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*Ind. Eng. Chem. Res.*, **1995**, 34 (5), 1835-1841 • DOI: 10.1021/ie00044a034 • Publication Date (Web): 01 May 2002

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# Revision of the Group Contribution–Flory Equation of State for Phase Equilibria Calculations in Mixtures with Polymers. 2. Prediction of Liquid–Liquid Equilibria for Polymer Solutions

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The group contribution–Flory equation of state (GC-Flory EoS) is applied to the prediction of the phase behavior of monodisperse polymer/single solvent systems. The model is capable of predicting with satisfactory accuracy the most common types of phase diagrams typical of liquid–liquid equilibria of polymer solutions (i.e., phase diagrams of the UCST, LCST, combined (UCST + LCST), and hourglass types). Combinatorial effects derived from differences in size, shape, and structure of the polymer and the solvent molecules strongly influence the phase behavior of the systems, but the type of a phase diagram of a specific polymer/solvent system is primarily governed by the nature of the molecular energy interactions. The GC-Flory EoS predicts the significant effect of the free-volume contributions at high temperatures, which is in very good agreement with the nature of the liquid-phase separation at temperatures near the gas–liquid critical temperature of the solvent, where the highly expanded state of the solvent leads to LCST behavior.

## Introduction

Due to their modular molecular structure, the polymers attain specific physical, chemical, and thermal properties, which make them suitable for the development of a very large variety of new materials. Knowledge of the phase behavior of polymer solutions is of special importance in the design of separation and polymerization processes, where liquid–liquid phase separations markedly influence the characteristics of the final polymer product. During the past decades, great attention has been devoted to quantitative and qualitative descriptions of the phase behavior of mixtures with polymers and, since the first works of Flory (1953), Huggins (1941), and Guggenheim (Guggenheim, 1952) in the 1940s and 1950s, many theories of thermodynamics of phase separation in polymer systems (solutions, blends and melts) have been proposed.

Essentially, *two different approaches* have been followed:

(a) In the first approach, the liquid–liquid equilibrium (LLE) is described semiquantitatively in terms of the polymer solubility; the goal is to be able to predict whether, at a certain temperature, a monodisperse polymer is soluble in a specified solvent or mixture of solvents. The Flory–Huggins model (in the case of the binary polymer solutions) and the generalized three-dimensional solubility parameter theory by Hansen (1969) have been used for this purpose.

(b) The second approach aims to describe qualitatively and quantitatively the LLE of polymer systems, and focuses on its temperature, composition, and, for EoS models, pressure dependence. Group contribution (GC) models have only been recently applied for the description of liquid–liquid equilibrium (LLE) in polymer solutions. Kontogeorgis et al. (1994) have shown that UNIFAC-based activity coefficient models are capable of describing the most common type of phase diagrams for polymer solutions, including the combined upper and lower critical solution temperature (UCST + LCST) and hourglass types.

The group contribution–Flory equation of state (GC-Flory EoS) proposed by Chen et al. (1990) has been used for the prediction of vapor–liquid equilibrium (VLE) in polymer solutions. In order to improve the performance of the model and extend its applicability to a wider range of polymer systems, Bogdanic and Fredenslund (1993) revised and further simplified the model. The purpose of this work is to evaluate and further understand the capability of the revised GC-Flory EoS in predicting liquid–liquid phase equilibria in monodisperse polymer/single solvent systems.

## Some Aspects of Polymer Solution Thermodynamics

The classical lattice theory of Flory and Huggins contains many of the essentials of polymer solution phase equilibria, but is not capable of describing, even qualitatively and in a generalized way, the different types of phase diagrams found in polymer–solvent systems. The major failure of the theory is its inability to describe the thermally induced phase separation or lower-critical-solution-temperature (LCST) phenomena at high temperatures (an almost universal property of polymer solution liquid–liquid phase equilibria), the reason being the (incompressible) nature of the model itself. In general (with the exception of water) the free-volume percentage (or compressibility) of a low molecular weight compound is greater than the free-volume percentage of a macromolecule (see, for example, Elbro, 1992). In the case of polymer solutions, the difference in the degree of thermal expansion between the polymer and the solvent becomes more pronounced as the temperature is increased, attaining very high values at temperatures near the gas–liquid critical temperature of solvent, where phase separation is induced by the expansion of the solvent that take place at these conditions. The appearance of a LCST in systems with strong molecular energy interactions, including systems with hydrogen bonds (Sandler, 1993), is due to the reduction of rotational freedom of the molecules at relatively low temperatures. In both cases, LCST at high and at low temperatures, the phase separation is

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entropy-driven, and is associated to a negative excess entropy of mixing.

The lattice model of Flory–Huggins is a theory of incompressible fluids and is unable to describe the temperature, the pressure, and the composition dependence of a liquid mixture density. Since the pioneer work of Prigogine (Prigogine, 1957) on the analysis of the influence of the PVT properties of the compounds on the thermodynamics of polymer solutions, several theories have been proposed during the past 25 years that attempt to describe the LCST in polymer solutions. While several of them are able to correlate the different types of phase diagrams found among polymer solutions, only a few show predictive or semipredictive capabilities. These theories may be divided in two main groups: (a) group contribution and (b) non group contribution models. A comprehensive and detailed description of the performance of different models in predicting phase equilibria in mixtures with polymers will be presented by Saraiva et al. (1995) in a future publication and, for this reason, this point will not be further discussed here.

### The Group Contribution–Flory Equation of State (GC-Flory EoS)

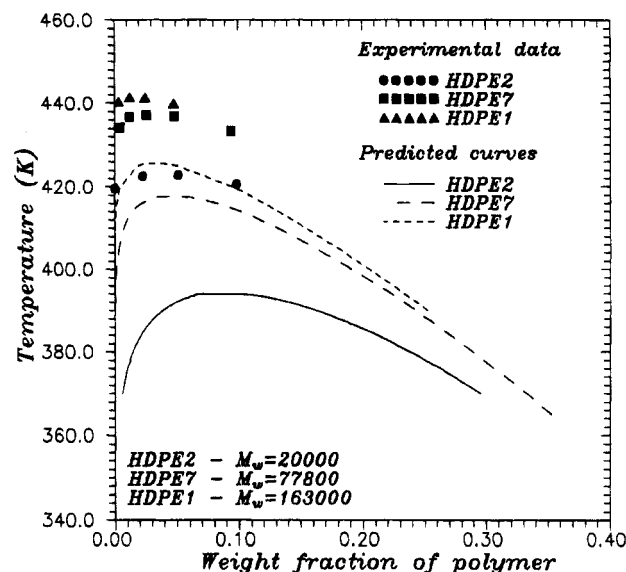
In 1985, John Holten-Andersen (JHA) extended the work of Prigogine (1957), Patterson (1967), and Flory (Flory et al., 1964; Flory, 1970) and developed a group contribution model for prediction of phase equilibria in polymeric systems (Holten-Andersen, 1987). In order to overcome problems originating from the degree of complexity of the JHA model and still keeping the prediction capabilities at the same level, Chen et al. (1990) proposed the group contribution–Flory equation of state (GC-Flory EoS), a simplified and modified version of the JHA model (Chen et al., 1990). The GC-Flory EoS has been used to predict VLE in polymer solutions. In order to improve the performance of the model and extend its applicability to a wider range of polymer systems, the model has been recently revised and further simplified by Bogdanic and Fredenslund (1994).

Here, only general comments on the basic assumptions of the GC-Flory EoS will be outlined; a detailed description of the model is presented elsewhere (Bogdanic and Fredenslund, 1994). In its present form, the model is a modified Flory–Prigogine liquid-phase EoS, which differs from the original Flory EoS in the following points: free-volume and attractive terms of the configurational partition function, and predictive capabilities (group contribution concept).

**1. Free-Volume Partition Function.** The free-volume partition function,  $Z^{FV}$ , adopted in the GC-Flory EoS accounts for the difference between the internal and the translational motions of the molecules.

The internal motions of the molecules are considered to be restricted by the space around the center of mass of the molecules, while the translational motions of the center of mass are influenced by the total volume available for the system (Holte-Andersen, 1985). This leads to a configurational-FV partition function that, unlike the Flory term (Flory et al., 1964; Flory, 1970), gives the correct ideal gas limit: at zero densities, the  $Z^{FV}$  is equal to  $V^n$  ( $n$  is the number of molecules and  $V$  the total volume of the system). It is found that the new  $Z^{FV}$  expression improves the temperature dependence of the model.

**2. Attractive Partition Function.** In order to account for the effect of nonzero energy interactions



**Figure 1.** Coexistence curves predicted by the GC-Flory EoS for the HDPE/1-octanol system. Symbols: cloud-point experimental data.

between the compounds in the mixing process, the GC-Flory EoS has a nonrandom UNIQUAC-like attractive partition function. The assumption of random mixing is particularly poor in the dilute region where, due to their modular molecular structure, the polymer molecules tend to form regions of higher concentration than the overall concentration of the mixture.

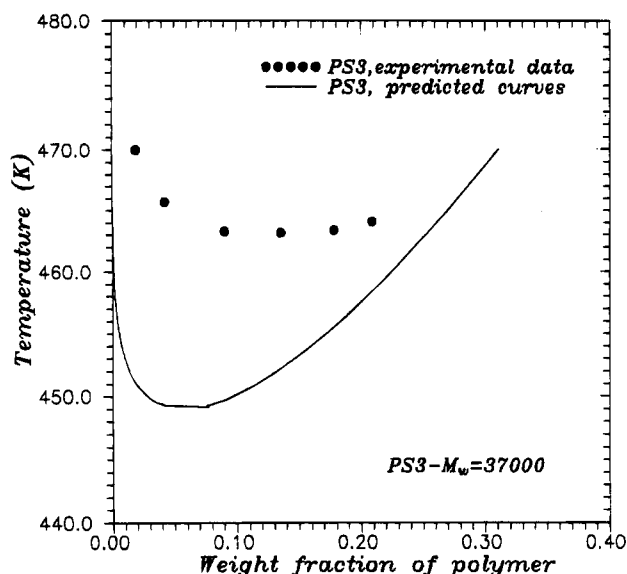
**3. The Group Contribution Approach.** In the Flory EoS, the estimation of the pure component (polymer and solvent) EoS parameters requires pure component experimental data. In the GC-Flory EoS, the pure component model parameters are estimated through group contribution expressions, which enhances the predictive nature of the model. The capability of the GC-Flory EoS to describe the phase equilibria in mixture with polymers can be considered a major achievement of the group contribution concept.

### LLE in Monodisperse Polymer/Single Solvent Systems

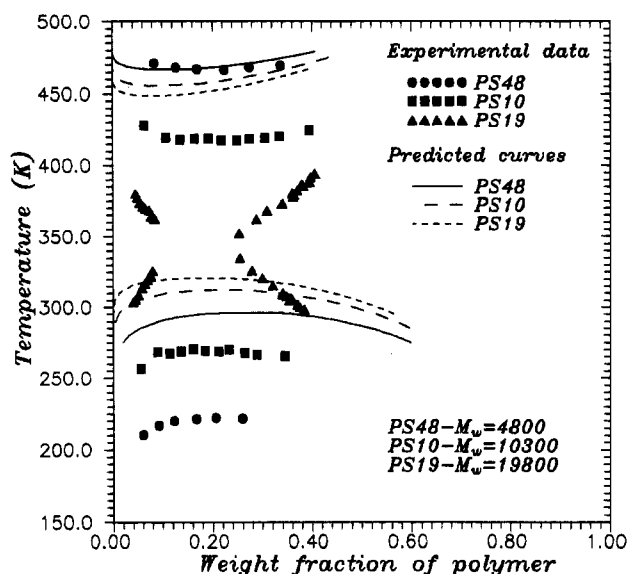
**1. Coexistence Curves.** Figures 1–8 show experimental and calculated coexistence curves for several polar and nonpolar polymer solutions. The experimental cloud-point curves have been retrieved from the DECHEMA (Hao et al., 1992) and DIPPR (High and Danner, 1992) Data Banks. The results are analyzed and discussed below.

**Polar Systems. (a) Polymer Solutions with Specific Energy Interactions.** Figure 1 refers to HDPE/1-octanol solutions, a system with specific energy interactions (i.e., H-bonds). The UCST's are underestimated approximately 15–30 °C and, for these types of systems, the predictions are more accurate for high molecular weight polymer solutions. The shape of the UCST curves is reasonably reproduced, as well.

The model predicts total miscibility for aqueous polymer solutions (like PEG/water), once the description of the specific energy interactions characteristic of aqueous systems are beyond the predictive capabilities of the model in its present form. However, it might be possible to extend the applicability of the model to these type of systems by adding (developed) an extra term specific for hydrogen bonds.

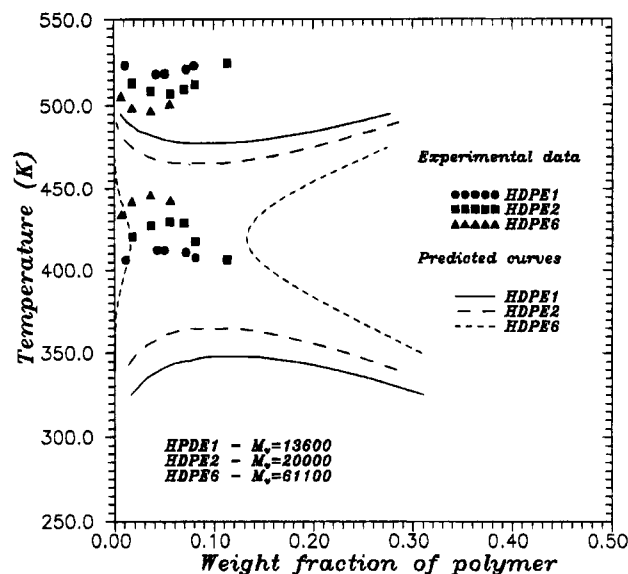


**Figure 2.** Coexistence curves predicted by the GC-Flory EoS for the PS/MEK system. Symbols: cloud-point experimental data.

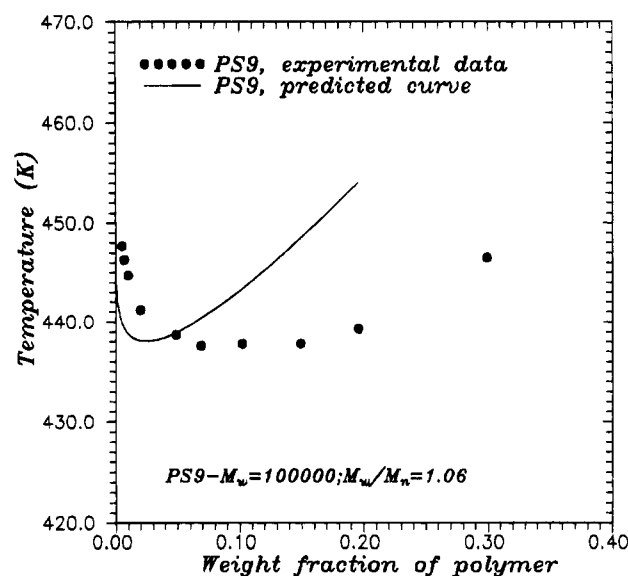


**Figure 3.** Coexistence curves predicted by the GC-Flory EoS for the PS/acetone system. Symbols: cloud-point experimental data.

**(b) Polymer Solutions without Specific Energy Interactions.** Figures 2–6 show coexistence curves for five different polar polymer solutions that do not exhibit specific energy interactions. The GC-Flory EoS is able to describe qualitatively the phase equilibria behavior for this type of systems. Particularly accurate are the LCST's predicted for the PS/MEK (Figure 2) and PS/ethyl acetate (Figure 6) solutions. For the systems which show phase diagrams of the combined (UCST + LCST) type, the difference between the calculated and the experimental critical points is within 10–80 °C, which may be still considered quantitatively satisfactory for some applications. The model correctly predicts the decrease of polymer solubility with the increase of polymer size, but it is not accurate enough to describe this dependence quantitatively. An increase of the molecular weight of the polymer leads to an increase of the UCST and a decrease in the LCST. For some systems, at a certain high value of the polymer molecular weight, the UCST and LCST branches intersect mutually, and the phase diagram is transformed in a hourglass type. Although the experimental hourglass

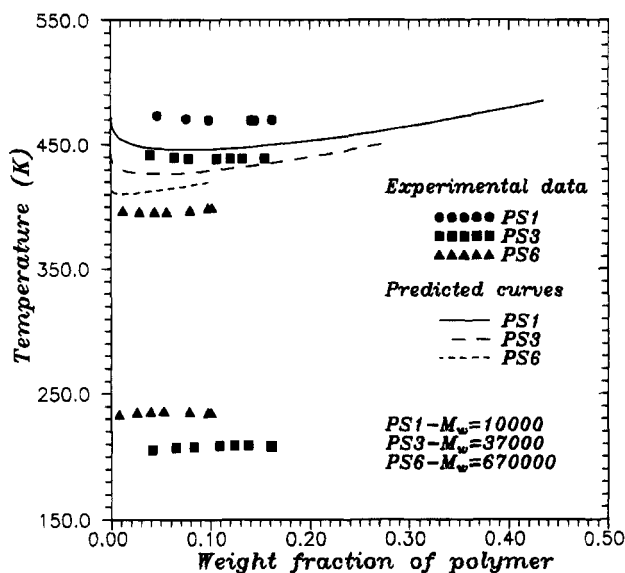


**Figure 4.** Coexistence curves predicted by the GC-Flory EoS for the HDPE/*n*-butyl acetate system. Symbols: cloud-point experimental data.

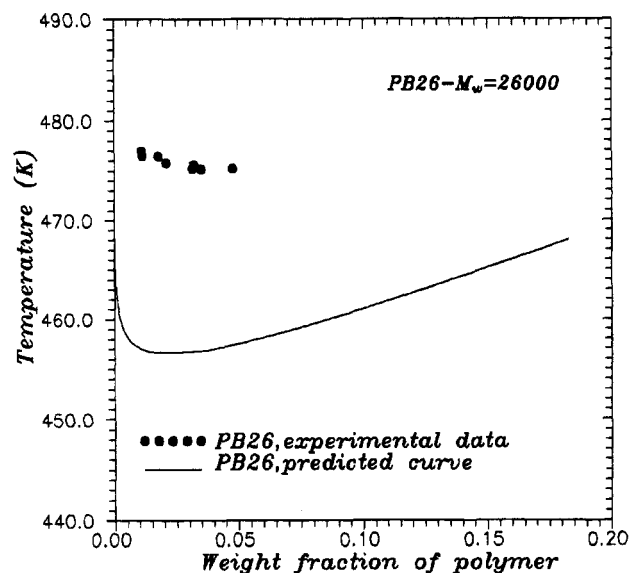


**Figure 5.** Coexistence curves predicted by the GC-Flory EoS for the PS/ethyl acetate system. Symbols: cloud-point experimental data.

for the PS( $M_w = 19800$ )/acetone solution (Figure 3) cannot be predicted by GC-Flory EoS, the model is, in general, capable of describing hourglass behavior, as can be concluded from the results obtained for the HDPE ( $M_v = 61\,100$ )/*n*-butyl acetate (Figure 4) solution. For the PS/ester systems considered in this work, the GC-Flory EoS predicts only LCST curves. This is in agreement with the experimental data for the PS ( $M_w = 96\,000$ )/ethyl acetate system (Figure 5) but is not valid for the PS/branched acetate solutions (Figure 6) for which UCST curves exist. The failure of the model to describe the UCST of the branched acetate systems might be due to steric effects in molecules with side groups, as is the case of isopropyl acetate (and *tert*-butyl acetate), which are not correctly described by the model. Due to the difference in size between a polymer and a solvent, the critical points (upper and lower) are located in the polymer dilute region and are further dislocated toward the zero-polymer-concentration area as the polymer molecular weight increases; the GC-Flory EoS



**Figure 6.** Coexistence curves predicted by the GC-Flory EoS for the PS/isopropyl acetate system. Symbols: cloud-point experimental data.



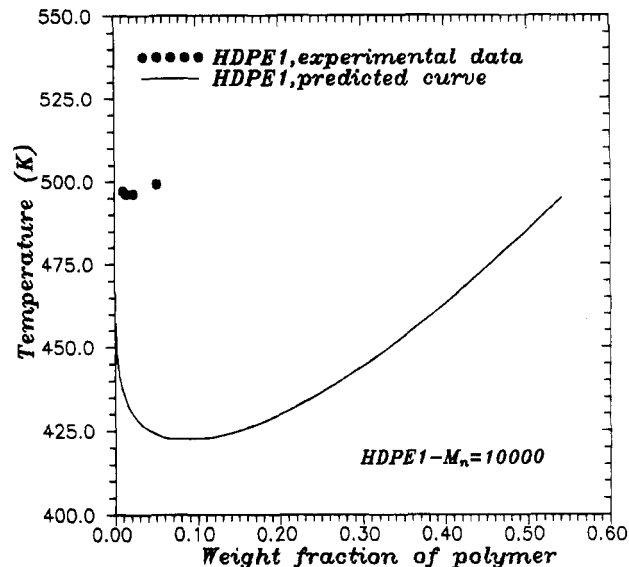
**Figure 7.** Coexistence curves predicted by the GC-Flory EoS for the PB/*n*-hexane system. Symbols: cloud-point experimental data.

is able to account, qualitatively, for this dependence (Figures 2–6).

**Nonpolar Systems. (a) Nearly Athermal Polymer Solutions.** Figures 7 and 8 show results obtained for two different polymer solutions where only energy interactions of the alkane–alkane type exist. Due to the weakness of the dispersive energy interactions, these systems have low enthalpies of mixing and, for this reason, are often called nearly athermal polymer solutions. The lower-critical-solution temperature for the PB/*n*-hexane system is predicted with good accuracy. The predictions for the HDPE/*n*-octane solution are rather poor, but the model qualitatively predicts the LCST behavior.

**2.  $\Delta G^{\text{mix}}$  versus  $X$  and the Polymer Molar Activity Coefficients.** The PS/acetone system will be used to illustrate a few interesting aspects of LLE in polymer solutions.

Due to the significant difference in size between the polymer and solvent molecules, the critical solution point(s) are located in the extremely dilute polymer mole

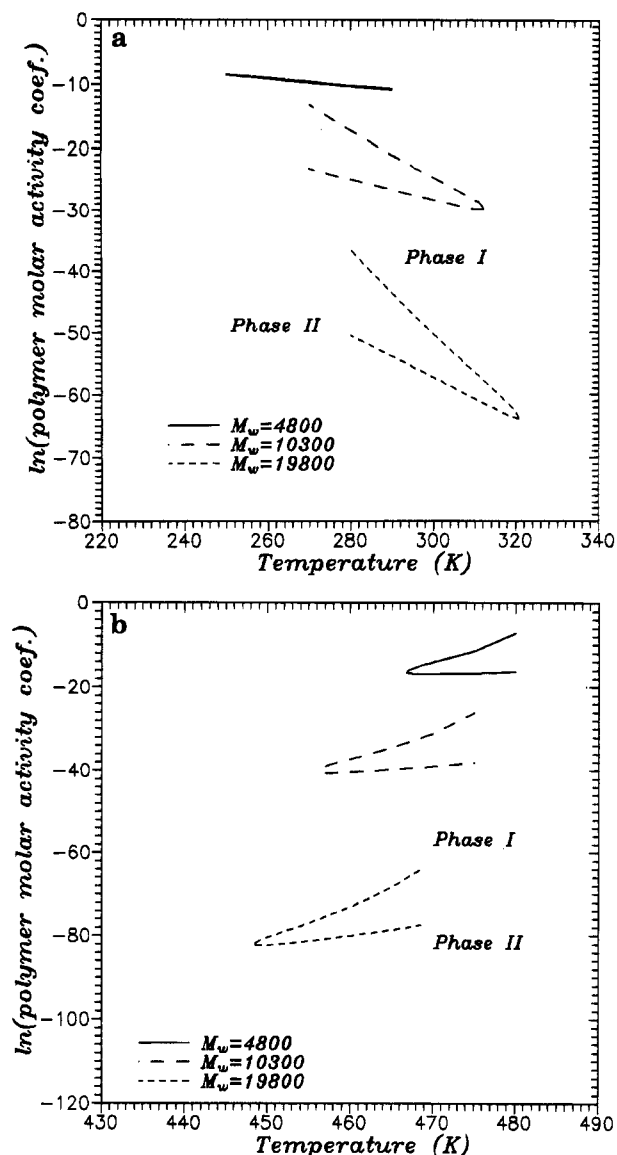


**Figure 8.** Coexistence curves predicted by the GC-Flory EoS for the HDPE/*n*-octane system. Symbols: cloud-point experimental data.

fraction area. On a molar basis, the liquid mixture is essentially pure solvent (i.e., the mole fraction of the solvent is close to unity), and the polymer molar thermodynamic partial functions are close to the polymer solution properties at infinite dilution. As a consequence, the solvent molar activity coefficient is close to unity. The polymer molar activity coefficient,  $\gamma_{\text{pol}}$ , can have any value, from extremely low to extremely high, depending on the nature of the system and of the polymer molecular weight. Figure 9 presents typical values for  $\ln \gamma_{\text{pol}}$  in the LLE range. It is important to point out here that, since experimental data of polymer activity coefficients are not available, the magnitude of the  $\gamma_{\text{pol}}$  that is predicted by the GC-Flory EoS (and by theory, in general) cannot be checked experimentally. In the LCST branch of the phase diagram (Figure 9b),  $\gamma_{\text{pol}}$  is an increasing function of the temperature, having its minimum value at the lower critical solution point where  $\gamma_{\text{pol}}$  in the two coexisting liquid phases become equal. In the UCST branch (Figure 9a), the situation is reversed, and  $\gamma_{\text{pol}}$  is a decreasing function of the temperature. It is clear that, unlike for VLE, LLE in polymer solutions is (almost) totally governed by the polymer molar activity coefficient.

Figure 10 shows two  $\Delta G^{\text{mix}}$  curves for the same PS/acetone solution at two different temperatures within the liquid–liquid immiscibility region. The curve at 310 K refers to equilibrium points in the UCST branch while the curve at 460 K is related to equilibrium points in the LCST branch. The symbols mark the points of stable equilibrium. A liquid mixture will only separate in two (or more) phases if the process leads to a decrease of the total Gibbs free energy. At the equilibrium state, the system Gibbs free energy is minimum, and the chemical potential of each of the components is equal in the two stable coexisting-liquid phases (Gibbs, 1948). If, at a certain temperature, a given liquid binary mixture is immiscible, the system  $\Delta G^{\text{mix}}$  must have, at least, two inflection points. The change of curvature of the molar  $\Delta G^{\text{mix}}$  curve of a polymer solution is very difficult to identify graphically (Figure 10). In order to be able to detect the curvatures in the  $\Delta G^{\text{mix}}$  function, the numerical difference between the  $\Delta G^{\text{mix}}$  function and the straight line that connects the points of stable

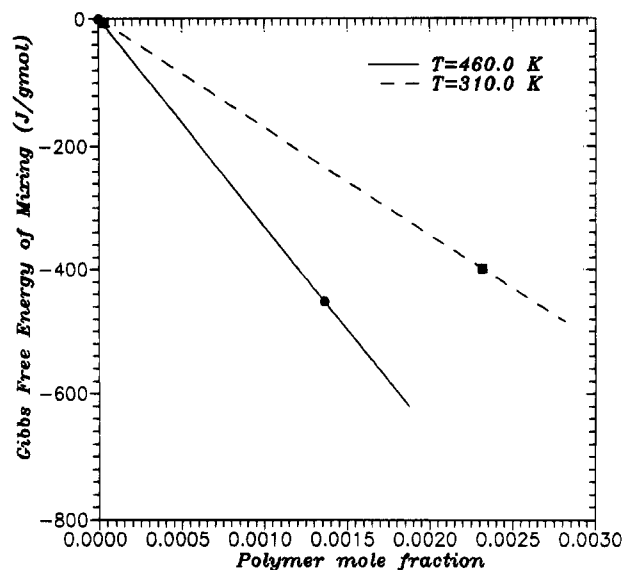




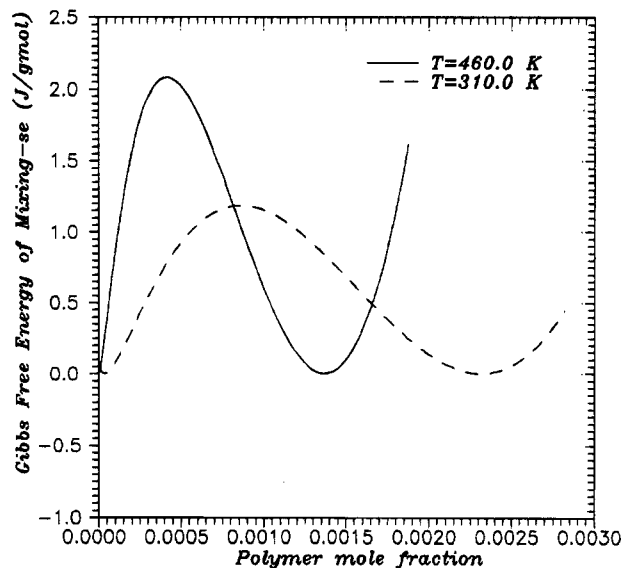
**Figure 9.** Predicted  $\ln \gamma_{\text{pol}}$  for the PS/acetone system by the GC-Flory EoS, in the  $(T, \text{composition})$  region of immiscibility. The upper lines refer to the liquid-phase one and the lower lines to the liquid-phase two: (a) UCST curves; (b) LCST curves.

equilibrium (for practical purposes, that function is here called  $\Delta G^{\text{mix-se}}$ ) has been calculated and the results are presented in Figure 11. As expected, two inflection points can be clearly identified in each of the curves. However, the  $\Delta G^{\text{mix-se}}$  functions assume values of a order of magnitude not greater than 2.5, while the absolute  $\Delta G^{\text{mix}}$  functions achieve values of a order of magnitude 300 times higher, which explains why the inflections in the  $\Delta G^{\text{mix}}$  plot could not be detected visually. The apparent linearity of the molar  $\Delta G^{\text{mix}}$  versus  $X$  plot is a universal feature of LLE of polymer solutions; in general, the magnitude of the inflection point differences, and the total  $\Delta G^{\text{mix}}$ , differs significantly.

**3. UCST versus LCST.** In the GC-Flory EoS, the difference in size, shape, configurational structure and energy interactions between the molecules of the compounds in a mixture are described by three separate terms: a combinatorial, a FV, and an attractive term (Bogdanic and Fredenslund, 1994). By evaluating the contribution to the total  $\gamma_{\text{pol}}$  of each of the terms in the region where the model predicts liquid-liquid immiscibility, it is possible to get a better understanding of the nature of the different types of phase diagrams



**Figure 10.**  $\Delta G^{\text{mix}}$  curves predicted by the GC-Flory EoS for the PS ( $M_w = 19\,800$ )/acetone solution at two different equilibrium temperatures: 460 K (point in the LCST curve) and 310 K (point in the UCST curve). The symbols mark the points of stable phase equilibrium, at the specified temperature.



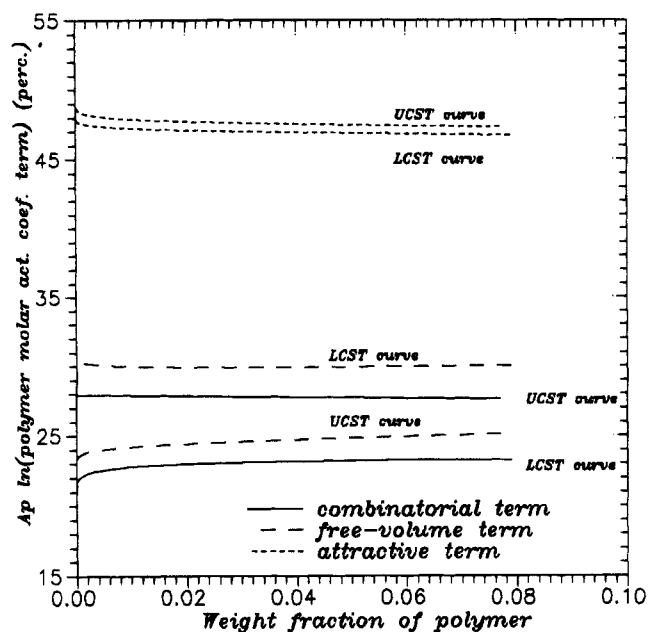
**Figure 11.**  $\Delta G^{\text{mix-se}}$  functions for the PS ( $M_w = 19\,800$ )/acetone solution at two different equilibrium temperatures: 460 K (point in the LCST curve) and 310 K (point in the UCST curve). At the points of stable phase equilibrium,  $\Delta G^{\text{mix-se}}$  is equal to zero.

typically found in LLE of polymer solutions. Here, we will show how the GC-Flory EoS describes a combined upper-critical-solution (UCS)/lower-critical-solution (LCS) behavior in terms of combinatorial, FV, and attractive contributions. The system PS(10300)/acetone will be used as example.

**Combinatorial, Free-Volume, and Attractive Contributions.** Figure 12 presents the absolute percentage contributions to the  $\ln \gamma_{\text{pol}}$  defined as

$$\ln \gamma_{\text{pol}}^{i-\text{ap}} = \frac{|\ln \gamma_{\text{pol}}^i|}{\sum_i |\ln \gamma_{\text{pol}}^i|} \times 100 \quad i = \text{comb, FV, attract} \quad (1)$$

for the PS (10300)/acetone system. The absolute percentage contributions defined by eq 1 are a measure of



**Figure 12.** Predicted absolute percent combinatorial, free-volume, and attractive terms of  $\ln \gamma_{\text{pol}}$  in the diluted coexisting-liquid phase for the PS ( $M_w = 10\,300$ )/acetone system, by GC-Flory EoS. Polymer solution with unlike-nonspecific energy interactions; phase diagram of the combined (UCST + LCST) type.

the degree with which each of the terms influence the solution properties. They are closely related to the type of energy interactions existent in solution, and are practically independent on the polymer molecular weight.

#### Systems without Specific Energy Interactions.

For a certain polymer molecular weight range, polar polymer solutions without specific energy interactions exhibit a phase diagram of the combined (UCST + LCST) type. In both branches of the phase diagram, the attractive term contributes significantly, and in a similar way, and the upper and lower branches differ in the degree with which the combinatorial and the FV effects influence the phase behavior of the solution (Figure 12). In the LCST curves, the  $\ln \gamma_{\text{pol}}^{\text{FV-ap}}$  has a higher value than in the UCST curves, which is in good agreement with the physics of the phase separation at both low (UCST) and high (LCST) temperatures for this type of polymer solutions.

#### Conclusions

The revised GC-Flory EoS is a powerful tool for prediction of phase equilibria in polymer solutions. The model is capable of describing the most common types of phase diagrams found in polymer solutions, UCST, LCST, combined (UCST + LCST), and hourglass types, and is particularly accurate in predicting the lower-critical-solution behavior of polymer solutions. In general, the predicted LCS and UCS temperatures deviate from the experimental values within 10–80 °C; this may be considered a satisfactory result regarding the group contribution nature of the model, and the methodology followed in the estimation of the model parameters (group and subgroup parameters have been evaluated from low molecular weight pure component volumetric and VLE mixture experimental data). The GC-Flory EoS is capable of predicting the significant influence of the FV effects in the polymer–solvent incompatibility at high temperatures, which is in very good agreement with the nature of the liquid-phase separation at

temperatures near the gas–liquid critical temperature of the solvent (LCST).

Despite the fact that it converges to the ideal-gas limit, the GC-Flory EoS in its present form is only capable of describing with good accuracy the PVT behavior of the liquid phase. In particular, the pure component vapor pressures predicted by the GC-Flory EoS deviate significantly from the experimental values. This deficiency of the GC-Flory EoS is expected, since no pure component vapor pressure data have been used in the estimation of the group and subgroup model parameters.

Further work will focus in the extension and evaluation of the capabilities of the model in predicting LLE in copolymer solutions and (co)polymer blends.

#### Acknowledgment

The authors are grateful to Docent Michael L. Michelsen for his constructive and inspiring ideas. Special thanks are extended to Georgios M. Kontogeorgis for his support and interest in this work.

#### Abbreviations

EoS = equation of state  
 FH = Flory–Huggins  
 FV = free volume  
 GC = group contribution  
 H = hydrogen  
 HDPE = high-density polyethylene  
 LLE = liquid–liquid equilibrium  
 LCS = lower critical solution  
 LCST = lower critical solution temperature  
 MEK = methyl ethyl ketone  
 MWD = molecular weight distribution  
 PB = poly(1-butene)  
 PE = polyethylene  
 PEG = poly(ethylene glycol)  
 PS = polystyrene  
 PVT = pressure–volume–temperature  
 UCS = upper critical solution  
 UCST = upper critical solution temperature  
 vdW = van der Waals  
 VLE = vapor–liquid equilibrium

#### Symbols

$\Delta G^{\text{mix}}$  = Gibbs free energy of mixing  
 $\Delta G^{\text{mix-se}}$  = Gibbs free energy of mixing minus straight line connecting the values of the Gibbs free energy of mixing corresponding to the points of liquid–liquid stable equilibrium conditions  
 $M_n$  = number-average molecular weight  
 $M_v$  = viscosity-average molecular weight  
 $M_w$  = weight-average molecular weight  
 $T$  = absolute temperature  
 $V$  = total volume  
 $Z$  = configurational partition function  
 $W$  = polymer weight fraction

#### Greek Letters

$\gamma$  = molar activity coefficient  
 $\chi$  = Flory–Huggins binary energy interaction parameter

#### Superscripts

attract = attractive contribution  
 attract-ap = absolute percentage attractive contribution  
 comb = combinatorial contribution  
 comb-ap = absolute percentage combinatorial contribution  
 FV = free-volume contribution



FV-ap = absolute percentage free-volume contribution  
mix = mixing

#### Subscripts

pol = polymer  
n = number  
v = viscosity  
w = weight

#### Mathematical Functions and Operators

ln = natural logarithm  
|| = absolute value  
 $\Sigma$  = summation

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Received for review April 4, 1994

Revised manuscript received December 6, 1994

Accepted January 17, 1995\*

IE9402224

\* Abstract published in *Advance ACS Abstracts*, March 1, 1995.