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GROUP CONTRIBUTION METHODS FOR ESTIMATING THE PROPERTIES OF POLYMER SYSTEMS

Polymer materials are nowadays used in a wide range of technological applications. Reliable knowledge of the thermophysical properties of pure polymers and their mixtures in the whole composition and a wide temperature and pressure range determines whether a given polymer is suitable for a specific application. On the other hand, accurate knowledge of the thermodynamic properties of the systems is a vital prerequisite for computer–aided syntheses, design, and the optimization of industrial polymer processes. However, the experimental data on polymer solubility are often scarce, and at this point, thermodynamics provide a powerful tool for modeling and extrapolating the experimental data. These models, together with factual data banks, are powerful software tools for the reliable development of chemical processes and other applications of industrial interest. The status of the different approaches and important applications of industrial interest using thermodynamic information derived from data banks or by using predictive thermodynamic models are presented in this review.

Dedicated with affection and the highest appreciation to Bobo on his 70th birthday

The continuous development of modern process industries has made it increasingly important to have information about the properties of materials, including many new chemical substances whose physical properties have never been measured experimentally. This is especially true of polymeric substances. The design of manufacturing and processing equipment requires considerable knowledge of the processed materials and related compounds. This knowledge is also essential for their application and final use.

Some handbooks and similar compilations [1–6] contain a part of the data required, but in many cases the property needed cannot be obtained from such sources.

The aim of this paper is to give a review of methods based on structure–properties relationships for the estimation and/or prediction of more important properties of polymers in the solid, liquid and dissolved states, in cases where experimental values are not found. In other words, this paper addresses predictions. These are usually based on correlations of the properties of known polymers with their chemical structure, with interpolation or extrapolation, as required.

A so called semi–empirical approach (partly empirical, but based on theoretical models or concepts) is the most common and sometimes even the only possible way in a relatively new field of macromolecular matter. Fundamental theory is generally too remote from the phenomena which have to be described. What is needed in practice is a formulation which is designed to deal directly with the phenomena and which makes use of the language of observation. This is a pragmatic approach that is designed for specific use; it is a completely non–speculative procedure.

Reid, Prausnitz and Sherwood [7] have performed this task in the low–molecular field, as far as gases and liquids are concerned. For molecular crystals and glasses Bondi [8] gave a similar contribution which partly covers the polymeric field, too. Literature on the macromolecular field is already extremely large. Nevertheless, the researcher is often confronted with the problem that neither directly measured properties, nor reliable methods to calculate them, can be found. This is the justification of the present paper.

The simplest and yet very successful method is based on the concept of additive group contributions and the purpose of this paper is to show that group contribution models may be used for estimating properties of pure polymers, polymer–solvent and polymer–polymer mixtures.

The underlying idea is that there are thousands of chemical compounds of interest in science and practice; however, the number of structural and functional groups which constitute all these compounds is much smaller. The assumption that a physical property of a compound, e.g. a polymer, is in some way determined by a sum of contributions made by the structural and functional groups in the molecule or in the repeating unit of the polymer, forms the basis of a method for estimating and correlating the properties of a very large number of compounds or polymers, in terms of a much smaller number of parameters which characterize the contributions of individual groups. These group contributions are often called increments.

Such a group contribution or increment method is necessarily an approximation, since the contribution of a

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given group in one surroundings is not necessarily the same as that in another environment.

The fundamental assumption of the group contribution technique is additivity. If the group values are known for a specific property F, then the total value of the property for the whole molecule is often expressed by a general additive rule of the form:

$$F = \sum_i n_i F_i \tag{1}$$

or similar additive equations. In Equation (1) n_i is the number of groups of type *i* and F_i is the corresponding group value. It is obvious that the general group contribution equation has a more complicated form than that indicated by Equation (1).

This assumption, however, is valid only when the influence of any one group in a molecule or in a structural unit of a polymer is not affected by the nature of the other groups. If there is mutual interaction, it is sometimes possible to find general rules for corrections to be made in such a case of interaction (e.g. conjugation of double bonds or aromatic rings). Every correction or distinction in the contribution of a group, however, means an increase in the number of parameters. As more and more distinctions are made, finely the ultimate group will be recovered, namely the molecule or the structural unit of the polymer itself. Then the advantage of the group contribution method is completely lost.

So the number of distinct groups must remain reasonably small, but not so small as to neglect significant effects of molecular structure on physical properties. For practical utility always a compromise must be attained; it is this compromise that determines the potential accuracy of the method.

It is obvious that reliable experimental data are always to be preferred to values obtained by an estimation method. In this respect all the methods proposed in this paper have a restricted value.

GROUP CONTRIBUTION METHODS FOR ESTIMATING PROPERTIES OF PURE POLYMERS

This section will deal mainly with the group contribution (GC) methods for estimating more important properties of polymers, required later for estimating phase equilibrium for polymer solutions and blends. It is not the purpose of this chapter to give a complete review of group contribution methods for estimating the properties of polymers. For this, the reader is referred to references 9–11. Examples of properties for which GC methods have been developed and presented here are the density, the solubility parameter, the melting and glass transition temperatures.

Methods for estimating the densities of polymers

Experimental density data are now available for many polymers [12,13]. However, the number of polymers of interest is much greater than the number of those for which data are available. The density of some polymers can be estimated using one of the GC methods discussed below.

The van Krevelen method

Van Krevelen [9] suggested the following equations for estimating the volume of polymers using group contributions, which are based on their physical state (amorphous, glassy, crystalline):

– for amorphous polymers:

$$V_a(T) = V_w(1.30 + 10^{-3}\,T) \tag{2a}$$

– for glassy polymers:

$$V_g(T) = V_w(1.30 + 0.5510^{-3}\,T_g + 0.4510^{-3}\,T) \tag{2b}$$

– for completely crystalline polymers:

$$V_c(T) = V_w(1.30 + 0.4510^{-3}\,T) \tag{2c}$$

In the above equations, T is the temperature in K, T_g is the glass transition temperature in K, and V_w is the van der Waals volume of the repeating unit.

Parameter tables and detailed explanation of calculation are presented in reference 9.

The van der Waals volume, originally introduced by Bondi [8], is defined as the actual volume of a molecule and can be easily estimated using GCs via Equation (1), where $F = V_w$, and the parameter tables are available in many references [7,14,15]. In these tables, which have been developed for the UNIFAC activity coefficients model, the van der Waals volume is given in terms of a dimensionless parameter R_k. Group van der Waals volumes (in cm^3/gmol) can be estimated from R_k values as follows:

$$V_{w,k} = R_k \cdot 15.17\,V_{w,k} \tag{3}$$

The Askadskii method

The calculation of the volume of polymers proposed by Askadskii [10,16] is based on the chemical structure of the repeating unit via group contributions and on their physical state (amorphous, glassy, crystalline):

$$V = \frac{V_w}{k} \tag{4a}$$

where V_w is the van der Waals volume of the repeating unit of the polymer and k is the coefficient of packing.

Regardless of the chemical structure of a polymer, the coefficient of packing of an amorphous polymer has been shown to be approximately the same, and equal ~ 0.681 at 293.15K. Hence, the Equation (4a) for amorphous polymers has been rewritten as:

$$V_a = \frac{V_w}{k_{av}} \tag{4b}$$

where $k_{av} = 0.681$.

Crystalline polymers were found to have a rather broad curve of distribution of the coefficient of packing. Investigations by Askadskii [10,16] show that the temperature dependences of the coefficient of packing for polymers have a form of:

$$k(T) = \frac{V_w}{MV_g\,[1 + \alpha_G\,(T - T_g)]}\quad T < T_g \qquad (4c)$$

where V_g is the specific volume at glass transition temperature, T_g, α_G is the coefficient of thermal expansion of the polymer before glass transition temperature, and M is the molar mass of polymer repeating unit. A noteworthy property of this temperature dependence is that the coefficient of packing in the first approximation is the same for all polymers at any temperature below the glass transition temperature. In the second, more accurate approximation, the coefficient of packing is the same for each polymer at its glass transition temperature and equals k_g = 0.667. At low temperatures (T_0 ~ 6K) the coefficient of packing of polymers are also approximately the same, and equal k_0 = 0.731.

Parameter tables and details of calculations are available in references 10 and 16.

The GCVOL method

The group contribution volume (GCVOL) method has been proposed by Elbro et a1. [17]. The method is based on GCs according to the following equations:

$$V = \sum_i n_i\,V_i \qquad (5a)$$

$$V_i = A_i + B_i\,T + C_i\,T^2 \qquad (5b)$$

Tsimbanogiannis et al. [18] and Ihlmes and Gmehling [19] later extended the GCVOL method for the already existing 36 original groups with 24 new groups. The extension included the densities of tertiary alcohols, alkynes, carboxylic acids, allenes, cycloalcanes, fluorides, bromides, iodides, thiols, sulfides, sulfates, amines and nitrocompounds. The new A_i, B_i and C_i group parameters are given in reference 19.

Constantinou et al. [20] developed an alternative GC method for the density of polymers (restricted to 25°C). An important advantage of the works by Elbro et al. [17], and Ihlmes and Gmehling [19] and Constantinou et al. [20] over that of van Krevelen [9] and Askadskii [10,16] is that these authors showed that the same consistent GC method can be applied in the prediction of density for low-molar-mass compounds (solvents), oligomers, and polymers.

The performance of the GCVOL method is quite satisfactory, with an average mean deviation of 1.5% for the database of 1040 compounds. Using this method very good results are also obtained for the density of copolymers, as shown by Bogdanić and Fredenslund [21]. A comparison with the van Krevelen method for a number of polymers is shown in reference 22.

The solubility parameter of polymers

The solubility parameter, δ, is a very important property, and has found a widespread use in many fields and not just in the study of polymer–solvent thermodynamics. It is associated with the Flory–Huggins model as well, but can also be used independent of it. The solubility parameter is defined as

$$\delta = \sqrt{\frac{\Delta E^{vap}}{V}} \qquad (6a)$$

where V is the liquid molar volume and ΔE^{vap} is the internal energy of vaporization, which equals the heat of vaporization minus RT (the product of gas constant and temperature). This quantity has traditionally been called *cohesive energy*. The solubility parameters of solvents can be measured by direct experimental measurements using this definition (Equation 6a). However, polymers are not volatile and they degrade long before reaching their vaporization temperatures. Their solubility parameters are experimentally assessed via various indirect methods (especially swelling and viscometric studies). This often results in different values of the solubility parameters of polymers, as shown by van Krevelen [9].

Methods for estimating the solubility parameters

In the absence of experimental data, the solubility parameters of both solvents and polymers can be estimated using the GC methods. Three the most widely used methods are those by Hoftyser–van Krevelen [9], Small [23] and Askadskii [10,16]. All three methods are similar, but are based on somewhat different assumptions.

The Hoftyser–van Krevelen method

Hoftyzer and van Krevelen proposed [9] group values for cohesive energy, i.e., for the ratio $\frac{\Delta E^{vap}}{V}$. The total cohesive energy is estimated from the group values via Equation (1). Then the solubility parameter is estimated using Equation (6a).

Parameter tables and details of calculations are presented in reference 9.

The Small method

Small [23] proposed an additive method for the so-called molar attraction constant F:

$$F = \sqrt{E_{coh,i}\,V_i} \qquad (6b)$$

Small considered that the F quantity of Equation (6b) shows better "additive" characteristics than cohesive energy. The total molar attraction constant is calculated from Equation (6b) and the solubility parameter is calculated from the equation:

$$\delta = \frac{F}{V} \qquad (6c)$$

Parameter tables and details of calculations are presented in references 23 and 9.

The Askadskii method

Askadskii [10,16] suggested the calculation of increments of the density of cohesive energy not by relating it to the molar, but to the van der Waals atom volume:

$$\delta = \sqrt{\frac{E^{*}}{V_w}} \tag{6d}$$

The parameter tables with details of calculation are given in references 10 and 16.

All three methods described above are have comparable accuracy (their differences keep within 10 % in most cases).

The Hansen method

Hansen [9,24] proposed an extension of the solubility parameter concept which is particularly suitable for solubility assessments for strongly polar and hydrogen bonding fluids. He identified three contributions to the cohesive energy and thus to the solubility parameter, one stemming from nonpolar (dispersion or van der Waals forces), (d), one from (permanent) polar (p), and one from hydrogen bonding forces (h). Hansen suggested that these three effects contribute additively to the cohesive energy density (i.e., the ratio of the cohesive energy to the volume):

$$E_{coh} = E_d + E_p + E_h \tag{7a}$$

Therefore, using Equation (7a), the total solubility parameter is estimated from the equation:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{7b}$$

Thus, the solubility parameter may be thought of as a vector in a three–dimensional d–p–h space. The above equation provides the magnitude of this vector. Each solvent and each polymer can be characterized by the three "solubility parameter increments", δ_d, δ_p, δ_h.

Hansen has presented extensive tables with the solubility parameter increments (d,p,h) in his recent book [24]. Van Krevelen [9] has proposed methods for all three increments according to the following equations:

$$\delta_d = \frac{\sum_i F_{di}}{V} \tag{7c}$$

$$\delta_p = \frac{\sum_i F_{pi}^2}{V} \tag{7d}$$

$$\delta_h = \frac{\sum_i F_{hi}}{V} \tag{7f}$$

Transition temperatures

It is impossible to understand the properties of polymers if the transitions that occur in such materials and specifically the temperatures at which these occur are not known. The main transitions are glass–rubber transition and the crystalline melting point. However, several other transitions of secondary importance may often be observed, e.g. the temperature of melting of "liquid crystals". Transition temperatures are extremely structure–sensitive, partly due to steric effects, partly due to intra– and inter–molecular interactions.

The glass transition is by far the most important among the many transitions and relaxations observed in amorphous polymers. When an amorphous polymer undergoes the glass transition, almost all of its properties significant for processing and/or performance change dramatically.

In addition, the glass transition plays a role in determining the physical properties of semicrystaline polymers, whose amorphous portions "melt" or "soften" at T_g while the crystaline portions remain "solid" up to the melting temperature T_m. A semicrystaline polymer can be treated as a solid below T_g, as a composite consisting of solid and rubbery phases of the same chemical composition above T_g but below T_m, and as a fluid above T_m. The effect of glass transition on the physical properties of semicrystalline polymers decreases with increasing crystallinity.

The observed value of T_g is a function of rate measurements. There is an important rate–dependent (kinetic) aspect of the glass transition. Nonetheless, the glass transition undoubtedly has an underlying fundamental thermodynamic basis. Theories of the glass transition invariably treat the observed value of T_g as a kinetic (rate–dependent) manifestation of an underlying thermodynamic phenomenon; however, they differ significantly in their description of the nature of this phenomenon at a fundamental level. Differences of opinion also exist concerning the issue of whether or not the discontinuities observed at T_g in the second derivatives of the Gibbs free energy (i.e., the coefficient of thermal expansion and the heat capacity) justify referring to the glass transition as a "second–order phase transition". A detailed treatment of these fundamental issues is outside the scope of this paper.

At a relatively simplified practical and operational (and thus theoretically nonrigorous) level of treatment, T_g can be defined as the temperature at which the forces holding distinct components of an amorphous solid together are overcome, so that these components become able to undergo large–scale viscous flow, limited mainly by the inherent resistance of each component to such flow. Despite its apparent simplicity, this operational definition actually comprehends both of the key aspects of the physics of the glass transition. It states that, when a solid is heated up to T_g, it acquires enough thermal energy to be able to overcome two types of resistance to the large–scale motions of its components: the cohesive forces holding its different components together and attributes of the individual components (chain segments in polymers) which resist viscous flow.

Based on considerations summarized above, it is not surprising that most theories of the glass transition describe this phenomenon in terms of key physical ingredients whose values strongly depend on the chain stiffness and/or the cohesive forces. The same statement can also be made for all empirical correlations for T_g, which either explicitly or implicitly attempt to account for the effects of chain stiffness and cohesive forces. One such empirical correlation is the relationship of van Krevelen [9], which will be reviewed briefly below. Many other empirical correlations, which usually express T_g as a function of quantities calculated using group contribution methods, have also been used with limited success.

A detailed review article by Lee [25] provides quantitative critical assessments, and extensive lists of original references, for some of the best-known empirical correlations for T_g. Some of the many other interesting attempts to estimate T_g, which were not reviewed by Lee [25], include the method of Askadskii and Slonimskii [26,27].

Methods for estimating glass transition temperature

The van Krevelen–Hoftyzer method

The equation for calculation the glass transition temperature proposed by van Krevelen and Hoftyter [9] is as follows:

$$T_g = \frac{Y_g}{M} = \frac{\sum\limits_i Y_{gi}}{M} \tag{8a}$$

where

$$Y_g = \sum_i Y_{gi} = T_g \cdot M \tag{8b}$$

Y_{gi} is called molar mass transition function. Y_{gi} group parameters together with a detailed explanation of T_g estimations are shown in reference 9.

The Askadskii metod

The starting equation relating T_g to the structure of the repeating unit proposed by Askadskii [10,16,26,27] is as follows:

$$T_g = \frac{\sum\limits_i \Delta V_i}{\sum\limits_i K_i \Delta V_i} \tag{9a}$$

where coefficients of packing for polymers are k_0 = 0.731 and k_g = 0.667, as described earlier, and

$$K_i = \alpha_i / (k_0 / k_g - 1) \tag{9b}$$

The values of K_i characteristic for each atom and each type of molecular interactions are given in references 10 and 16.

Methods of estimation of the melting point

The van Krevelen–Hoftyzer method

The equation for calculation the melting point of polymers proposed by van Krevelen and Hoftyter [9] is as follows:

$$T_m = \frac{Y_m}{M} = \frac{\sum\limits_i Y_{mi}}{M} \tag{10a}$$

where

$$Y_m = \sum_i Y_{mi} = T_m M \tag{10b}$$

Y_m is molar melt transition function. Y_{mi} group parameters altogether with detailed explanation of T_m estimations are shown in reference 9.

GROUP CONTRIBUTION METHODS FOR ESTIMATING THE PROPERTIES OF POLYMER MIXTURES

Vapor–liquid equilibrium

Group contribution methods may also be used for semiquantitative prediction of phase equilibrium compositions, not only for mixtures with normal–boiling components, but also for mixtures containing polymers [28–33,44–46]. Some recent significant developments of the available methods for mixtures with polymers will be reviewed with an emphasis on application.

Just as for mixtures with low molar mass components, two different approaches have been used for predicting vapor–liquid equilibrium (VLE) in mixtures which contain polymers: activity coefficient models (γ–models) and equation of state (EOS). In both cases, the starting point is the equality of the fugacity of each species in the two phases:

$$\hat{f}_i^V = \hat{f}_i^L \qquad i = 1,2,\ldots,N \tag{11}$$

where, for an *N*–component mixture, $\hat{f}_i^V$ is the fugacity of component *i* in the vapor phase and $\hat{f}_i^L$ is the fugacity of component *i* in the liquid phase. In the activity coefficient approach (and neglecting the Poynting correction factor), Equation (11) is usually rewritten as follows:

$$y_i \hat{\varphi}_i^V P = x_i \gamma_i \varphi_i^{sat} P_i^{sat} \tag{12}$$

where γ_i is the activity coefficient of component *i* and $\hat{\varphi}_i^V$ is its fugacity coefficient. If the vapor phase is an ideal gas, $\hat{\varphi}_i^V = \varphi_i^{sat} = 1$, and Equation (12) reduces to the often–used expression:

$$y_i P = x_i \gamma_i P_i^{sat} \tag{13}$$

In the EOS approach, Equation (11) is rewritten as:

$$y_i \hat{\varphi}_i^V = x_i \hat{\varphi}_i^L \tag{14}$$

where $\hat{\varphi}_i^V$ and $\hat{\varphi}_i^L$ are the fugacity coefficients of component i in the vapor and the liquid phase. $\hat{\varphi}_i^V$ and $\hat{\varphi}_i^L$ in Equation (14) [and $\hat{\varphi}_i^V$ and φ_i^{sat} in Equation (12)] may be obtained from any equation of state, using well–known relationships from classical thermodynamics, for example:

$$\ln \hat{\varphi}_i = \int_{\infty}^{V} -\left[\left(\frac{\partial P}{\partial N_i}\right)_V - \frac{RT}{V}\right] dV - \ln\left(\frac{PV}{NRT}\right) \tag{15}$$

where N_i is number of mole of species i and V is total volume. The key elements in VLE computations are the liquid–phase activity coefficients, or the fugacity coefficients in both phases obtained from equations of state. Both equations of state and activity coefficient models are used as bases for group contribution prediction of phase equilibrium in polymer solutions.

Group contribution versions of both approaches are given below.

The models reviewed in this paper will not be fully described here. The equations, the calculation procedure and the parameters can be found in publications by Oishi and Prausnitz [31] for the UNIFAC–FV model, by Elbro et al. [32] and Kontogeorgis et al. [33] for the Entropic–FV model, by Bogdanić and Fredenslund [43] for the GC–Flory EOS, and by High and Danner [44,45] for the GC–LF EOS.

As the mole fraction of the solvent in a polymer, apart from the very dilute region of the solvent, is very close to unity, the mass fraction concentration scale is more convenient than the mole fraction scale:

$$w_i = \frac{m_i}{\sum_j m_j} = \frac{x_i M_i}{\sum_j x_j M_j} \tag{16}$$

where w_i, m_i and x_i are the mass fraction, the mass and the mole fraction of component *i* in the solution, respectively, and M_i is the molar mass of the component *i*. Due to the large difference in the molar masses of the solvents and polymers, one often uses activity coefficients based on mass fraction rather than mole fraction. The mass fraction activity coefficient, Ω_i, of a solvent in a solution containing polymers is defined as follows:

$$a_i = x_i \gamma_i = w_i \omega_i \tag{17}$$

where α_i and γ_i are the activity and the mole fraction activity coefficient of the component *i*.

Activity coefficient models

The UNIFAC–FV model

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$$

where C and R refer to, respectively, the combinatorial and residual contribution

$$\ln \gamma_i^C = \left(\frac{\ln \phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}\right) - \frac{1}{2} z\, q_i \left(\frac{\ln \phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right)$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \qquad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

where the summation is over all components

$$r_i = \sum \nu_{ki} R_k \qquad q_i = \sum_k \nu_{ki} Q_k$$

where the summation is over all groups

R_k = volume parameter for group k
Q_k = surface area parameter for group k
ν_{ki} = number of groups of type *k* in molecule *i*
x_i = liquid mole fraction of component *i*
z = coordination number = 10

$$\ln \gamma_i^R = \sum_k \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right)$$

where the summation is over all groups

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_m \theta_n \psi_{nm}}\right]$$

$$\psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad X_m = \frac{\sum_j \nu_{mj} x_j}{\sum_j \sum_n \nu_{nj} x_j}$$

a_{mn} = group interaction parameter for the interaction between *m* and *n*
Γ_k = the residual activity coefficient of group *k* in a reference solution containing only molecules of type *i*

Figure 1. Original UNIFAC equations [*14*]

Oishi and Prausnitz [31] modified the UNIFAC model [14,15] by including a contribution for free volume differences between polymer and solvent molecules to arrive at the following expression for the activity coefficient of a solvent, *i*, in a polymer:

$$\ln\gamma_i = \underset{\text{combinatorial}}{\ln\gamma_i^{comb}} + \underset{\text{residual}}{\ln\gamma_i^{attr}} + \underset{\text{free–volume}}{\ln\gamma_i^{FV}} \tag{18}$$

where γ_i is the activity coefficient of the solvent *i* at the solution temperature T, γ_i^{comb} is the combinatorial contribution to the activity coefficient (providing the contributions due to differences in molecular size), and γ_i^{attr} is the attractive contribution (frequently named residual, providing contributions due to molecular interactions) to the activity coefficient. Both contributions are identical to the original UNIFAC model [14] contribution (Figure 1). The free volume contribution to the activity coefficient, γ_i^{FV}, is calculated by means of the Flory expression,

$$\ln\gamma_i^{FV} = 3C_i \ln\left[\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_M^{1/3} - 1}\right] - C_i\left[\left(\frac{\tilde{v}_i}{\tilde{v}_M} - 1\right)\left(1 - \frac{1}{\tilde{v}_i^{1/3}}\right)^{-1}\right] \tag{19}$$

where C_i is an external degree of freedom parameter, and $\tilde{v}_i$ is the reduced volume of component *i*.

Molecules are divided into groups as defined by the method. The model parameters for these groups (group areas and volumes and the group interactions parameters for all possible binary pairs of groups) are obtained from the UNIFAC tables [14,15,29].

The Entropic–FV model

Elbro et al. [32] and Kontogergis et al. [33] have shown that the two terms $\ln\gamma_i^{FV}$ and $\ln\gamma_i^{comb}$ in Equation (18) may be replaced by a much simpler expression for the so–called entropic activity coefficient, γ_i^{entr}:

$$\ln\gamma_i = \ln\gamma_i^{entr} + \ln\gamma_i^{antr} \tag{20}$$

where this entropic part is:

$$\ln\gamma_i^{entr} = \ln\frac{\phi_i^{FV}}{x_i} + 1 - \frac{\phi_i^{FV}}{x_i} \tag{21}$$

and ϕ_i^{FV} is the free–volume fraction associated with component *i*:

$$\phi_i^{FV} = \frac{x_i v_{f,i}}{\sum\limits_j x_j v_{f,j}} \tag{22}$$

The Entropic–FV model [33] is based on the free–volume definitions given by:

$$v_{f,i} = v_i - v_i^* \tag{23}$$

where

$$v_i^* = v_{w,i} \tag{24}$$

and on the attractive term of modified UNIFAC [34] with linear temperature dependent UNIFAC parameters [34]:

$$a_{mn} = a_{mn,1} + a_{mn,2}\,(T - T_0) \tag{25}$$

v_i, v_i^* and $v_{w,i}$ in the above expressions are the liquid molar volume, the "inaccessible volume" and van der Waals volume, respectively.

For the UNIFAC–FV and the Entropic–FV models the densities of the pure solvent and pure polymer at the temperature of the mixture of interest, the structure of the solvent and polymer and the molar masses of all components are required. The densities of both solvent and polymers may be predicted within an average mean deviation of only 1.5% using a contribution method by Elbro et al. [17], and Ihlmes and Gmehling [19].

More recent approach in the FV term

Despite the overall successful performance of Entropic–FV and UNIFAC–FV models for a number of systems and types of phase equilibria, a number of researchers [35–43] have shown over the last several years that the combinatorial–FV terms of both the Entropic–FV and UNIFAC–FV models have a number of deficiencies. Their intention was to improve the expression for different systems, different purposes or particular cases only. The aim of this section is not to give a complete review of these models. For this, the reader is referred to references 35–43.

Equations of state

The GC–Flory EOS

The GC–Flory EOS [44,47,48] is a group contribution extension of the Flory equation [49], and like the EOS of Flory it is derived from the generalized van der Waals partition function. The group contribution modification permits the prediction of solvent activity, given only the structures of polymers and solvent involved. The GC–Flory equation contains a free–volume and attractive energy term:

$$P = \frac{nRT}{V}\left(\frac{\tilde{v}^{1/3} + C}{\tilde{v}^{1/3} - 1}\right) + \frac{E^{attr}}{V} \tag{26}$$

where n, $\tilde{v}$, V and C are the total number of moles in the system, the reduced volume, the total volume and the number of the external degree of freedom parameter, respectively. The attractive energy term of the partition function similar to the Flory expression has been adopted, but a non–random UNIFAC–like group contribution approach for the molecular parameters has been applied instead of the random mixing expression of the Flory model.

Expressions for the activity coefficients are derived from the EOS using classical thermodynamics. Writing the three contributions to the activity coefficients separately

$$\ln\gamma_i = \underset{\text{combinatorial}}{\ln\gamma_i^{comb}} + \underset{\text{free volume}}{\ln\gamma_i^{FV}} + \underset{\text{attractive}}{\ln\gamma_i^{attr}} \tag{27}$$

then

$$\ln\gamma_i^{com} = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \tag{28}$$

$$\ln\gamma_i^{attr} = 1/2zq_i\left\{\frac{1}{RT}\left[\varepsilon_{ii}(\tilde{v}) - \varepsilon_{ii}(\tilde{v}_i)\right] + 1 - \ln\sum_j \theta_j \exp(-\Delta\varepsilon_{ji}/RT) - \right.$$
$$\left.\left\{\sum_j \frac{\theta_j \exp(-\Delta\varepsilon_{ji}/RT)}{\sum\limits_k \theta_k \exp(-\Delta\varepsilon_{ki}/RT)}\right\}\right. \tag{29}$$

$$\ln\gamma_i^{FV} = 3\,(1 + C_i)\ln\left(\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) - C_i\ln\frac{\tilde{v}_i}{\tilde{v}} \tag{30}$$

where ϕ_i and θ_i are the segment volume fractions, and ε_{ii} and $\Delta\varepsilon_{ij}$ are energy interaction parameters. Equation (26) can in principle be applied at all pressures and temperatures, but it can be simplified for normal–pressure applications by solving for the volume roots at zero pressure instead of the pressure of the system.

The GC–lattice–fluid EOS

A group contribution lattice–fluid equation of state [45,46] (GC–LF EOS) is a modification of the equation of state derived by Panayiotou and Vera [50] which is based on the lattice statistics development of Guggenheim

[51]. Shown below is only the exact equation in terms of reduced variables:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+q/r-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \tag{31}$$

where $\tilde{P}$ is reduced pressure of the mixture, z is coordination number (z = 10), q is surface area parameter for the pure component of mixture and r is number of occupied lattice sites in the lattice for the pure component or the mixture.

From this equation of state, using classical thermodynamics, the mass fraction activity coefficient of a solvent in a solution is obtained:

$$\ln\Omega_i = \ln\phi_i - \ln w_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i\ln\left[\frac{\tilde{v}}{(\tilde{v}-1)}\,\frac{(\tilde{v}_i-1)}{\tilde{v}_i}\right] + $$
$$+ q_i\left(\frac{2\theta_{i,p}}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\Gamma_{ii} \tag{32}$$

where $\tilde{T}$ and $\tilde{T}_i$ are the reduced temperatures of the mixture and of the component *i*, $\theta_{i,p}$ is the surface area fraction of the component *i* in the pure state at the temperature and pressure of mixture, and Γ_{ii} is the nonrandomness parameter of a molecule of the component *i* surrounding a central molecule of the component *i*.

GC–Flory and GC–LF EOS calculations require structures of the solvent and polymer and the molar masses of all compounds. It should be stressed that an equation of state does not require pure component and mixture densities.

Discussion

The purpose of this section is to present an extensive evaluation of the capability of the described models in predicting activity coefficients for mixture with polymers. Extensive examples of predicted solvent activity coefficients will be shown, both at infinite dilution and finite concentrations. These are compared with the corresponding experimental values. All mentioned models: the UNIFAC–FV, the Entropic–FV, the GC–Flory EOS and GC–LF EOS were investigated for activity calculations in numerous systems of different solvents with different polymers in references 52–55. All models are based on the group contribution approach; the UNIFAC–FV and Entropic–FV models are activity coefficient models while the GC–Flory and GC–LF models are equation of state models. It should be underlined that all these models are purely predictive in the absence of any adjustable parameter.

Figures 2–5 show the results [52] for solvent activity coefficients at infinite dilution for more than 100 polymer solution.

Each model has its advantages and shortcomings for different types of systems. The advantages and disadvantages of equations of state and activity coefficient models have been discussed elsewhere [52–55] and will not be repeated here, except to underline that an equation of state does not require pure component and mixture densities. The accuracy of activity coefficient models is rather sensitive to pure component and mixture densities. The major drawback of these models is that they require accurate density data for the polymer at the temperature of the system, which is difficult to find. The major drawback of GC–Flory EOS and the GC–LF EOS is that, compared to

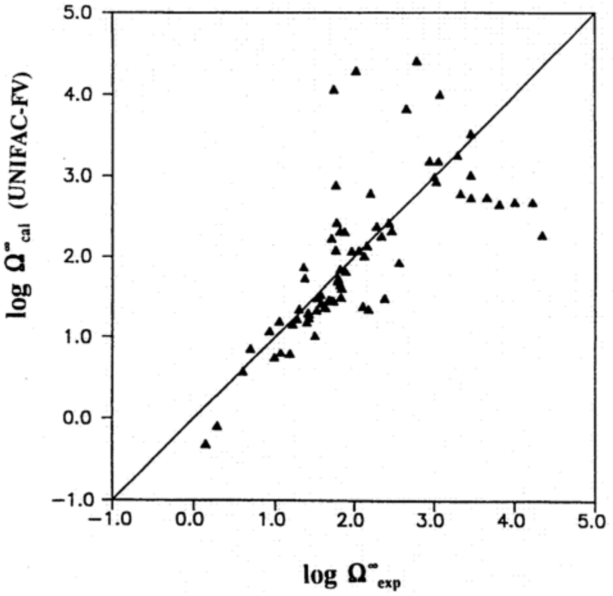

Figure 2. Calculated activity coefficients at infinite dilution using the UNIFAC–FV, $\log\Omega^\infty_{cal}$*, versus experimental data,* $\log\Omega^\infty_{exp}$ *for polymer solutions* [52]

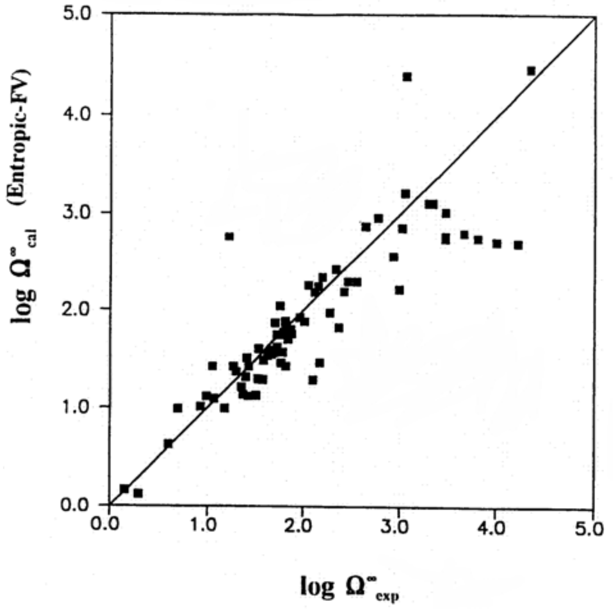

Figure 3. Calculated activity coefficients at infinite dilution using the Entropic–FV model, $\log\Omega^\infty_{cal}$*, versus experimental data,* $\log\Omega^\infty_{exp}$*, for polymer solutions* [52]

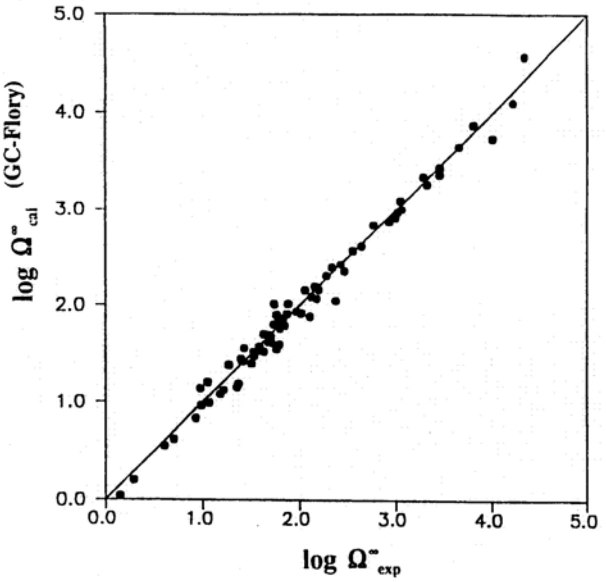

Figure 4. Calculated activity coefficients at infinite dilution using the GC–Flory, $\log\Omega^{\infty}_{cal}$, *versus experimental data,* $\log\Omega^{\infty}_{exp}$, *for polymer solutions* [52]

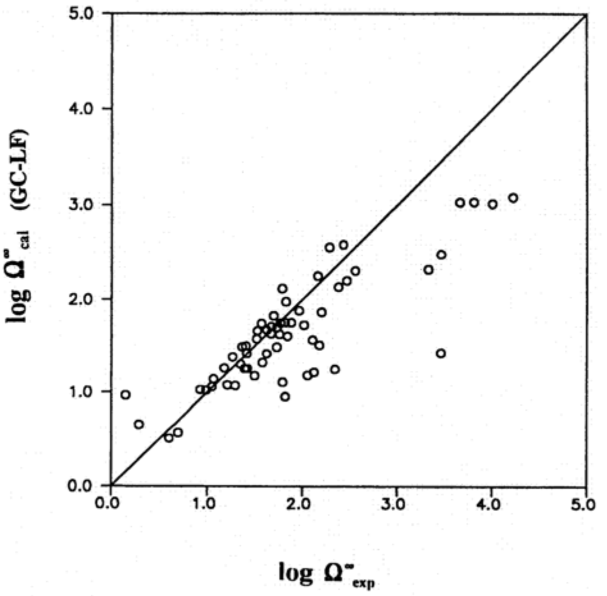

Figure 5. Calculated activity coefficients at infinite dilution using the GC–LF model, $\log\Omega^{\infty}_{cal}$, *versus experimental data,* $\log\Omega^{\infty}_{exp}$, *for polymer solutions.*

activity coefficient models, only a relatively small number of group parameters have been determined.

The activity coefficient approach may be preferred for VLE at low pressures due to its simplicity. This has led Kontogeorgis et al. [33] to investigate the applicability of Equation (20) for interacting systems, where the term $\ln\gamma_i^{attr}$ is not equal to zero. It was found that using the entropic activity coefficient model by Elbro et al. [32] combined [33] with $\ln\gamma_i^{attr}$ from UNIFAC gives superior results compared to those of Oishi and Prausnitz [31]. For example, UNIFAC–FV is not capable of representing phase behavior of strongly associating systems. At high pressures, the EOS approach could be used.

The results obtained with the GC–LF EOS model are of the same quality as the results obtained by the Entropic–FV model for finite concentrations as well as for dilute regions. Relatively poor prediction of the Entropic–FV model for solutions which contain the chloro groups may be attributed to uncertainties in the group contribution interaction parameters for CCl_2 and CCl_3 groups in new temperature–dependent UNIFAC parameter tables [34]. The GC–Flory model was found to be the best for solutions with alcohols and acetic acid. This is a significant result, especially if we consider that no additional hydrogen bonding parameters are used in the revised GC–Flory model. It can be seen that the GC–Flory model is capable of solving troublesome cases described earlier such as PVC solutions and alcohol–polymer solutions. Until now, the GC–Flory model has been the only model tested which can reasonably predict VLE behavior for solutions with PVC and hydrocarbons. Over the whole spectrum of polymer–solvent systems investigated here, there is not a single model that is superior to the GC–Flory EOS.

Liquid–liquid equilibrium

Knowledge and reliable estimates of the behavior of polymers and polymer solutions is very important for the prediction of process performances, primarily because many polymeric materials are produced in a solution with a solvent. A problem which often arises is how to remove (devolatilize) low molar mass constituent(s) from the final product, i.e. polymer. A part of this problem involves solving VLE problems, usually encountered at low concentrations of the solvent, whereas liquid–liquid equilibrium (LLE) often takes place in the opposite concentration range, i.e. at low concentrations of the polymer. The activity of the polymer is a predominant factor in LLE calculations for polymer solutions.

For mixtures of low–molar mass compounds only, it can be stated that mixing is the rule and the presence of two liquid phases is the exception. The contrary typically occurs for polymer solutions, for which the presence of two liquid phases is evidenced very often.

Phase separation in polymer solutions may occur upon cooling to low temperatures – upper critical solution temperatures (UCST) behavior, or upon heating to high temperatures – lower critical solution temperature (LCST) behavior. A system containing a poor solvent exhibits both UCST and LCST. UCST behavior is due to an unfavorable energy effect that arises from component differences in chemical nature and molecular force fields between the components. LCST is detected even for nonpolar or nearly athermal systems, usually at temperatures approaching solvent critical temperatures and at pressures above atmospheric. LCST behavior is due to an unfavorable entropic effect that overcomes the favorable enthalpies of mixing. For polymer solutions, LCST behavior is due to a difference in free volume between the polymer and the solvent. Unlike UCST, LCST behavior tends to be very pressure–dependent. Usually, LCST lies above UCST. However, when specific interactions are present (e.g. aqueous polymer solutions), a closed–loop phase behavior is observed. The LLE phase behavior depends significantly on the molar mass and the molar mass distribution of the polymer.

In the case of LLE, Equation (14) often takes the following form:

$$(\gamma_i x_i)^a = (\gamma_i x_i)^b \quad i = 1, 2, \ldots \tag{33}$$

or is expressed more generally, in terms of fugacity coefficients:

$$(\varphi_i x_i)^a = (\varphi_i x_i)^b \quad i = 1, 2, \ldots \tag{34}$$

where a and b represent the two liquid phases.

Equations (33) and (34) imply that LLE can be calculated if a suitable model for the activity coefficient (or an equation of state) is available.

According to thermodynamics, complete miscibility is achieved if

$$\left(\frac{\partial^2 \Delta G}{\partial \varphi_1^2}\right)_{T,P} \geq 0 \tag{35}$$

If a system is miscible, then $\Delta G < 0$ (the Gibbs energy of mixing is negative), but the second derivative criterion, Equation (35) offers a more rigorous criterion for miscibility. At critical solution temperatures (onset of two–phase appearance) the following equations hold true:

$$\left(\frac{\partial^2 \Delta G}{\partial \varphi_2^2}\right) = \left(\frac{\partial^3 \Delta G}{\partial \varphi_2^3}\right) = 0 \tag{36}$$

or

$$\left(\frac{\partial \ln \alpha_1}{\partial \varphi_2}\right) = \left(\frac{\partial^2 \ln \alpha_1}{\partial \varphi_2}\right) = 0 \tag{37}$$

It should be mentioned that, due to a significant difference in size between the polymer and solvent molecules, critical solution point(s) are located in the extremely diluted polymer mole fraction area. On the molar basis, the liquid mixture is essentially a pure solvent (i.e. the mole fraction of the solvent is close to unity), and the polymer molar thermodynamic functions are, in practice, 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 coefficients can have extremely low values, depending on the nature of the system and on the polymer molar mass. It is important to point out that, since experimental data of polymer activity coefficients are not available, the magnitude of the polymer activity coefficients cannot be checked experimentally.

Figure 6a shows the variation of the Gibbs energy of mixing (ΔG^M) curve for PVAL/water system at 420 K within the liquid–liquid immiscibility region. The curve refers to equilibrium points in the UCST branch. 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 energy has a minimum, and the chemical potential of each of the components is equal in the two stable coexisting phases. If, at certain temperature, a given liquid binary mixture is immiscible, the system ΔG^M must have at least two inflection points. It is very difficult to graphically identify a change of curvature in the molar ΔG^M curve of a polymer solution (see Fig. 6a). In order to be able to detect curvatures in ΔG^M function, the numerical difference between the ΔG^M function and the straight line that connects two points on the curve (in our case it was for $x_{polym} = 0$ and $x_{polym} = 0.18$) (for practical purposes, that function is here called (ΔG^M – se) has been calculated, and the results are presented in Figure 6b. As expected, two inflection points can cle-

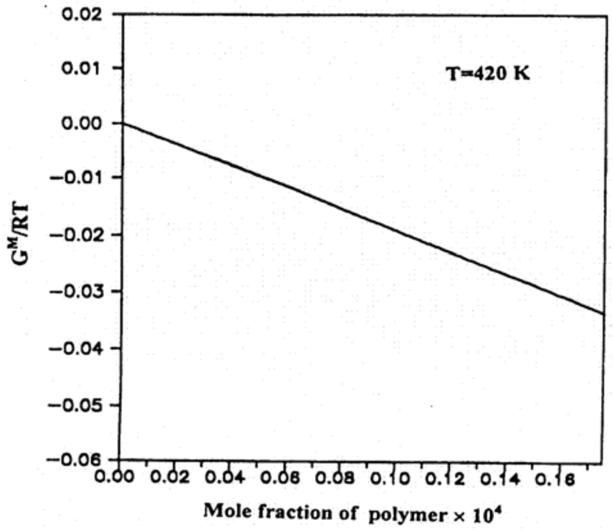

Figure 6a. Plot of $\Delta G^M/RT$ versus molar fraction of the polymer for PVAL/water binary mixture [56] at 420 K.

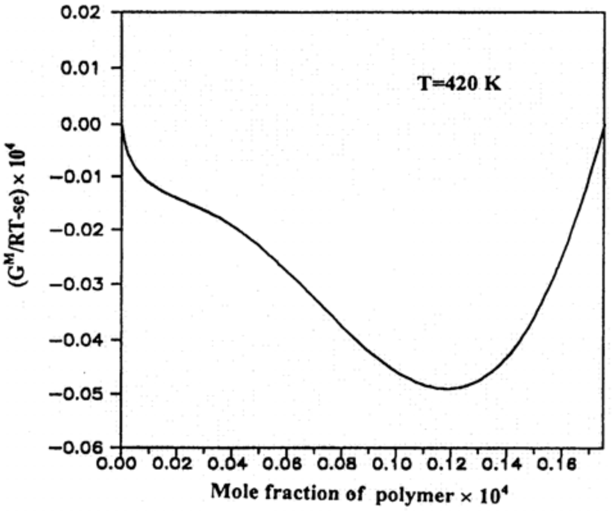

Figure 6b. Plot of ($\Delta G^M/RT$–se) versus molar fraction of the polymer for PVAL/water binary mixture [56] at 420 K.

arly be identified. The apparent linearity of the molar ΔG^M versus molar fraction of the polymer is a universal phenomenon of LLE of polymer solution.

Polymer solutions

Practical phase equilibrium calculations are performed using either activity coefficient or EOS models. In EOS models, a single equation is used to represent all the fluid phases. From the thermodynamic point of view, this is a more powerful approach than the activity coefficient approach, as a single equation provides uniform representation of the thermodynamic properties in the two-phase and one-phase regions. It is not only applicable to wide pressure and temperature ranges, including critical and supercritical conditions, but also makes it possible to calculate various properties other than those associated with phase equilibrium.

In principle, LLE compositions may be calculated using any model for Gibbs energy. Models relying on a group contribution approach, such as the UNIFAC model [14,15,29], have been applied to low molar mass compound mixtures, but they require a special set of parameters [57]. Recently, γ-model and EOS relying on a group contribution approach have been extended to LLE calculations for polymer solutions using parameters based on VLE by Kontogeorgis et al. [58] and Saraiva et al. [59], but only qualitative results were obtained. Better results were obtained by Lee and Danner [60], using the GC-LF EOS. However, experimental evidence by Vukoviå et al. [61] shows that small structural changes, such as ortho and para substitution on the aromatic ring, may induce large modifications to the miscibility maps of blends. Defining the groups as it is usually done in, for example in UNIFAC method [14,15,29] cannot take into account such effects. Models which are based on the repeating units of the polymer are more flexible and may provide correlation and predictive methods for polymer solution behavior, as a function of chain length, and for copolymer solutions dependence on copolymer composition.

Activity coefficient models

The segmental interaction UNIQUAC-FV models

The segmental interaction UNIQUAC model proposed by Bogdanić and Vidal [62-64] is derived from the Entropic-FV model [32,33], applying the approach to associate the nonideality of a polymer-solvent mixture with polymer segment-solvent interaction parameters rather than with the polymer-solvent interaction parameters or functional group interaction parameters. The groups are defined as segments, or monomer repeating units of polymers or copolymers, or as the solvent molecule. This is usual for the application of the mean field theory [65]. Such choice reduced the flexibility of the model, but it is a price one should accept for a fair predictive power. This principle has also been applied by Chen [66], but, as underlined by the author, free-volume effects were not considered, and therefore lower critical solution temperatures (LCST) could not be represented.

The activity coefficients of the segmental interaction UNIQUAC-FV model [62-64] are given by the Equation (18). Free-volume (FV) contributions are combined in a single term, the so-called entropic-FV part, described by the Equation (21). Free-volume is defined as by Kontogeorgis et al. [33].

For the calculation of the residual term, $\ln\gamma_i^{res}$, the mixture is considered as a solution of segments, and the molar fraction of each segment is calculated as:

$$X_k = \frac{\sum\limits_{i}^{ncomp} x_i \upsilon_k^{(i)}}{\sum\limits_{j}^{ncomp} \sum\limits_{m}^{nseg} x_j \upsilon_m^{(j)}} \tag{38}$$

where x_i and x_j are the mole fractions of the components *i* and *j*. The summations are extended to the total number of components, *ncomp*, and to the total number of segments, nseg. $\nu_k^{(i)}$ and $\nu_m^{(j)}$ are the numbers of segments *k* in the component *i*, and of segments *m* in the component *j*. Their values are equal to the number of repeating units for a homopolymer, and to one for the solvent. For a copolymer, the value of $\nu_k^{(i)}$ is obtained from the molar mass of the copolymer, M_i, from the molar fraction, $X_k^{(i)}$, of each copolymer segment *k*, which characterizes the copolymer composition, and from the molar mass of each segment M_k:

$$v_k^{(i)} = \frac{M_i}{\sum\limits_{m}^{nseg} X_m^{(i)} M_m} X_k^{(i)} \tag{39}$$

From the molar fractions X_k, the activity coefficients of the segments Γ_k in the mixture are calculated by applying a model of nonideality. Authors have used the residual term of the UNIQUAC model [67]. For a binary mixture the expression of $ln\,\Gamma_k$ is:

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_{m}^{nseg} \Theta_m \tau_{mk}\right) - \sum_{m}^{nseg} \frac{\Theta_m \tau_{km}}{\sum\limits_{n}^{nseg} \Theta_n \tau_{nm}}\right] \tag{40}$$

In this expression Q_k represents the surface parameters of the segments, derived from the van der Waals area, and Θ_n and Θ_m their surface fractions:

$$\Theta_m = \frac{X_m Q_m}{\sum\limits_{n}^{nseg} X_n Q_n} \tag{41}$$

The values of τ_{nm} are derived from the interaction parameters between segments, a_{nm}, by the relation:

$$\tau_{nm} = \exp\left(\frac{a_{nm}}{RT}\right) \tag{42}$$

The segmental interaction parameters are assumed to have a linear temperature dependency, which is expressed as:

$$a_{nm} = a_{nm,1} + a_{nm,2}\,(T - T_0) \tag{43}$$

where *m* and *n* denote segments in the UNIQUAC table, and T_0 is a reference temperature equal to 298.15 K.

The activity coefficients of the segments $\Gamma_k^{(i)}$ in the pure components must also be evaluated. For a solvent or a homopolymer, they are equal to one and for copolymer they are calculated using Equation (40), where the surface fractions will be obtained from the mole fractions of the segments in the pure copolymer, $X_k^{(i)}$.

Finally, the activity coefficients of the components, solvent, homopolymer or copolymer, are obtained by the relation:

$$\ln\gamma_i^{res} = \sum_k \upsilon_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(1)}\right) \tag{44}$$

It should be underlined that the term $\ln\Gamma_k^{(i)}$ in Eq. (40) takes into account the internal repulsion effect in copolymers [65,61].

The procedure requires the densities of the solvent and of the polymer at the temperature of the mixture, the van der Waals volumes for the calculation of the free volume–combinatorial contribution, and the molecular surface parameters of the segments for the application of the UNIQUAC model.

The segmental interaction parameters are presented references 62–64, together with references to data used in parameter estimations.

Pappa et al. [68] proposed a very similar segmental interaction UNIQUAC–FV model, which takes into account the pressure effect on LLE, due to the fact that pressure–dependent molar volumes are incorporated in the free–volume term. This model will not be described here, due to its great similarity to the UNIQUAC–FV model by Bogdanić and Vidal. The equations, the calculation procedure and the parameters can be found in publications by Pappa et al. [68].

The empirical method for predicting the LLE of a binary polymer system

Vetere [69,70] proposed combining the Flory–Huggins equation (empirically modified to account for free–volume effects) with the NRTL expression for energetic effects. The two NRTL parameters were correlated with the solubility parameters of components. The relative importance of the combinatorial and residual contributions was analyzed and satisfactory results (for both VLE and LLE) were obtained for some binary systems, including aqueous polymer solutions. This recent approach is under development.

Equation of state models

The GC–Flory EOS

GC–Flory EOS has been used to calculate activity coefficients in polymer–solvent mixtures for several years now. As mentioned earlier, using the parameters based on VLE, GC–Flory EOS has also been applied to predict the miscibility/immiscibility phenomena of monodisperse polymer–solvent systems. This model was shown [59] to be limited to qualitative prediction of the phase behavior of such systems. A recent adaptation of the GC–Flory EOS model for LLE calculations [71] relies on experimental LLE data parameter estimation. The prediction of the LLE phase behavior of polymer solutions with the new LLE parameter table showed a significant improvement over the ones obtained using the VLE parameter tables. The comparison of prediction accuracies showed that the model is capable of quantitatively predicting the most relevant types of phase diagrams typical of LLE of polymer solutions.

The problem of fitting the GC–Flory EOS to experimental LLE data was reduced to finding the ε_{nn} and $\Delta\varepsilon_{nm}$ parameter values that will predict LLE composition as closely as possible to the experimental values. In all examined cases the overall mean absolute deviation between the experimental and calculated LLE compositions was no more than 1.5 wt.%. The obtained ε_{mm} and ε_{mn} parameter values are listed in reference 71. It is worth noting that all these parameters were estimated only from low–molar mass pure components and mixtures thereof.

Discussion

Most polymer solutions are typically highly nonideal; i.e., both an expression for the entropy and the enthalpy of mixing need to be known. However, a few nonpolar solutions where the repeating unit of the polymer is structurally similar to the solvent (e.g., polyethylene/alcanes, polystyrene/benzene, polyvinyl acetate/ethyl acetate) can be considered to be athermal; i.e., the heat of mixing is approximately zero. These polymers and solvents have the same or very similar solubility parameters. Thus, experimental phase equilibrium data for athermal polymer solutions can help checking expressions for the entropy of mixing. For regular solutions, e.g., benzene/heptane, carbon monoxide/methane, only an expression for the heat of mixing need be developed; the entropy of mixing has the ideal value. Finally, ideal solutions, e.g., hexane/heptane, ethanol/propanol, have the ideal value for the entropy of mixing and zero enthalpy of mixing. This suggests that even the simplest nonpolar polymer solutions are nonideal due to a nonideal value of the entropy of mixing.

As it was mentioned earlier, the extension of existing VLE models to LLE, as shown by Kontogeorgis et al. [58] and Saraiva et al. [59], led only to qualitative results of LLE phase behavior. Better results were obtained using the GC–LF EOS model by Lee and Danner [60]. Models which are based on the repeating units of the polymer are more flexible, providing correlation and predictions for polymer solution behavior, as was shown by Chen [66], but, as underlined by the author, free–volume effects were not considered, and therefore LCST could not be represented.

Figures 7–10 illustrate the ability of the UNIQUAC–FV segmental interaction model [62] and the GC–Flory EOS [64] to calculate LLE for binary polymer solutions.

A detailed investigation of the results shows that LLE correlation/prediction of nonpolar, moderately polar and polar systems with strong specific interactions is possible using the UNIQUAC type models. The results obtained with the segmental interaction UNIQUAC–FV models proposed by Bogdanić and Vidal [62–64] are of the same quality as the results obtained by Pappa et al. [68]. The lower and upper critical solution temperatures as well as the closed loop diagrams for numerous systems are well correlated/predicted, using weakly temperature dependent UNIQUAC–FV parameters. Probably the main limitation is the immediate proximity of the critical point of the solvent, where the excess volume

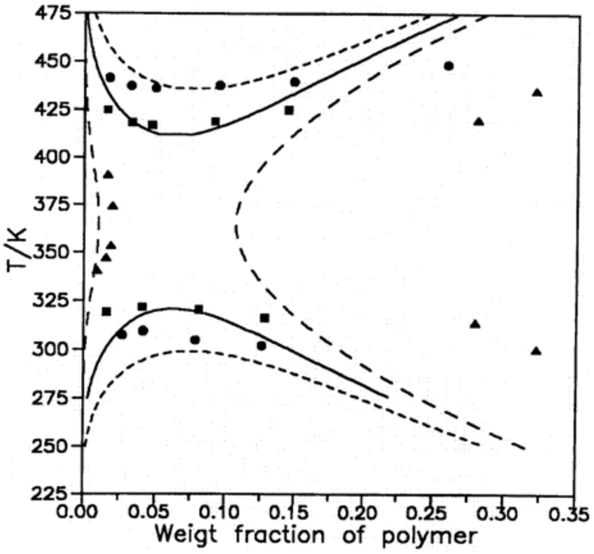

Figure 7. Correlation and prediction of LLE for PBD/1–octane system by the UNIQUAC–FV segmental interaction model [62] *(Exp. data by G. Delmas, P. Saint–Romain, Eur. Polym. J.,* ***10*** *(1974) 1133).*

■ Exp. data (M_v=65000 g/mol), —— correlation;

▲ Exp. data (M_v=135000 g/mol), — — prediction;

• Exp. data (M_w=44500 g/mol), - - - - - - prediction.

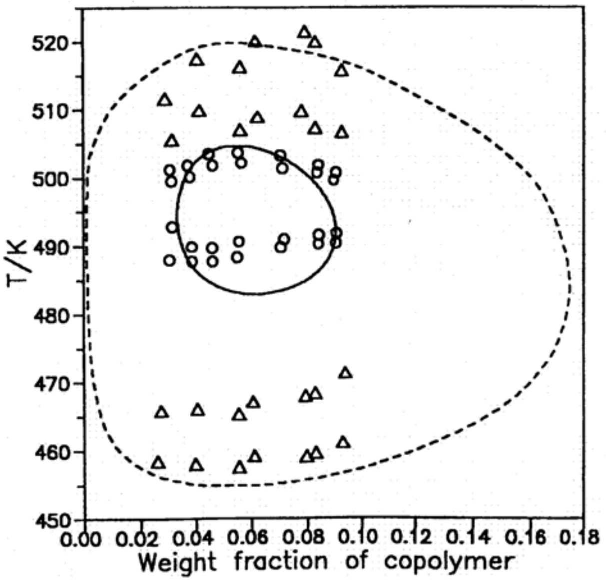

Figure 8. Correlation and prediction of LLE for poly(S–co–BMA)/MEK system by the UNIQUAC–FV segmental interaction model [62] *(Exp. data by M. Kyoumen, Y. Baba, A. Kagemoto, Macromolecules,* ***23*** *(1999)1085).*

o Exp.data [poly($S_{0.54}$–co–$BMA_{0.46}$), M_w=40000 g/mol), ——correlation;

△ Exp.data [poly($S_{0.80}$–co–$BMA_{0.20}$), M_w=250000 g/mol), - - - - - prediction.

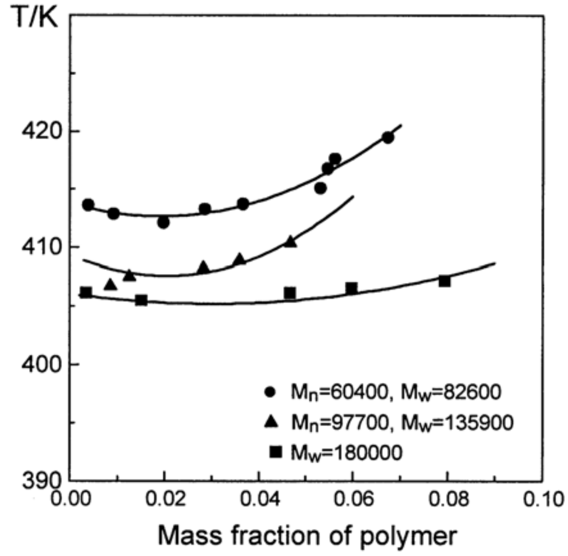

Figure 9. Coexistence curves for HDPE/n–hexane systems as predicted by GC–Flory EOS [64] *(——).*

Exp. data *(•,▲)* by Kodama, Y.; Swinton, F.L. Brit. Polym. J., **10** (1978) 191, and *(■)* by Orwol, R.A.; Flory, P.J. J. Am. Chem. Soc., **89** (1967) 6822.

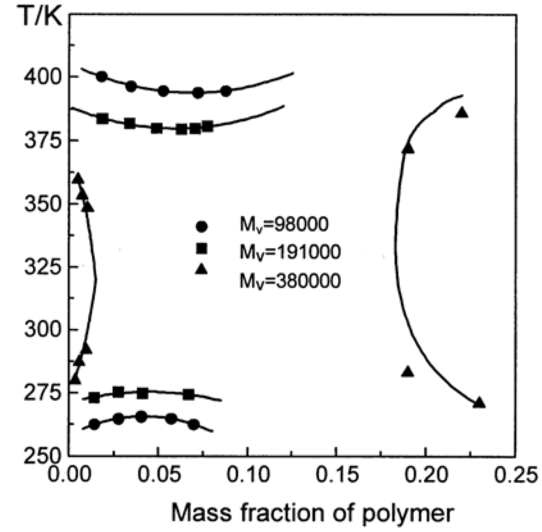

Figure 10. Coexistence curves for PIB/n–hexane systems as predicted by GC–Flory EOS [64] *(——).*

Exp. data by Delmas, G.; Saint–Romain, P. Eur. Polym. J., **10** (1974) 1133.

of the solution cannot be described. The results obtained by the GC–Flory EOS are also very good. However, the major drawback of using GC–Flory EOS is only a relatively small number of group parameters determined until now, however this recent approach is under development.

Polymer blends

Over the years, there has been a strong interest in understanding the principles governing the miscibility and phase domain formation of multicomponent polymer systems. Simple models that provide a useful framework for describing blends with controlled phase behavior have emerged, among which the Flory–Huggins equation [72,73] and the empirical Flory–Huggins χ models [74,75] have been the most popular.

It is known that miscibility in polymer blends is strongly dependent on the chain microstructure. Composition and sequence distribution in a copolymer, stereo–configuration, branching and crosslinking are structural features affecting local environments, whereas the size (molar mass) and shape of molecules (chain flexibility) have long–range effects. The effect of molecular size on miscibility is clearly described [76]; miscibility decreases with increasing molar mass. The combinatorial part in the Flory–Huggins theory [74,75] accounts for this effect.

The term miscibility has widely been used [65] to describe multicomponent polymer blends whose behavior is similar to that expected of a single–phase system. The term does not necessarily imply mixing at a segmental level, but suggests that the level of such mixing is adequate to yield macroscopic properties expected of a single–phase material. It should also be noted that mixing polymers to obtain a blend invariably involves not only thermodynamic consideration, but also the thermal and mechanical histories of the system which impact the kinetic aspects associated with the attainment of equilibrium processes. This paper discusses only the equilibrium thermodynamic aspect.

The mean–field theory

More than a decade ago, a simple mean–field theory of random copolymer blends was proposed, based on a mixture of polymer segment concept [77,65]. It was shown that using the mean–field approach, phase behavior of blends could be described by pair interactions between all segments in the blends. This theory also provided a general explanation for the effect of chemical composition on miscibility.

In studies of polymer–polymer miscibility by Amherst and Zagreb group (see for example references 61 and 78), the mean–field model [77,65] was applied. This model is reliable for correlating and describing the phase behavior of polymer blends. It has become widely used in the description of miscibility/immiscibility phenomena. It will be briefly describe here.

Based on a lattice theory, the Flory–Huggins expression for the Gibbs energy of mixing [72,73] of a mixture of two polymers can be written as:

$$\frac{\Delta G^M}{RT} = \underbrace{\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2}_{\text{combinatorial term}} + \underbrace{\chi_{\text{blend}}\,\phi_1\phi_2}_{\text{residual term}} \qquad (45)$$

where N_1 and N_2 are the number of lattice cells occupied by polymer 1 and 2, Φ_1 and Φ_2 their volume fractions calculated on the basis of lattice occupancy, and χ_{blend} is a dimensionless overall interaction parameter for the polymer–polymer system. In practice, the χ_{blend} parameter exhibits considerable variation with temperature, pressure and blend composition. The combinatorial contribution of the Equation (45) to the Gibbs energy of mixing is due to the differences in sizes of molecules, while the residual contribution is essentially due to energetic interaction.

The mean–field theory provided the evaluation of χ_{blend} parameter in a group contribution framework in terms of segmental interactions, where segments are usually defined as monomer–repeating units. This is an arbitrary assignation and implies that χ_{blend} parameters must be the function of segmental definition. In this model, a polymer molecule is assumed to consist of a given number of segments, while a polymer blend is a mixture of these segments. Further, it is assumed that each segment occupies one lattice site. The excluded volume effect is taken into account by a single–site occupancy requirement. The residual term of Equation (45) assumes that molecular segments are randomly mixed on a lattice. The model neglects free–volume contributions to the Gibbs energy of mixing and does not take into account any possible directional interactions.

For the most general case of mixtures of two random copolymers of the type $(A_{1-x}B_x)_{N1}/(C_{1-y}D_y)_{N2}$, the overall interaction parameter χ_{blend} can be expressed as a linear combination of segmental interaction parameters, χ_{ij}:

$$\begin{aligned}\chi_{\text{blend}} = {} & (1-x)\,(1-y)\,\chi_{AC} + (1-x)\,y\,\chi_{AD} + \\ & + x\,(1-y)\,\chi_{BC} + x\,y\,\chi_{BD} - x\,(1-x)\,\chi_{AB} - \\ & - y\,(1-y)\,\chi_{CD}\end{aligned} \qquad (46)$$

where the definition of the respective χ_{ij} parameters is obvious from their subscript, and copolymer compositions x and y should be expressed on the basis of lattice site occupancy.

The first four terms on the right–hand side of Equation (46) define additive intermolecular interactions between the non–bonded component monomers in the mixture of two copolymers, weighted according to the copolymer compositions, whereas the remaining two terms define the intramolecular forces between the two different monomers comprising each of the copolymers. In Equation (46), x and y should be used in terms of volume fractions, but very often mass or mole fractions are used. Furthermore, it was pointed out by Nishimoto et al. [78] and Salamons et al. [79] that in many papers in which Equation (46) has been used, authors failed to report the basic segmental units. In papers cited in references 61 and 78, the calculation employed volume fractions based on Bondi's van der Waals volumes [8] which may be considered as the best expression for the lattice occupancy.

The basic criterion for miscibility of blends is that χ_{blend} must be less than a critical value $\chi_{\text{blend}}^{\text{crit}}$, which for monodisperse polymers may be calculated on the basis of the number of lattice cells occupied [81]:

$$\chi_{\text{blend}}^{\text{crit}} = 0.5(N_1^{-0.5} + N_2^{-0.5})^2 \qquad (47)$$

where N_1 and N_2 are the number of lattice cells occupied by a molecule of polymer 1 and 2, respectively. Equation (47) may be interpreted as defining N_1 and N_2 as the degrees of polymerization or the number of repeating units of polymers, if the molar volumes of all repeating units have similar values. It turns out that this is a valid approach for many polymer systems, and that $\chi_{\text{blend}}^{\text{crit}}$ calculated from the number of repeating units is quite satisfactory in many cases. However, it is obvious that segmental interaction parameters depend on $\chi_{\text{blend}}^{\text{crit}}$ and on the van der Waals volumes used.

The boundary between miscibility and immiscibility domains for copolymer–copolymer system is described by a function expressed in terms of x and y, such that:

$$f(x,y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} = 0 \qquad (48)$$

The mean–filed approximation is fairly satisfactory when the mixture consists only of long chain molecules. The most noteworthy conclusion from this analysis is that a net exothermic heat of mixing promoting miscibility can be attained even when none of the individual interaction parameters are negative, i.e., favoring miscibility, provided that one or both constituents are copolymers. This means that a favorable specific interaction between the two component macromolecules may not be an absolute requirement for their miscibility. It is of course not suggested that such specific interactions do not exists in certain cases, but miscibility, as defined here, can occur in many cases where such a strong interaction mechanism is absent.

In many of studies cited in reference 61 and 78, the mean–field model was comprehensively tested and proved to provide a very useful framework for describing phase behavior of polymer blends, and no attempt is made here to discuss the results in detail. Figures 11 and 12 are used only to illustrate the prediction of miscibility domains in comparison with experimental data for binary polymer blends of poly(S–co–oClS) and poly(S–co–pClS) with SPPO copolymers using the mean–field model [78].

Experimental evidence from the figures above indicates that small structural changes, such as ortho and para substitution on the aromatic ring may largely modify miscibility maps of polymer blends, yet the mean–field model can still give a good description of the phase behavior of such systems.

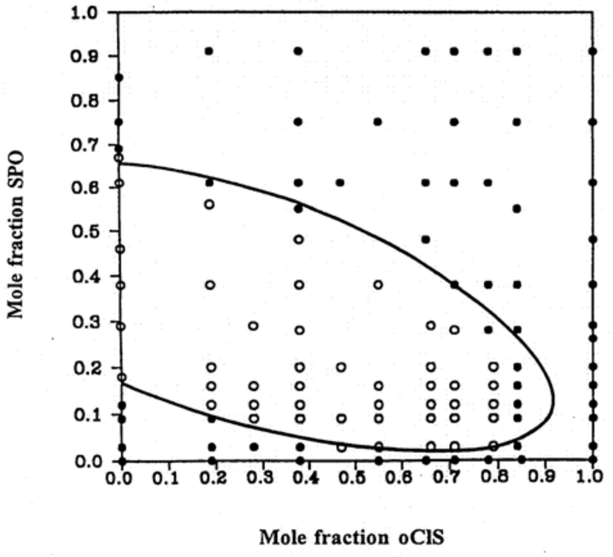

Figure 11. Miscibility of 50/50 wt% blends of poly(S–co–pClS) and SPPO copolymers. (o) one phase; (•) two phases; (—–) predicted miscibility/immiscibility boundary [78]. (Exp. data by R. Vuković, G. Bogdanić et al., Thermochim. Acta, **306** (1997) 135).

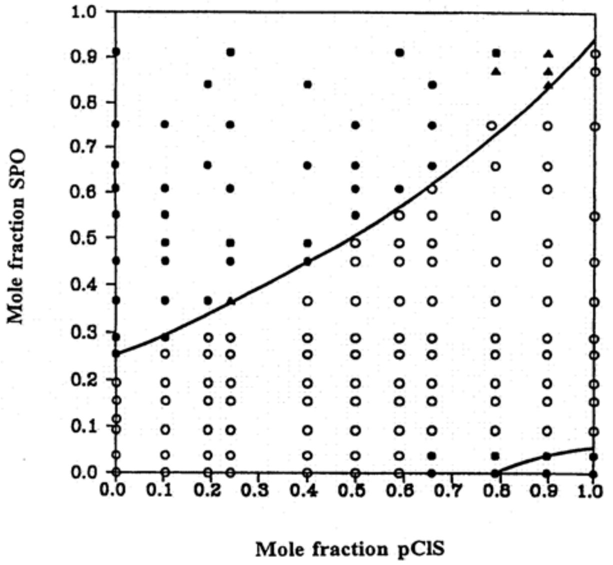

Figure 12. Miscibility of 50/50 wt% blends of poly(S–co–pClS) and SPPO copolymers. (o) one phase; (•) two phases; (▲) intermediate situation; (—–) predicted miscibility/immiscibility boundary [78] (Exp. data by R. Vuković, G. Bogdanić et al., Thermochim. Acta, **306** (1997) 135).

The Coleman–Graf–Painter model

After the mean–field model, which does not take into account specific interaction, worth mentioning are the Coleman–Graf–Painter model [82] and practical guidelines for predicting and designing miscible polymer mixtures, taking into account specific interactions. This model can be recommended for semiquantitative predictions in polymer blends. This paper has no intention to review this model. For a thorough description of this model the reader is referred to reference 82.

The segmental interaction UNIQUAC–FV model

The segmental interaction UNIQUAC–FV model described earlier [62] has also been successfully applied in correlating phase behavior of polymer blends, as demonstrated by Figures 13–14.

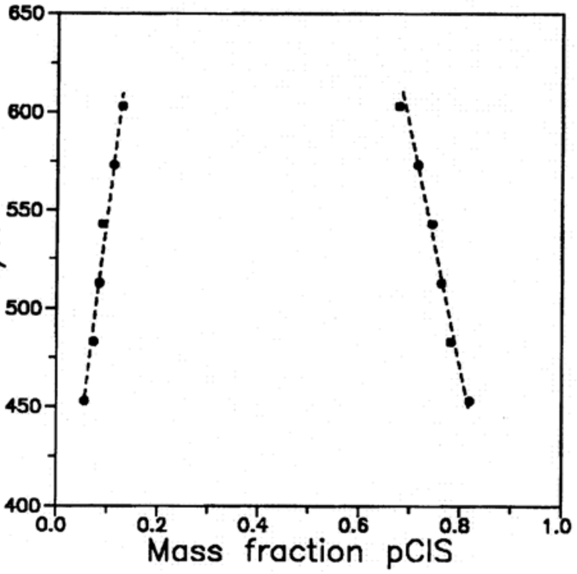

Figure 13. Miscibility behavior of homopolymer/copolymer PPO/poly(oFS–co–pClS) system as correlated (-------) by segmental interaction UNIQUAC–FV model (Exp. data by R. Vuković et al., J. Appl. Polym. Sci., **30** (1985) 317).

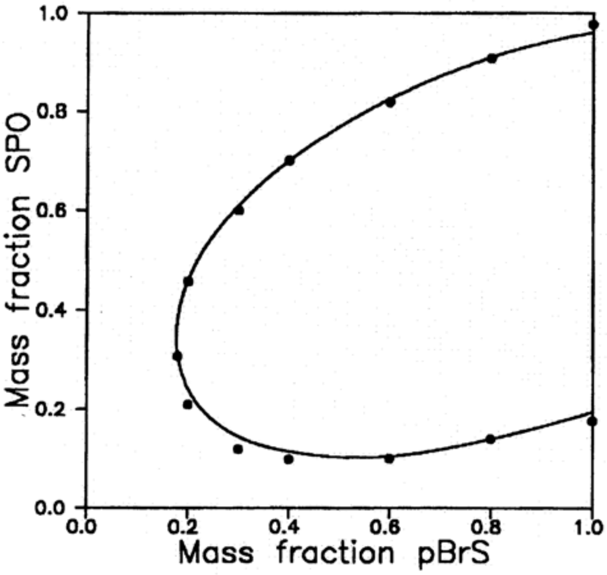

Figure 14. Miscibility behavior of copolymer/copolymer SPPO/poly(oBrS–co–pBrS) system as correlated (——) by segmental interaction UNIQUAC–FV model (Exp. data by R. Vuković, G. Bogdanić et al., J. Appl. Polym. Sci., **195** (1992) 351).

It is encouraging that the model can successfully predict LLE for polymer blends, which will be shown in part 3 of the series of papers dealing with the segmental interaction UNIQUAC–FV model.

THERMODYNAMIC DATABASES FOR POLYMERS

Extensive databases for thermodynamic polymer properties are now available, and a significant amount of experimental data has been reported in literature. Unfortunately, there is an overall paucity of available information on the thermodynamic properties of polymers. The type of data for different polymer systems varies considerably in quantity, quality and in the nature of experimental information provided, which makes tabulation of the data difficult. The key information which is usually unavailable is the distribution of polymer molar mass (polydispersity significantly affect LLE calculations).

Pure polymer densities

Experimental data for a number of polymers are correlated using the Tait equation and are summarized in the DIPPR Polymer Project [12]. Recently, an extensive compilation of polymer densities using the Tait equation has been presented by Rodgers [13].

Polymer and solvent solubility parameters

The most extensive compilation is provided in the recent book by Hansen [24] and in the handbooks by Barton [83,84].

Polymer–solvent VLE

Vapor–liquid data, both at intermediate concentrations and at infinite dilution of the solvent, are available in two extensive databases: DECHEMA and DIPPR Polymer Project [12,85]. These databases are also available in electronic form. The data are restricted to single solvent systems and often cover various temperatures. A more recent compilation of VLE has been published by Wohlfarth [86].

Polymer–solvent LLE

Many data are stored in the two above–mentioned databases [12,85]. In DECHEMA database, data are only cited as LCST/UCST temperatures and restricted to single solvents. The DIPPR project provides full binodal curves. In addition, LLE data are reported for a few systems (mostly with polystyrene) with two solvents.

It could be concluded that commonly available literature lacks systematic reports on polymer–mixed solvents data (VLE or LLE), especially in the form of full–phase equilibrium measurements. Data are often reported simply as "soluble/nonsoluble" or as "theta temperatures" (critical solution temperature at infinite polymer molar mass). Original papers are sometimes difficult to interpret because data are presented in graphs and other forms with problematic conversion.

CONCLUSION

Why have so many different models been developed for polymer systems? The state–of–the–art can be easily considered if taking into account that polymer solutions and blends are complicated systems with frequent occurrence of LLE in many forms (UCST, LCST, closed loop), significant effect of temperature and polymer molar mass in phase equilibrium, free–volume effects, and other factors causing these difficulties.

The choice of a suitable model depends on the actual problem and demand, but especially on the type of mixture (solution or blend, binary or multicomponent), type of phase equilibrium (VLE, LLE, SLE), temperature, pressure, concentration, and calculation (accuracy, speed, yes/no answer, or complete design). This paper discusses the performance of various models and their range of application. Bokis et al. [87] in their recent review paper list polymer models currently supplied in the ASPEN–Plus Process Simulator.

The following can be concluded:

Many databases (some available in electronic form) and reliable group contribution methods are available for estimating many pure polymer properties and phase equilibrium of polymer solutions such as densities, solubility parameters, glass and melting temperatures, and solvent activity coefficients.

Simple group contribution models based on UNIFAC, containing corrections for the FV effects, as well as group contribution EOS satisfactorily predict solvent activities and VLE for binary and ternary polymer solutions.

The combination of a simple FV expression such as that employed in the Entropic–FV model and a local composition energetic term such as that of UNIQUAC seems to be a very promising tool for both VLE and LLE in polymer solutions. It should be expected that such tools may find a widespread practical use in the future.

Some of the future challenges in the area of polymer thermodynamics should involve the correlation and prediction of phase equilibrium of solutions containing polar and hydrogen bonding solvents and polymers, more emphasis on multicomponent systems including both mixed solvents and blend–solvent systems, more emphasis on condensed phases especially LLE and SLE as well as water–soluble polymer systems, emphasis on high–pressure systems involving both typical nonpolar and polar macromolecules, development of new polymeric and "special materials", proper account for the effects of crystallinity and cross–linking with special attention to swelling phenomena, and closer collaboration between academic institutions and the polymer industries in order to further advancements in the area of polymer thermodynamics.

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IZVOD

PRIMJENA METODA DOPRINOSA ATOMNIH SKUPINA ZA PROCJENU SVOJSTAVA POLIMERNIH SUSTAVA

(Naučni rad)

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Posljednjih se godina intenzivno radi na izučavanju principa faznog ponašanja polimernih sustava i razvijanju termodinamičkih modela koji mogu dati kvantitativne informacije o svojstvima polimernih materijala ili o faznoj ravnoteži polimernih otopina/mješavina. Modelima koji se temelje na metodama molekulske simulacije može se vrlo dobro opisati fazno ponašanje kompleksnih spojeva, otopina ili mješavina, u kojima su izraženi različiti tipovi interakcija između kemijski različitih atomskih skupina ili molekulskih segmenata. Međutim, takovi su modeli u principu vrlo složeni, s velikim brojem parametara, a zahtijevaju i veliki broj eksperimentalnih podataka.

U ovom radu prikazani su novi, takozvani "inženjerski modeli". Svi se temelje na metodama doprinosa atomskih skupina ili segmenata molekula. Opisivanje faznog ponašanja polimernih sustava primjenom bilo kojeg modela svodi se na pronalaženje pogodnog izraza za Gibbsovu energiju miješanja, ΔG^M, koji povezuje termodinamička svojstva čistih tvari sa sastavom mogućih faza, uzimajući u obzir neidealnost svih faza u ravnoteži. Na nizu je primjera pokazano da se, poznavajući parametre relativno malog broja funkcionalnih skupina, mogu predvidjeti svojstva velikog broja kompleksnih kemijskih spojeva ili smjese spojeva (otopine/mješavine). Ukazano je i na probleme koji se susreću pri proračunima fazne ravnoteže, a posljedica su ekscesnih svojstava otopina/mješavina. Analizirane su mogućnosti novih termodinamičkih modela za predviđanje faznog ponašanja polimernih sustava i prikazani najnoviji rezultati istraživanja.

Ključne riječi: Metode doprinosa atomskih skupina • Korelacija • Predviđanje • Ravnoteža kapljevina–para (VLE) • Ravnoteža kapljevina–kapljevina (LLE) • Svojstava polimernih sustava •

Key words: Group contribution methods (GC) • Correlation • Estimation • Vapor–liquid equilibrium (VLE) • Liquid–liquid equilibrium (LLE) • Polymeric system properties •