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References and Notes

(1) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961.
(2) Mattice, W. L.; Skolnick, J. *Macromolecules* **1981**, *14*, 863.
(3) Mattice, W. L.; Napper, D. H. *Macromolecules* **1981**, *14*, 1066.
(4) Smith, R. P. *J. Chem. Phys.* **1965**, *42*, 1162.
(5) Mattice, W. L.; Santiago, G. *Macromolecules* **1980**, *13*, 1560.
(6) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(7) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1098.
(8) Lide, D. R., Jr. *J. Chem. Phys.* **1960**, *33*, 1519.
(9) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(10) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1976**, *9*, 53.
(11) Mattice, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 3466.
(12) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4165.
(13) Mattice, W. L. *Macromolecules* **1980**, *13*, 506.
(14) Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1713.
(15) Mattice, W. L. *Macromolecules* **1981**, *14*, 143.
(16) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4178.
(17) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(18) Orofino, T. A. *Polymer* **1961**, *2*, 305.
(19) Solc, K. *Macromolecules* **1978**, *6*, 378.

Estimation of the χ Parameter for Poly(dimethylsiloxane) Solutions by the UNIFAC Group Contribution Method

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ABSTRACT: The UNIFAC group contribution method is used to calculate the reduced residual chemical potential χ for poly(dimethylsiloxane) solutions in alkanes, aromatic hydrocarbons, and dimethylsiloxane oligomers. The correct dependence of χ on polymer segment fraction is obtained for all solvents. In most cases the computed value of χ differs by less than 10% from the experimental data. No adjustable parameters or solution data are required for the calculation. The UNIFAC method is shown to be a promising tool for systems with small "free volume" effects and unavailable experimental data.

The thermodynamics of polymer solutions have attracted the interest of many investigators. Several theories have been put forward in an effort to explain the various phenomena occurring when large polymer molcules are mixed with small solvent molecules.[1-5] Traditionally, the chemical potential (μ) or activity (a) of the solvent is described as the sum of two terms—a combinatorial term and a residual term:[2]

$$\ln a_1 = (\mu_1 - \mu_1^\circ)/RT = \{(\mu_1 - \mu_1^\circ)_{comb}/RT\} + \{(\mu_1 - \mu_1^\circ)_{res}/RT\} = \{\ln \phi_1 + (1 - 1/r)\phi_2\} + \chi\phi_2^2 \quad (1)$$

Here the subscripts 1 and 2 refer to the solvent and polymer, respectively, r is the ratio of molar volumes of polymer to solvent, and ϕ is the segment fraction defined as[3]

$$\phi_i = m_i v^*_{sp,i}/(m_1 v^*_{sp,1} + m_2 v^*_{sp,2}) \quad (2)$$

where m_i is the mass of component i and $v^*_{sp,i}$ is the core volume or characteristic volume per gram.

The combinatorial term in eq 1 is obtained from the Flory–Huggins lattice model. The residual term incorporates two distinct contributions: an "interactional" contribution due to differences in chemical nature between solvent and solute molecules and a "free volume" contribution due to volume changes involved in the mixing process.

The reduced residual chemical potential χ, defined by eq 1, is a key parameter in describing solution properties of non-cross-linked polymer molecules and swelling behavior of cross-linked materials.[6] Hence, the ability to predict its value over the entire range of polymer concentrations ($0 < \phi_2 < 1$) is the utmost test for the practical utility of any model. The lack of sufficient data on solution behavior for many important polymer–solvent pairs only emphasizes the need for a reliable predictive tool for the χ parameter.

Poly(dimethylsiloxane) (PDMS) is one of the most thoroughly studied polymers.[7] The relative abundance of data for various solvent–PDMS systems facilitates comparison of theory to experimental data. In addition, "free volume" effects are relatively small in PDMS solutions.[8] Such effects depend on the difference in free volume between the solution components. Most polymers exhibit considerably smaller free volume than those of typical solvents whereas PDMS, due to its high degree of thermal expansion, has a relatively large free volume. The negligible "free volume" contribution to χ enables one to study the "interactional" contribution independently. These two factors, combined with the practical importance of PDMS systems,[9] prompted us to concentrate in this work on PDMS solutions. Treatment of systems with large "free volume" effects will be considered in forthcoming publications.

Flory and Shih[10] have investigated the behavior of PDMS solutions in benzene, cyclohexane, and chlorobenzene. Utilizing their own data as well as data by Kuwahara et al.,[11] they have shown good agreement between experiment and Flory's theory.[2] The agreement is obtained with the aid of two adjustable parameters, X_{12} and Q_{12}, and manipulation of a third parameter s_1/s_2 between two limiting values. Chahal et al. in a recent publication[8] have compared 15 different PDMS–solvent systems to various one- and two-adjustable-parameter versions of Flory's theory. Their conclusions are that this theory fails to provide a reliable prediction of χ for each one of the tested solutions. Several other experimental studies on PDMS solutions are available,[7,22] but most of them are limited to

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Table I
Reduced Bondi Parameters for Groups Used in This Work

functional group	main group[a]	R_k	Q_k	sample group assignment	ref
SiO	SiO	1.1044	0.466	PDMS repeat unit: 1 SiO, 2 CH_3	18
Si	SiH_2	1.0470	0.410	octamethyltrisiloxane: 2 SiO, 1 Si, 8 CH_3	18
CH_3		0.9011	0.848		
CH_2	CH_2	0.6744	0.540	2,2,4-trimethylpentane: 5 CH_3, 1 CH_2, 1 CH, 1 C	13
CH		0.4469	0.228		
C		0.2195	0.000		
ACH	ACH	0.5313	0.400	benzene: 6 ACH	13
$ACCH_3$	$ACCH_2$	1.2663	0.968	xylene: 4 ACH, 2 $ACCH_3$	13
$ACCH_2$		1.0396	0.660	ethylbenzene: 5 ACH, 1 $ACCH_2$, 1 CH_3	13

[a] Main group includes all functional groups of similar chemical structure which have identical interaction parameter values with respect to members of other main groups and zero interaction among group members.

a narrow range of polymer concentrations.

In this work we demonstrate the ability of the UNIFAC group contribution method to predict the value of χ, over the entire range of polymer concentrations, for PDMS in a variety of solvents. No adjustable parameters are required in this calculation.

The UNIFAC Method

The UNIFAC method, developed and extended by Fredenslund and co-workers[12-14] and recently applied to polymer solutions,[15] is based on the concept that the solution is a collection of groups. Thus, a liquid mixture is considered as a solution of functional groups rather than a solution of molecules. This concept allows calculation of solution properties for a large number of different materials constructed from a relatively small set of functional groups. (This idea was also utilized by Derr and Deal[24] in their work on polymer solutions.)

Three quantities associated with each functional group are required for the application of the UNIFAC method. The first two quantities, R_k and Q_k, are the reduced Bondi group volume and surface area parameters, respectively. They are calculated from the van der Waals radii and covalent bond lengths as outlined by Bondi[16] and normalized with respect to the polyethylene repeat unit.[17] The reduced Bondi group parameters for several groups used in this work are listed in Table I. A more extensive list of parameter values[13] and a discussion of their calculation for silicone groups[18] are given elsewhere.

The third type of parameter associated with each group is the interaction parameter a_{mn}, related to the interaction between a group of type m and a group of type n ($a_{mn} \neq a_{nm}$ and $a_{mm} = 0$). This parameter has to be determined from experimental data but is independent of the particular system at hand. Once the interaction parameter between two groups has been determined, its value will remain unchanged for all systems in which they will occur. A comprehensive list of interaction parameters is given by Skjold-Jørgensen et al.[14] A similar list for several silicone groups is also available.[18] The a_{mn} values for the groups pertinent to this work are given in Table II.

In what follows, a summary of the basic relations needed for application of the UNIFAC method is given. A detailed discussion of the method and its underlying assumptions is available in two recent publications.[13,15]

The molar volume r_i and molar surface area q_i for molecule i are given in terms of the functional groups composing it by

$$r_i = (\sum_k \nu_k^i R_k)/M_i \quad (3)$$

$$q_i = (\sum_k \nu_k^i Q_k)/M_i \quad (4)$$

where ν_k^i is the number of occurrences of group type k in molecule i (repeat unit in case of a polymer molecule) and M_i is the molecular weight of molecule i (repeat unit for polymer).

Table II
Interaction Parameters (a_{mn}) for Main Groups Used in This Work[a]

m \ n	CH_2	ACH	$ACCH_2$	SiO	SiH_2
CH_2	0	61.13	76.50	327.0	407.2
ACH	−11.12	0	167.0	254.3	551.9
$ACCH_2$	−69.70	−146.8	0	355.5	683.3
SiO	109.3	293.8	221.8	0	639.3
SiH_2	97.9	−184.3	191.6	498.8	0

[a] Values for last two columns and last two rows from ref 18. All other values from ref 14.

The segment fraction ϕ_i' and molar surface fraction θ_i' for molecule i in the solution are now defined

$$\phi_i' = m_i r_i/(\sum_j m_j r_j) \quad (5)$$

$$\theta_i' = m_i q_i/(\sum_j m_j q_j) \quad (6)$$

The activity of the solvent is then calculated by[15] (ignoring free volume effects)

$$\ln a_1 = \ln \phi_1' + \phi_2' + (z/2)M_1 q_1[\ln(\theta_1'/\phi_1') - 1 + \phi_1'/\theta_1'] + \sum_k \nu_k^1(\ln \Gamma_k - \ln \Gamma_k^{(1)}) \quad (7)$$

The lattice coordination number, z, is set equal to 10 throughout this work. The summation in the last term on the right-hand side of eq 7 is carried out over all functional groups composing the solvent molecule. The group activity Γ_k is computed from

$$\ln \Gamma_k = Q_k[1 - \ln(\sum_m \Theta_m \Psi_{mk}) - \sum_m(\Theta_m \Psi_{km}/(\sum_n \Theta_n \Psi_{nm}))] \quad (8)$$

Summations are over all different functional groups in the solution.

$$\Psi_{mn} = \exp(-a_{mn}/T) \quad (9)$$

The group surface fraction Θ_m is calculated in a fashion similar to θ_m'

$$\Theta_m = (W_m Q_m/M_m)/(\sum_k W_k Q_k/M_k) \quad (10)$$

where W_k is the weight fraction of group k in the solution and M_k is the molecular weight of group k. The summation is over all groups in the solution.

In eq 7 $\Gamma_k^{(1)}$ is the group activity in a reference solution of pure solvent. It is computed by replacing Θ_k with $\Theta_k^{(1)}$ in eq 8 and W_k with $W_k^{(1)}$ in eq 10.

Table III
Experimental and Computed Interaction Parameter Values for Several PDMS Solutions[a]

material	$\phi_2 = 0.01$			$\phi_2 = 0.25$			$\phi_2 = 0.50$			$\phi_2 = 0.75$			$\phi_2 = 0.99$		
	χ_{exptl}	χ_{UN}	χ_{UFV}	χ_{exptl}	χ_{UN}	χ_{UFV}	χ_{exptl}	χ_{UN}	χ_{UFV}	χ_{exptl}	χ_{UN}	χ_{UFV}	χ_{exptl}	χ_{UN}	χ_{UFV}
n-pentane		0.42	0.51		0.42	0.51	0.47	0.42	0.52	0.48	0.41	0.53	0.50	0.41	0.54
n-heptane		0.53	0.57	0.50	0.52	0.57	0.47	0.52	0.56	0.49	0.51	0.56	0.50	0.51	0.56
n-octane		0.59	0.62	0.52	0.58	0.61	0.50	0.57	0.60	0.51	0.56	0.59	0.55	0.56	0.59
benzene	0.49	0.44	0.47	0.55	0.48	0.50	0.68	0.52	0.55	0.77	0.56	0.60	0.90	0.62	0.66
toluene	0.43	0.42	0.42	0.51	0.46	0.47	0.63	0.52	0.53	0.72	0.60	0.61	0.85	0.71	0.72
p-xylene		0.48	0.48		0.51	0.52	0.56	0.56	0.57	0.65	0.65	0.65	0.77	0.77	0.77
ethylbenzene		0.47	0.47	0.50	0.50	0.50	0.60	0.54	0.54	0.67	0.60	0.60	0.78	0.66	0.67
hexamethyldisiloxane		0.32	0.36	0.34	0.32	0.36	0.33	0.32	0.37	0.33	0.33	0.38	0.32	0.34	0.39
octamethyltrisiloxane		0.23	0.25	0.29	0.23	0.25	0.25	0.24	0.26	0.22	0.24	0.26	0.18	0.24	0.27

[a] χ_{exptl} = experimental value. If more than one value is available, average value is given. χ_{UN} = prediction of UNIFAC without the free volume contribution. χ_{UFV} = prediction of the modified UNIFAC including free volume contribution.

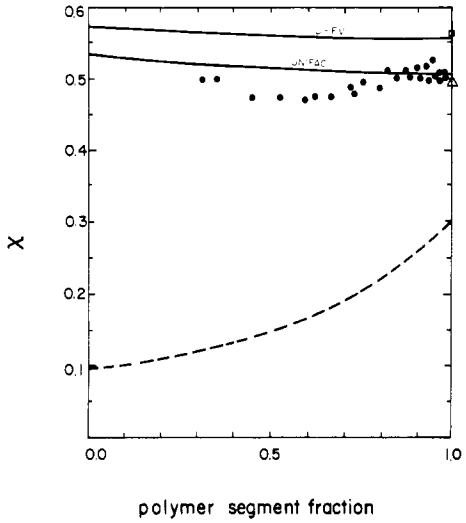

Figure 1. Plot of χ against polymer segment fraction for the system *n*-heptane/PDMS. Theoretical curves: UNIFAC, eq 7; UFV, eq 14 of ref 15; broken line, Flory's theory computed by Chahal et al.[8] Experimental points: filled circles, ref 8 (20 °C); open triangle, ref 20 (55 °C); open square, ref 21 (25 °C).

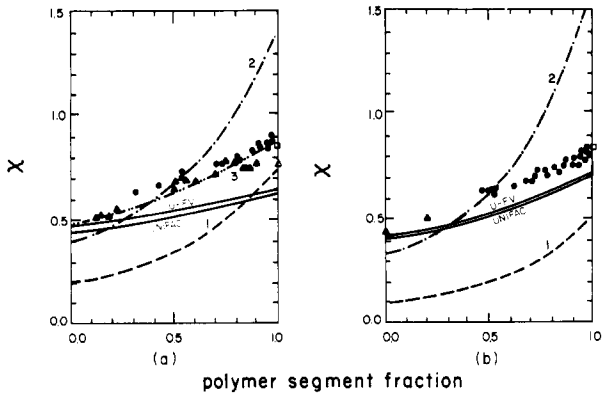

Figure 2. Plot of χ against polymer segment fractions for aromatic solvents. Theoretical curves: UNIFAC, eq 7; UFV, eq 14 of ref 15; broken lines 1 and 2, Flory's theory with one (X_{12}) and two (X_{12}, Q_{12}) adjustable parameters, respectively, as computed by Chahal et al.;[8] broken line 3, two-parameter Flory theory as computed by Flory and Shih.[10] (a) Benzene/PDMS. Experimental points: circles, ref 8 (20 °C); filled triangles, ref 10 (25 °C); square, ref 21 (25 °C); open triangle, ref 20 (55 °C). (b) Toluene/PDMS. Experimental points: circles, ref 8 (20 °C); triangles, ref 11 (20 °C); square, ref 21 (25 °C).

When applied to polymer solutions the UNIFAC model has to be modified to include a "free volume" term. This has been done recently by Oishi and Prausnitz.[15] (We will subsequently refer to their model as UFV.) One additional parameter is now required, namely, the number of external

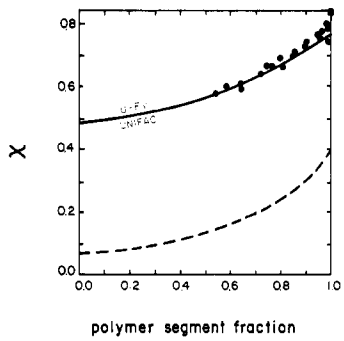

Figure 3. Plot of χ against polymer segment fraction for *p*-xylene/PDMS. Experimental points: circles, ref 8 (25 °C); square, ref 21 (25 °C). Solid line, computed by eq 7 (UNIFAC) and eq 14 of ref 15 (UFV). Dashed line, Flory's theory computed by Chahal et al.[8]

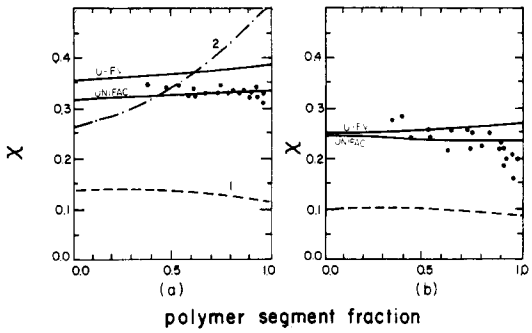

Figure 4. Plot of χ against polymer segment fraction for PDMS oligomers. Solid lines: prediction of the UNIFAC (eq 7) and UFV (eq 14 of ref 15) models. Dashed lines, Flory's model as computed by Chahal et al.[8] with one (dashed line 1) and two (line 2) adjustable parameters. (a) Hexamethyldisiloxane/PDMS. Experimental points, ref 8 (20 °C). (b) Octamethyltrisiloxane/PDMS. Experimental points, ref 8 (23.2 °C).

degrees of freedom per solvent molecule, $3c_1$. Oishi and Prausnitz have suggested $c_1 = 1.1$ for all of the solvents studied by them, which included most of the ones discussed here.

Results and Discussion

The solvent activities for the systems reported by Flory and Shih[10] and by Chahal et al.[8] were computed[23] by using eq 7 and Tables I and II. The χ parameter was then obtained from eq 1, using v^*_{sp} values available in the literature.[8,10,12] The computed χ values (solid lines labeled UNIFAC) are compared to experimental data in Figures 1–4 and in Table III (χ_{UN}). The experimental points shown in these figures were obtained from vapor solution,[8,10] osmotic pressure,[10,11] or gas–liquid chromatography[20,21] measurements of the chemical potential. The experimental data are also compared to the predictions of Flory's theory

as computed by Flory and Shih[10] and by Chahal et al.[8] (dashed lines).

The computation was repeated with eq 14 and 16 of ref 15 to include "free volume" effects. The results of these computations are indicated in Figures 1–4 (by the solid lines labeled U-FV) and in Table III (χ_{UFV}). The value $c_1 = 1.1$ was used in all calculations.

Nine solvents from three chemical families were utilized in this work: alkanes, aromatic hydrocarbons, and dimethylsiloxane oligomers.

From the three tested alkanes, *n*-pentane, *n*-heptane (Figure 1), and *n*-octane, only the first one shows a large disagreement between the prediction of UNIFAC and the experimental data. For this system the UNIFAC model is predicting a consistently lower value of χ with an average error of 12%. A much better agreement is obtained for the two other alkane systems. In all three systems the value of χ is almost independent of ϕ_2. This behavior is correctly predicted by UNIFAC for the three solvents.

The relatively poor results in the case of pentane may be due to the "free volume" effect. As pointed out by Chahal et al.[8], the high degree of thermal expansion of PDMS, being close to that of the solvents, makes free volume contribution unimportant. Yet, examination of the thermal expansion coefficient values for alkanes reveals that *n*-pentane has a much larger thermal expansion coefficient than the two other alkanes discussed here (1.55×10^{-3} deg^{-1} for pentane compared with 1.22×10^{-3} deg^{-1} for heptane, 1.15×10^{-3} deg^{-1} for octane, and 0.91×10^{-3} deg^{-1} for PDMS). The addition of a "free volume" term to the expression for the chemical potential of the solvent will increase the value of χ predicted by it. When this is done employing the UFV model, values which are 5–10% higher than experiment are obtained. An even larger error (always overestimating χ) is obtained in the case of heptane (cf. Figure 1) and octane (cf. first three rows in Table III). Using a larger c_1 value will increase the discrepancy between calculated and experimental values even further.

Four aromatic hydrocarbons were tested: benzene, toluene, *p*-xylene, and ethylbenzene. In Figures 2 and 3 the prediction of the UNIFAC and UFV models are compared to experimental data for the first three. For all four systems χ is strongly dependent on ϕ_2. The trend of increasing χ values with increasing ϕ_2 is correctly predicted by both models. The agreement between UNIFAC and experiment varies from a close match for the *p*-xylene system to a relatively poor agreement for the benzene system (20% average error). The inclusion of free volume effects has no influence on the theoretical predictions in the case of *p*-xylene and ethylbenzene and is not significant for the other two.

A better agreement can be obtained with the UFV model if the value of c_1 for benzene and toluene in increased considerably ($c_1 > 5.0$). But these values will be inconsistent with values used successfully by Oishi and Prausnitz[15] for other benzene/polymer and toluene/polymer systems. High c_1 values are also inconsistent with the physical interpretation of this parameter.

In Figure 4 the behavior of two dimethylisiloxane oligomers is depicted. Here χ is only slightly dependent on ϕ_2. But in this case its value is decreasing with increasing polymer segment fraction. There is good agreement in both cases between the χ values calculated by UNIFAC and the depicted experimental data. Here again, UFV overcompensates for the free volume effects, especially in the case of the hexamethyldisiloxane solution.

Conclusions

From the results of this work it is clear that the UNIFAC model is capable of predicting quite accurately the value of χ for different PDMS/solvent systems.

In all cases, the correct dependence of χ on ϕ_2 is obtained and in most systems the computed values are within 10% of the experimental data. In all systems, except the benzene/PDMS system, the a priori UNIFAC calculation is in much better agreement with experiment than available models employing one or two adjustable parameters. Inclusion of the "free volume" effects by means of the UFV model yields in most of the cases tested here too large χ values.

The fact that no solution data are required for the UNIFAC computation makes its use very attractive for systems in which experimental information is scarce.

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References and Notes

(1) Prigogine, I. "The Molecular Theory of Solutions"; North-Holland Publishing Co.: Amsterdam, 1957.
(2) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(3) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
(4) Patterson, D. *Discuss. Faraday Soc.* **1970**, *49*, 98.
(5) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(6) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953; pp 576.
(7) Bonner, D. C. *J. Macromol. Sci., Rev. Macromol. Chem.* **1975**, *C13*, 263.
(8) Chahal, R. S.; Kao, W. P.; Patterson, D. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 1834.
(9) Morton, M. "Rubber Technology"; Van Nostrand-Reinhold: New York, 1973.
(10) Flory, P. J.; Shih, H. *Macromolecules* **1972**, *5*, 761.
(11) Kuwahara, N.; Okazawa, T.; Kaneko, M. *J. Polym. Sci., Part C* **1968**, *23*, 543.
(12) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(13) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: Amsterdam, 1977.
(14) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714.
(15) Oishi, T.; Prausnitz, J. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 333.
(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(17) The method described by Bondi is for the calculation of the van der Waals volume V_w and surface area A_w. The reduction parameters used are 15.17 cm^3/mol and 2.5×10^9 cm^2/mol, respectively.[12]
(18) Herskowitz, M.; Gottlieb, M. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 407.
(19) Shih, H.; Flory, P. J. *Macromolecules* **1972**, *5*, 758.
(20) Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 565.
(21) Summers, W. R.; Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 12.
(22) Orwoll, R. A. *Rubber Chem. Technol.* **1976**, *50*, 451.
(23) Pertinent computer programs are available from the authors upon request.
(24) Derr, E. L.; Deal, C. H. *Adv. Chem. Ser.* **1973**, *No. 124*, 11.