Optimization of Polymer-Solvent Interaction in a Multisolvent System by the UNIFAC Group-Contribution Method

CHI-MING TSENG, MOHAMED S. EL-AASSER, and JOHN W. VANDERHOFF, *Emulsion Polymers Institute and Departments of Chemical Engineering and Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015*

Synopsis

The solubility parameter scheme is an exceptionally useful tool for predicting the solubility behavior of simple polymer systems. However, this scheme is unable to handle well enough complicated systems, such as those involving donor-acceptor interactions and those containing more than two solvents. More advanced thermodynamic treatments and computer techniques, such as UNIFAC, can be a key to solving these kinds of problems.

The UNIFAC group-contribution method utilizes a volume parameter and a surface-area parameter for each structural group and a pair of interaction-energy parameters for each pair of groups, which can be deduced from experimental activity data. The method was originally derived for mixtures of ordinary liquids and has been extended to polymer solutions by adding a free-volume correction. The modified UNIFAC method can be used to estimate the activities of solvents in a polymer solution, even when no experimental data are available for the mixture.

In the present study, the UNIFAC method was applied to optimize polymer-solvent interactions in three-solvent systems. A three-dimensional plot, displaying polymer activity as a function of the solvent composition, was constructed for each polymer system. The minimum in polymer activity was used as the criterion for maximum polymer-solvent interaction. Dissolution rate and solution clarity were used to test the polymer-solvent interaction experimentally. Comparison of theoretical predictions with experimental results indicated that a better agreement could be obtained by using the UNIFAC method rather than the solubility parameter method.

INTRODUCTION

Dissolving a polymer in a mixture of solvents is a common practice in industrial processing. The solubility parameter concept is often used to estimate solubility behavior. Froehling et al.[1] have shown how the three-dimensional solubility parameter scheme may be used to predict the proportions of a two-solvent mixture that would give maximum swelling of a given polymer. They applied the method to predict the swelling behavior of polyvinyl chloride in swelling agent-nonsolvent mixtures. The predictions agreed well with the experimental results, except the cases of donor-acceptor solvent pairs.

The solubility parameter concept was formalized and extended to a three-solvent mixture by Rigbi[2] using vector algebra. The maximum polymer-solvent interaction was given by the intersection of the perpendicular line from the polymer value to the plane defined by the values of the three solvents in the mixture. Froehling and Hillegens[3] later presented a more

TABLE I
Comparison of Rigbi's and Froehling's Optimal Compositions for the Polybutadiene System

Polymer-solvent	Solubility parameters[a]			Optimal volume fractions		Distance[a]	
	δ_d	δ_p	δ_h	Rigbi	Froehling et al.	Rigbi	Froehling et al.
Polybutadiene	17.00	0	1.02				
Toluene	18.05	1.4	2.0	0	0.558		
Hexane	14.78	0	0	0.717	0.442	1.66	0.88
Chlorobenzene	19.00	4.3	2.0	0.283	0		

[a] $J^{1/2}$ cm$^{-3/2}$.

concise and mathematically satisfying algorithm for three-solvent systems. Table I compares the optimal solvent compositions and polymer-solvent distances on the solubility parameter map for the polybutadiene system calculated using the methods of Rigbi[2] and Froehling and Hillegens.[3] Both methods gave a negative volume fraction for one component, which indicated that the perpendicular line did not intersect the triangle of the three solvents; therefore this solvent was omitted, and the optimal two-solvent mixture was calculated instead of a three-solvent mixture.

Thus the three-dimensional solubility parameter scheme can be used to optimize polymer-solvent interactions for systems containing three (or even more) solvents, using a computer; the results become less reliable as the number of components increases. An alternative approach, which has a more sound theoretical basis, is the UNIFAC (universal functional-group activity coefficients) model proposed by Fredenslund et al.[4] Hansen, who developed the three-dimensional solubility parameter scheme,[5] recently expressed his hope in the UNIFAC model[6]: "I feel that advanced computer techniques such as UNIFAC will improve predictive ability for solubility relations still more for those with access to such computers."

The UNIFAC model uses a volume parameter R_k and a surface-area parameter Q_k for each structural group and a pair of interaction-energy parameters (a_{mn} and a_{nm}) for each pair of groups, which can be deduced from experimental activity data. The activity of each component in a liquid mixture can thus be calculated by treating the mixture as a solution of groups. For a multicomponent mixture, the activity of component i is given by

$$\ln a_i = \underset{\text{combinatorial}}{\ln a_i^C} + \underset{\text{residual}}{\ln a_i^R} \tag{1}$$

$$= \ln \phi_i + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + \iota_i - \frac{\phi_i}{x_i} \sum_j x_j \iota_j + \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

and

$$\iota_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$$

$$r_i = \sum_k \nu_k^{(i)} R_k$$

$$q_i = \sum_k \nu_k^{(i)} Q_k$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right]$$

$$\Theta_m = \frac{Q'_m W_m}{\sum_n Q'_n W_n}$$

$$\Psi_{mn} = \exp \left(-\frac{a_{mn}}{T} \right)$$

where r and q are the volume parameter and the area parameter of the molecule, ϕ and θ are the average segment fraction and the average area fraction of the molecule, x is the mole fraction, z is the coordination number ($\equiv 10$), Q' is the group area parameter per gram, Θ is the area fraction of the group, W is the weight fraction of the group, $\nu_k^{(i)}$ is the number of groups of type k in one molecule of i, Γ_k is the residual activity of the group k, and $\Gamma_k^{(i)}$ is the residual activity of the group k in a reference solution containing only molecules i.

The UNIFAC model was originally derived for mixtures of ordinary liquids and has been applied to predictions of vapor-liquid equilibria,[7,8] liquid-liquid equilibria,[9–12] solvent effects on chemical reactions,[13] and the design of distillation columns.[14]

Thus far the UNIFAC method has found only limited application in polymer systems. In 1977, Oishi and Prausnitz[15,16] modified the model by adding a free-volume correction based on Flory's equation-of-state theory for polymer solutions. The modified UNIFAC model (UNIFAC-FV) can be used to estimate the activities of solvents in a polymer solution, even when no experimental data are available for the mixture. The activity of component i in a multicomponent polymer solution is thus given by

$$\ln a_i = \underset{\text{combinatorial}}{\ln a_i^C} + \underset{\text{residual}}{\ln a_i^R} + \underset{\text{free volume}}{\ln a_i^{FV}} \tag{2}$$

and

$$\ln a_i^{FV} = 3c_i \ln \frac{\mathbf{v}_i^{1/3} - 1}{\mathbf{v}_m^{1/3} - 1} - c_i \frac{\mathbf{v}_i/\mathbf{v}_m - 1}{1 - 1/\mathbf{v}_i^{1/3}} \tag{3}$$

where

$$\mathbf{v}_i = \frac{v_i}{v_i^*}$$

and

v_i = volume of solvent per gram

v_i^* = hard-core volume of solvent per gram

$3c_i$ = number of external degrees of freedom per solvent molecule

The reduced volume for the solvent and the mixture are given by

$$\mathbf{v}_i = \frac{v_i}{15.17 b r_i'} \tag{4}$$

$$\mathbf{v}_m = \frac{\sum_j v_j w_j}{15.17 b \sum_j r_j' w_j} \tag{5}$$

where w_j is the weight fraction, r_j' is the group-volume parameter per gram, and b and c_i are set to 1.28 and 1.10, respectively.

When the model prediction of solvent activity in polymer solutions was compared with literature results for 13 binary solvent-polymer systems, the calculated and observed solvent activities agreed to within 10%.[15,16]

Recently, Arai and Iwai[17] applied the UNIFAC-FV model to predict the weight fraction Henry's constants of hydrocarbons in polystyrene, and Gottlieb and Herskowitz[18,19] applied the UNIFAC model to silicone compounds.

THEORETICAL PREDICTIONS

A FORTRAN program based on the UNIFAC-FV model to calculate the activities of solvents and polymer in a three-solvent system was written and run on a CDC Cyber 730 computer, and the activity of the polymer was plotted as a function of solvent composition. Tables II and III give the group volume and surface-area parameters and group-interaction parameters used in this work, as taken from Magnussen et al.[12]

Three polymer systems were evaluated: polybutadiene-toluene-hexane-chlorobenzene, polymethyl methacrylate-chloroform-benzene-methyl ethyl ketone, and polystyrene-benzene-cyclohexane-ethyl acetate. The first two systems were studied previously by Rigbi[2] and Froehling and Hillegens.[3] In all the calculations, the polymer concentration was set at 10 volume percent, and the molecular weight of the polymer was set at 1.0×10^6. The minimum in polymer activity was used as the criterion for optimal polymer-solvent interaction.

TABLE II
Group Volume (R_k) and Surface-Area (Q_k) Parameters Used in This Work

Main group	Subgroup	R_k	Q_k
1 CH_2	CH_3	0.9011	0.848
	CH_2	0.6744	0.540
	C	0.2195	0.000
2 $C=C$	$CH=CH$	1.1167	0.867
3 ACH	ACH	0.5313	0.400
	AC	0.3652	0.120
4 $ACCH_2$	$ACCH_3$	1.2663	0.968
	ACCH	0.8121	0.348
10 CH_2CO	CH_3CO	1.6724	1.488
14 COOC	CH_3COO	1.9031	1.728
18 CCl_3	$CHCl_3$	2.8700	2.410
20	ACCl	1.1562	0.844

Figures 1, 2, and 3 show the three-dimensional plots of the polymer activity for the three polymer systems in a prism-shaped coordinate system. The two triangles (top and bottom) in each plot give the composition of solvent mixture, and the height of the prism gives the logarithm of the polymer activity, ranging from 0 (top) to -2.0×10^4 (bottom).

In Fig. 1, the solvent composition that gave the minimum polymer activity for the polybutadiene system was the pure solvent, toluene. Another pure solvent, chlorobenzene, also gave a low polymer activity, just slightly higher than that for toluene. This indicated that the pure solvents, toluene and chlorobenzene, were the best solvent compositions in this system. Any solvent mixture containing a significant amount of hexane was worse than the pure solvents, toluene, or chlorobenzene.

In Fig. 2, the solvent composition that gave the minimum polymer activity for the polymethyl methacrylate system was pure chloroform. A secondary minimum, with a much higher level of polymer activity, was also found at the solvent composition, benzene-MEK (0.68:0.32). This indicated that chloroform was the best solvent among all solvent combinations, and benzene-MEK (0.68:0.32) (▼) was the best combination when only those two solvents were used.

In Fig. 3, two minima with comparable polymer activity levels were found for the polystyrene system at solvent compositions: benzene-ethyl acetate (0.90:0.10) (/\) and cyclohexane-ethyl acetate (0.76:0.24) (▲). This indicated that these two solvent mixtures were the best among all the solvent combinations.

For comparison, Table IV summarizes the optimal solvent combinations from this work with those calculated according to the methods of Rigbi[2] and Froehling et al.[1,3] The values for the latter two methods were those recalculated for the two-solvent mixtures. Note that two results given for the polymethyl methacrylate system were calculated using two sets of partial solubility parameters from different sources. In only one case (polystyrene) did the solubility parameter method (Froehling et al.) and the UNIFAC method give results that were reasonably close: benzene-ethyl acetate (0.89:0.11) versus benzene-ethyl acetate (0.90:0.10).

TABLE III
Group-Interaction Parameters Used in This Work

	1 CH$_2$	2 C=C	3 ACH	4 ACCH$_2$	10 CH$_2$CO	14 COOC	18 CCl$_3$	20 ACCl
1 CH$_2$	0	74.5	-114.8	-115.7	472.6	972.4	7.5	924.8
2 C=C	292.3	0	340.7	4102.0	343.7	-577.5	4583.0	99.6[a]
3 ACH	156.5	-94.8	0	167.0	593.7	6.0	-231.9	-878.1
4 ACCH$_2$	104.4	-269.7	-146.8	0	916.7	5688.0	-12.1	-107.3
10 CH$_2$CO	66.6	306.1	-78.3	-73.9	0	258.7	12.0	902.6
14 COOC	-320.1	485.6	114.8	-170.0	58.8	0	-209.7	629.0
18 CCl$_3$	21.2	-185.1	288.5	33.6	342.2	176.5	0	NA
20 ACCl	-59.1	-24.4[a]	777.8	-47.1	190.5	-246.3	NA	0

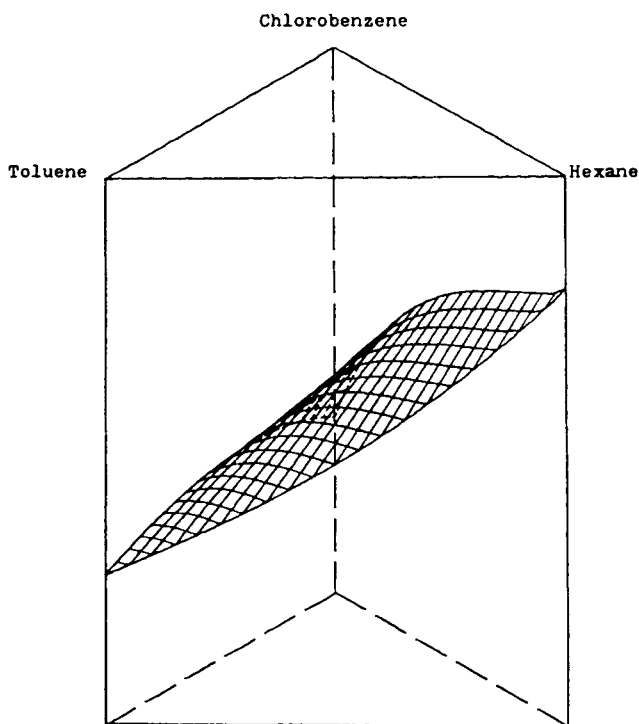[a] Data not available; use the values for the pair CCl and C=C.

Fig. 1.   Three-dimensional plot of polymer activity from UNIFAC method for the polybutadiene-toluene-hexane-chlorobenzene system.

EXPERIMENTAL OBSERVATIONS

The dissolution behavior of the calculated optimal solvent combinations predicted using the UNIFAC and solubility parameter methods was compared experimentally for each polymer system. For each solvent combination, a polymer sample with a calculated volume of 10 ml was weighed in an 8-oz glass bottle, and 90 ml of the solvent mixture was added. The bottles were rotated end over end at about 30 rpm. Solution samples were taken periodically, and the solids content was measured to determine the proportion of polymer dissolved. The clarity of the final solution was also used as an indication of solvent power. The polymers used were: cis-1,4-polybutadiene slab (Polyscience, Inc.) cut into pieces of 1-cm size, polymethyl methacrylate beads (6.35 mm in diameter, American Cyanamid Co.), and polystyrene granules (3–4 mm diameter, high MW, Monomer-Polymer & Dajac Lab.).

Figures 4, 5, and 6 show the dissolution rates of the three polymer systems. The appearance of the final solutions is compared in Table V. For the polybutadiene system, the dissolution rates were ambiguous. Of the five solvent mixtures, four had approximately the same dissolution rate (Fig. 4), but the solution clarity (Table V) clearly indicated that the pure toluene and chlorobenzene were better solvents than hexane or the solvent mixtures containing hexane. This observation agreed with the prediction from the UNIFAC method, but not the solubility parameter method. Note that the
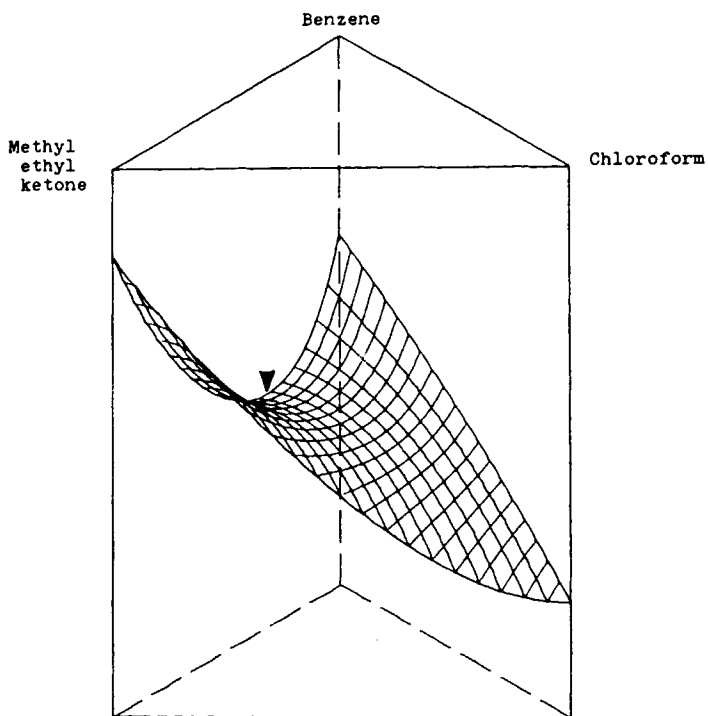
Fig. 2.   Three-dimensional plot of polymer activity from UNIFAC method for the polymethyl methacrylate-chloroform-benzene-methyl ethyl ketone system.
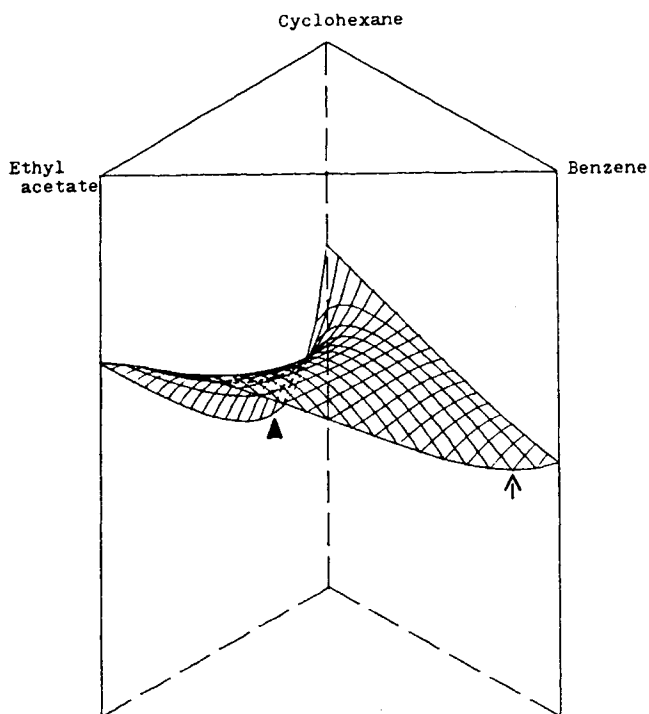

Fig. 3.   Three-dimensional plot of polymer activity from UNIFAC method for the polystyrene-benzene-cyclohexane-ethyl acetate system.

TABLE IV
Optimal Solvent Compositions Calculated from the Solubility Parameter Method and the UNIFAC Method

Polymer-solvent	δ_d	δ_p	δ_h	Rigbi	Froehling et al.	UNIFAC
1　Polybutadiene[a]	17.00	0	1.0			
Toluene	18.05	1.4	2.0	0	0.558	1.0
Hexane	14.78	0	0	0.717	0.442	0
Chlorobenzene	19.00	4.3	2.0	0.283	0	0
2　Polymethyl methacrylate[b]	15.74	8.2	6.7			
Chloroform	17.70	3.1	5.7	0	0.147	1.0
Benzene	18.32	1.0	2.0	0.019	0	0
MEK	15.70	9.0	5.1	0.981	0.853	0
2'　Polymethyl methacrylate[a]	17.62	5.7	7.8			
Chloroform	17.70	3.1	5.7		0.636	1.0
Benzene	18.32	1.0	2.0		0	0
MEK	15.70	9.0	5.1		0.364	0
3　Polystyrene[b]	18.34	1.0	3.3			
Benzene	18.33	1.0	2.1		0.89	0.90
Cyclohexane	16.76	0	0		0	0
Ethyl acetate	15.24	5.3	9.2		0.11	0.10

[a] Solubility parameters from Koenhen and Smolders.[20]
[b] Solubility parameters from Hansen.[5]
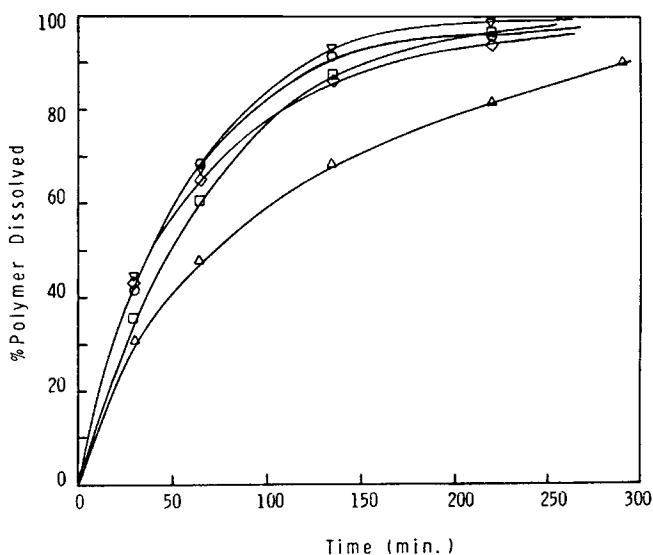
Fig. 4. Dissolution of polybutadiene chunks in various solvent combinations: ○ toluene; □ chlorobenzene; △ hexane; ◇ hexane-chlorobenzene (0.717:0.283); ▽ toluene-hexane (0.558:0.442).
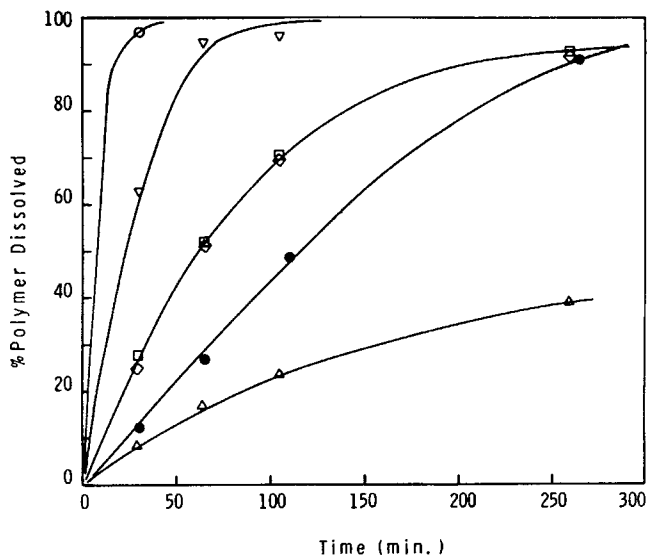

Fig. 5. Dissolution of polymethyl methacrylate beads in various solvent combinations: ○ chloroform; △ benzene; □ MEK; ▽ chloroform-MEK (0.636:0.364); ◇ chloroform-MEK (0.147:0.853); ● benzene-MEK (0.68:0.32).

group-interaction parameters for the pair (C = C and ACCl) were not available from the literature.[12] In the calculations, these were given the values for the pair (C = C and CCl). Even with this limitation, the UNIFAC method still predicted the optimal solvent composition accurately for the polybutadiene system.
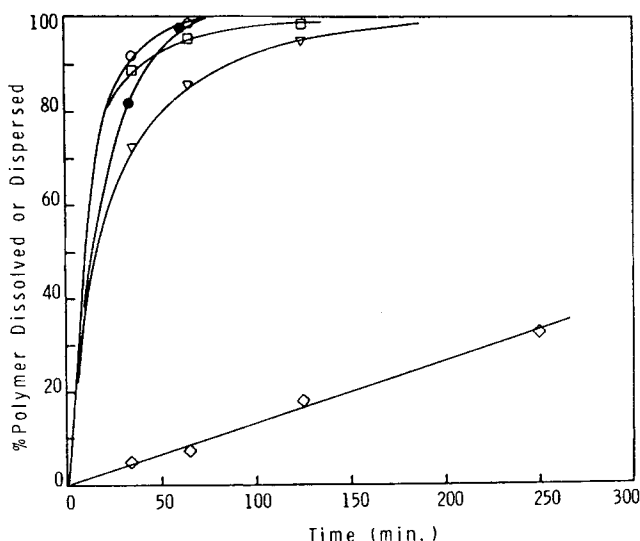
Fig. 6.   Dissolution of polystyrene granules in various solvent combinations: □ benzene; ▽ ethyl acetate; ◇ cyclohexane; ○ benzene-ethyl acetate (0.90:0.10); ● cyclohexane-ethyl acetate (0.76:0.24).

For the polymethyl methacrylate system, a fast dissolution rate (Fig. 5) and a clear solution (Table V) indicated that chloroform was the best solvent among all the solvent combinations. Again, this result agreed with the prediction from the UNIFAC method but not the solubility parameter method. The solvent mixture benzene-MEK (0.68:0.32) had an initial dissolution rate between those of the pure solvents MEK and benzene. After about 2 h, its dissolution rate (slope of the curve) overtook that of MEK, and eventually the solvent mixture completed dissolution of the polymer slightly faster than MEK. This finding also agreed with the secondary minimum obtained in the UNIFAC activity plot.

In the polystyrene system, two solvent mixtures, benzene-ethyl acetate (0.90:0.10) and cyclohexane-ethyl acetate (0.76:0.24), gave the fastest dissolution rates (Fig. 6). Again, the dissolution rate and solution clarity proved that the UNIFAC method gave accurate predictions. The solubility parameter method (Froehling et al.[1,3]) also gave a correct prediction for the polystyrene system.

DISCUSSION

From the results of this study, it appears that the use of the UNIFAC method in treating complicated polymer solution problems is quite promising. The computer program may be further modified to optimize polymer-solvent interactions in a polymer system containing more than three solvents. The applicability is limited only by the availability and accuracy of the group-interaction parameters. A group-interaction parameter table derived mainly from activity data of polymer solutions (instead of those from mixtures of low-molecular-weight compounds) would probably improve the

TABLE V
Appearance of Final Polymer Solutions (10 vol%)

Polymer-solvent	Appearance of solution
1. Polybutadiene	
Toluene	Clear
Hexane	Cloudy
Chlorobenzene	Clear
Hexane-chlorobenzene (0.717:0.283)	Slightly cloudy
Toluene-hexane (0.558:0.442)	Slightly cloudy
2. Polymethyl methacrylate	
Chloroform	Clear
Benzene	Very slightly cloudy
MEK	Clear
Chloroform-MEK (0.636:0.364)	Clear
Chloroform-MEK (0.147:0.853)	Clear
Benzene-MEK (0.68:0.32)	Clear
3. Polystyrene	
Benzene	Clear
Cyclohexane	Milky, polymer swollen and dispersed instead of being dissolved
Ethyl acetate	Cloudy
Benzene-ethyl acetate (0.90:0.10)	Clear
Cyclohexane-ethyl acetate (0.76:0.24)	Slightly cloudy

accuracy of prediction and further extend the range of application. Further extension of the UNIFAC method to other applications, such as prediction of the intrinsic viscosity of a polymer in a solvent mixture and construction of phase diagrams for multipolymer and multisolvent systems, is foreseen.

References

1. P. E. Froehling, D. M. Koenhen, A. Bantjes, and C. A. Smolders, *Polymer*, **17**, 835 (1976).
2. Z. Rigbi, *Polymer*, **19**, 1229 (1978).
3. P. E. Froehling and L. T. Hillegens, *Polymer*, **22**, 261 (1981).
4. A. Fredenslund, R. L. Jones, and J. M. Prausnitz, *AIChE J.*, **21**, 1086 (1975).
5. C. M. Hansen, *J. Paint Technol.*, **39**, 505 (1967).
6. C. M. Hansen, *Preprints, ACS Div. Org. Coat. Plast. Chem.*, **45**, 227 (1981).
7. S. Skjold-Jørgensen, B. Kolbe, J. Gmehling, and P. Rasmussen, *Ind. Eng. Chem., Process Des. Develop.*, **18**, 714 (1979).
8. J. Gmehling, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem., Process Des. Develop.*, **21**, 118 (1982).
9. J. M. Sørensen, T. Magnussen, P. Rasmussen, and A. Fredenslund, *Fluid Phase Equilibra*, **2**, 297 (1979).
10. J. M. Sørensen, T. Magnussen, P. Rasmussen, and A. Fredenslund, *Fluid Phase Equilibra*, **3**, 47 (1979).
11. T. Magnussen, J. M. Sørensen, P. Rasmussen, and A. Fredenslund, *Fluid Phase Equilibra*, **4**, 151 (1980).

12. T. Magnussen, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem., Process Des. Develop.*, **20**, 331 (1981).

13. J. Gmehling and J. Fellensiek, *Z. Phys. Chem.* (Wiesbaden), **122**, 251 (1980).

14. A. Fredenslund, J. Gmehling, M. L. Michelsen, P. Rasmussen, and J. M. Prausnitz, *Ind. Eng. Chem., Process Des. Develop.*, **16**, 450 (1977).

15. T. Oishi, Master's thesis, University of California, Berkeley, 1977.

16. T. Oishi and J. M. Prausnitz, *Ind. Eng. Chem., Process Des. Develop.*, **17**, 333 (1978).

17. Y. Arai and Y. Iwai, *Ind. Eng. Chem., Process Des. Develop.*, **19**, 508 (1980).

18. M. Gottlieb and M. Herskowitz, *Macromolecules*, **14**, 1468 (1981).

19. M. Herskowitz and M. Gottlieb, *Ind. Eng. Chem., Process Des. Develop.*, **20**, 407 (1981).

20. D. M. Koenhen and C. A. Smolders, *J. Appl. Polym. Sci.*, **19**, 1163 (1975).