

A Comparison of Methods for the Estimation of Polymer/Monomer Interaction Parameters: The Polystyrene/*n*-Butyl Methacrylate System

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SYNOPSIS

To measure the polymer/monomer interaction parameter as a function of composition, a set of partially cross-linked synthetic latices has been produced by batch and semicontinuous emulsion polymerization. The degrees of cross-linking have been measured by DMA and also predicted by computer simulation based on kinetic data. With equilibrium monomer swelling experiments achieved on films made from these polymers, two curves of the interaction parameter vs. the polymer fraction have been computed. These curves compare favorably with a theoretical model based on a Unifac procedure for the estimation of monomer activity. Two different data bases, liquid-liquid and liquid-vapor equilibria, have been used in the Unifac model. For the polystyrene/*n*-butyl methacrylate system, a linear relationship found between the interaction parameter and composition is both predicted and measured experimentally. In all cases, this interaction parameter is found to increase with polymer concentration. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Knowledge of the compositional dependence of the polymer-monomer interaction parameter is required in a variety of applications, especially those involved with equilibrium phenomena in reacting systems. Examples may be found in determining monomer partitioning in phase-separating polymerizations (e.g., HIPS, ABS, rubber-modified polyesters) and, much to our interest, in assessing monomer compositions in swollen polymer latex particles. For all the discussions of interaction parameters (χ 's) in the literature and in handbooks, there are relatively few reports on the compositional dependence of χ values involving polymer-monomer pairs, especially when the monomer is not the repeating unit within the polymer. Although one might anticipate that such χ values could be closely approximated by finding data for the polymer interaction with carefully selected solvent analogs to the monomer, our

experience is that this is difficult for vinyl monomers due to the influence of unsaturation within the molecule. Thus, we have chosen to work directly with the polystyrene/*n*-butyl methacrylate system of interest to us in our work on polymer latex morphology control.

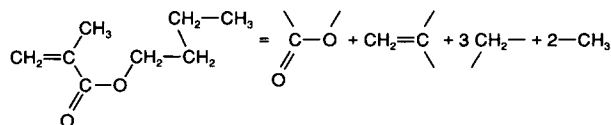
The compositional dependence of the polymer-solvent χ is well known to vary in different ways depending upon the "goodness" of the solvent for the polymer. In some cases, the χ value does not vary appreciably with composition, as in the polyisobutylene/cyclohexane system.¹ In most instances, however, the χ value changes with composition, usually increasing with polymer concentration. This is characteristic of a "poor" solvent for the polymer. The objective of the present study was first to apply the Unifac method² of predicting monomer activity within the polymer solution and, in turn, to predict the interaction parameter and its compositional dependence. Second, these predictions were to be contrasted with experimental determinations of χ based upon equilibrium swelling of cross-linked polystyrene (PS) by *n*-butyl methacrylate (nBuMA) monomer. Cross-link densities

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were predicted from a computer simulation using the kinetic parameters of the polymer synthesis and from measurements of the polymer shear modulus via dynamic mechanical analysis (DMA). Figure 1 represents the manner in which the different methods were used to compute the interaction parameters.

UNIFAC METHOD

Unifac means “*UNI*versal *F*unctional Group *A*ctivity *C*oefficient.” It is a highly powerful method that allows the prediction of activities of any component in any mixture, with no experimental data. The applications of such predictions are numerous and useful.²⁻¹⁰ Here, this method is applied to polymer solutions, knowing that this field is the less accurate one for this theory.¹¹ To correlate thermodynamic properties, it can be appropriate to consider a molecule as an association of functional groups. For example, BuMA can be decomposed into four groups:



Polystyrene is decomposed using the same idea. It is to be noted that the degree of polymerization does not affect this decomposition procedure, because the

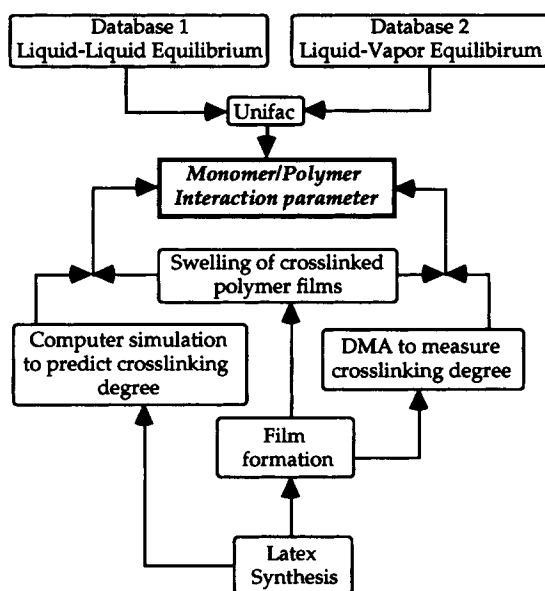
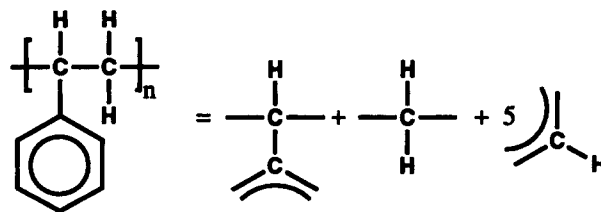


Figure 1 Flow chart representing the relation between the different methods.

idea of the Unifac is to break the molecules in small functional groups:



The properties of the groups are of two kinds: The first ones are references for the group (molecular weight, volume, surface . . .) and the second ones are interaction parameters and are coupled (group 1/group 2). Interaction parameters have been computed by several authors¹²⁻¹⁴ through equilibrium measurements. The first database compiled was based on vapor-liquid-equilibrium¹² (VLE) and is the one widely used for many applications. The second one is based on liquid-liquid-equilibrium¹³ (LLE) and seems more appropriate to polymer solutions, but the number of different groups referenced is smaller and not all groups are in the second database. Application of Unifac involves numerous calculations, and because of their complexity, the equations are in the Appendix.

The relation between the activity of the monomer a_M^{Unifac} in the polymer solution and the interaction parameter is derived from the Flory-Huggins theory¹⁵ and reads

$$\chi_{M/P} = \frac{\ln a_M^{\text{Unifac}} - \ln \Phi_M + (1 + \Phi_M)(1 - m)}{(1 - \Phi_M)^2} \quad (1)$$

with $\chi_{M/P}$ the monomer/polymer interaction parameter and Φ_M the monomer volume fraction in the polymer system. All notations are listed at the end of the article. Applications to the PS/BuMA system with the two databases (VLE and LLE) are presented in Figure 2.

POLYMER SWELLING METHOD

Theory of Swelling

Homopolystyrene is completely soluble in nBuMA and therefore polystyrene was cross-linked with a bifunctional monomer to reduce its swelling in the monomer. Ethylene glycol dimethacrylate (EGDMA) was chosen for this purpose because the second double bond of this monomer has a reactivity

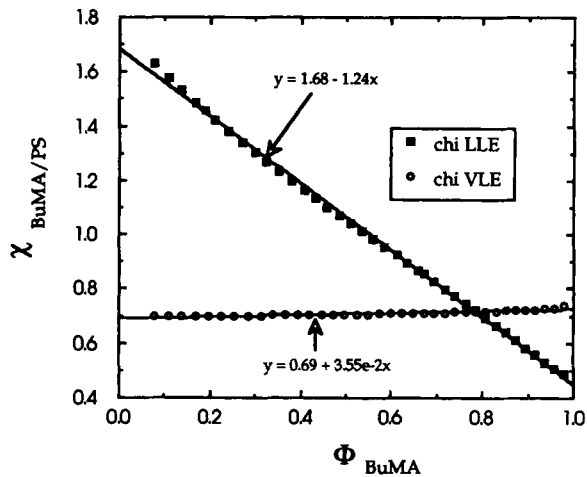


Figure 2 Dependence of the interaction parameter BuMA/PS on the volume fraction of BuMA obtained by Unifac with two different databases (LLE and VLE).

similar to the first double bond. In this way, the rapid rise of cross-linking that one often sees at the end of the polymerization is minimized. A variation of the ratio EGDMA/styrene changes the degree of cross-linking and the swelling capacity of the copolymer. The ratio EGDMA/styrene was kept low to minimize the effect of the presence of EGDMA and to be able to make the assumption that this effect is negligible on the value of χ .

To calculate χ , the following equations have been applied: The chemical potential of a monomer in a cross-linked polymer μ_M^{PP} can be written as^{15,16}

$$\begin{aligned} \mu_M^{PP} = & \mu_M^0 + RT[\text{Ln } \Phi_M^{\text{sat}} + (1 - m)(1 - \Phi_M^{\text{sat}}) \\ & + \chi_{M/P}(1 - \Phi_M^{\text{sat}})^2] + \frac{RT}{L_{\text{ret}}} [(1 - \Phi_M^{\text{sat}})^{1/3} \\ & - (1 - \Phi_M^{\text{sat}})/2] \quad (2) \end{aligned}$$

where the last term accounts for the elastic contribution to the chemical potential. L_{ret} is the distance in monomeric units between two cross-links; T is the temperature in Kelvin. When this cross-linked polymer is swollen to saturation, the monomer is in equilibrium between two phases: the polymer phase and the pure monomer (taken as the reference):

$$[\mu_M^{PP}]^{\text{sat}} = \mu_M^0 = 0 \quad (3)$$

By solving (2) for $\chi_{M/P}$ at saturation, the final equation is

$$\chi_{M/P} = - \frac{\text{Ln } \Phi_M^{\text{sat}} + (1 - m)(1 - \Phi_M^{\text{sat}}) + [(1 - \Phi_M^{\text{sat}})^{1/3} - (1 - \Phi_M^{\text{sat}})/2]/L_{\text{ret}}}{(1 - \Phi_M^{\text{sat}})^2} \quad (4)$$

To obtain the dependence of $\chi_{M/P}$ on Φ_m , one needs to determine L_{ret} and (Φ_M^{sat}) of different cross-linked polystyrene.

Polymer Synthesis

All cross-linked polymers were synthesized by emulsion polymerization, with sodium dodecyl sulfate (SDS) as surfactant and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) as initiator. The emulsion polymerizations were carried out at 70°C using a 1 L jacketed reactor and syringe pumps for the semicontinuous process. Styrene and EGDMA (Aldrich) were freshly vacuum-distilled and stored at -18°C before use. SDS, $\text{K}_2\text{S}_2\text{O}_8$ (Aldrich) and NaHCO_3 (Fluka) were used as received, with no further purification. To remove oxygen from the DDI water, nitrogen was bubbled in the water (in the reactor) for 1 h before the beginning of the polymerization. During the reaction, latex samples were taken from the reactor and quenched by the addition of hydroquinone (Fluka). These samples were analyzed (solid content and size by light scattering) to provide polymerization kinetic data. Table I presents all the recipes used in this synthesis.

In the four first copolymers in Table I, the entire amount of styrene was added before the beginning of the polymerization (batch) but the cross-linker (EGDMA) was added semicontinuously. For the last four copolymers, both styrene and EGDMA were added semicontinuously with an initial small charge.

All the latices displayed a relatively constant number of particles from the beginning to the end of the polymerization and conversion curves are similar for each process family. Glass transition temperatures were determined by differential scanning calorimetry (DSC) and sizes by dynamic light scattering and dynamic centrifugation of particles (DCP). All samples were found to be nearly monodisperse in size distribution. The size differences between the four first latices and the last four are due to the process (initial ratio of monomer/water). These measurements are summarized in Table II.

Film Formation and Swelling

The monomer fraction at saturation Φ_{BuMA} was determined by the following method: The latex was

Table I Recipes Used to Prepare Cross-linked Polymer by Emulsion Polymerization

	EP1	EP2	EP3	EP4	EP5	EP6	EP7	EP8
H ₂ O (g)	941.94	942.77	945.1	946.7	947.8	944.5	949	939.79
SDS (g)	0.9545	0.9497	0.951	0.9526	0.9548	0.9583	0.9541	0.9532
NaHCO ₃ (g)	0.7621	0.7643	0.7589	0.7606	0.7615	0.7593	0.7611	0.7586
K ₂ S ₂ O ₈ (g)	0.7598	0.7600	0.7619	0.7653	0.7607	0.7599	0.7600	0.7597
Styrene								
Total (g)	89.91	90.45	90.13	89.91	81.81	81.81	81.81	83.63
First (g)	89.91	90.45	90.13	89.91	5.45	5.45	5.45	6.97
Speed (g/h)	0	0	0	0	32.72	32.72	32.72	41.81
Duration (h)	0	0	0	0	2.33	2.33	2.33	1.83
EGDMA								
Total (g)	1.72	3.15	5.25	7.87	5.25	2.63	1.31	4
First (g)	0	0	0	0	0.35	0.17	0.09	0.33
Speed (g/h)	1.57	1.05	2.1	3.15	2.1	1.05	0.525	2
Duration (h)	1.09	3	2.5	2.5	2.33	2.33	2.33	1.83
Ratio EGDMA/styrene (%)	1.91	3.48	5.82	8.76	6.42	3.21	1.60	4.78
Ending time (h)	6	6	6	6	5	5	5	5

dried at 110°C and turned into films by a hydraulic press at 170°C under 50 atm for 2 min. Then, the films were swollen at room temperature for 18 h by BuMA and Φ_{BuMA} was measured by the weight difference on the film.

DYNAMIC MECHANICAL ANALYSIS (DMA)

The relation between the sinusoidal strain $\gamma^* = \gamma_0 \times \exp(j\omega t)$ of a polymer and the sinusoidal shear stress $\sigma^* = \sigma_0 \exp[j(\omega t + \delta)]$ can be expressed by a complex function

$$G^* = \frac{\sigma^*}{\gamma^*} = G' + jG'' = \frac{\sigma_0}{\gamma_0} \exp(j\delta)$$

When G' is plotted vs. the frequency of the stress ω (Fig. 3), one finds a plateau between the glass transition area and the flow area called the rubbery stage.¹⁷⁻¹⁹ The width of this plateau increases with the molecular weight and decreases with the polydispersity. The effect of cross-linking on this plateau is very strong and its position is conversely proportional to the cross-link distance by the relation¹²

$$L_{\text{ret}} = \frac{\rho RT}{M_M G_N^0} \quad (5)$$

where ρ is the polymer density; M_M , the monomer molecular weight; and G_N^0 , the shear modulus of the plateau.

To apply this simple relation, two assumptions are made:

Table II Characterization of the Cross-linked Latices

	EP1	EP2	EP3	EP4	EP5	EP6	EP7	EP8
T_g (°C)	106.6	109.6	111.4	117	115.5	106.7	102.5	106.2
Size (nm)	267	219	258	251	161		143	
Solid content (wt %)	8.7	9	8.9	8.5	8.7	7.9	7.1	6.1
Φ_{BuMA}	0.78	0.75	0.72	0.66	0.7	0.78	0.82	
L_{ret} DMA	290	435	240	245	140	726	2186	143
L_{ret} simulation	460	260	180	100	150	280	500	220
χ_{DMA}	0.55	0.58	0.59	0.63	0.59	0.57	0.56	
$\chi_{\text{simulation}}$	0.57	0.57	0.58	0.60	0.59	0.55	0.54	

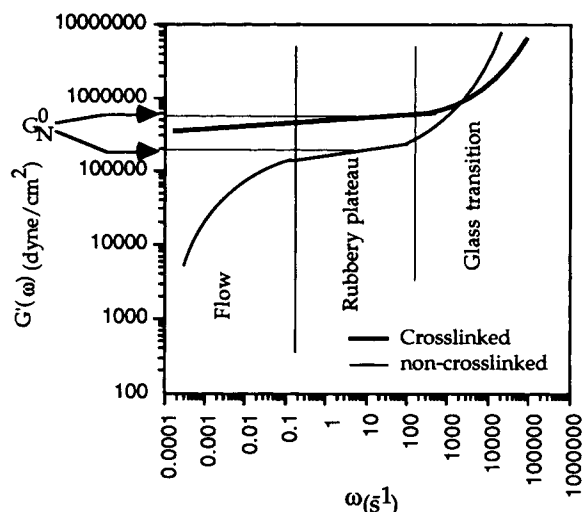


Figure 3 General DMA spectrum showing the rubbery plateau on a cross-linked and on an uncross-linked polymer.

1. All cross-links are chemical ones, meaning that the physical cross-links (i.e., entanglements) are not taken into account.
2. The under rubbery plateau is the same as the rubbery plateau for a cross-linked polymer.

The DMA samples have been prepared by the following method: The latex was vacuum-dried under 0.021 atm at 40°C, then the powder was compacted in a small disc under 0.001 atm vacuum and 5000 psi mechanical pressure at room temperature.

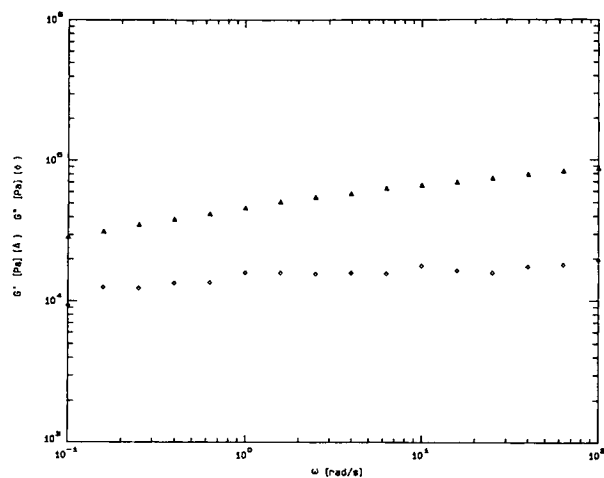


Figure 4 DMA of sample EP9 at 180°C. Disc thickness was 1.8 mm.

Then, the polymer was melted in the DMA instrument itself at 250°C.

The DMA tests were run at 180°C (Fig. 4) and 250°C (Fig. 5) in a range of frequency from 10^{-1} to 10^2 rad/s. The distance between cross-links vs. the ratio EGDMA/styrene used in the synthesis is presented in Figure 6.

COMPUTER SIMULATION

A computer simulation that predicts cross-linking density as a function of polymer conversion during reaction was developed by Muller-Mathey and Guillot,^{19,20} initially for the polystyrene/polybutadiene case. All simulations predict a wide plateau in the conversion range from 20 to 80%. The value of this plateau is assumed to be representative of the whole polymer and is taken as an average value.

Four main assumptions were used in the simulation model:

1. All double bonds have the same reactivity.
2. Each double bond acts independently of the others.
3. There is no inside cross-linking on a terminated macromolecule.
4. The termination reaction is by disproportionation and the coupling reaction is neglected.

The predicted average distances between cross-links for the whole polymers are shown in Figure 6 as a function of the ratio EGDMA/styrene used in the synthesis. The agreement of L_{ret} obtained by DMA and simulation is reasonable, considering the precision of the DMA measurements and the diversity of the samples.

DISCUSSION

Application of eq. (4) to obtain the dependencies of χ on Φ_{BuMA} with L_{ret} obtained by DMA experiments and by computer simulation gave very similar results (Fig. 7). It is interesting to note that the dependency of χ on Φ is linear over the region studied. The Unifac model also predicts a linear dependence, but the slopes obtained with the two databases are very different and of opposite sign. This is apparently due to the low capacity of Unifac to predict polar-aro-

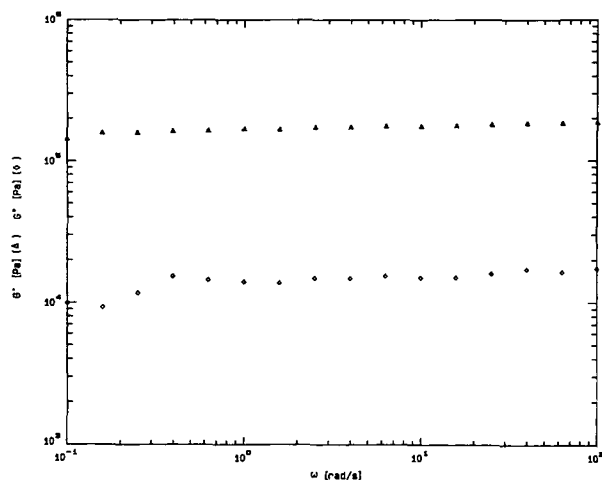


Figure 5 DMA of sample EP6 at 250°C. Disc thickness was 1.07 mm.

matic interactions. Following suggestions made by Price and Ashworth,³ the straight line obtained from Unifac can be shifted to go through one experimental point. Because of the inability to decide which database is better in this application, a slope resulting from the average of the two predictions has been used (wide line in Fig. 8). Considering that the distance between cross-links is difficult to obtain, a very lightly cross-linked polymer can be synthesized (1–2% of cross-linker) in order to neglect the contribution of the elastic term to the interaction parameter in eq. (4). Then, only one swelling experiment needs to be run. This idea applied to polymer EP7

gives $\chi = 0.57$ for $\Phi_{\text{BuMA}} = 0.82$. The line going through this point, with its slope coming from the average of the Unifac predictions, gives reasonably good agreement with the two experimental lines (Fig. 8). For this PS/BuMA system, we suggest that the linear relation derived from DMA data analysis (i.e., $\chi = 0.90 - 0.43 \Phi_{\text{BuMA}}$) be used to describe the variation in χ with monomer concentration.

CONCLUDING REMARKS

The polymer–monomer interaction parameter for the PS–BuMA system has been predicted to be linearly dependent upon polymer concentration over the entire range of compositions. The Unifac method yielded different, but linear results depending upon which database was used for the calculations. It would thus appear that the compilation of a new database from polymer–solvent interactions would be a useful advancement. Experimentally derived values of the interaction parameter also showed a linear dependence over the range of compositions achieved from monomer swollen, cross-linked polymer films. All the methods used to obtain the compositional dependence of the interaction parameter resulted in its value increasing with polymer concentration, indicating that *n*-BuMA is a “poor” solvent for polystyrene. For this polymer–monomer system, one obtains a fair approximation to the experimentally derived compositional dependency of

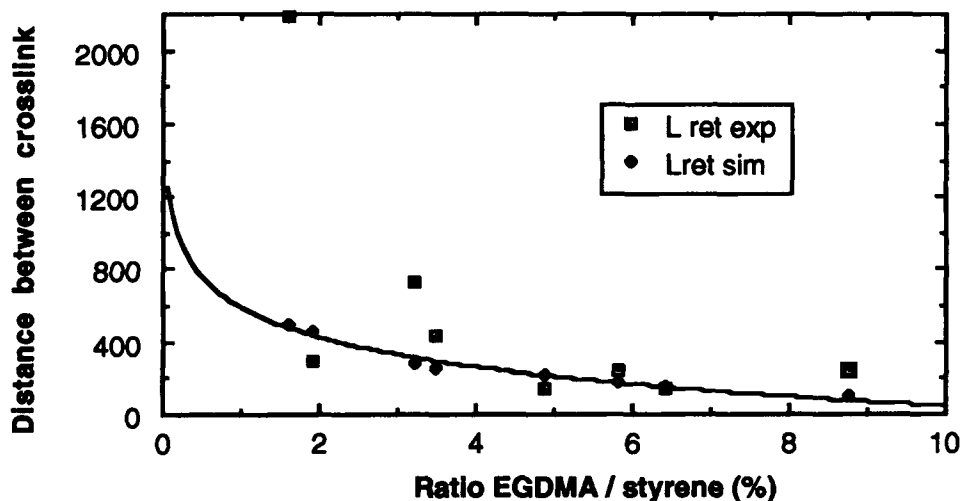


Figure 6 Distance between cross-links obtained by DMA (squares) and by simulation (diamond) vs. the ratio cross-linker/styrene.

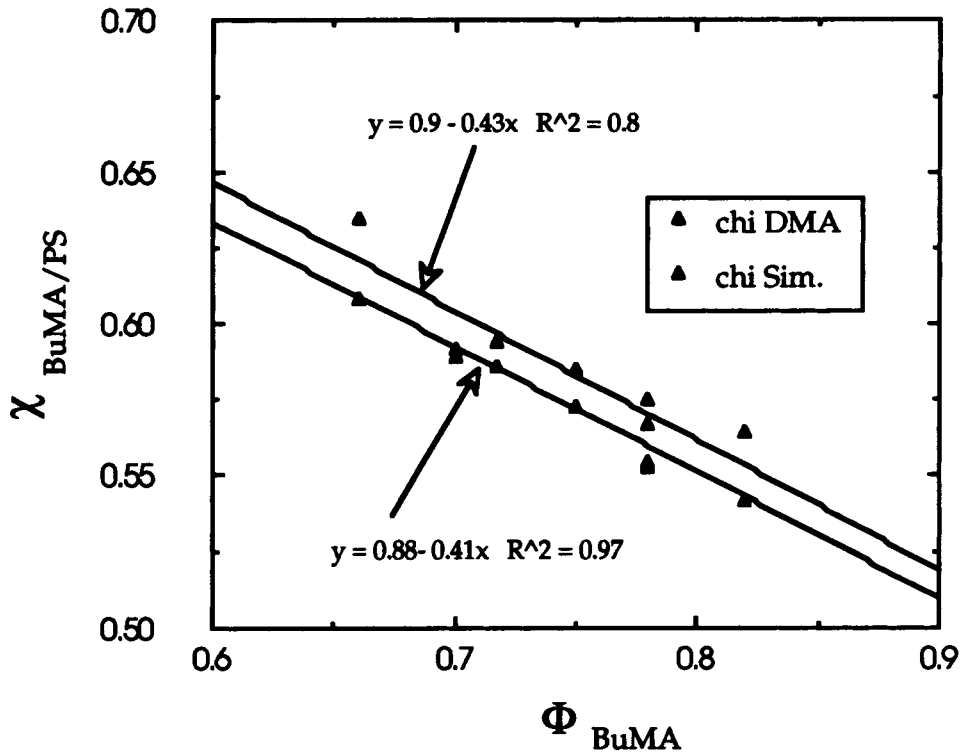


Figure 7 Comparison of the interaction parameter BuMA/PS obtained by swelling experiment when the distance between cross-links is determined by DMA (close triangles) or by computer simulation (open triangles).

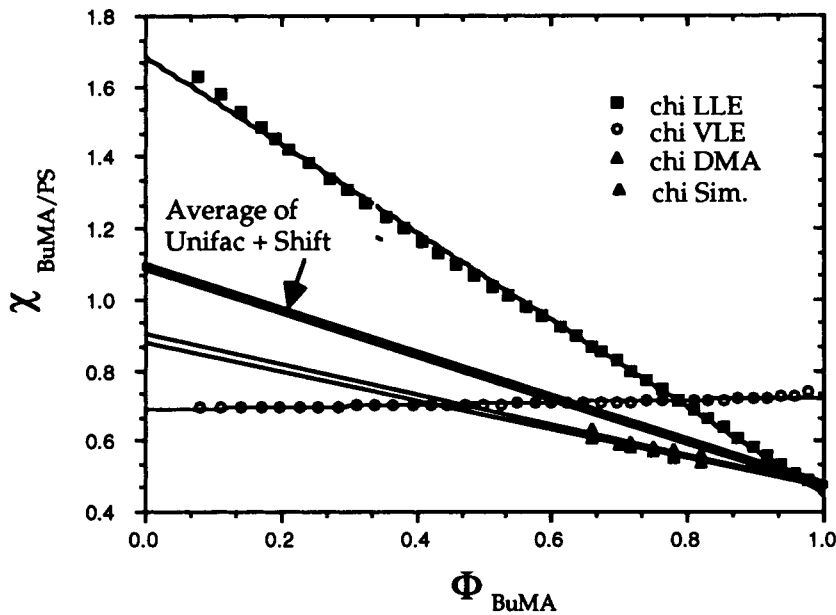


Figure 8 Interaction parameter BuMA/PS as a function of the BuMA fraction Φ_{BuMA} . Open triangles are points where L_{ret} was obtained by simulation. Closed triangles are points where L_{ret} was obtained by DMA. Circles are points obtained with a UNIFAC model using a vapor-liquid equilibrium database. Closed squares are points obtained with a UNIFAC model using a liquid-liquid equilibrium database. Wide line represents the suggested method³ (“Unifac + one point”) using the average slope of the two Unifac curves.

χ by averaging the Unifac predictions from the two available databases. Closer agreement with the experimental values can be achieved by using the average slope of the Unifac predictions and forcing the curve through a single data point.

ABBREVIATIONS AND SYMBOLS

G^*	complex shear modulus
G'	shear storage modulus
G''	shear loss modulus
G_N^0	shear modulus of the rubbery plateau
L_{ret}	distance in monomeric units between two cross-links
m	molar volume ratio between monomer and polymer
M_M	monomer molecular weight
R	perfect gas constant
T	temperature (K)
γ^*	complex strain
γ_0	maximum amplitude of the strain
δ	loss angle
σ^*	complex stress
σ_0	maximum amplitude of the stress
Φ_M	monomer volume fraction in the polymer particles
Φ_M^{sat}	monomer volume fraction in the polymer particles at saturation
μ_M^{PP}	monomer chemical potential in the polymer particles
μ_M^0	monomer chemical potential in its pure phase—taken as reference
ρ	polymer density
$\chi_{M/P}$	monomer/polymer interaction parameter
ω	frequency of the stress

APPENDIX

It is very difficult to find all the equations that constitute the Unifac model in one place, because authors use different conventions and modify the basic equations and there are errors in the final publications. Here follows a succession of equations that was compiled from different sources^{2-6,11-14,21,22} and might be a good estimation of useful equations.

The system is composed of Ndm different molecules. Each molecule is decomposed into groups. All those groups are Ndg different groups, and for a molecule i , a group k has a multiplicity of ν_k^i (this number equals 0 if group k

is not present in molecule i). For polymers, $\nu_k^i = DPn_x$ (ν_k^i of the minimum repeating unit), with Dpn the number-average degree of polymerization. For each molecule, the concentration as weight fraction (w_i), the density in g/cm^3 (D_i), and the degree of freedom (C_i) are required. The activity, a_i , of each molecule can be written as the sum of three different terms. For every i belonging to N (natural numbers), with $0 < i < Ndm + 1$,

$$\text{Ln } a_i = \text{Ln } a_i^C + \text{Ln } a_i^{\text{FV}} + \text{Ln } a_i^R \quad (\text{A.1})$$

where the term with C means combinatorial, the one with FV means free volume, and the last one with R means residual.

Combinatorial Term, Referenced as the Staverman Form

For every i belonging to N , with $0 < i < Ndm + 1$,

$$\text{Ln } a_i^C = \text{Ln } \Phi_i + 1 - \Phi_i + \frac{1}{2} Z M_i q_i \left\{ \text{Ln } \frac{\theta_i}{\Phi_i} - 1 + \frac{\Phi_i}{\theta_i} \right\} \quad (\text{A.2})$$

$$\Phi_i = \frac{r_i w_i}{\sum_{j=1}^{Ndm} r_j w_j} \quad \theta_i = \frac{q_i w_i}{\sum_{j=1}^{Ndm} q_j w_j} \quad (\text{A.3, A.4})$$

where w_i is the weight fraction of molecule i in the mixture and $Z = 10$ for organic molecules.

$$r_i = \frac{1}{M_i} \sum_{k=1}^{Ndg} \nu_k^i R_k \quad q_i = \frac{1}{M_i} \sum_{k=1}^{Ndg} \nu_k^i Q_k$$

$$M_i = \sum_{k=1}^{Ndg} \nu_k^i M g_k \quad (\text{A.5, A.6, A.7})$$

where R_k , Q_k , and $M g_k$ come from the first table of the chosen database.

When eq. (A.2) is used to calculate the combinatorial activity of a polymer, one frequently finds that a_i^C is greater than unity. To overcome this difficulty, a modification made by Kikic et al.^{7,10} might be used. Equations (A.8) and (A.9) replace eqs. (A.2), (A.3), (A.4), and (A.6). For every i belonging to N , with $0 < i < Ndm + 1$,

$$\text{Ln } a_i^C = \text{Ln } \phi_i + 1 - \phi_i, \quad (\text{A.8})$$

where

$$\phi_i = \frac{r_i^{3/4} w_i}{\sum_{j=1}^{Ndm} r_j^{3/4} w_j} \quad (\text{A.9})$$

Free Volume Term

For every i belonging to N , with $0 < i < Ndm + 1$,

$$\text{Ln } a_i^{\text{FV}} = C_i \left\{ 3 \text{Ln} \left[\frac{V_i^{1/3} - 1}{V_m^{1/3} - 1} \right] - \left[\frac{V_i/V_m - 1}{1 - V_m^{1/3}} \right] \right\} \quad (\text{A.10})$$

with

$$V_i = \frac{1}{D_i 15.17 b r_i} \quad (\text{A.11})$$

and

$$V_m = \frac{\sum_{i=1}^{Ndm} \frac{W_i}{D_i}}{15.17 b \sum_{i=1}^{Ndm} w_i r_i} \quad (\text{A.12})$$

Residual Term

For every i belonging to N , with $0 < i < Ndm + 1$,

$$\text{Ln } a_i^R = \sum_{k=1}^{Ndg} \nu_k^i [\text{Ln } \Gamma_k - \text{Ln } \Gamma_k^i] \quad (\text{A.13})$$

In the term $\text{Ln } \Gamma_k$, the group k has to be considered relatively to its concentration in the global mixture of Ndm molecules.

For every k belonging to N , with $0 < k < Ndg + 1$,

$$Wr_k = Mg_k \sum_{i=1}^{Ndm} \nu_k^i \frac{w_i}{M_i} \quad (\text{A.14})$$

and $\text{Ln } \Gamma_k$ is calculated by the following equations:

$$\text{Ln } \Gamma_k = Q_k \left[1 - \text{Ln} \left(\sum_{m=1}^{Ndg} \theta_m \Psi_{m,k} \right) - \sum_{m=1}^{Ndg} \frac{\theta_m \Psi_{k,m}}{\sum_{n=1}^{Ndg} \theta_n \Psi_{n,m}} \right] \quad (\text{A.15})$$

For every m belonging to N , with $0 < m < Ndg + 1$,

$$\theta_m = \frac{q_m Wr_m}{\sum_{n=1}^{Ndg} q_n Wr_n} \quad (\text{A.16})$$

Then, in the term $\text{Ln } \Gamma_k^i$, the concentration of the group k is considered in the pure molecule i . This yields to (A.17) and (A.19).

For every i, k belonging to N , with $0 < i < Ndm + 1$, $0 < k < Ndg + 1$,

$$Wr_k^i = \frac{\nu_k^i Mg_k}{\sum_{m=1}^{Ndg} \nu_m^i Mg_m} \quad (\text{A.17})$$

$$\text{Ln } \Gamma_k^i = Q_k \left[1 - \text{Ln} \left(\sum_{m=1}^{Ndg} \theta_m^i \Psi_{m,k} \right) - \sum_{m=1}^{Ndg} \frac{\theta_m^i \Psi_{k,m}}{\sum_{n=1}^{Ndg} \theta_n^i \Psi_{n,m}} \right] \quad (\text{A.18})$$

For every i, m belonging to N , with $0 < i < Ndm + 1$, $0 < m < Ndg + 1$,

$$\theta_m^i = \frac{q_m Wr_m^i}{\sum_{n=1}^{Ndg} q_n Wr_n^i} \quad (\text{A.19})$$

In eqs. (A.15) and (A.18), $\Psi_{m,n}$ has the following definition: For every m, n belonging to N , with $0 < m < Ndg + 1$, $0 < n < Ndg + 1$,

$$\Psi_{m,n} = e^{-a_{mn}/T} \quad (\text{A.20})$$

with “ T ” for the temperature of the mixture in Kelvin degrees and a_{mn} comes from the interaction parameter database.

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