curve, which is a fit. The experimental data by Chen et al.<sup>17</sup> are shown as points. Copolymer SAFT correctly captures not only the effect of decreasing cloud point pressures but also the shift from U-LCST to LCST as the degree of branching increases.

## Conclusion

The TPT1 formalism developed in this work provides a basis for a Copolymer SAFT equation of state. This equation of state is demonstrated to account for the effects of the short-chain branching on the cloud-point pressures of poly(ethylene-*co*-butene) solutions in supercritical propane.

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## Appendix

Derivation of eq 14:

$$\begin{aligned} \frac{P - P_R}{k_B T \rho} &= - \sum_{i=1}^r \sum_{j=1}^{m_i-1} X_i \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_j^i(L_j^i) \right] \\ &= - \sum_{i=1}^r X_i \sum_{k_i=1}^{\bar{B}_i} n_i^{k_i} \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_i^{k_i}(L_i^{k_i}) \right] \\ &= - \sum_{i=1}^r X_i (1 - m_i) \sum_{k_i=1}^{\bar{B}_i} \frac{n_i^{k_i}}{1 - m_i} \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_i^{k_i}(L_i^{k_i}) \right] \\ &= - \sum_{i=1}^r X_i (1 - m_i) \sum_{k_i=1}^{\bar{B}_i} B_i^{k_i} \left[ 1 + \rho \frac{\partial}{\partial \rho} \ln g_i^{k_i}(L_i^{k_i}) \right] \\ &= - \sum_{i=1}^r X_i (1 - m_i) \left[ 1 + \sum_{k_i}^{\bar{B}_i} B_i^{k_i} \rho \frac{\partial}{\partial \rho} \ln g_i^{k_i}(L_i^{k_i}) \right] \quad (A1) \end{aligned}$$

From the mass-action equation it follows

$$\frac{1}{X_j^i} = 1 + \rho^i X_j^i \Delta_j^i$$

or

$$1 - X_j^i = \rho^i (X_j^i)^2 \Delta_j^i \quad (A2)$$

or

$$\frac{1}{(X_j^i)^2} - \frac{1}{X_j^i} = \rho^i \Delta_j^i$$

After differentiating both sides of the previous equation, we have

$$\frac{\partial X_j^i}{\partial \rho_s} \left( -\frac{2}{(X_j^i)^3} + \frac{1}{(X_j^i)^2} \right) = \frac{\rho^i}{\rho_s} \Delta_j^i + \rho^i \frac{\partial \Delta_j^i}{\partial \rho_s}$$

which is equivalent to

$$\frac{\partial X_j^i}{\partial \rho_s} \left( \frac{1}{X_j^i} - \frac{1}{2} \right) = -\frac{1}{2} (X_j^i)^2 \left[ \frac{\rho^i}{\rho_s} \Delta_j^i + \rho^i \frac{\partial \Delta_j^i}{\partial \rho_s} \right] \quad (A3)$$

Since the Helmholtz molar energy,  $\tilde{a}_R^{res}$ , and  $\bar{g}^i$  depend explicitly on  $[x_{\alpha}; \alpha=1, M]$ , we need  $(\partial x_{\alpha}/\partial X_j^i)$  derivatives to calculate the fugacities. These derivatives are given below:

$$\frac{\partial x_{\alpha}}{\partial X_j^i} = \frac{\gamma_{\alpha}^i m_i \left( \sum_{j=1}^r m_j X_j^i \right) - m_i \left( \sum_{j=1}^r \gamma_{\alpha}^j m_j X_j^i \right)}{\left( \sum_{j=1}^r m_j X_j^i \right)^2} \quad (A4)$$

## Nomenclature

$a$	molar Helmholtz energy
$\tilde{a}$	dimensionless molar Helmholtz energy in $RT$ units
$A$	total Helmholtz energy
$B_i^{k_i} (=n_i^{k_i}/(m_i - 1))$	number fraction of bonds of type $k_i$ in chain $i$
$b_j^i$	number fraction of the formed bonds $j$ on chain $i$
$\bar{B}_i$	number of types of bonds in chain $i$
$f_j^i(\mathbf{r})$	Mayer function of association potential $\phi_j^i(\mathbf{r})$
$g_j^i(\mathbf{r})$	radial distribution function of segments forming a bond $j$ on chain $i$
$g_i^{k_i}$	radial distribution function of bond of type $k_i$ on chain $i$
$\bar{g}^i$	effective contact value of pair correlation function on chain $i$
$k_B$	Boltzmann's constant
$L_j^i$	bond length of bond $j$ on chain $i$
$L_i^{k_i}$	bond length of bond of type $k_i$ on chain $i$
$m_i$	number of segments in chain $i$
$M$	number of types of segments in chain $i$ ( $\alpha = 1, \dots, M$ )
$n_i^{k_i}$	number of bonds of type $k_i$ in chain $i$
$N_s$	total number of segments
$N_s^{\alpha}$	number of segments $\alpha$ , $\sum_{\alpha} N_s^{\alpha} = N_s$
$N$	total number of chains (molecules)
$N_i$	number of chains of type $i$ , $\sum_i N_i = N$
$P$	pressure
$r$	total number of types of segments
$R$	gas constant
$T$	temperature

$V$	total volume
$x_j^i$	number fraction of to-be-formed $j$ -bonds on chain $i$ (eqs 1–11)
$x_\alpha$	mole fraction of the type- $\alpha$ segments in the whole system (eq 20)
$X_i = \rho_i^i/\rho$	mole fraction of component (chain) $i$
$Z$	compressibility factor
$\gamma_\alpha^i$	number fraction of segment of type $\alpha$ in chain $i$
$\phi_j^i(\mathbf{r})$	association potential
$\varphi_i$	fugacity coefficient of component $i$ , e.g. chain $i$ , in a mixture
$\rho_s = N_s/V$	total segment number density
$\rho_s^\alpha = N_s^\alpha/V$	number density of segment $\alpha$
$\rho = N/V$	total number density; $\bar{\rho}$ is treated as an integration variable in eq 18
$\rho_c^i = N_i/V$	number density of chain $i$
<b>Subscripts</b>	
$c$	chain properties
$i$	chain type
$j$	bond type
$R$	reference-fluid properties
$s$	segment properties
$\alpha$	segment type
<b>Superscripts</b>	
$i$	chain type
$k_i$	bond type on chain $i$
$res$	residual properties
$\alpha$	segment type

## References and Notes

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- While applying the copolymer chain term to the original SAFT, we note that  $a^{hs}/RT$  in eq 3 of ref 15 (eq 3<sup>15</sup>) is a molar property (i.e. per mole of molecules). Hence, the  $a^{hs}/RT$  corresponds to the *whole* first term on the right-hand side of eq 19 in this paper (including its summation part, and not just  $a_R^{res}/RT$  that is defined here as being a segmental property, i.e. per mole of segments). We also note a typographical error in eq 3<sup>15</sup>; the  $6/\pi\rho$  factor should be  $6/N_A\pi\rho$ .
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