

# A Predictive Group-Contribution Simplified PC-SAFT Equation of State: Application to Polymer Systems

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A group-contribution (GC) method is coupled with the molecular-based perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EoS) to predict its characteristic pure compound parameters. The estimation of group contributions for the parameters is based on a parameter database of 400 low-molecular-weight compounds estimated by fitting experimental vapor pressures and liquid densities. The method has been successfully used for estimating the PC-SAFT parameters for common polymers. Specifically, using the new polymer parameters as calculated from the proposed GC scheme, the simplified PC-SAFT yields rather good predictions of polymer densities and gives promising modeling results of various binary polymer mixtures exhibiting both vapor–liquid and liquid–liquid phase equilibria. In summary, the data required for calculating polymer phase equilibria with the proposed method are the molecular structure of the polymer of interest in terms of functional groups and a single binary interaction parameter for accurate mixture calculations.

## 1. Introduction

The thermodynamics and phase behavior of polymer systems play a key role in the integration of polymer production, processes, and material development.<sup>1</sup> The more advanced the properties and performances of the final polymer product are, the more complex its phase behavior may be. Accurate prediction of the phase equilibria of polymer mixtures requires thermodynamic models that are able to deal with large size differences between molecules, to deal with polydisperse polymers, and to account for strong deviations from ideal behavior over wide ranges of operating conditions. For the past several decades, investigations of polymer systems with equations of state show that such models are efficient tools but their application is often constrained by the availability of the required input parameters.

Advances in statistical mechanics have allowed developments of different semiempirical equations of state based on molecular principles with a strong theoretical foundation. Among the different approaches available to date, those based on the Wertheim perturbation theory<sup>2–5</sup> resulted in a family of equations of state (EoS) known as statistical association fluid theory (SAFT). Since the original SAFT model,<sup>6–8</sup> several modifications have appeared with one of the most recent versions being perturbed-chain SAFT (PC-SAFT).<sup>9</sup> Two reviews<sup>10,11</sup> provide more detailed discussions of recent developments and applications of the various types of SAFT. In order to reduce the computational time and programming efforts without essentially affecting the performance of the model, we have modified the original PC-SAFT<sup>9</sup> and developed the simplified PC-SAFT<sup>12</sup> EoS that has already been applied to vapor–liquid (VLE) and liquid–liquid equilibria (LLE) of various polymer systems.<sup>13–15</sup>

Both those versions of the PC-SAFT model, the original and simplified, are able to predict the effects of molecular weight, copolymerization, and hydrogen bonding on the thermodynamic

properties and phase behavior of complex fluids including solvents, monomers, and polymer solutions and blends. Complete description of these systems requires three physically meaningful temperature-independent parameters: the segment number ( $m$ ), the hard-core segment diameter ( $\sigma$ ), and the segment–segment interaction energy parameter ( $\epsilon/k$ ) for each pure nonassociating fluid. They are typically fitted to vapor pressure and liquid density data. Associating fluids require two additional compound parameters, the association energy ( $\epsilon^{AB}$ ) and the association volume ( $\kappa^{AB}$ ).

Since high-molecular-weight compounds, such as polymers, do not have a detectable vapor pressure and commonly undergo thermal degradation before exhibiting a critical point, determination of EoS parameters is often based solely on experimental density data.<sup>16</sup> Unfortunately, derivation of polymer parameters based only on density usually results in poor prediction of phase equilibria with the SAFT EoS. Recent publications demonstrate that this shortcoming remains even in the newest versions of the SAFT EoS, such as PC-SAFT and simplified PC-SAFT.<sup>17–21</sup> Hence, there is a need for a predictive calculation method for polymer EoS parameters.

As PC-SAFT models molecules as chains of united atom segments with their own parameters, the model is adaptable for developing a group-contribution scheme. Group-contribution (GC) methods are the most widely used techniques for estimating and predicting thermophysical properties of pure compounds and mixtures.<sup>22</sup> Use of the GC principle in models for phase equilibrium calculations can greatly enhance their predictive capabilities. The GC methods can be divided into two classes. Methods in the first class are those that estimate the property of a compound as a summation of the contributions of simple first-order groups (FOG) that may occur in the molecular structure, such as  $\text{CH}_2$  and  $\text{OH}$ . This approach is necessary where there is no theoretical basis for the groups' identification and the groups are not able to capture proximity effects or isomer differences. The second class includes methods that attempt to capture fine structural differences by additionally

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**Table 1. Modifications of the Simplified PC-SAFT<sup>12</sup> EoS Compared to the Original PC-SAFT<sup>9</sup> EoS**

original PC-SAFT <sup>9</sup>	simplified PC-SAFT <sup>12</sup>
$g_{ij}^{\text{hs}} = \frac{1}{1 - \zeta_3} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{3\zeta_2}{(1 - \zeta_3)^2} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1 - \zeta_3)^3}$	$g^{\text{hs}}(\eta) = \frac{1 - \eta/2}{(1 - \eta)^3}$
$a^{\text{hs}} = \frac{1}{\zeta_0} \left[ \frac{3\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} + \left( \frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) \right]$	$a^{\text{hs}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}$

**Table 2. First-Order Group (FOG) Contributions for the  $m$ ,  $m\sigma^3$ , and  $m\epsilon/k$  Parameters**

first-order groups (FOG)	contributions			sample group assignment (occurrences)
	$m$	$m\sigma^3$ [ $\text{\AA}^3$ ]	$m\epsilon/k$ [K]	
"—CH <sub>3</sub> "	0.644 362	34.169 55	129.3866	propane (2)
"—CH <sub>2</sub> "	0.384 329	24.339 81	102.3238	butane (2)
"—CH<"	0.043 834	13.953 91	68.2084	isobutene (1)
">C<"	−0.492 080	2.3254 15	−10.9830	neopentane (1)
"CH <sub>2</sub> =CH—"	1.031 502	52.086 40	240.7577	propylene (1)
"—CH=CH—"	0.900 577	39.686 39	257.6914	<i>cis</i> -2-butane (1)
"CH <sub>2</sub> =C<"	0.739 720	40.857 26	214.9811	isobutene (1)
"—CH=C<"	0.513 621	29.695 89	208.6538	2-methyl-2-butene (1)
">C=C<"	0.377 151	17.070 79	212.3236	2,3-dimethyl-2-butene (1)
"CH <sub>2</sub> =C=CH—"	1.588 361	67.460 85	412.7788	1,2-butadiene (1)
"CHEC—"	1.172 342	41.800 54	287.8396	propyne (1)
"CEC"	0.715 504	33.171 67	276.7768	2-butyne (1)
"ACH"	0.366 330	19.817 53	106.9481	benzene (6)
"AC"	0.010 721	10.514 68	87.93008	naphthalene (2)
"ACCH <sub>3</sub> "	0.836 861	43.574 97	235.0636	toluene (1)
"ACCH <sub>2</sub> —"	0.389 760	34.498 23	171.3898	<i>m</i> -ethyltoluene (1)
"ACCH<"	−0.036 170	27.226 17	109.9270	<i>sec</i> -butylbenzene (1)
"CH <sub>3</sub> CO"	1.793 821	61.903 47	496.6067	methyl ethyl ketone (1)
"CH <sub>2</sub> CO"	1.552 067	52.185 21	444.9888	cyclopentanone (1)
"CHO"	1.889 630	31.066 93	436.2165	1-butanal (1)
"CH <sub>3</sub> COO"	2.362 557	65.594 42	538.0440	ethyl acetate (1)
"CH <sub>2</sub> COO"	1.952 796	54.809 90	462.7927	methyl propionate (1)
"HCOO"	1.745 841	43.392 09	426.2767	<i>n</i> -propyl formate (1)
"COO"	1.439 110	32.513 28	351.1344	ethyl acetate (1)
"CH <sub>3</sub> O"	1.527 003	38.226 02	330.7321	methyl ethyl ether (1)
"CH <sub>2</sub> O"	1.226 298	28.979 37	277.2849	ethyl vinyl ether (1)
"CHO"	1.544 171	16.263 32	321.8993	diisopropyl ether (1)
"CH <sub>2</sub> O (cyclic)"	1.101 871	32.855 69	307.6912	1,4-dioxane (2)
"CH <sub>3</sub> S"	1.391 979	61.468 31	428.3381	methyl ethyl sulfide (1)
"CH <sub>2</sub> S"	0.970 886	51.070 98	341.3012	diethyl sulfide (1)
"CHS"	0.928 117	40.554 89	363.4252	diisopropyl sulfide (1)
"I"	0.890 179	49.922 70	341.5094	isopropyl iodide (1)
"Br"	0.888 904	35.942 99	276.4405	2-bromopropane (1)
"CH <sub>2</sub> Cl"	1.209 673	53.658 76	368.3897	<i>n</i> -butyl chloride (1)
"CHCl"	0.810 132	43.140 92	272.4527	isopropyl chloride (1)
"ACCl"	0.713 602	41.178 43	273.3549	<i>m</i> -dichlorobenzene (2)
"ACF"	1.458 050	49.349 37	254.5195	fluorobenzene (1)
"CF <sub>3</sub> "	0.615 750	46.220 00	118.2550	perfluorohexane (2)
"CH <sub>2</sub> NO <sub>2</sub> "	2.210 123	65.583 54	702.2415	1-nitropropane (1)
"ACNO <sub>2</sub> "	2.340 985	48.053 76	687.6930	nitrobenzene (1)
"CF <sub>2</sub> "	0.933 850	35.658 25	153.7675	perfluoromethylcyclohexane (5)
"CH <sub>2</sub> =C=C<"	1.328 356	57.764 90	375.6868	3-methyl-1,2-butadiene (1)
"CH=C=CH—"	1.479 486	56.356 90	408.9468	2,3-pentadiene (1)
"CHCO"	1.085 097	15.635 89	347.6752	diisopropyl ketone (1)
"O (except as above)"	−0.088 640	14.502 39	−21.2312	divinyl ether (1)

introducing, in a consistent manner, so-called second-order groups (SOG).

Throughout the past decades, different group-contribution approaches in the form of GC EoS have been proposed. Among the first attempts, one may find the GC-EoS by Skjold-Jorgensen,<sup>23</sup> later modified by Gros et al.,<sup>24</sup> who added an additional associating term. High and Danner<sup>25,26</sup> developed a group-contribution lattice-fluid (GCLF) EoS for polymer solutions. A number of modifications followed their original paper in order to apply the method to vapor–liquid equilibria of

polymers–solvents.<sup>27,28</sup> Another approach proposed by Elvasore et al.<sup>29</sup> combines a GC method with the perturbed-hard-sphere-chain (PHSC) EoS developed by Song et al.<sup>30</sup> The characteristic molecular EoS parameters were obtained by fitting both vapor pressures and saturated liquid densities from which the GC values were determined. This approach provided satisfactory results and improved the PHSC theory, allowing modeling of VLE and LLE of mixtures of high-molecular-weight compounds. Elliott and Natarajan<sup>31</sup> developed a group-contribution form of the Elliott–Suresh–Donohue (ESD) EoS

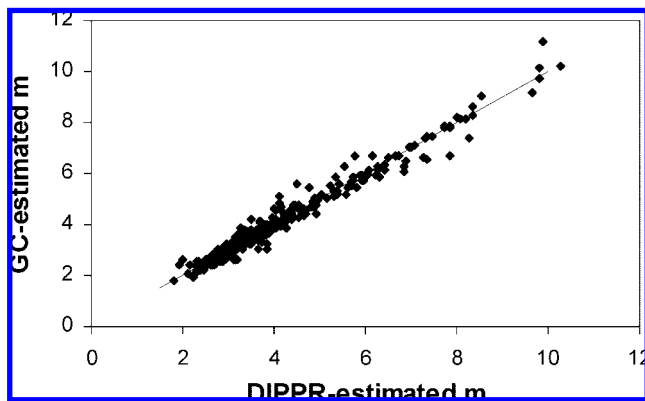
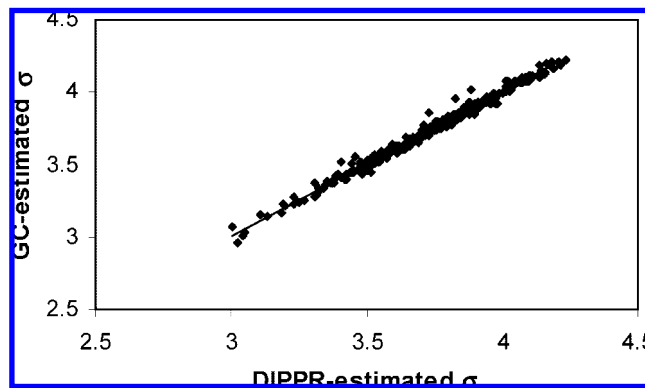
**Table 3. Second-Order Group (SOG) Contributions for Each of the  $m$ ,  $m\sigma^3$ , and  $m\epsilon/k$  Parameters**

second-order groups (SOG)	contributions			sample group assignment (occurrences)	total no. occurrences
	$m$	$m\sigma^3$ [ $\text{\AA}^3$ ]	$m\epsilon/k$ [K]		
"(CH <sub>3</sub> ) <sub>2</sub> -CH—"	0.016 263	0.280 872	−9.836 15	isobutane (1)	38
"(CH <sub>3</sub> ) <sub>3</sub> -C—"	0.041 437	1.472 296	−6.895 16	neopentane (1)	18
"-CH(CH <sub>3</sub> )-CH(CH <sub>3</sub> )—"	−0.046 340	−2.464 521	−6.814 56	2,3-dimethylbutane (1)	9
"-CH(CH <sub>3</sub> )-C(CH <sub>3</sub> ) <sub>2</sub> —"	−0.101 480	−1.913 722	−4.680 34	2,2,3-trimethylpentane (1)	4
"-C(CH <sub>3</sub> ) <sub>2</sub> -C(CH <sub>3</sub> ) <sub>2</sub> —"	−0.183 290	−7.464 243	23.727 92	2,2,3,3-tetramethylpentane (1)	3
"ring of 3 carbons"	0.672 813	5.826 574	121.088 7	cyclopropane (1)	3
"ring of 4 carbons"	0.506 911	2.643 507	101.789 8	cyclobutane (1)	3
"ring of 5 carbons"	0.309 498	1.015 915	61.402 57	cyclopentane (1)	8
"ring of 6 carbons"	0.064 237	−0.636 912	29.246 73	cyclohexane (1)	12
"ring of 7 carbons"	0.121 577	−4.990 554	52.689 76	cycloheptane (1)	9
"-C=CC=C—"	−0.112 200	−0.955 843	−19.75 39	1,3-butadiene (1)	9
"CH <sub>3</sub> -C="	0.013 538	0.342 635	1.528 91	isobutene (2)	27
"-CH <sub>2</sub> -C="	−0.043 500	0.658 982	−5.937 27	1-butene (1)	54
">C{H or C}-C="	0.087 414	−0.806 591	−0.989 85	3-methyl-1-butene (1)	6
"string in cyclic"	−0.145 510	−0.220 100	−5.719 82	ethylcyclohexane (1)	6
">CHCHO"	0.254 933	4.322 626	24.838 24	2-methyl butyraldehyde (1)	5
"CH <sub>3</sub> (CO)CH <sub>2</sub> —"	−0.038 690	−1.234 490	−6.906 54	2-pentanone (1)	3
"C(cyclic)=O"	−0.030 920	−0.169 280	32.299 44	cyclopentanone (1)	4
"CH <sub>3</sub> (CO)OC{H or C}<"	0.088 960	−1.218 040	−18.939 80	isobutyric acid (1)	4
"(CO)C{H <sub>2</sub> }COO"	−0.010 910	3.553 918	47.566 69	ethyl acetoacetate (1)	3
"(CO)O(CO)"	−0.077 070	3.242 018	−13.212 50	propanoic anhydride (1)	4
"ACHO"	−0.242 220	−0.310 420	−8.358 46	benzaldehyde (1)	4
"ACBr"	−0.123 261	0.424 762	−37.976 0	bromotoluene (1)	5
"ACCOO"	−0.080 001	1.303 279	−23.830 3	benzoic acid ethyl ester (1)	18
"AC(ACH <sub><i>m</i></sub> ) <sub>2</sub> AC(ACH <sub><i>n</i></sub> ) <sub>2</sub> "	−0.000 133	0.665 582	5.950 01	naphthalene (1)	4
"O(cyclic)-C(cyclic)=O"	0.363 529	3.423 997	−0.922 22	diketene (1)	2

**Table 4. Statistical Results with the GC Method**

parameter	data points	standard deviation <sup>a</sup>		AAE <sup>a</sup>		AAPE <sup>a</sup> (%)	
		first order	second order	first order	second order	first order	second order
$m$	399	0.27	0.26	0.19	0.18	5.11	4.54
$m\sigma^3$	399	4.11	3.94	2.77	2.55	1.38	1.25
$m\epsilon/k$	399	41.7	36.6	31.1	27.8	3.26	2.87

<sup>a</sup> Standard deviation =  $\sqrt{\sum(X_{\text{est}} - X_{\text{exp}})^2 / (N - 1)}$ ; AAE =  $(1/N)\sum|X_{\text{est}} - X_{\text{exp}}|$ ; AAPE =  $(1/N)\sum(|X_{\text{est}} - X_{\text{exp}}|/X_{\text{exp}}) 100\%$ .  $N$  is the number of experimental data,  $X_{\text{est}}$  is the estimated value of the property  $X$ , and  $X_{\text{exp}}$  is the experimental value of the property  $X$ .

**Figure 1.** Scatter plot of GC estimated versus DIPPR-estimated  $m$  parameter.**Figure 2.** Scatter plot of GC estimated versus DIPPR-estimated  $\sigma$  parameter.

and applied it to various polymer solutions. Eighty-eight group contributions were presented to estimate the ESD shape parameter, complementing in this way existing GC methods for the solubility parameters and molar volume. This GC EoS has been applied primarily to polymer solutions (mostly VLE). In 2004, a GC method presented by Tamouza et al.<sup>32</sup> was coupled with two versions of SAFT: the original SAFT<sup>6</sup> and SAFT-VR.<sup>33</sup> The three molecular parameters were calculated through averages using the Lorentz–Berthelot combining rules, where energy parameters are averaged geometrically and size parameters are averaged arithmetically. During recent years, this GC SAFT approach has been extended to binary mixtures,<sup>34</sup> esters,<sup>35</sup> and aromatic compounds,<sup>36</sup> and also applied to the PC-SAFT

model.<sup>37</sup> Despite the fact that this method yields good results for several classes of compounds, the method has not been tested for polymer systems. To our knowledge based on personal communication, present efforts in developing GC SAFT equations are quite extensive in different research groups, but until now, only limited results have been published.

In this study we have chosen to use the Constantinou–Gani GC method<sup>38</sup> in combination with simplified PC-SAFT<sup>12</sup> to determine the three characteristic molecular PC-SAFT parameters. This choice is made because, unlike other approaches found in the literature, this GC methodology includes two levels of contributions, both FOG and SOG, that can, to some extent, capture the proximity effects and distinguish among structural

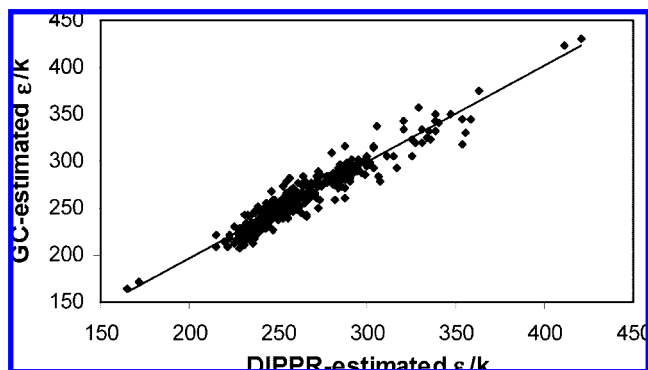


Figure 3. Scatter plot of GC estimated versus DIPPR-estimated  $\epsilon/k$  parameter.

Table 5. PC-SAFT Parameters for Polymers and the Percentage Average Absolute Deviation (AAD %) between Calculated and Experimental Liquid Densities<sup>44</sup> of the Studied Polymers<sup>a</sup>

polymer	<i>m</i> /MW	$\sigma$ [Å]	$\epsilon/k$ [K]	AAD $\rho$ [%]
PMMA	0.0262	3.6511	267.64	4.1
PBMA	0.0269	3.7598	267.21	1.9
PIPMA	0.0259	3.7543	267.41	2.1
PVAc	0.0292	3.3372	227.68	2.0
PS	0.0202	4.1482	367.17	2.9
PP	0.0255	4.0729	279.64	2.7
PIB	0.0210	4.3169	296.46	3.4
PMA	0.0292	3.4704	259.21	1.3
BR	0.0293	3.8413	284.70	1.1
PBA	0.0286	3.6486	261.43	2.2
PEA	0.0289	3.5478	260.15	1.9
PB	0.0297	3.7548	276.98	2.0
PPA	0.0287	3.6048	260.86	1.5

averagedeviation

2.24

<sup>a</sup> These polymer parameters are calculated from the group-contribution method.

isomers. The method and groups are presented in the next section. Polymer parameters are calculated from the GC scheme and are compared with the parameters available in the literature. We then test them against experimental polymer density data. Finally, the model is applied to various polymer systems that exhibit both vapor–liquid and liquid–liquid phase equilibria.

## 2. The Proposed Method

**2.1. Simplified PC-SAFT Equation of State.** The equation of state employed in this work for mixtures is the simplified version of the original PC-SAFT model<sup>9</sup> developed by von Solms et al.<sup>12</sup> This model is identical to the original PC-SAFT model for pure compounds, and the only difference lies in the simpler mixing rules employed.

PC-SAFT is expressed, in terms of the Helmholtz energy, for a mixture of associating molecules:

$$\tilde{a} = \frac{A}{NkT} = \tilde{a}^{\text{id}} + \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{assoc}} \quad (1)$$

where  $\tilde{a}^{\text{id}}$  is the ideal gas contribution,  $\tilde{a}^{\text{hc}}$  is the contribution of the hard sphere chain reference system, and  $\tilde{a}^{\text{disp}}$  and  $\tilde{a}^{\text{assoc}}$  are the contributions of dispersion forces and association (not used here, since all systems examined are nonassociating). The expressions for the contributions from the ideal gas and dispersion were used as in the original PC-SAFT version.<sup>9</sup> The reader is referred to the original articles for more details about these expressions.

The modifications of von Solms et al.<sup>12</sup> affect the hard-sphere term and, through the radial distribution function, the chain term and the association term. The first assumption is that all

Table 6. PC-SAFT Parameters Polymer Obtained Using the GC Scheme and from Other Methods, and the Percentage Average Absolute Deviations (AAD %) between Calculated and Experimental Liquid Densities ( $\rho$ )<sup>44</sup>

polymer	<i>m</i> /MW	$\sigma$ [Å]	$\epsilon/k$ [K]	reference	AAD $\rho^a$ [%]
PMMA	0.0262	3.6511	267.64	this work	4.1
	0.027	3.5530	264.60	53	1.0
	0.0262	3.60	245.0	54	1.8
PBMA	0.0269	3.7598	267.21	this work	1.9
	0.0241	3.8840	264.70	53	1.0
	0.0268	3.75	233.8	54	3.4
PVAc	0.0292	3.3372	227.68	this work	2.0
	0.0299	3.4630	261.60	53	0.4
	0.0321	3.3970	204.60	19	6.0
PS	0.0202	4.1482	367.17	this work	2.9
	0.0205	4.1520	348.20	53	0.6
	0.1900	4.1071	267.00	18	1.2
PP	0.0255	4.0729	279.64	this work	2.7
	0.0248	4.1320	264.60	53	1.1
	0.0231	4.1000	217.00	18	5.5
PIB	0.0270	4.0215	289.33	55	1.4
	0.0210	4.3169	296.46	this work	3.4
	0.0233	4.1170	267.60	53	1.4
PMA	0.0235	4.1000	265.50	18	1.0
	0.0292	3.4704	259.21	this work	1.3
	0.0292	3.5110	268.30	53	0.5
BR	0.0292	3.50	243	54	5.2
	0.0309	3.5000	275.00	19	3.3
	0.0293	3.8413	284.70	this work	4.9
PBA	0.0245	4.1440	275.50	53	0.9
	0.0140	4.2000	230.00	19	7.0
	0.0286	3.6486	261.43	this work	2.2
PEA	0.0259	3.9500	224.00	54	4.5
	0.0289	3.5478	260.15	this work	1.9
	0.0271	3.6500	229.00	54	3.1
PPA	0.0287	3.6048	260.86	this work	1.5
	0.0262	3.8000	225.00	54	2.4

<sup>a</sup> The temperature range for the melt polymer density calculations for PMMA and PVAc is 305–385 K and for the other polymers is 390–470 K.

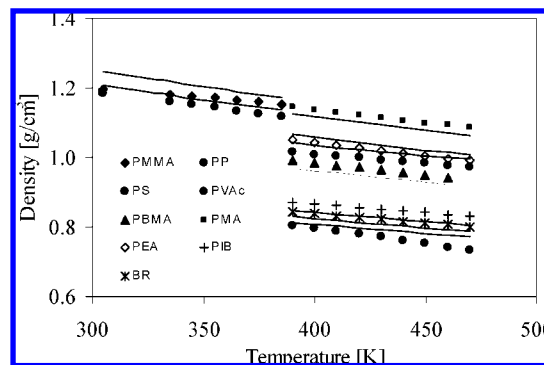


Figure 4. Polymer density predictions (lines) with PC-SAFT using GC-estimated parameters as a function of temperature at  $P = 1$  bar. Experimental data<sup>44</sup> are indicated with points.

segments in the mixture have the same mean diameter calculated by

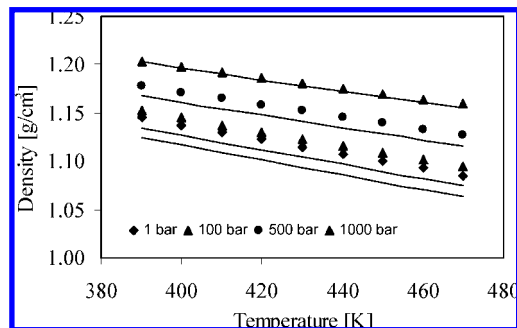
$$d_{\text{av}} = \left( \frac{\sum_i x_i m_i d_i^3}{\sum_i x_i m_i} \right)^{1/3} \quad (2)$$

where  $x_i$  is the mole fraction of compound  $i$ , and the individual  $d_i$  variables are temperature-dependent segment diameters

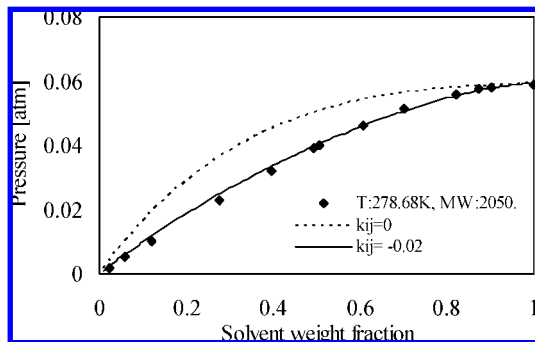
$$d_i = \sigma_i \left[ 1 - 0.12 \exp\left(-\frac{3\epsilon_i}{kT}\right) \right] \quad (3)$$

Using eq 2, the term  $\zeta_n$ , used in the radial distribution function ( $g^{\text{hs}}$ ), can be recalculated to

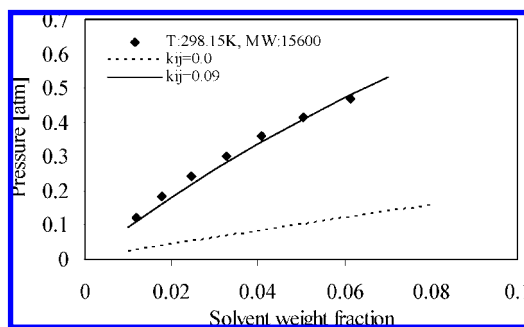
$$\zeta_n = d_{\text{av}} \frac{n\pi}{6} \rho \sum_i x_i m_i \quad (4)$$



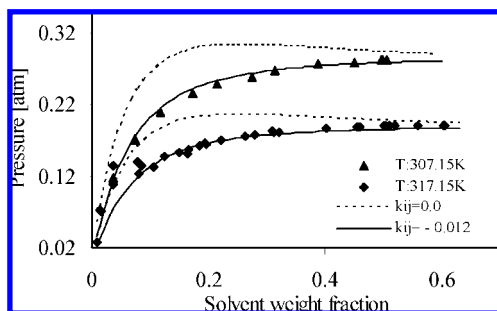
**Figure 5.** PC-SAFT density predictions (lines) using GC-estimated parameters for PMA at various pressures and temperatures. Experimental data<sup>44</sup> are indicated with points.



**Figure 6.** VLE for the system PP-CCl<sub>4</sub>. Experimental data are from Kershaw et al.<sup>45</sup> Lines are simplified PC-SAFT correlations with PP parameters obtained from the proposed GC method (Table 5).

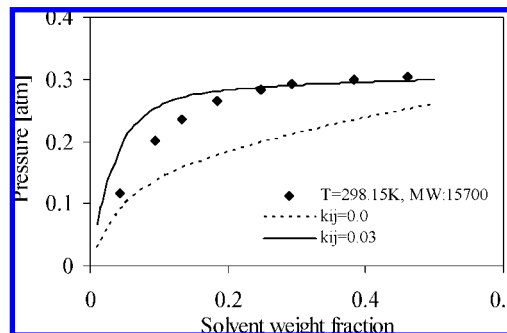


**Figure 7.** VLE for the system PP-CH<sub>2</sub>Cl<sub>2</sub>. Experimental data are from Kershaw et al.<sup>45</sup> Lines are simplified PC-SAFT correlations with PP parameters obtained from the proposed GC method (Table 5).

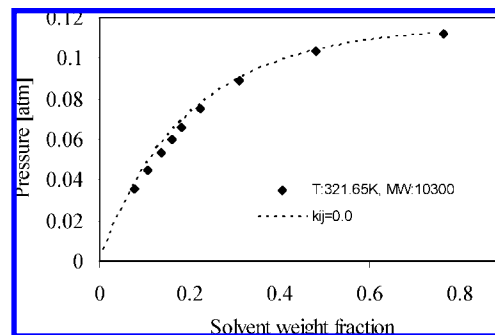


**Figure 8.** VLE for the system PS (MW = 440 000)-cyclohexane. Experimental data are from Kriegbaum et al.<sup>46</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained from the proposed GC method (Table 5).

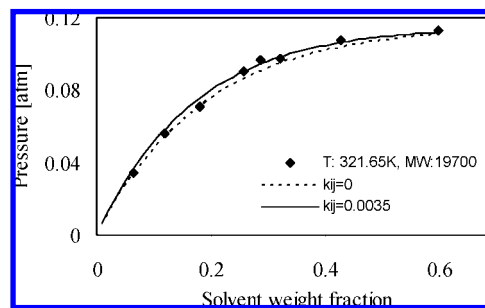
By setting the volume fraction  $\eta \equiv \zeta_3$ , a simpler expression for  $g^{\text{hs}}$  is obtained and  $\hat{a}^{\text{hs}}$  (hard-sphere term of the Helmholtz energy) reduces to the Carnahan–Starling equation, as shown in Table 1.



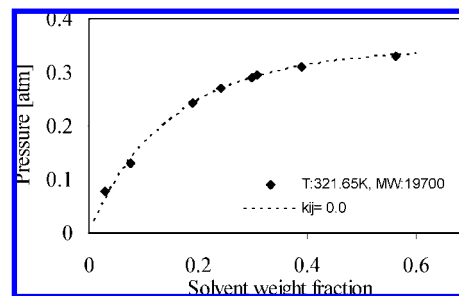
**Figure 9.** VLE for the system PS-acetone. Experimental data are from Bawn and Wajid.<sup>47</sup> Lines are simplified PC-SAFT correlations with PS parameters obtained from the proposed GC method (Table 5).



**Figure 10.** VLE for the system PS-toluene. Experimental data are from Tait and Abushihada.<sup>48</sup> Lines are simplified PC-SAFT predictions with PS parameters obtained from the proposed GC method (Table 5).



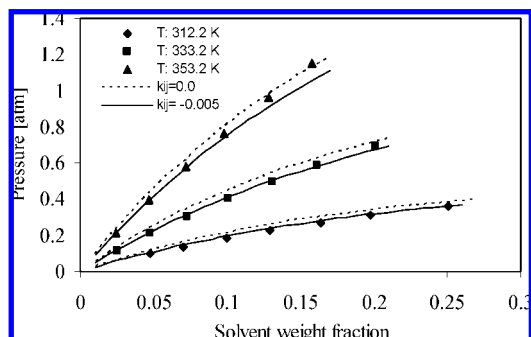
**Figure 11.** VLE for the system PMMA-toluene. Experimental data are from Tait and Abushihada.<sup>48</sup> Lines are simplified PC-SAFT predictions with PMMA parameters obtained from the proposed GC method (Table 5).



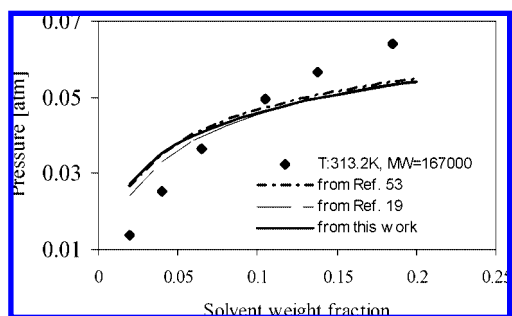
**Figure 12.** VLE for the system PMMA-methyl ethyl ketone. Experimental data are from Tait and Abushihada.<sup>48</sup> Lines are simplified PC-SAFT correlations with PMMA parameters obtained from the proposed GC method (Table 5).

Finally, consistent with the earlier simplifications, the radial distribution function is replaced with the simpler expression where the temperature-independent  $\sigma_{ij}$  is used instead of the temperature-dependent segment diameter  $d_{ij}$ .

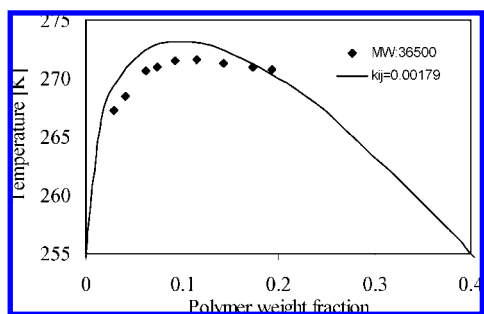




**Figure 13.** VLE for the system PVAc (MW = 167 000)–methyl acetate. Experimental data are from Wibawa et al.<sup>49</sup> Lines are simplified PC-SAFT correlations with PVAc parameters obtained from the proposed GC method (Table 5).



**Figure 14.** VLE for the system PVAc–1-propanol. Experimental data are from Kokes et al.<sup>50</sup> Lines are simplified PC-SAFT correlations ( $k_{ij} = -0.025$ ) with PVAc parameters taken from Table 6.



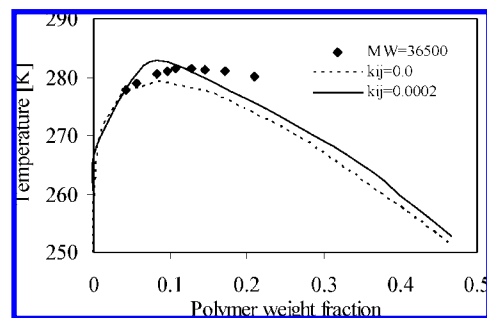
**Figure 15.** LLE for the system PMMA–4-heptanone. Experimental data are from Wolf et al.<sup>51</sup> Lines are simplified PC-SAFT correlations with PMMA parameters obtained from the proposed GC method (Table 5).

Extension to mixtures requires combining rules for the segment energy and diameter. The Lorentz–Berthelot rules, shown in eq 5

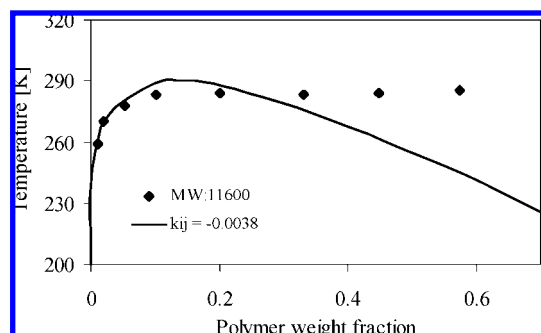
$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}(1 - k_{ij}) \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (5)$$

are employed for the calculations. For mixtures where experimental data are available, a binary interaction parameter,  $k_{ij}$ , can be used as a correction to the geometric mean rule.

**2.2. Estimation of Group Contributions.** Only the basic principle behind the GC method developed by Constantinou and Gani<sup>38</sup> is presented in the following. For more details, the reader is referred to the original paper. As previously mentioned, this GC method is used for predicting physical and thermodynamic properties of compounds at two levels. The basic level includes contributions from first-order functional groups such as those currently applied for the



**Figure 16.** LLE for the system PMMA–chlorobutane. Experimental data are from Wolf et al.<sup>51</sup> Lines are simplified PC-SAFT correlations with PMMA parameters obtained from the proposed GC method (Table 5).



**Figure 17.** LLE for the system PBMA–octane. Experimental data are from Saraiva et al.<sup>52</sup> Lines are simplified PC-SAFT correlations with PBMA parameters obtained from the proposed GC method (Table 5).

**Table 7. Comparison of the Predictive Performance of the Simplified PC-SAFT (with  $k_{ij} = 0$ ) for Vapor–Liquid Equilibria of PS Mixtures with and without SOG Contributions for the Calculation of PS Parameters**

system <sup>a</sup>	AAD (%), simplified PC-SAFT	
	excl SOG	incl SOG
PS+ benzene	52.4	53.2
PS+ethylbenzene	6.28	18.3
PS+ xylene	34.2	31.1
PS+ acetone	29.0	28.3
PS+ diethylketone	21.2	14.7

<sup>a</sup> PC-SAFT parameters for solvents are taken from refs 9 and 41.

estimation of mixture properties. The next level considers a set of simple and small second-order groups (SOG), which use the first-order groups (FOG) as building blocks. The definition and identification of SOG are theoretically based on the concept of conjugation operators according to the Atoms and Bonds in the properties of Conjugate forms (ABC) theory of molecular structures,<sup>39</sup> whose basic property is the standard enthalpy of formation at 298 K. On the basis of this method, Constantinou and Gani have presented extensive lists of FOG and SOG.<sup>38</sup> Every molecule definitely has FOG, but it may or may not have SOG.

The specific methodology applied in this study is as follows.

1. The identification and occurrence of FOG and SOG in each compound of interest are defined. In order to obtain a list covering various functional groups, several different families of chemical compounds are included.

2. An extensive parameter table for PC-SAFT for numerous nonassociating compounds has been developed by fitting vapor pressure and liquid density data obtained from DIPPR<sup>40</sup> correlations in a reduced temperature ( $T_r$ ) range of  $0.5 \leq T_r \leq 0.9$ . Here only experimental data of low-MW compounds (with  $N_c > 5$ ) within the 5% experimental uncertainty for vapor

pressure and 3% for liquid density are used. A large part of this extended parameter table has already been published.<sup>41</sup> The values obtained were found to have a linear relation with their molecular parameters.<sup>6,41</sup> This linear relationship of the parameter groupings is used as the basis for developing the present GC method.

3. Fitting of each of the three GC based parameters to the corresponding DIPPR fitted parameters is done by means of linear regression, and the objective function is the residual of the sum of squares of the differences between the DIPPR fitted values and the GC based values.

Assuming that a given molecule contains  $n_i$  groups of type  $i$ , the following relations are applied using the first-order and second-order group contributions:

$$m_{\text{molecule}} = \sum_i (n_i m_i)_{\text{FOG}} + \sum_j (n_j m_j)_{\text{SOG}} \quad (6)$$

$$(m\sigma^3)_{\text{molecule}} = \sum_i (n_i m_i \sigma_i^3)_{\text{FOG}} + \sum_j (n_j m_j \sigma_j^3)_{\text{SOG}} \quad (7)$$

$$(m\epsilon/k)_{\text{molecule}} = \sum_i (n_i m_i \epsilon_i/k)_{\text{FOG}} + \sum_j (n_j m_j \epsilon_j/k)_{\text{SOG}} \quad (8)$$

where  $m_i$ ,  $\sigma_i$ , and  $\epsilon_i/k$  are the contributions of the first-order group (FOG) of type  $i$  that appears  $n_i$  times, and  $m_j$ ,  $\sigma_j$ , and  $\epsilon_j/k$  are the contributions of the second-order group (SOG) of type  $j$  that appears  $n_j$  times.

A linear-least-squares analysis is carried out to determine the contributions of FOG and SOG for each of the three parameter groupings,  $m$ ,  $m\sigma^3$ , and  $m\epsilon/k$ .

The first-order and second-order group contributions for each of the PC-SAFT parameters are shown in Tables 2 and 3. It is noted that a few FOG contributions exhibit negative values. Similar behavior has been observed by Elbro et al.<sup>42</sup> and Stefanis et al.<sup>43</sup> Table 4 gives the standard deviation, the average error, and the average absolute percentage error for the FOG and SOG approximations.

Using the above approximations (eqs 7 and 8), the  $\sigma$  and  $\epsilon/k$  parameters for each investigated compound can then be calculated. Calculated average errors for the  $\sigma$  and  $\epsilon/k$  parameters, when compared to DIPPR fitted values, are about 0.47 and 3.28%, respectively, when only FOG are included, and 0.43 and 2.81% when both FOG and SOG contributions are taken into account. The observed improvement of 10% when using SOG is typical for the Constantinou–Gani GC method.<sup>38</sup> It must be underlined that the performance of the second order group is directly related to the extent of the database's having molecular structures with second order groups. The smaller the number of those compounds, the lower the contribution of the SOG. Figures 13 illustrate the correlation of the GC estimated values with the corresponding DIPPR fitted values for each of the molecular parameters.

All reference values used in this work are drawn from DIPPR.<sup>40</sup> These data are referred to as "experimental" even though they may include compilations of real experiments and computational results, and are therefore, in fact, only pseudoexperimental in nature with well-established uncertainties. This must be kept in mind when interpreting the performance of the current method and the deviations from the so-called "experimental values".

### 3. Results and Discussion

On the basis of Tables 2 and 3, it is now possible to calculate the pure polymer parameters of simplified PC-SAFT EoS where the only input needed is the molecular structure in terms of

present functional groups and the molecular weight. Detailed examples of the application of the method to the calculation of molecular parameters for PMMA and PIPMA are given in the Appendix. Table 5 presents PC-SAFT parameters for 12 commonly used polymers and their average absolute deviations of liquid densities. Additionally, Table 6 includes other previously published polymer PC-SAFT parameters, estimated with various methods, and the results of absolute deviations of liquid densities obtained by simplified PC-SAFT compared to the present method. Pure-compound parameters for the solvents are taken from the literature.<sup>9,41</sup>

**3.1. Density Predictions of Pure Polymers.** As observed in Table 6, the GC method is able to reproduce the experimental densities over a wide range of temperatures and pressures with an average error of 2.24%. Figure 4 reports predictions of densities of all the investigated polymers at the pressure of 1 bar. In the particular case of poly(methyl acrylate) (PMA), the average error in density prediction by simplified PC-SAFT is only about 1.0% over a wide range of pressures, as shown in Figure 5.

For a purely predictive method the accuracy of the density predictions is considered to be reasonably good. The accuracy is similar and in some cases even smaller than the ones obtained with parameters from other literature methods, several of which employ mixture data in pure parameter estimations, as presented in Table 6. In the next section, the new polymer parameters obtained by the GC method are evaluated for a variety of polymer–solvent systems exhibiting both VLE and LLE.

**3.2. Vapor–Liquid Equilibria.** VLE calculations are performed for six binary polymer–solvent systems. Figures 6 and 7 show VLE for the systems of polypropylene (PP) with carbon tetrachloride and methylene chloride, respectively. A single binary interaction parameter is needed in order to obtain accurate correlations of these two systems. As shown in Figures 8–12, promising results can also be obtained when the GC-predicted polymer parameters are used for other polymer systems, e.g., polystyrene (PS) and poly(methyl methacrylate) (PMMA). In all cases, the interaction parameters have reasonably low values. For both PS–toluene and PMMA–methyl ethyl ketone systems, pure predictions ( $k_{ij} = 0.0$ ) with simplified PC-SAFT give excellent results with an average deviation for vapor pressure within 1.0%. Presented in Figure 13 is the VLE phase diagram of the poly(vinyl acetate) (PVAc)–methyl acetate system at three temperatures. This system is rather well predicted at all three temperatures, and excellent correlations are achieved using a small negative temperature-independent binary interaction parameter ( $k_{ij} = -0.005$ ).

Although the methodology presented in this work is primarily targeted at polymer solutions without hydrogen bonding (where group-contribution values are presented only for  $m$ ,  $\sigma$ , and  $\epsilon/k$ ), the VLE phase diagram for the system PVAc–propanol is shown in Figure 14 using three different PVAc parameters from Table 6. A comparison of the obtained correlations is chosen for the evaluation of the PVAc parameters and to show that the presented method is applicable to polymer systems involving self-associating solvents but requires a binary interaction parameter to improve accuracy. The performance is not very satisfactory, but similar accuracy for correlating the phase behavior of this system was obtained by Elliott and Natarajan.<sup>31</sup>

Most often, comparisons of modeled results with experimental LLE data provide a much more rigorous test and challenge for a model and its parameters than comparison with experimental VLE data. Some LLE results are presented next.

**3.3. Liquid–Liquid Equilibria.** Liquid–liquid equilibria (LLE) calculations of a few polymer–solvent systems have been performed. Mixtures with poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) have been considered. Figures 15 and 16 show different PMMA solutions with 4-heptanone and chlorobutane, respectively. Both systems display upper critical solution temperature behavior and are well correlated using small positive binary interaction parameters. However, the flatness of the curve toward increased polymer weight fractions cannot be accurately described. This is a weakness of the model rather than of the polymer parameters. Very similar behavior is observed for the PBMA–octane system in Figure 17 using a small negative value of  $k_{ij} = -0.0038$ .

Most of the VLE and LLE results presented for various polymer–solvent systems have already been tested with simplified PC-SAFT using another set of polymer parameters estimated by Kouskoumvekaki et al.,<sup>53</sup> and the results are rather similar. The results demonstrate that properly calculated pure predictive GC-estimated polymer parameter values can result in quite accurate modeling of mixture phase equilibria. For many systems investigated, a small  $k_{ij}$  value is needed so that the model can accurately correlate experimental data.

As a final remark, Table 7 has been included to illustrate the influence of SOG contributions on model predictions of VLE of PS mixtures. These preliminary calculations show that SOG have a small impact on the modeling of the phase behavior of polymer systems; this issue calls for further evaluation.

#### 4. Conclusions

Calculation of thermodynamic properties using EoS requires molecular parameters that are difficult to estimate when experimental data, e.g., vapor pressures, are deficient. In this work, a GC method is developed for predicting the simplified PC-SAFT parameters and it is applied to polymers. The proposed technique requires only information in terms of structural properties, the presence of FOG and SOG, the compounds of interest, and the molecular weight.

Simplified PC-SAFT predicts liquid densities of the polymers considered with a deviation of 2.24% when using the presented GC scheme. Moreover, simplified PC-SAFT is able to correlate VLE and LLE equilibria for various polymer–solvent systems within reasonable accuracy using the newly estimated parameters.

The combination of the Constantinou–Gani group-contribution method with the simplified PC-SAFT equation of state gives a reliable tool for accurate modeling of polymer phase equilibria over a wide range of temperatures and compositions. With a few exceptions, the results are satisfactory. This approach will greatly extend the applicability of PC-SAFT to model systems with different degrees of the chemical complexities, a direction that will be pursued in the future.

It is emphasized that our newly developed GC scheme used to calculate the parameters for complex compounds can make the simplified PC-SAFT model a relevant and useful tool in the design and development of complex products, e.g., detergents or food ingredients, pharmaceuticals, and some other specialty chemicals, where predictions of various thermodynamic and phase equilibrium properties are required, but for which vapor pressure and/or liquid density may not be available.

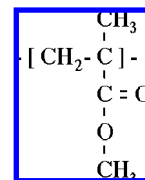
#### Acknowledgment

The authors are grateful to the Danish Technical Research Council (STVF) for financial support of this work as part of the grant entitled “Advanced Thermodynamic Tools for Computer-Aided Product Design”.

#### Appendix

Typical examples of the application of the proposed group-contribution method for calculating the PC-SAFT parameters for the polymers are presented.

**1. Example: Poly(methyl methacrylate) (PMMA).** The repeating unit of the polymer is



The molecular weight of the repeating unit is 100.12 g/mol. There are only first-order groups (FOG) present. Using the values of the FOG contributions from Table 2, the following results are obtained:

FOG( <i>i</i> )	<i>n<sub>i</sub></i>	<i>m<sub>i</sub></i>	<i>m<sub>i</sub>σ<sub>i</sub><sup>3</sup></i>	<i>m<sub>i</sub>ε<sub>i</sub>/k</i>
CH <sub>3</sub>	2	1.288 724	68.3391	258.7732
CH <sub>2</sub>	1	0.384 329	24.339 81	102.3238
C	1	−0.492 08	2.325 415	−10.983
COO	1	1.439 11	32.513 28	351.1344
		Σ <i>n<sub>i</sub>m<sub>i</sub></i> = 2.620 08	Σ <i>n<sub>i</sub>m<sub>i</sub>σ<sub>i</sub><sup>3</sup></i> = 127.5176	Σ <i>n<sub>i</sub>m<sub>i</sub>ε<sub>i</sub>/k</i> = 701.2483

From those values, the following PC-SAFT parameters are calculated:

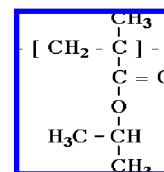
$$m/M_w = 2.62008/100.12 = 0.0262$$

$$\sigma = \sqrt[3]{(m\sigma^3)/m} = \sqrt[3]{127.51760/2.62008} = 3.6511 \text{ \AA}$$

$$\epsilon/k = (m\epsilon/k)/m = 701.24832/2.62008 = 267.64 \text{ K}$$

With this parameter set calculated from the group-contribution scheme, the percentage average absolute deviation (% AAD) between simplified PC-SAFT calculations and the experimental liquid density is 4.1%, in the temperature range 300–400 K and pressures up to 1000 bar.

**2. Example: Poly(isopropyl methacrylate) (PIPMA).** The repeating unit of the polymer is



The molecular weight of the repeating unit is 128.17 g/mol. There are both first-order groups (FOG) and second-order groups (SOG) present. Using the values of the FOG and SOG contributions from Table 2 and 3, the following results are obtained:

FOG( <i>i</i> )	<i>n<sub>i</sub></i>	<i>m<sub>i</sub></i>	<i>m<sub>i</sub>σ<sub>i</sub><sup>3</sup></i>	<i>m<sub>i</sub>ε<sub>i</sub>/k</i>
CH <sub>3</sub>	3	1.933 09	102.5086	388.1598
CH <sub>2</sub>	1	0.384 329	24.339 81	102.3238
CH	1	0.043 834	13.953 91	68.208 42
C	1	−0.492 08	2.325 415	−10.983
COO	1	1.439 11	32.513 28	351.1344
		Σ <i>n<sub>i</sub>m<sub>i</sub></i> = 3.308 28	Σ <i>n<sub>i</sub>m<sub>i</sub>σ<sub>i</sub><sup>3</sup></i> = 175.641 07	Σ <i>n<sub>i</sub>m<sub>i</sub>ε<sub>i</sub>/k</i> = 898.8434
SOG( <i>j</i> )	<i>n<sub>j</sub></i>	<i>m<sub>j</sub></i>	<i>m<sub>j</sub>σ<sub>j</sub><sup>3</sup></i>	<i>m<sub>j</sub>ε<sub>j</sub>/k</i>
(CH <sub>3</sub> ) <sub>2</sub> CH	1	0.016 26	0.280 87	−9.836 15
		Σ <i>n<sub>j</sub>m<sub>j</sub></i> = 0.016 26	Σ <i>n<sub>j</sub>m<sub>j</sub>σ<sub>j</sub><sup>3</sup></i> = 0.280 87	Σ <i>n<sub>j</sub>m<sub>j</sub>ε<sub>j</sub>/k</i> = −9.836 15

From those values, the following PC-SAFT parameters are calculated:



$$m/Mw = (3.30828 + 0.01626)/128.17 = 0.02594$$

$$\sigma = \sqrt[3]{(m\sigma^3)/m} = \sqrt[3]{(175.922/3.3245)} = 3.7543 \text{ \AA}$$

$$\epsilon/k = (m\epsilon/k)/m = 889.0073/3.3245 = 267.41 \text{ K}$$

With this parameter set calculated from the group-contribution scheme, the percentage average absolute deviation (% AAD) between simplified PC-SAFT calculations and the experimental liquid density is 2.1%, in the temperature range 300–400 K and pressures up to 1000 bar.

## Abbreviations

AAD = average absolute deviation  
 AAE = average absolute error  
 AAPE = average absolute percent error  
 ABC = atoms and bonds in the properties of conjugate forms  
 BR = butadiene rubber (polybutadiene)  
 DIPPR = Design Institute for Physical Properties  
 EoS = equation of state  
 ESD = Elliott–Suresh–Donohue  
 FOG = first-order groups  
 GC = group contribution  
 GC-EoS = group-contribution equation of state  
 GCLF = group-contribution lattice fluid  
 LCST = lower critical solution temperature  
 LLE = liquid–liquid equilibrium  
 MW = molecular weight, g/mol  
 PBMA = poly(butyl methacrylate)  
 PC-SAFT = perturbed-chain statistical associating fluid theory  
 PE = polyethylene  
 PHSC = perturbed hard sphere chain  
 PIB = polyisobutylene  
 PIPMA = poly(isopropyl methacrylate)  
 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  
 SOG = second-order groups  
 UCST = upper critical solution temperature  
 VLE = vapor–liquid equilibrium

## Parameters

$\tilde{a}$  = reduced Helmholtz energy  
 $A$  = Helmholtz energy, J  
 $d$  = temperature-dependent segment diameter  
 $g$  = radial distribution function  
 $k$  = Boltzmann's constant, J/K  
 $m$  = segment number  
 MW = molecular weight, g/mol  
 $N_c$  = number of carbon atoms  
 $n_i$  = occurrence of the type  $i$  first-order group in a compound  
 $n_j$  = occurrence of the type  $j$  second-order group in a compound  
 $P$  = pressure, bar/atm  
 $T$  = temperature, °C or K  
 $T_r$  = reduced temperature  
 $x$  = mole fraction

## Greek Symbols

$\zeta_n$  = parameters in eq 4 ( $n = 0, 1, 2$ , or  $3$ )  
 $\epsilon$  (energy parameter) = depth of the dispersion potential, J  
 $\epsilon^{AB}$  = association energy, J  
 $\eta$  = volume fraction  
 $\kappa^{AB}$  = association volume

$\rho$  = liquid density, g/cm<sup>3</sup>

$\sigma$  (size parameter) = segment diameter, Å

## Superscripts

assoc = association

disp = dispersion

hc = hard chain

hs = hard sphere

id = ideal

## Subscripts

$i, j$  = components  $i, j$

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Received for review August 7, 2007

Revised manuscript received October 8, 2007

Accepted October 17, 2007

IE0710768