# Influence of polymer molecular weight on selected thermodynamic properties of polymer/solvent systems and the application of the UNIFAC theory

## H. S. Tseng and Douglas R. Lloyd
*Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA*

The intrinsic viscosities of eleven narrow molecular weight distribution polystyrene samples ranging from number-average molecular weight 1820 to 1 292 000 have been determined in pure solvents of tetrahydrofuran and chloroform with a Ubbelohde No. 1 viscometer at 25°C. By combining the original and modified Fox–Flory viscosity treatments, respectively, with the Flory–Huggins Lattice theory, the interaction parameters were calculated. With the aid of original and modified UNIFAC methods the solvent activity, clustering function of the solvent, and the interaction parameter were computed and compared with the experimental data. It was established that the influence imposed by the polymer molecular weight on the activity of the solvent, the clustering function of solvent, and interaction parameter is insignificant. The modified UNIFAC method satisfactorily predicted the solvent activity as illustrated by previous investigators. However, both UNIFAC methods failed to predict the interaction parameter.

## INTRODUCTION

Due to small entropies of mixing, polymer dissolution is a highly non-ideal process except at the extreme dilute case where Raoult's Law is still applicable. To explain polymer solution properties, a special theoretical treatment is required. The widely used Flory–Huggins[1,2] theory of polymer solution thermodynamics leads to an equation for the free energy of mixing which contains combinatorial and non-combinatorial parts. In the original form, the theory contains one adjustable parameter, i.e. the interaction parameter which represents the non-combinatorial free energy of interaction. The significance of determining the interaction parameter is that it serves as a criterion of miscibility in solvent/polymer system.

The interaction parameter may be obtained experimentally by measuring the activity of the solvent. The activity of the solvent may be determined by a number of techniques such as vapour pressure lowering, freezing point depression, light scattering, osmotic pressure, inverse gas chromatography and intrinsic viscosity measurement. The unique feature of the intrinsic viscosity technique is that it only generates information in the limiting case of infinite dilution of the polymer. However, inverse gas chromatography measurement provides information at the other extreme of infinite dilution of the probe molecule. Both methods are relatively easy to carry out and require little time. While other techniques provide accurate thermodynamic information in the concentration range from 0.1 to 0.9, the variation of interaction parameter over the entire concentration range is suitably revealed via the intrinsic viscosity and inverse gas chro-

matography methods. Several review papers in this field are available in the literature[3-9].

Fredenslund et al.[10] derived the group-contribution method, UNIFAC($U_n$), to estimate the activity of vapour–liquid and liquid–liquid equilibrium systems of low molecular weight species. The basic assumption is that the group behaviour is independent of molecular environment. It is known that this assumption is often not true, making this method an approximate one. Oishi and Prausnitz[11] proposed the modified UNIFAC($U_{fv}$) method by introducing the free volume correction to the original UNIFAC. They demonstrated that the predicted solvent activity of solvent/polymer systems agree to within 10% error of observed values. The correlation equation presented by van Krevelen and Hoftyzer[12] for evaluating the solubility of solvent in polymer requires additional information at the glass transition temperature. Gottlieb and Herskowitz[13] used the modified UNIFAC method to obtain satisfactory prediction of interaction parameters for several solvent/polydimethyl siloxane(PDMS) systems. The attraction of the modified UNIFAC method is that it does not require any experimental data. However, this method has no provision for predicting the effect of polymer molecular weight on the thermodynamic properties of the system.

It is well known that the molecular parameters of polymers such as degree of polymerization, degree of branching, and molecular weight distribution have pronounced effects on the rheological properties of polymer systems. From both practical and academic points of view, it is instructive and valuable to study the thermodynamic properties of solvent/polymer systems. In

most studies, the effect of polymer molecular weight distribution on the thermodynamic properties can be minimized by using polymer samples having narrow molecular weight distribution. Outer, Carr, and Zimm[14] carried out light scattering experiments for dichloroethane and butanone, respectively, with a wide range of molecular weights of polystyrene at 25°C. Their results indicated that, except for very low molecular weight samples, the interaction parameter remains constant for different molecular weight polystyrenes. Bawn and Wajid[15] investigated the thermodynamic properties of chloroform/polystyrene(PS) systems at 25°C. It was observed that for low molecular weight polystyrene, the interaction parameter is greater at low polymer concentrations and smaller at high polymer concentrations. Muramoto[16] reported the interaction parameter for solutions of poly(dimethylsiloxane) of different molecular weights in methyethylketone by means of the vapour pressure method at 30°C. It was found that the $\chi$ values were to be almost independent of the polymer molecular weight.

The purpose of this study was to re-examine the applicability of the modified UNIFAC method to predict the interaction parameter and the effect of polymer molecular weight on the solvent activity and the interaction parameter. In view of other work being carried out in the authors' laboratory[17-19], the experimental portion of this work is concerned with the dilute polymer solution characterization.

## EXPERIMENTAL

The intrinsic viscosities of eleven narrow molecular weight distribution polystyrene samples ranging from number-average molecular weight 1820 to 1 292 000 have been determined in pure solvents of tetrahydrofuran and chloroform with a Ubbelohde No. 1 viscometer. The polystyrene samples were obtained from Pressure Chemical Company. Polymer solutions were prepared by weighing the polymer in a 50 ml flask and diluting at 25°C; the concentration, $C$, in g dl$^{-1}$ was calculated. The solutions were filtered into the viscometer through a Millipore 0.5 $\mu$m filter. Viscosities of polymer solutions at a series of concentrations by successive dilution were measured at 25°C with the aid of Haake constant temperature bath. The efflux time was kept long enough to minimize the

need for applying a kinetic energy correction. Duplicate measurements on a given solution agreed to within approximately 0.1% of the average flow time. For highest precision in extrapolating to zero concentration, the solution concentration was adjusted to the range that gave relative viscosities between 1.1 and 1.5. The characteristics of polymers are listed in the *Table 1*.

## DATA TREATMENT

It can be shown, by combining the Fox–Flory viscosity treatment[20] with the Flory–Huggins lattice theory, that the interaction parameter, $\chi$, of a solvent/polymer system is given by the expression:

$$\chi = \frac{1}{2} - \frac{V_1}{2C_M'KM}\left\{\frac{[\eta]^{5/3}}{[\eta]_0^{2/3}} - [\eta]\right\} \quad (1)$$

A similar equation can be derived by applying the modified Fox–Flory viscosity treatment proposed by Kurata, Stockmayer, and Riog[21]:

$$\chi = \frac{1}{2} - \frac{V_1}{2C_M'KM}\left\{\left(\frac{[\eta]^5}{[\eta]_0^{2.57}}\right)^{1/2.43} - \left(\frac{[\eta]^3}{[\eta]_0^{0.57}}\right)^{1/2.43}\right\} \quad (2)$$

where $V_1$ is the molar volume of the solvent and $C_M'K$ is a constant dependent only on the specific volume of the polymer at a given temperature and is equal to 2.4 × 10$^{-3}$ for polystyrene[20]. $[\eta]$ and $[\eta]_0$ are the intrinsic viscosities in the solvent and the theta solvent, respectively, of a uniform chain length of molecular weight $M$. The intrinsic viscosity at theta conditions can be evaluated by means of:

$$[\eta]_0 = KM^{1/2} \quad (3)$$

provided the $K$ value is known. $K$ is a constant for a given polymer, independent of solvent and molecular weight. In this study, a $K$ value of 8.0 × 10$^{-4}$ was used for polystyrene, as given in ref. 20. As illustrated by Fox and Flory[22], the specific volume of polystyrene below the glass transition temperature is essentially independent of the molecular weight. Therefore, a constant specific volume of polystyrene was used for the different molecular weight samples. The difference between equations (1) and (2) is that the latter takes the non-Gaussian character of polymer chains into account.

**Table 1** Characteristics of polystyrene samples

| Sample no. | $M_n{}^a$ | $M_w/M_n{}^a$ | $M_v{}^a$ | $M_n{}^b$ | $M_w/M_n{}^b$ | $M_v{}^b$ |
|---|---|---|---|---|---|---|
| 1 | 1790 | 1.06 | 2111 | 1822 | 1.17 | 2090 |
| 2 | 3570 | 1.06 | 3600 | 3115 | 1.15 | 3520 |
| 3 | 9050 | 1.06 | 9100 | 6550 | 1.18 | 7570 |
| 4 | 17 440 | 1.04 | – | 17 500 | 1.09 | 17 400 |
| 5 | 34 100 | 1.06 | – | 31 160 | 1.07 | 28 240 |
| 6 | 51 150 | 1.06 | 47 400 | 51 130 | 1.06 | 45 620 |
| 7 | 92 600 | 1.06 | 98 700 | 87 770 | 1.09 | 93 550 |
| 8 | 217 600 | 1.06 | 233 000 | 220 520 | 1.06 | 252 030 |
| 9 | ~600 000 | 1.10 | – | 511 880 | 1.21 | 633 960 |
| 10 | ~800 000 | 1.10 | . | 692 610 | 1.19 | 810 240 |
| 11 | ~1 600 000 | 1.30 | 1 750 000 | 1 292 500 | 1.46 | 1 729 000 |

*a* Data supplied by Pressure Chem. Co., Pittsburgh, PA 15201, USA
*b* This study. Characterized by using g.p.c. (Waters Assoc. Model 244) which had been calibrated for molecular weight through the use of polystyrene standards (Waters Associates) in tetrahydrofuran

In the literature, three concentration scales have been used in reporting thermodynamic properties of polymer solution: volume fraction, segment fraction, and site fraction. In this study, interaction parameters are expressed solely in terms of segment fraction, which is defined as:

$$\rho_i = \frac{\omega_i v_i^*}{\omega_i v_i^* + \omega_j v_j^*} \tag{4}$$

where $\omega_i$ and $v_i^*$ are the weight fraction and hard-core volume of component $i$. The hard-core volume can be calculated by:

$$v_i^* = \frac{1}{\rho_i \tilde{v}_i} \tag{5}$$

where $\rho_i$ is the density of component $i$. The reduced volume, $\tilde{v}_i$, can be calculated by:

$$\tilde{v}_i^{1/3} = 1 + \frac{\alpha T}{3(1 + \alpha T)} \tag{6}$$

where $\alpha$ is the thermal expansion coefficient and $T$ is the temperature in Kelvin. The segmental concentration scale requires the thermal expansion coefficient of the solvent as well as that of the polymer. For the commonly used solvents and polymers, the thermal expansion coefficient can be found in the literature[23-31]. If the thermal expansion coefficient of solvent is not available, it can be best estimated using density information compiled by Timmerman[32]. In this paper, the thermal expansion coefficients of acetone and chloroform at 25°C, as well as acetone, benzene, ethylacetate, and methanol at 30°C were evaluated to be $1.41 \times 10^{-3}$, $1.25 \times 10^{-3}$, $1.43 \times 10^{-3}$, $1.23 \times 10^{-3}$, $1.44 \times 10^{-3}$, and $1.21 \times 10^{-3}$, respectively.

## RESULTS AND DISCUSSIONS

The results are presented in *Figures 1-7* and *Tables 2-6*. The binary polymer systems selected for study were based on the availability of experimental interaction parameter data in the literature. The results of the viscosity measurements may be represented well, with the exception of lower polymer molecular weight samples, by the Mark–Houwink relation as shown in the *Figure 1*. Based on the viscosity average molecular weight, the Mark–Houwink constants $K'$ and $a$ obtained by regression analysis were $9.439 \times 10^{-5}$ and $0.736$ for the PS/THF solutions and $7.264 \times 10^{-5}$ and $0.750$ for the PS/CHCl$_3$ solutions,
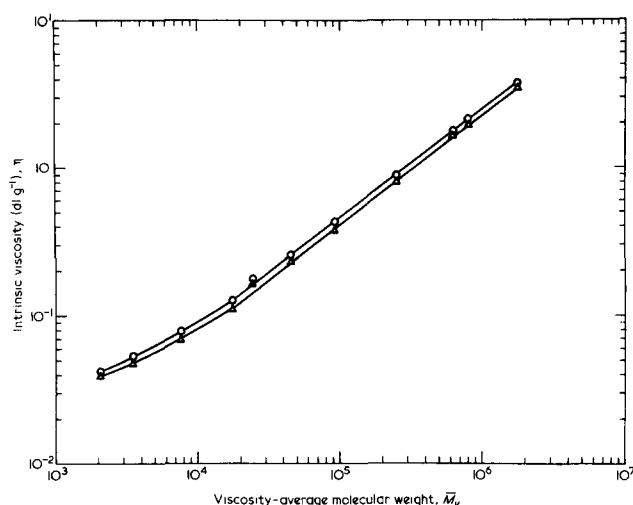


**Figure 1** Intrinsic viscosity–molecular weight relations for polystyrene in tetrahydrofuran and chloroform at 25°C.
○, tetrahydrofuran/PS solution; △, chloroform/PS solution

respectively. The intrinsic viscosity and the interaction parameter data for these two systems are shown in *Table 2*.

As shown in *Table 2*, the difference in interaction parameters calculated from equations (1) and (2) show that the value from equation (1) is always greater than the value from equation (2) and the difference increases as the polymer molecular weight increases. This may indicate that the non-Gaussian character of polymer chains becomes more important as the length of polymer chain increases. Apparently, a slight increase then decrease of the interaction parameter with polymer molecular weight is present in all 4 columns. This variation may be attributed to the inherent uncertainty of the experimental technique and inadequacies in the theories. The need for further study on this subject seems to be indicated. The values of experimental interaction parameters in the *Tables 3-6* were obtained by interpolation or by short extrapolation of data taken from this study and from the literature.

The modified UNIFAC method is briefly described here, detailed information is given elsewhere[11]. In the modified UNIFAC, the activity $a_i$ of solvent $i$ is calculated by:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} \tag{7}$$

where superscripts C, R, and FV represent combinatorial, residual, and free volume. The combinatorial part of the

**Table 2** Intrinsic viscosity and interaction parameter data for PS/THF and PS/CHCl$_3$ systems at 25°C

| Polymer code no. | PS/THF | | | PS/CHCl$_3$ | | |
|---|---|---|---|---|---|---|
| | $[\eta]$ (dl g$^{-1}$) | $\chi$ calculated from equation (1) | $\chi$ calculated from equation (2) | $[\eta]$ (dl g$^{-1}$) | $\chi$ calculated from equation (1) | $\chi$ calculated from equation (2) |
| 1 | 0.042 | 0.470 | 0.462 | 0.040 | 0.483 | 0.478 |
| 2 | 0.054 | 0.475 | 0.467 | 0.048 | 0.497 | 0.496 |
| 3 | 0.079 | 0.483 | 0.478 | 0.070 | 0.498 | 0.498 |
| 4 | 0.126 | 0.485 | 0.480 | 0.118 | 0.492 | 0.489 |
| 5 | 0.178 | 0.477 | 0.468 | 0.168 | 0.484 | 0.477 |
| 6 | 0.254 | 0.471 | 0.460 | 0.231 | 0.481 | 0.474 |
| 7 | 0.430 | 0.464 | 0.447 | 0.376 | 0.478 | 0.468 |
| 8 | 0.894 | 0.457 | 0.432 | 0.819 | 0.467 | 0.449 |
| 9 | 1.763 | 0.454 | 0.421 | 1.640 | 0.462 | 0.436 |
| 10 | 2.112 | 0.453 | 0.419 | 1.950 | 0.462 | 0.435 |
| 11 | 3.690 | 0.452 | 0.418 | 3.474 | 0.459 | 0.425 |

**Table 3** Comparison of computed and experimental interaction parameter for polystyrene/solvent systems as a function of segment fraction of polymer ($\phi_2$) at 25°C

| Solvent | $\phi_2 = 0.0$ | | | $\phi_2 = 0.25$ | | | $\phi_2 = 0.50$ | | | $\phi_2 = 0.75$ | | | $\phi_2 = 1.00$ | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | |
| Chloroform | 0.45 | 0.28 | 0.47 | 0.53 | 0.077 | 0.21 | 0.40 | -0.125 | 0.10 | 0.30 | -0.20 | 0.026 | 0.275 | -0.265 | 0.025 | a,b,f |
| Acetone | NA | 0.70 | 0.90 | NA | 0.70 | 0.92 | 0.775 | 0.70 | 0.955 | 0.94 | 0.70 | 1.00 | 1.30 | 0.70 | 1.075 | a |
| Methyl ethyl ketone | 0.51 | 0.53 | 0.69 | 0.58 | 0.53 | 0.71 | 0.665 | 0.53 | 0.74 | 0.81 | 0.53 | 0.775 | NA | 0.53 | 0.825 | b,c,d |
| Straight-chain propyl acetate | NA | 0.48 | 0.695 | NA | 0.46 | 0.695 | 0.71 | 0.42 | 0.685 | 0.75 | 0.36 | 0.66 | 0.82 | 0.26 | 0.555 | a |
| Benzene | 0.46 | 0.085 | 0.175 | NA | 0.078 | 0.205 | NA | 0.071 | 0.255 | NA | 0.064 | 0.270 | NA | 0.055 | 0.32 | b |
| Toluene | 0.46 | -0.01 | 0.145 | 0.45 | -0.02 | 0.16 | 0.435 | -0.03 | 0.180 | 0.41 | -0.04 | 0.205 | NA | -0.050 | 0.23 | c |
| Ethyl benzene | 0.39 | 0.04 | 0.165 | 0.48 | 0.04 | 0.175 | NA | 0.04 | 0.195 | NA | 0.04 | 0.205 | NA | 0.04 | 0.23 | e |

$^a$ Ref. 15, $\bar{M}_n = 2.9 \times 10^5$ and $\bar{M}_n = 9.0 \times 10^4$
$^b$ Ref. 33, $\bar{M}_n = 2.47 \times 10^5$
$^c$ Ref. 34, $\bar{M}_n = 2.9 \times 10^5$
$^d$ Ref. 35, $\bar{M}_n = 5.1 \times 10^4$
$^e$ Ref. 36, $\bar{M}_n = 5.1 \times 10^4$
$^f$ This study
$U_n$ indicates values computed using the UNIFAC method (ref. 10)
$U_{fv}$ indicates values computed using the modified UNIFAC method (ref. 11)

**Table 4** Comparison of computed and experimental interaction parameter for natural rubber/solvent systems as a function of segment fraction of polymer ($\phi_2$) at 25°C

| Solvent | $\phi_2 = 0.0$ | | | $\phi_2 = 0.25$ | | | $\phi_2 = 0.50$ | | | $\phi_2 = 0.75$ | | | $\phi_2 = 1.00$ | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | |
| Straight-chain hexane | 0.43 | -0.078 | 0.15 | NA | -0.077 | 0.18 | NA | -0.075 | 0.24 | NA | -0.070 | 0.31 | 0.658 | -0.065 | 0.40 | b,c |
| Straight-chain heptane | 0.416 | -0.077 | 0.13 | NA | -0.073 | 0.17 | NA | -0.073 | 0.21 | NA | -0.068 | 0.26 | 0.607 | -0.062 | 0.33 | b,c |
| Straight-chain octane | 0.422 | -0.075 | 0.125 | NA | -0.070 | 0.15 | NA | -0.065 | 0.19 | NA | -0.606 | 0.26 | 0.575 | -0.055 | 0.285 | b,c |
| Benzene | 0.42 | 0.39 | 0.58 | 0.43 | 0.35 | 0.58 | 0.45 | 0.33 | 0.59 | 0.485 | 0.315 | 0.61 | 0.56 | 0.30 | 0.65 | a,b,c,d |
| Toluene | 0.38 | 0.15 | 0.325 | NA | 0.16 | 0.35 | NA | 0.175 | 0.385 | 0.393 | 0.20 | 0.435 | 0.433 | 0.23 | 0.50 | b,c,e |

$^a$ Ref. 37, $\bar{M}_n = 4.0 \times 10^4$
$^b$ Ref. 38, $\bar{M}$ not available
$^c$ Ref. 39, $\bar{M}_n = 2.23 \times 10^5$
$^d$ Ref. 40, $\bar{M}$ not available
$^e$ Ref. 41, $\bar{M}$ not available
$U_n$ indicates values computed using the UNIFAC method (ref. 10)
$U_{fv}$ indicates values computed using the modified UNIFAC method (ref. 11)

**Table 5** Comparison of computed and experimental interaction parameter for polyisobutylene/solvent systems as a function of segment fraction of polymer ($\phi_2$) at 25°C

| Solvent | $\phi_2 = 0.0$ | | | $\phi_2 = 0.25$ | | | $\phi_2 = 0.50$ | | | $\phi_2 = 0.75$ | | | $\phi_2 = 1.00$ | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | |
| Straight-chain pentane | 0.465 | -0.118 | 0.23 | 0.565 | -0.115 | 0.31 | 0.66 | -0.112 | 0.42 | 0.75 | -0.110 | 0.58 | 0.87 | -0.103 | 0.85 | a,b,c,i, k,l |
| Straight-chain hexane | NA | -0.115 | 0.23 | NA | -0.113 | 0.30 | NA | -0.110 | 0.395 | NA | -0.106 | 0.53 | 0.78 | -0.105 | 0.78 | a,b,i |
| Straight-chain heptane | 0.468 | -0.112 | 0.23 | NA | -0.110 | 0.29 | NA | -0.105 | 0.37 | NA | -0.10 | 0.48 | 0.67 | -0.10 | 0.66 | a,b,e,i,m |
| Straight-chain octane | NA | -0.110 | 0.22 | 0.48 | -0.108 | 0.277 | 0.55 | -0.105 | 0.35 | NA | -0.10 | 0.45 | 0.63 | -0.098 | 0.585 | a,b,i |
| Cyclohexane | 0.42 | -0.043 | 0.23 | 0.44 | -0.043 | 0.275 | 0.46 | -0.043 | 0.33 | 0.50 | -0.043 | 0.40 | 0.59 | -0.043 | 0.50 | a,b,c,g, h,i |
| Benzene | 0.51 | 0.43 | 0.76 | 0.60 | 0.42 | 0.79 | 0.73 | 0.40 | 0.85 | 0.91 | 0.38 | 0.93 | 1.02 | 0.36 | 1.03 | a,b,c,d, e,f |

[a] Ref. 42, $\bar{M}_v = 4.0 \times 10^4$
[b] Ref. 43, $\bar{M}_v = 4.0 \times 10^4$
[c] Ref. 44, $\bar{M}_v = 6.6 \times 10^4$
[d] Ref. 45, $\bar{M}_v = 4.0 \times 10^4$
[e] Ref. 20, $\bar{M}_v = 1.88 \times 10^6$ and $\bar{M}_v = 1.46 \times 10^6$
[f] Ref. 46, $\bar{M}_v = 9.0 \times 10^4$
[g] Ref. 47, $\bar{M}_v = 4.0 \times 10^4$
[h] Ref. 33, $\bar{M}_n = 2.23 \times 10^5$
[i] Ref. 48, $\bar{M}_v = 1.46 \times 10^6$
[j] Ref. 49, $\bar{M}$ not available
[k] Ref. 50, $\bar{M} = 2.25 \times 10^6$
[l] Ref. 51, $\bar{M}_v = 4.0 \times 10^4$
[m] Ref. 52, $\bar{M}_v = 4.7 \times 10^6$ at 23.5°C
$U_n$ indicates values computed using the UNIFAC method (ref. 10)
$U_{fv}$ indicates values computed using the modified UNIFAC method (ref. 11)

**Table 6** Comparison of computed and experimental interaction parameter for polyvinyl acetate/solvent systems as a function of segment fraction of polymer ($\phi_2$) at 25°C

| Solvent | $\phi_2 = 0.0$ | | | $\phi_2 = 0.25$ | | | $\phi_2 = 0.50$ | | | $\phi_2 = 0.75$ | | | $\phi_2 = 1.00$ | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | Exp | $U_n$ | $U_{fv}$ | |
| Acetone | NA | -0.13 | 0.16 | NA | -0.13 | 0.185 | 0.42 | -0.11 | 0.26 | 0.52 | -0.065 | 0.385 | NA | 0.055 | 0.625 | a |
| Ethyl acetate | NA | 0.022 | 0.27 | NA | 0.022 | 0.305 | 0.45 | 0.022 | 0.35 | 0.52 | 0.022 | 0.415 | NA | 0.022 | 0.50 | a |
| Benzene | NA | 0.053 | 0.255 | NA | 0.055 | 0.28 | 0.475 | 0.55 | 0.31 | 0.44 | 0.055 | 0.35 | NA | 0.055 | 0.40 | a,b,c |
| Methanol | NA | 0.33 | 0.555 | NA | 0.417 | 0.67 | NA | 0.55 | 0.842 | 0.775 | 0.78 | 1.125 | 1.78 | 1.21 | 1.635 | a |

[a] Ref. 53, $\bar{M}_n = 1.1 \times 10^5$
[b] Ref. 54, $\bar{M}_v = 1.7 \times 10^5$
[c] Ref. 55, $\bar{M}_n = 1.43 \times 10^5$ and $\bar{M}_n = 4.8 \times 10^4$
$U_n$ indicates values computed using the UNIFAC method (ref. 10)
$U_{fv}$ indicates values computed using the modified UNIFAC method (ref. 11)

activity is given by

$$\ln a_i^C \approx \ln \phi_i' + \sum_P \phi_P' + \sum_S \phi_S' \left(1 - \frac{r_i}{r_s}\right)$$

$$+ \frac{Z}{2} M_i q_i' \ln \frac{\theta_i'}{\phi_i'} - \frac{Z}{2} M_i q_i' \left(1 - \frac{\phi_i'}{\theta_i'}\right)$$

(8)

where $i$ represents a particular solvent, P and S stand for polymers and solvents, respectively. The lattice co-ordinate number $Z$ is set equal to 10 and $M_i$ is the molecular weight of component $i$. $q_i'$ is the area parameter of component $i$ per gram and $r_i$ is the volume parameter of component $i$ per mole. The molar surface fraction, $\theta_i'$, and segment fraction, $\phi_i'$, of component $i$ based on the weight fraction $\omega_i$ are defined as:

$$\theta_i = \frac{q_i' \omega_i}{\sum_j q_j' \omega_j'} \quad ; \quad \phi_i = \frac{\gamma_i' \omega_i}{\sum_j \gamma_j' \omega_j'}$$

(9)

Parameters $\gamma_i'$ and $q_i'$ are computed from the sum of the molar functional group volume and functional group area parameters, $R_k$ and $Q_k$.

$$\gamma_i' = \frac{1}{M_i} \sum_k v_i^{(i)} R_k \quad ; \quad q_i' = \frac{1}{M_i} \sum_i v_i^{(i)} Q_k$$

(10)

In equation (10), $v^{(i)}$ is the number of occurrences of groups of type $k$ in molecule $i$. Group parameters $R_k$ and $Q_k$ can be obtained from the van der Waals group volume and surface areas given by Bondi[56]. The residual part of the activity is given by:

$$\ln a_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

(11)

where $\Gamma_k$ is the residual activity coefficient of group $k$ and $\Gamma_k^{(i)}$ is the residual activity coefficient of group $k$ in the reference solution containing only molecules of type $i$. The group activity coefficient $\Gamma_k$ can be computed by:

$$\ln \Gamma_k = Q_k' M_k \left[ 1 - \ln \left( \sum_m \theta_m' \psi_{mk} \Big/ \sum_n \theta_n' \psi_{nm} \right) \right]$$

(12)

where $\theta_m'$ is the area fraction of the group $m$, and summations are over all different functional groups in the solution. $Q_k'$ is the group area parameter per gram. $\theta_m'$ is computed by:

$$\theta_m' = \frac{Q_m' \omega_m}{\sum_n Q_n' \omega_n} = \theta_m$$

(13)

where $\omega_m$ is the weight fraction of group $m$ in the mixture. In equation (12), the group interaction parameter $\psi_{mn}$ is computed by:

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

(14)

where the group interaction parameter $a_{mn}$ is given by Fredenslund *et al.*[10]. The free volume part of the activity is given by:

$$\ln a_i^{FV} = 3c_i \ln \left(\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_M^{1/3} - 1}\right)$$

$$- c_i \left[ \left(\frac{\tilde{v}_i}{\tilde{v}_M} - 1\right) - \left(1 - \frac{1}{\tilde{v}_i^{1/3}}\right)^{-1} \right]$$

(15)

where $3c_i$ is the number of external degrees of freedom of solvent $i$ per mole. The reduced volumes for the solvent $i$ is computed by:

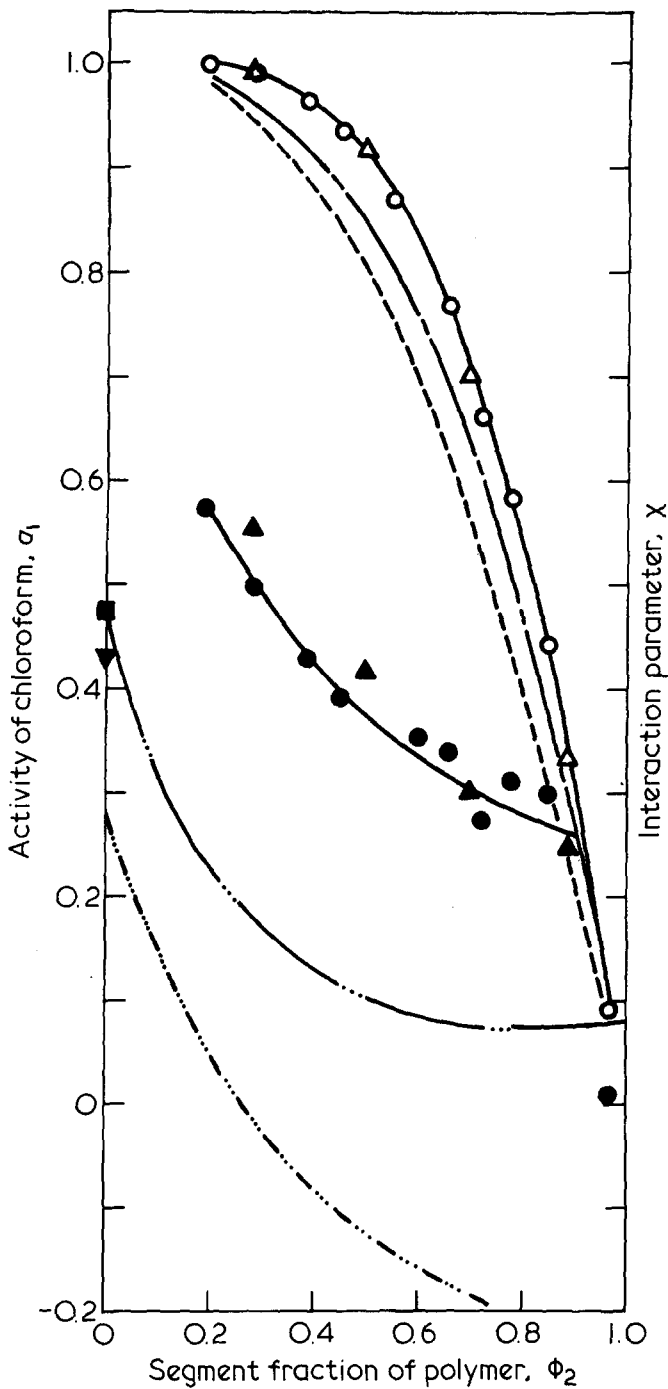$$\tilde{v}_i = \frac{v_i}{15.17 b \gamma_i'}$$

(16)

where $b$ is a proportionality constant of order unity. The reduced volume for the mixture is computed by:

$$\tilde{v}_M = \frac{\sum_j v_j \omega_j}{15.17 b \left(\sum_j \gamma_j' \omega_j\right)}$$

(17)

The required parameters of $c = 1.1$ and $b = 1.28$ are used in the UNIFAC approaches as suggested by previous investigators[11].

By examining *Figures 2–5*, it is found that the influence of polymer molecular weight on the solvent activity and interaction parameter is insignificant in all cases. The UNIFAC method predicted activity values which are much lower than the experimental results. With inclusion of the free volume correction to the UNIFAC, called the modified UNIFAC method[11], the discrepancy between computed and observed activities are greatly reduced. This observation agrees with the findings of Oishi and Prausnitz[11]. Once the activity of solvent is known, the $\chi$ can be easily evaluated. It is recognized that there are two factors contributing to $\chi$, i.e. the energetic interaction term, $\chi_h$, which is associated with a difference in chemical nature, and the free volume term, $\chi_s$, which is associated with a difference in thermal expansion coefficients between polymer and solvent molecules. It is known that the magnitude of $\chi$ is dominated by $\chi_s$ in most instances[57]. As noted by Flory[57], the typically large positive values of $\chi$ are the consequence of the difference in liquid-state properties of the polymeric solute compared with the low molecular weight solvent.
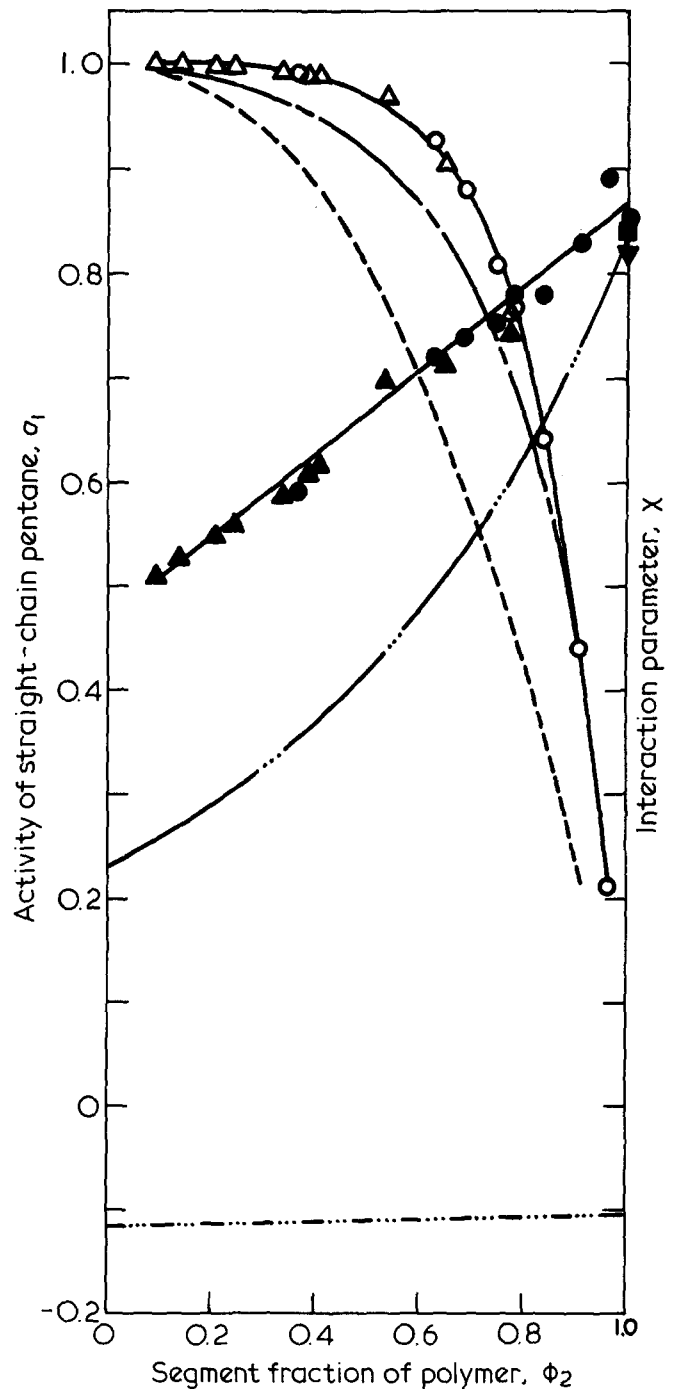
Gottlieb and Herskowitz[13] computed the interaction parameter for several PDMS/solvent systems applying both UNIFAC and modified UNIFAC methods. It was found that the modified UNIFAC method always over-estimated the $\chi$ except in the case for PDMS/straight-chain pentane. This may be attributed to the large difference in thermal expansion coefficients between pentane and PDMS. As the original UNIFAC method mainly takes the difference in chemical nature upon mixing into account, it is reasonable to expect that the $\chi$ computed by this method should mainly reflect the interactional term, $\chi_h$. The difference in the $\chi$ values computed by UNIFAC and modified UNIFAC methods should be characterized by the corresponding $\chi_s$. Due to the exceptionally high degree of thermal expansion coefficient of PDMS, $\chi_h$ should exhibit a dominating effect over $\chi_s$ to the interaction parameter, $\chi$, in most of the hydrocarbon/PDMS systems. When the results of Gottlieb and Herskowitz[13] are compared with the experimental data reported by Chahal, Kao, and Patterson[58], it is found that this trend qualitatively agreed. For the oligomer/PDMS systems, this trend was not observed. The reasons other than free volume effect are discussed and suggested elsewhere[58]. In the present study, neither the UNIFAC nor the modified UNIFAC approach satisfactorily predicted $\chi$ in all cases (see *Figures 2–5* and *Tables 3–6*). These discrepancies may be partially ascribed to the significant differences in thermal expansion coefficients between components.
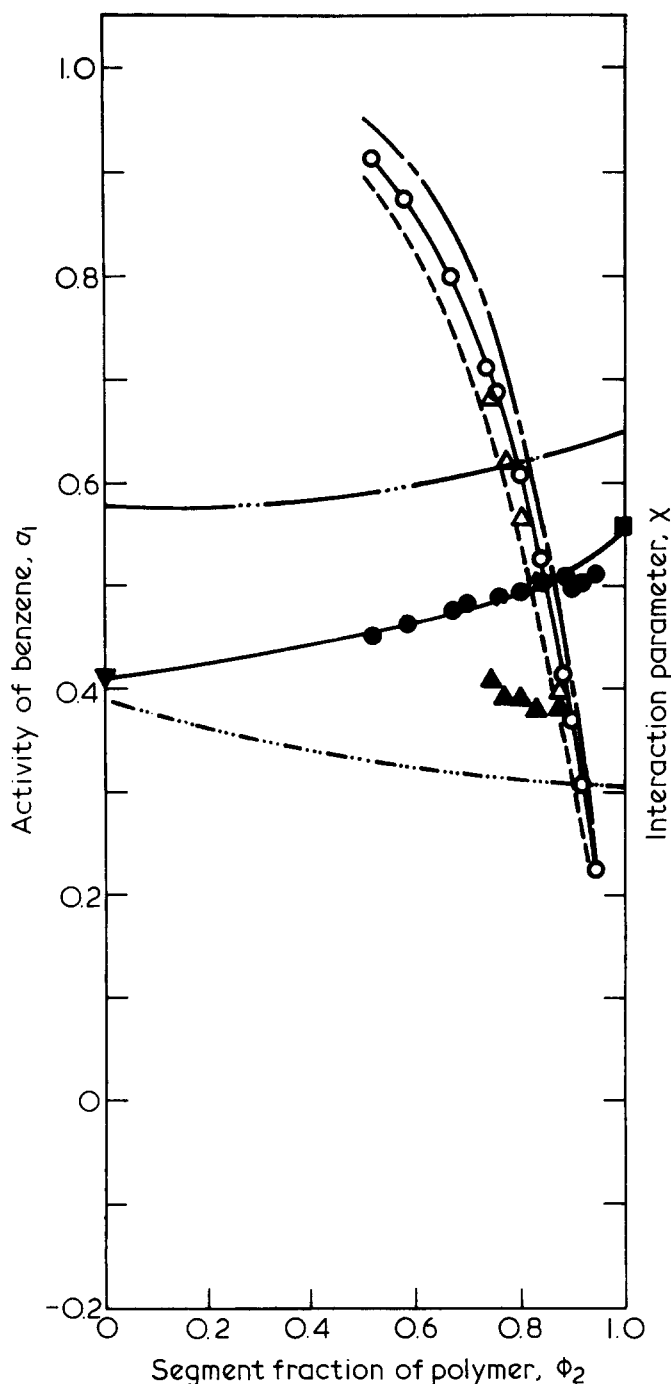
polyisoprene/benzene systems at 25°C studied by Eiching and Flory[37] with the polyisoprene/benzene systems (95% of cis-1,4 addition) at 23.5°C reported by Saeki, Holste, and Bonner[41], significant differences in $\chi$ are observed. This disagreement may be due to the differences in microstructure of the polymers used. For the PVAc/benzene system at 30°C[53], the $\chi$ values scattered considerably as shown in
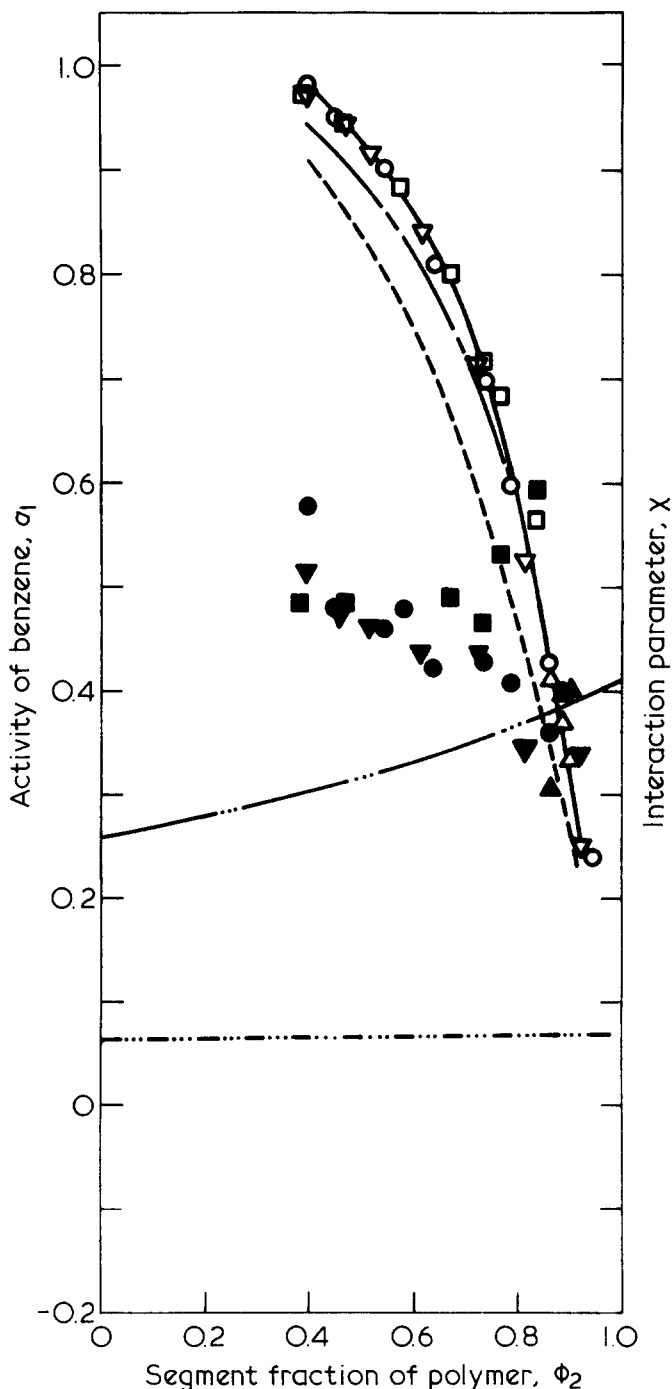


**Figure 2** Activity of solvent and interaction parameter *versus* segment fraction of polymer in chloroform/PS solution at 25°C. ○,●, $\bar{M}_n$=2.9×10⁵; △▲; $\bar{M}_n$=9.0×10⁴ taken from ref. 15; ▼, $\bar{M}_v$=2.47×10⁵ taken from ref. 33; and ■, this study. Curve descriptions: for the activity of solvent, the solid line with open symbols represents experimental data obtained from the literature; ——, computed from modified UNIFAC; and ——, computed from UNIFAC; for the interaction parameter, the solid line with closed symbols represents experimental data obtained from the literature; —···, computed from modified UNIFAC; and —···, computed from UNIFAC



**Figure 3** Activity of solvent and interaction parameter *versus* segment fraction in pentane/PIB solution at 25°C. ■, $\bar{M}_v$=4.0×10⁴ taken from ref. 47; ▼, $\bar{M}_v$=6.6×10⁴ taken from ref. 44; △,▲, M=2.25×10⁶ taken from ref. 50; and ○,●, $\bar{M}_v$=4.0×10⁴ taken from ref. 51. Curve descriptions: for the activity of solvent, the solid line with open symbols represents experimental data obtained from the literature; ——, computed from modified UNIFAC; and ——, computed from UNIFAC; for the interaction parameter, the solid line with closed symbols represents experimental data obtained from the literature; —···, computed from modified UNIFAC; and —···, computed from UNIFAC

It is instructive to present several interesting observations from this study. The polymer molecular weight apparently has only a minor effect on $\chi$. Within experimental error, $\chi$ is considered to be independent of molecular weight for the systems studied. Except for the polystyrene/chloroform system, the interaction parameter generated by the viscosity method fits well into the trend obtained by other techniques. When comparing the

**Figure 4** Activity of solvent and interaction parameter *versus* segment fraction of polymer in benzene/natural rubber solution at 25°C. ▼, $\bar{M}_n$=2.23×10$^5$ taken from ref. 33; ○,●, $\bar{M}_n$=7.5×10$^4$ taken from ref. 37; ■, $M$ (not available) taken from ref. 38; and △,▲, $M$ (not available) at 23.5°C taken from ref. 52. Curve descriptions: for the activity of solvent, the solid line with open symbols represents the experimental data obtained from the literature; ——, computed from modified UNIFAC; and ——, computed from UNIFAC; for the interaction parameter, the solid line with closed symbols represents the experimental data obtained from the literature; ——·, computed from modified UNIFAC

*Figure 5*. The modified UNIFAC method better represents the interaction parameter both qualitatively and quantitatively. The UNIFAC method predicted much lower values for $\chi$. This observation contradicts that of Gottlieb and Herskowitz[13]. For the aliphatic hydrocarbon with polyisobutylene (PIB) or natural rubber systems, $\chi$ decreases as the number of carbons in the solvent increases. Furthermore, the $\chi$ values computed by apply-

ing the UNIFAC method are all relatively small and negative as shown in *Tables 4* and *5*. This may be due to the similarity in the chemical nature between the polymer segment and the solvent molecules. It is noteworthy that for the PIB/straight-chain pentane system at 25°C, the experimentally determined[58] $\chi_h$ is a constant of approximately −0.1 compared with −0.11 computed by UNIFAC method. This may indicate that for chemically



**Figure 5** Activity of solvent and interaction parameter *versus* segment fraction of polymer in benzene/PVAc solution at 30°C. □,■, $\bar{M}_n$=1.1×10$^5$ taken from ref. 53; △,▲, $\bar{M}_v$=1.7×10$^5$ taken from ref. 54; ○,●, $\bar{M}_n$=1.43×10$^5$; and ▽,▼, $\bar{M}_n$=4.8×10$^4$ taken from ref. 55. Curve descriptions: for the activity of solvent, the solid line with open symbols represents the experimental data obtained from the literature; ——, computed from modified UNIFAC; and ——, computed from UNIFAC; for the interaction parameter, the solid line with closed symbols represents the experimental data obtained from the literature; ——·, computed from modified UNIFAC; and —·, computed from UNIFAC

similar mixtures, the small value of $\chi$ predicted by UNIFAC method may be closely related to $\chi_h$.

The cluster integral $G_{11}$ for the solvent suggested by Zimm and Lundberg[59] is given by:

$$G_{11}/\bar{v}_1 = -\phi_2\left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{P,T} - 1 \qquad (18)$$

where $\phi_1$ is the volume fraction of component 1 and $\bar{v}_1$ is the partial molar volume of the solvent. The clustering function, $\phi_1 G_{11}/\bar{v}_1$, is the mean number of type 1 molecules in excess of the mean concentration of type 1 molecules in the neighbourhood of a given type 1 molecules; thus, it measures the clustering tendency of the type 1 molecules. An increasing tendency toward cluster formation is reflected by an increasing or positive values of the quantity $\phi_1 G_{11}/v_1$. However, a decrease in cluster formation is characterized by decreasing or negative values of $\phi_1 G_{11}/\bar{v}_1$[41].

The clustering functions for several polymer/solvent solutions computed by the use of equation (18) with replacing the volume fraction by segment fraction with the modified UNIFAC and based on literature data are presented in *Figures 6* and *7*. It is found that in the PVAc/benzene and PS/chloroform solutions, the clustering functions are independent of polymer molecular weight. The clustering function increases with increasing concentration in PS/acetone solution. However, the function goes through a maximum in the concentration range between 0.4 and 0.6 for the PVAc/benzene, PS/chloroform, PIB/straight chain pentane, and PIB/cyclohexane solutions. For PS/acetone and PIB/pentane systems, the agreement between the modified UNIFAC and experimental results is good. For other systems, the difference in the clustering function between the computed and observed values increases as the polymer concentration decreases.

In spite of the fact that the modified UNIFAC approach is incapable of satisfactorily representing the interaction parameter, it is still worthwhile to consider this approach. A constant value of the so-called UNIFAC group interaction parameter was used throughout this study. This is not often true and may be directly responsible for this imperfection. Recently, progress has been made to include and revise the temperature and concentration dependence of the UNIFAC group interaction parameters by Skjold-Jørgensen, Rasmussen, and Fredenslund[60,61].

## CONCLUSIONS

Within the error and inadequacy involved in the experimental and theoretical treatment, there is no dependence of the interaction parameter on polymer molecular weight. Through treatment of experimentally generated data and interpretation of literature data, it has been concluded that the non-Gaussian character of polystyrene becomes more important as the polymer molecular weight increases. It was found that the influence imposed by the polymer molecular weight on the activity of solvent, the clustering function of solvent, and the interaction parameter is insignificant. In the present study, neither the UNIFAC nor the modified UNIFAC methods satisfactorily predicted $\chi$ in all cases, although both successfully predicted either activity or interaction para-
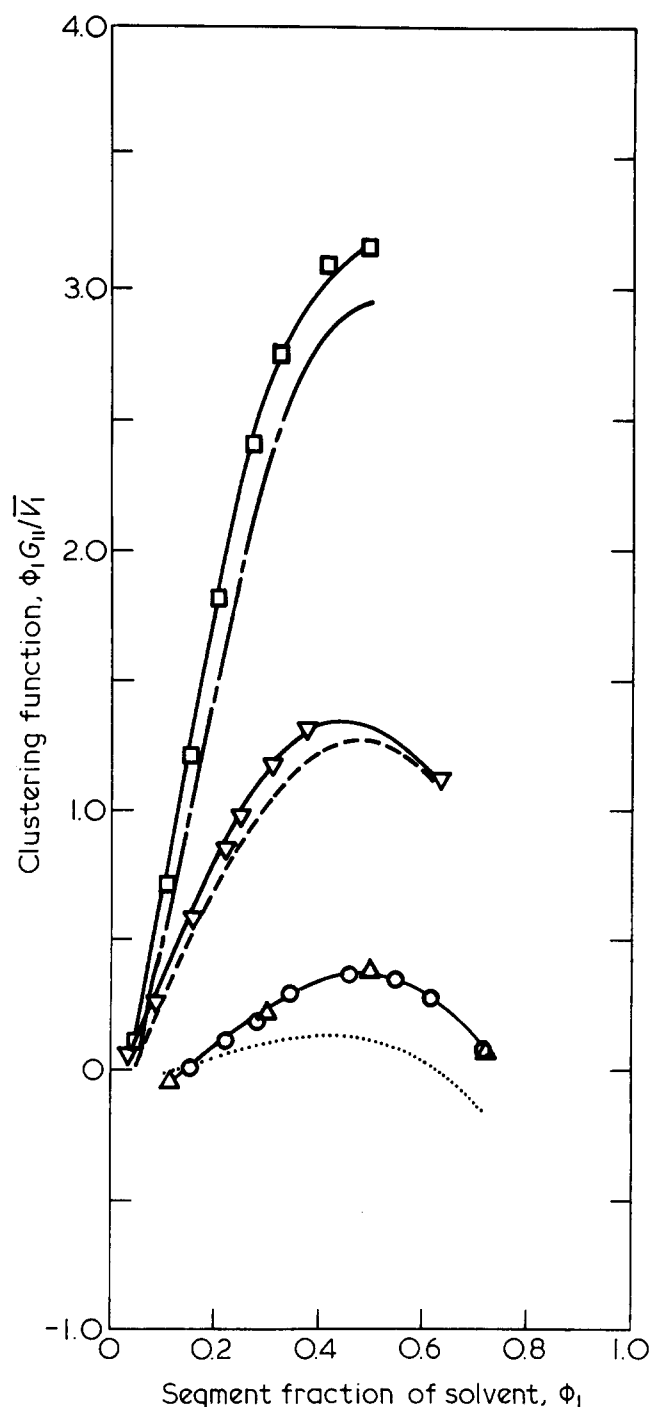


Figure 6 Clustering function *versus* segment fraction of solvent at 25°C. For acetone/PS solution: □, $M_n$=1.57×10$^4$ taken from ref. 15; and ———, computed from modified UNIFAC; for pentane/PIB solution: ∇, $M_v$=4.0×10$^4$ taken from ref. 51; and ——, computed from modified UNIFAC; for chloroform/PS solution: ○, $M_n$=2.9×10$^5$; and △, $M_n$=9.0×10$^4$ taken from ref. 15; and ········, computed from modified UNIFAC

meter in some cases as verified by previous investigators[11,13].

It should be emphasized that the constant values of UNIFAC group interaction parameter was used which may not be true. It is expected that the accuracy of modified UNIFAC method will be greatly improved with the advanced development of taking temperature and concentration dependence of the UNIFAC group interaction parameters into account.
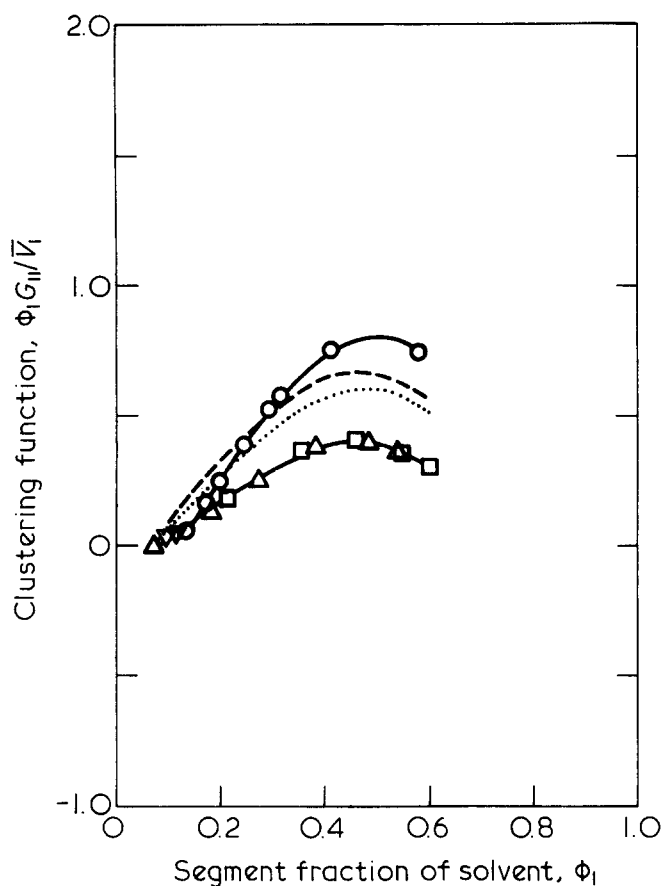
**Figure 7** Clustering function *versus* segment fraction of solvent. For cyclohexane/PIB solution at 25°C: $\bigcirc$, $\bar{M}_v = 4.0 \times 10^4$ taken from ref. 47; and — —, computed from modified UNIFAC; for benzene/PVAC at 30°C: $\triangle$, $\bar{M}_n = 4.8 \times 10^4$; and $\square$, $\bar{M}_n = 1.43 \times 10^5$ taken from ref. 55; $\bigtriangledown$, $\bar{M}_v = 1.7 \times 10^5$ taken from ref. 54; and $\cdots\cdots\cdots$, computed from modified UNIFAC

## ACKNOWLEDGEMENTS

## REFERENCES

1   Flory, P. J. *J. Chem. Phys.* 1942, **10**, 51
2   Huggins, M. L. *Ann. N.Y. Acad. Sci.* 1942, **43**, 1
3   Sheehan, C. J. and Bisic, A. L. *Rubber Chem. Tech.* 1966, **39**, 149
4   Bonner, D. C. *J. Macromol. Sci.-Revs. Macromol. Chem.* 1975, **C13**, 263
5   Braun, J. M. and Guillet, J. E. *Adv. Polym. Sci.* 1976, **21**, 107
6   Orwoll, R. A. *Rubber Chem. Tech.* 1977, **50**, 451
7   Blanks, R. F. *Polym.-Plast. Technol. Eng.* 1977, **8**(1), 13
8   Gray, D. G. in 'Prog. Polym. Sci.' (Ed. A. D. Jenkins), Pergamon Press, New York, N.Y. 1977, 5, 1
9   Tseng, H. S. MS Report, Polytech. Inst. N.Y. 1981
10  Fredenslund, A., Gmehling, J., Michelsen, M. L., Rasmussen, P. and Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* 1977, **16**, 450
11  Oishi, T. and Prausnitz, J. M. *ibid* 1978, **17**, 333
12  Van Krevelen, D. W. and Hoftyzer, P. T. 'Properties of Polymers: Correlations with Chemical Structure', Elsevier Pub. Co., New York, N.Y. 1972, Ch. 18
13  Gottlieb, M. and Herskowitz, M. *Macromol.* 1981, **14**, 1468
14  Outer, P., Carr, C. I. and Zimm, B. H. *J. Chem. Phys.* 1950, **18**, 830
15  Bawn, C. E. H. and Wajid, M. A. *Trans. Faraday Soc.* 1956, **52**, 1658
16  Muramoto, A. *Polymer* 1982, **23**, 1311
17  Narasimhan, V., Lloyd, D. R. and Burns, C. M. *J. Appl. Polym. Sci.* 1979, **23**, 749
18  Lloyd, D. R. and Burns, C. M. *J. Polym. Sci.-Polym. Lett. Ed.* 1981, **19**, 299
19  Robledo-Muniz, J. G. *M.S. Thesis* The University of Texas, December 1982
20  Fox, T. G. and Flory, P. J. *J. Am. Chem. Soc.* 1951, **73**, 1904; *J. Phys. Chem.* 1942, **46**, 151
21  Kurata, M., Stockmayer, W. H. and Roig, A. *J. Chem. Phys.* 1960, **33**, 151
22  Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
23  Allen, G., Gee, G. and Wilson, G. J. *Polymer* 1960, **1**, 456
24  Abe, A. and Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1838
25  Orwoll, R. A. and Flory, P. J. *J. Am. Chem. Soc.* 1967, **89**, 6814
26  Eichinger, B. E. and Flory, P. J. *Macromol.* 1968, **1**, 285
27  Othmer, K. 'Encyclopedia of Chemical Technology', 2nd Edn., Interscience Pub., New York, N.Y. 1969, Vol. 18
28  Hocker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251
29  Shih, H. and Flory, P. J. *Macromol.* 1972, **5**, 758
30  Brandrup, J. and Immergut, E. H. 'Polymer Handbook', John Wiley and Sons, New York, N.Y., 1974
31  Morimoto, S. *Makromol. Chemie.* 1970, **133**, 197
32  Timmerman, J. 'Physico-Chemical Constants of Pure Organic Compounds', Elsevier Pub. Co., New York, N.Y. 1950
33  Bristow, G. M. and Watson, W. F. *Trans. Faraday Soc.* 1958, **54**, 1742
34  Bawn, C. E. H., Freeman, R. F. J. and Kamaliddin, A. R. *Trans. Faraday Soc.* 1950, **46**, 677
35  Flory, P. J. and Hocker, H. *Trans. Faraday Soc.* 1971, **67**, 2258
36  Hocker, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2270
37  Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035
38  Tewari, Y. B. and Schreiber, H. P. *Macromol.* 1972, **5**, 329
39  Bristow, G. M. and Watson, W. F. *Trans. Faraday Soc.* 1958, **54**, 1567
40  Gee, G., Herbert, B. M. and Roberts, R. C. *Polymer* 1965, **6**, 541
41  Saeki, S., Holste, J. C. and Bonner, D. C. *J. Polym. Sci. Polym. Phys. Edn.* 1982, **20**, 793
42  Leung, Y.-K. and Eichinger, B. E. *J. Phys. Chem.* 1974, **78**, 60
43  Leung, Y.-K. and Eichinger, B. E. *Macromol.* 1974, **7**, 685
44  Newman, R. D. and Prausnitz, J. M. *J. Phys. Chem.* 1972, **76**, 1492
45  Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2053
46  Flory, P. J. and Daoust, H. *J. Polym. Sci.* 1957, **25**, 429
47  Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2061
48  Hammers, W. E. and Deligny, C. L. *Rec. Travi. Chim., Pays-Bas.* 1971, **90**, 912
49  Flory, P. J., Ellenson, J. L. and Eichinger, B. E. *Macromol.* 1968, **1**, 279
50  Baker, C. H., Brown, W. B., Rowlinson, J. S., Stubley, D. and Yeadon, R. D. *Polymer* 1962, **3**, 215
51  Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2066
52  Saeki, S., Holste, J. C. and Bonner, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 805
53  Matsumura, K. and Katayama, T. *Kagaku, Kogaku* 1974, **38**, 388
54  Kokes, R. J., Dipietro, A. R. and Long, F. A. *J. Am. Chem. Soc.* 1953, **75**, 6319
55  Nakajima, A., Yamakawa, H. and Sakuraca, I. *J. Polym. Sci.* 1959, **35**, 489
56  Bondi, A. 'Physical Properties of Molecular Crystals, Liquids, and Gases', Wiley, New York, N.Y. 1968
57  Flory, P. J. *Disc. Faraday Soc.* 1970, **49**, 7
58  Chahal, R. S., Kao, W.-P. and Patterson, D. *J. Faraday Trans.* 1973, **69**, 1834; 1973, **69**, 1849
59  Zimm, B. H. and Lundberg, J. L. *J. Phys. Chem.* 1956, **60**, 425
60  Skjold-Jørgensen, S., Rasmussen, P. and Fredenslund, A. *Chem. Eng. Sci.* 1980, **35**, 2389
61  Skjold-Jørgensen, S., Rasmussen, P. and Fredenslund, A. *Chem. Eng. Sci.* 1982, **37**, 99