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Statistical Thermodynamics of Polymer Solutions Based on Free Volume Theory‡

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ABSTRACT: The modified Flory theory proposed by authors is applied to both poly(dimethylsiloxane)–solvent systems, where agreements between values of excess volume calculated according to the Flory theory and experimental theories are poor, and polyisobutylene–solvent systems, where the Flory theory holds well. For the former systems, agreements with experimental values are favorable, while for the latter systems, agreements with experimental values are not so good. But if the additivity of volume is assumed for polyisobutylene–solvent systems, agreements with experimental values are excellent. These results agree well with those obtained assuming only the corresponding state principle found recently by Ogino et al.

Since the large deviation characteristic of polymer solutions from the ideal solution law was first elucidated by Flory[1] and Huggins,[2] principal thermodynamic properties of nonpolar solution have been qualitatively explained.[3] But the theory failed to interpret the phenomenon found first by Rowlinson et al.[4] that a certain nonpolar polymer–nonpolar solvent system exhibited a lower critical solution temperature. Also the theory could not describe volume changes on mixing.

Patterson et al.[5] enabled us to interpret such a phenomenon on the basis of the cell theory of Prigogine.[6] Flory[7] also succeeded in explaining it by proposing a new polymer solution theory based on free volume theory.

The feature of the Flory theory is that thermodynamic parameters are evaluated from the measurable parameters such as specific volumes, thermal expansivities, and thermal pressure coefficients of each component. This is a great advantage in applying this theory to polymer solutions. Therefore, the Flory theory was compared with experiments for many systems of polymer–solvent by Flory and his co-workers, and many other investigators.

The Flory theory agreed well with the experimental value for polyisobutylene (PIB)[8-13] and polyethylene[14,15] solutions, while for polystyrene[16] and poly(dimethylsiloxane) (PDMS)[17-21] solutions, it was necessary to introduce a correction parameter Q_{12} to obtain agreements between calculated and observed values. Although the correction term was considered to express exchange entropy on the basis of Guggenheim's assertion,[22] it is added only to the expression for the interaction parameter χ and its physical meaning remains obscure. Especially for mixtures of PDMS and solvent, it was found that the contribution of this term to χ was unusually large.[17-21] Also, excess volumes observed for PDMS–solvent systems were considerably different from those predicted by the theory.[17,20,21]

In the preceding papers,[23,24] we showed that the above two problems could be solved by the modification of the combining rules on mixing assumed by Flory. We modified his combining rules as follows: (i) the number of external degrees of freedom for mixtures is nonadditive with respect to segment fraction, and (ii) the sizes of the core volume per segment are different between two pure components and the core volume for mixtures is given by the expression similar to the van der Waals combining rule.

In this paper, we examine whether our modified Flory theory is applicable to various systems of polymer–solvent or not. For this purpose, we deal with PIB–solvent systems for which the original Flory theory was successful and with PDMS–solvent systems for which it was not. Further, the parameters introduced into the modified combining rules are discussed.

Theoretical

Following Prigogine,[6] the number of degrees of freedom of a molecule in a liquid can be separated into internal and external degrees of freedom. Then, the partition function of a liquid can be expressed as a product of factors related to both degrees of freedom as follows:

$$Z = Z_{\mathrm{int}} Z_{\mathrm{ext}} \tag{1}$$

The internal degrees of freedom depend only on valency forces, and then Z_{int} is a function of temperature only. The external degrees of freedom depend on the environment of the molecule. Therefore, a part of the rotational and vibrational degrees of freedom belongs to the external degrees of freedom. This subdivision of the degrees of freedom is important for polymeric liquids because rotation and vibration of a polymer molecule considerably influence the environment.

Now we consider a system comprising N r-mer molecules. Using Prigogine's approximation[6] that the external rotational and vibrational degrees of freedom can be considered to be equivalent to the translational degrees of freedom, we have

$$Z_{\mathrm{ext}} = (2\pi mkT/h^2)^{3Ncr/2} Z_{\mathrm{c}} \tag{2}$$

where $3c$ is the total number of external degrees of freedom per segment, m is the mass per segment, h is Planck's constant, and Z_{c} is the configurational partition function.

Following Flory,[7] we can write the configurational partition function as

$$Z_{\mathrm{c}} = Z_{\mathrm{comb}}[g(v^{1/3} - v^{*1/3})^3]^{Ncr} \exp(-E_0/kT) \tag{3}$$

where Z_{comb} is the combinatorial factor including the communal entropy, g is the geomentric factor, v is the volume per segment, v^* is the core volume per segment, and E_0 is the mean intermolecular energy given by the following van der Waals type

$$E_0 = -Nrs\eta/2v \tag{4}$$

where s is the number of intermolecular contact sites per segment and η is a constant characterizing the energy per contact site.

Then, the partition function can be written from eq 1 as

$$\begin{aligned} Z = Z_{\mathrm{comb}} q_{\mathrm{int}}(T)^{Nr} (2\pi mkT/h^2)^{3Ncr/2} [g(v^{1/3} - {} \\ v^{*1/3})^3]^{Ncr} \exp(Nrs\eta/2vkT) \end{aligned} \tag{5}$$

where

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‡Dedicated to Professor Dr. Paul J. Flory on his 70th birthday.

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$$q_{\mathrm{int}}(T)^{Nr} = Z_{\mathrm{int}} \quad (6)$$

From eq 5, we obtain the reduced partition function

$$Z = Z_{\mathrm{comb}}q_{\mathrm{int}}(T)^{Nr}[(2\pi mkT/h^2)^{1/2}(gv^*)^{1/3}]^{3Nrc}(\tilde{v}^{1/3} - 1)^{3Nrc}\exp(Nrc/\tilde{v}\tilde{T}) \quad (7)$$

which gives the reduced equation of state

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} -1) - 1/\tilde{v}\tilde{T} \quad (8)$$

where $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are the reduced variables of pressure, volume, and temperature, respectively, and they are defined by

$$\tilde{v} = v/v^* \quad (9)$$

$$\tilde{T} = T/T^* = 2v^*ckT/s\eta \quad (10)$$

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \quad (11)$$

where p^*, v^*, and T^* are the characteristic parameters.

For a binary mixture, assuming a random mixing, the energy E_0 can be given by

$$-E_0/\bar{r}N = (\sigma_1\theta_1 s_1\eta_{11} + \sigma_2\theta_2 s_2\eta_{22} + 2\sigma_1\theta_2 s_1\eta_{12})/2v \quad (12)$$

where σ_i is the segment fraction of component i (i = 1, 2) defined by

$$\sigma_i = r_iN_i/(r_1N_1 + r_2N_2) = r_iN_i/\bar{r}N \quad (13)$$

and θ_i is the site fraction of component i defined by

$$\theta_i = s_ir_iN_i/(s_1r_1N_1 + s_2r_2N_2) \quad (14)$$

Flory[7] assumed that segments of both molecules in the mixture were arbitrarily chosen to be of equal core volume. (This assumption leads to linearity of the molecular core volume in the mole fraction.) But considering the importance of the repulsive forces,[25] we should take into account difference in size of segments so that $v_1^* \neq v_2^*$. Prigogine[6] pointed out that the difference in size had large effects on the values of excess functions. By analogy with the van der Waals combining rule regarding a constant "b",[26] we assume the core volume of segments in the mixture as

$$v^* = \sigma_1^2v_1^* + 2\sigma_1\sigma_2v_{12}^* + \sigma_2^2v_2^* \quad (15)$$

where

$$v_{12}^* = \zeta[(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad (16)$$

in which ζ is unity for hard spheres. Equation 14 is equivalent to the van der Waals combining rule when $r_1 = r_2$.

We now evaluate the core volume per segment of pure liquids in the following way. According to Prigogine's approximation[6] for a flexible r-mer, only $r - 1$ internal stretching frequencies belong to the internal degrees of freedom. Then, the external degrees of freedom per molecule can be written as

$$3cr = 2r + 1 \quad (17)$$

For a polymer, putting r at infinity, we have $c = {}^2/_3$ from eq 17. Also, eq 10 and 11 give

$$p^*v^* = cRT^* \quad (18)$$

and

$$p^*rv^* = crRT^* \quad (19)$$

where rv^* is the core volume per mole and can be evaluated by the product of the molecular weight and the specific core volume v_{sp}^*. Thus, v^* of the component can be determined by the use of p^*, T^* and v_{sp}^*.

The characteristic pressures for the pure components are given by the following relation from eq 11:

$$p_1^* = s_1\eta_{11}/2v_1^{*2} \qquad p_2^* = s_2\eta_{22}/2v_2^{*2} \quad (20)$$

By analogy, we define

$$p_{12}^* = s_1\eta_{12}/2v_{12}^{*2} \quad (21)$$

By analogy with the relation between the energy and the characteristic parameters for a pure liquid, we define

$$-E_0/\bar{r}N = p^*v^*/\tilde{v} = ckT^*/\tilde{v} \quad (22)$$

Then, comparison of eq 22 with eq 12 after substitution of eq 20 and 21 into eq 11 gives

$$p^* = \sigma_1\theta_1p_1^*(v_1^*/v^*)^2 + \sigma_2\theta_2p_2^*(v_2^*/v^*)^2 + 2\sigma_1\theta_2p_{12}^*(v_{12}^*/v^*)^2 \quad (23)$$

Flory[7] assumed that the number of external degrees of freedom for the mixture was given by a linear form with respect to concentration. On the other hand, Lin[27] and others[23] took into consideration a departure from linearity. Recently, Ogino et al.[28,29] showed the experimental result that it deviates from linearity. Therefore, we write the number of external degrees of freedom for the mixture as

$$c = \sigma_1c_1 + \sigma_2c_2 - \sigma_1\theta_2c_{12} \quad (24)$$

where c_{12} is the parameter characterizing the deviation from additivity.

From eq 22 and 24, the characteristic temperature T^* for the mixture is given by

$$1/T^* = [\sigma_1p_1^*(v_1^*/v^*)/T_1^* + \sigma_2p_2^*(v_2^*/v^*)T_2^* - \sigma_1\theta_2kc_{12}/v^*]/p^* \quad (25)$$

Flory[7] defined the residual free energy as the free energy of mixing except for the combinatorial part. On the basis of eq 7 and the above combining rules in the one-fluid model, the residual chemical potential of component 1 is given by

$$\begin{aligned}(\mu_1 - \mu_1^0)^R ={}& 3p_1^*V_1^*\tilde{T}_1[{}^1\!/_2 \ln (m_1/m) + {}^1\!/_3 \ln (v_1^*/v^*)] - {}^3\!/_2\sigma_2p^*V^*\tilde{T}(m_1 - m_2)/m + 3r_1c_{12}RT\theta_2^2 \ln K + \\ & 3p_1^*V_1^*\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 3r_1c_{12}RT\theta_2^2 \ln (\tilde{v}^{1/3} - 1) + \\ & p_1^*V_1^*[1/\tilde{v}_1 - (\tilde{T}_1/\tilde{T})/\tilde{v}] + (V^*/\tilde{v})\{p_2^*(v_2^*/v^*)(\sigma_2/\sigma_1)[2(v_2^*/v^*)\theta_2 - \tilde{T}_2/\tilde{T}] + \\ & 2p_{12}^*(v_{12}^*/v^*)^2\theta_2 - p^*(\theta_2/\sigma_1)\} + 2\sigma_2p^*V^*(1/\tilde{v} - \tilde{T}) \times \\ & [\sigma_1v_1^* - (\sigma_1 - \sigma_2)v_{12}^* - \sigma_2v_2^*]/v^* + \theta_2r_1c_{12}RT/(\tilde{v}\tilde{T}) \quad (26)\end{aligned}$$

where

$$K = (2\pi mk/h^2)^{1/2}(gv^*)^{1/3}T^{1/2} \quad (27)$$

$$m = \sigma_1m_1 + \sigma_2m_2 \quad (28)$$

$$V_1^* = r_1v_1^* \qquad V^* = r_1v^* \quad (29)$$

Using Flory–Huggins expression as the combinatorial entropy, we would rather use the core volume fraction φ_i given by the following equation than σ_i.

$$\varphi_i = r_iN_iv_i^*/(r_1N_1v_1^* + r_2N_2v_2^*) \quad (30)$$

Then, the interaction parameter χ is defined by

$$\chi = (\mu_1 - \mu_1^0)^R/(RT\varphi_2^2) = (\mu_1 - \mu_1^0)/(RT\varphi_2^2) - [\ln (1 - \varphi_2) + (1 - r_1v_1^*/r_2v_2^*)\varphi_2]/\varphi_2^2 \quad (31)$$

At low pressure, the enthalpy of mixing is

$$\Delta H^{\mathrm{M}} \simeq \Delta E_0 = \bar{r}N[-(3/2)\sigma_1\theta_2r_1c_{12}RT + \sigma_1p_1^*v_1^*/\tilde{v}_1 + \sigma_2p_2^*v_2^*/\tilde{v}_2 - p^*v^*/\tilde{v}] \quad (32)$$

Table I
Equation-of-State Parameters for Pure Liquids

liquid[a]	temp, °C	$\tilde{v}$	v_{sp}^*, cm^3 g^{-1}	T^*, K	p^*, J cm^{-3}	v^*, cm^3 mol^{-1}	r	c
n-C_5H_{12}	25	1.3607	1.1828	4158	406	85.11	1.003	0.999
n-C_6H_{14}	20	1.3142	1.1540	4425	426	80.97	1.228	0.938
n-C_7H_{16}	25	1.2973	1.1347	4652	428	81.89	1.388	0.907
n-C_8H_{18}	20	1.2731	1.1183	4826	434	81.12	1.575	0.878
	25	1.2794	1.1193	4838	433	81.84	1.562	0.880
n-C_9H_{20}	20	1.2612	1.1047	4966	443	79.58	1.780	0.854
MEK	35	1.3216	0.9586	4588	577	64.71	1.068	0.979
MIBK	35	1.2838	0.9896	4951	470	82.77	1.198	0.945
EBK	35	1.2686	0.9798	5127	519	72.50	1.543	0.883
DIBK	35	1.2581	1.0007	5261	445	85.22	1.670	0.866
c-C_6H_{12}	25	1.2906	1.0012	4721	530	69.84	1.207	0.943
C_6H_6	25	1.2917	0.8860	4709	628	59.41	1.165	0.953
PDMS	20	1.2248	0.8381	5494	343	88.83	∞	0.667
	35	1.2354	0.8423	5596	337	92.09	∞	0.667
PIB	20	1.1463	0.9488	7552	447	93.65	∞	0.667
	25	1.1488	0.9493	7580	447	94.04	∞	0.667

[a] MEK, MIBK, EBK, and DIBK express methyl ethyl ketone, methyl isobutyl ketone, ethyl butyl ketone, and diisobutyl ketone, respectively.

By series expansion of eq 32 in powers of σ_2 or φ_2, the enthalpy of mixing $\Delta H^{M}(\infty)$ to infinite dilution can be written as

$$\begin{aligned}\Delta H^{M}(\infty) = {}& (p_1^* v_{sp,2}^*/\tilde{v}_1)(v_1^*/v_2^*)(1 + \alpha_1 T) \times \\ & [(s_2/s_1) + 2(v_{12}^*/v_1^*) - 2] + \\ & p_2^* v_{sp,2}^*[\alpha_1 T(T_1^*/T_2^*)/\tilde{v}_1 + 1/\tilde{v}_2] - \\ & 2(p_{12}^* v_{sp,2}/\tilde{v}_1)(v_1^*/v_2^*)(v_{12}^*/v_1^*)^2(s_2/s_1)(1 + \alpha_T) - \\ & (c_{12}RTv_{sp,2}^*/v_2^*)(s_2/s_1)[3/2 + \alpha_1 T/(\tilde{v}_1\tilde{T}_1)] \end{aligned} \quad (33)$$

where $v_{sp,2}^*$ is the specific characteristic volume of component 2 and α_1 the thermal expansion coefficient of component 1.

The ratio of the excess volume V^E to the sum V^0 of the volumes of the pure components is given by

$$V^E/V^0 = v^*\tilde{v}/(\sigma_1 v_1^* \tilde{v}_1 + \sigma_2 v_2^* \tilde{v}_2) - 1 \quad (34)$$

Results

The reduced and reduction parameters ($\tilde{v}$, $\tilde{T}$, v_{sp}^*, T^*, and p^*) for components were determined from the specific volume v_{sp}, the thermal expansivity α, and the thermal pressure coefficient γ according to Flory's method.[7] The values of v^*, r, and c for small molecules were evaluated from p^*, v_{sp}^*, T^*, and the molecular weight by the use of eq 17–19, and the values of v^* for polymers were determined by substituting $c = {}^2/_3$ into eq 18. They are shown in Table I.

As shown in the table, an n-pentane molecule corresponds to a segment. This seems to be more reasonable than the result obtained by Sanchez and Lacombe.[30] The number of segments of n-alkane is proportional to the number of methylene groups; the value of r per methylene group is about 0.2. The results for other components including polymers show the same tendency. Although the assumption of eq 17 may be inadequate for such spherical molecules as benzene and cyclohexane, the results for r and c obtained according to it do not appear to be unreasonable, though these values are somewhat arbitrary. The large sizes of core volumes per segment for PDMS and PIB may arise from the large cross sections due to the methyl groups.

The ratio s_2/s_1 of contact sites per segment for polymer molecule to that for solvent is evaluated by the approximation that it is equivalent to the ratio of surface areas estimated from molecular models and characteristic volumes.[10,31,32] The PDMS molecule was assumed as a cylinder with a radius 3.37 Å and a length 2.90 Å per monomer. These values were estimated from bond angles, bond lengths, and characteristic volume. The values of the PIB molecule were estimated as well as those of the PDMS molecule. Results obtained for PIB are the length, 2.59 Å per monomer, and the radius, 3.30 Å. The values of bond angles and bond lengths were taken from the literature.[33] The surface areas of n-alkanes, MEK, MIBK, EBK, and DIBK were also estimated by the approximation of a cylinder by the use of characteristic volumes of molecules, bond angles, and bond lengths. Those of cyclohexane and benzene molecules were estimated as spheres with the radius estimated from $(3r_1v_1^*/4\pi)^{1/3}$. The values of s_2/s_1 calculated by the use of the values so obtained are shown in the third column of Table II. The value of ζ in eq 16 was assumed to be unity for simplicity.

Calculation of thermodynamic quantities of mixtures requires two parameters, p_{12}^* and c_{12}, besides the reduced and reduction parameters of pure components and s_2/s_1. These values were chosen in order to give agreement between the experimental and calculated values of χ (shown in Figures 1 and 2) and $\Delta H^{M}(\infty)$ (shown in Table II). The geometric factor g was taken as $(4\pi/3)2^{1/2}$. p_{12}^*, c_{12}, and V^E/V^0 so obtained are shown in the fourth, fifth, and seventh columns of Table II.

It should be noted that the calculated values of χ and V^E/V^0 can reproduce rather well the observed ones for PDMS solutions, while the calculated values of V^E/V^0 for solutions of PIB are not good in comparison with those obtained by Flory et al.[10-12] But if a simple relation, which

$$v_{12}^* = (v_1^* + v_2^*)/2 \quad (35)$$

would be appropriate for chain molecules and where the additivity of volume holds,[34] is used instead of eq 16 for PIB–solvent systems, agreement with observed values is excellent, as shown in parentheses in Table II.

Discussion

Ogino et al.[28,29] measured the PVT relation for PDMS–solvent and PIB–solvent systems and examined the combining rules without using any model except the assumption of the corresponding state principle. According to their results, the number of external degrees of freedom for the mixtures varies in a nonlinear fashion with respect to concentration and is smaller than that obtained by the linear combination of the values for both pure components. Also it was shown that the additivity of volume does not hold. The nonadditivity is appreciable for PDMS–solvent systems, but the nonadditivities of the number of degrees

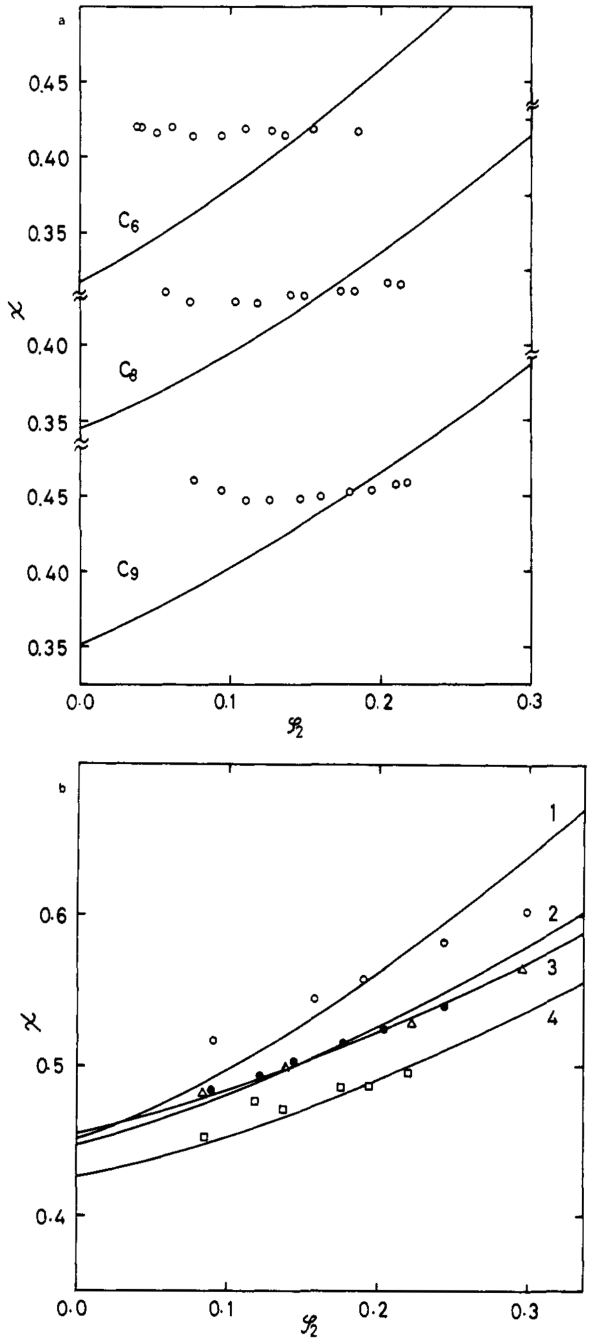

Figure 1. Comparison between the calculated and observed values of χ plotted against the core volume fraction for PDMS–solvent systems. The curves were calculated by the use of the parameters in Tables I and II according to the theory. The points are experimental. (a) The PDMS–*n*-alkane systems at 20 °C. The open circles represent osmometric results of Sugamiya et al.[19] (b) The PDMS–methyl ethyl ketone (1, open circles), PDMS–methyl isobutyl ketone (2, filled circles), PDMS–ethyl butyl ketone (3, triangles), and PDMS–diisobutyl ketone (4, squares) systems at 35 °C. The plots are data from ref 20.

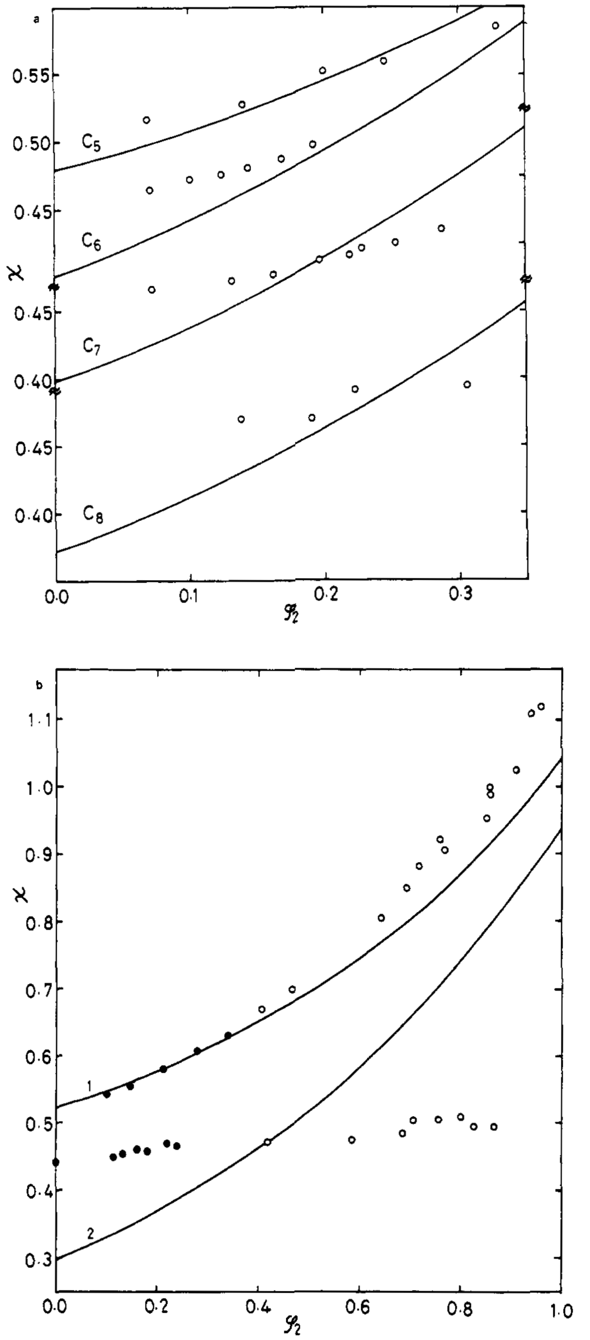

Figure 2. Comparison of calculated values of χ with experimental ones for PIB–solvent systems. (a) The PIB–*n*-alkane systems. The *n*-hexane system is the result at 20 °C and the other systems are at 25 °C. The circles for the *n*-pentane and *n*-octane systems show the experimental results of Barker et al.[36] and Flory et al.,[8] respectively, and those for the *n*-hexane and *n*-heptane systems show the results of Okazawa and Kaneko.[13] (b) The PIB–benzene (1) and PIB–cyclohexane systems (2) at 25 °C. The plots represent the values observed by Flory and his co-workers.[10,11,37,38] The filled circles for the benzene and cyclohexane systems show the results at 24.5 and 30 °C, respectively.

of freedom and volume are very small for PIB–solvent systems.

As shown in Table II, the parameter c_{12} is positive for every system considered here; that is, the number of external degrees of freedom for the mixtures is smaller than that obtained from the linear combination of the values for both pure components. Values of c_{12} for PDMS–solvent systems are quite large, while those for PIB–solvent systems are small. Also, for PDMS–solvent systems, values of V^E/V^0 calculated by using eq 16, where the volume is not additive, agree with the observed values better, while for PIB–solvent systems, V^E/V^0 from eq 35, where the additivity of volume holds, is better. These conclusions agree well with evidence found by Ogino et al.[29]

For PDMS–solvent systems, where the volume for a mixture is smaller than that obtained from linear combination of the volume of both components, the segments of both components must come closer together in solution than in pure liquids. This could be attributed to the fact that PDMS molecules may be able to minimize steric hindrance since Si–O–Si bond angles are "soft",[35] or may

Table II
Parameters Used for Calculations of Thermodynamic Quantities for Mixtures and Comparison between Calculated and Observed Values of $\Delta H^{M}(\infty)$ and V^{E}/V^{0}

system	temp, °C	s_2/s_1	p_{12}^{*},[l] J cm^{-3}	c_{12}[l]	$\Delta H^{M}(\infty)$, J g^{-1}		$V^{E}/V^{0} \times 10^{2}$	
					obsd	calcd[l]	obsd[m]	calcd[l]
PDMS-n-C_6H_{14}	20[n]	0.62	496.8	0.0316_3	0.65[a]	0.19	−0.056[b]	−0.031
			(498.0)	(0.0316_5)		(−1.41)		(−0.046)
PDMS-n-C_8H_{18}	20[n]	0.64	490.8	0.0214_4	2.56[a]	2.49	0.035[b]	0.069
			(490.8)	(0.0214_6)		(2.23)		(0.092)
PDMS-n-C_9H_{20}	20[n]	0.67	483.4	0.0177_0	3.37[a]	3.36		0.075
			(483.4)	(0.0177_9)		(2.95)		(0.11)
PDMS-c-C_6H_{12}	25	0.82	475	0.0211	5.2[c]	4.9	0.053[e]	0.13
			(473.3)	(0.0211)		(4.4)		(0.38)
PDMS-C_6H_6	25	0.90	492	0.0265	11,[d] 14.2[c]	9.0	−0.061[e]	−0.045
			(485.8)	(0.0265_8)		(9.5)		(0.64)
PDMS-MEK	35	0.72	530.2	0.0396_6	14.3[f]	12.0	−0.030[f]	0.224
			(530.2)	(0.0396_0)		(10.0)		(0.644)
PDMS-MIBK	35	0.63	507.0	0.0210_1	9.0[f]	7.1	−0.045[f]	0.258
			(507.0)	(0.0210_3)		(6.8)		(0.290)
PDMS-EBK	35	0.71	503.2	0.0147_8	8.8[f]	11.9	−0.116[f]	0.182
			(502.2)	(0.0147_5)		(11.0)		(0.381)
PDMS-DIBK	35	0.67	477.0	0.0133_2	6.1[f]	3.8	0.028[f]	0.096
			(477.0)	(0.0138_6)		(3.6)		(0.109)
PIB-n-C_5H_{12}	25	0.61	574.4	0.0096_8	−3.6[g]	−3.2	−1.28[h]	−1.62
			(574.0)	(0.0096_9)		(−3.2)		(−1.72)
PIB-n-C_6H_{14}	20[n]	0.66	560.0	0.0115_3	−2.5[g]	−1.2	−0.85[h]	−1.02
			(559.2)	(0.0115_5)		(−1.3)		(−0.93)
PIB-n-C_7H_{16}	25	0.67	555.8	0.0105_6	−1.8[g]	−0.9	−0.62[h]	−0.83
			(555.0)	(0.0105_7)		(−0.9)		(−0.75)
PIB-n-C_8H_{18}	25	0.68	553.2	0.0095_0	−1.2[g]	−0.5	−0.48[h]	−0.66
			(552.4)	(0.0095_1)		(−0.6)		(−0.59)
PIB-c-C_6H_{12}	25	0.88	517.6	0.0112_5	−0.61[g]	−0.58	−0.14[i]	−0.49
			(513.8)	(0.0115_3)		(−0.59)		(−0.13)
PIB-C_6H_6	25	0.97	517.9	0.0099_7	15.0,[j] 17.8[g]	17.1	0.34[k]	−0.29
			(508.0)	(0.0099_6)		(18.8)		(0.61)

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be due to Flory's explanation[19] that the obstruction of efficient packing of PDMS molecule in bulk is relaxed by solvent molecules. For PDMS–aliphatic ketones, the agreement of calculated values of V^E/V^0 with experimental values is poorer than that for PDMS–n-alkanes. This may be due to interaction of PDMS molecules with the carbonyl groups of aliphatic ketones.

Values of c_{12} for PDMS–solvent systems are much larger than that for PIB–solvent systems, as remarked earlier. This may also be elucidated by Flory's explanation[19] that the obstruction of efficient packing of PDMS molecules in bulk is relaxed and both molecules come closer together in solution and consequently the number of external degrees of freedom for mixture becomes smaller than in pure liquids. This explanation seems to be reasonable considering the irregularity of form of the PDMS chain, having pendant CH_3 groups spaced by comparatively long Si–O and Si–C bonds.

The concentration dependence of χ is not predicted well, as shown in Figures 1 and 2. The discrepancy between calculated and observed concentration dependence of χ is eliminated to some extent by allowing the contact ratio s_2/s_1 per segment to take arbitrary values. But we have avoided the additional arbitrariness of allowing the contact ratio to be adjustable.

Conclusion

Modified Flory theory can reproduce the experimental values of χ, $\Delta H^m(\infty)$, and V^E/V^0 for both PDMS and PIB systems by the use of two parameters, p_{12}^* and c_{12}. Adoption of the assumption of nonadditivity of the number of external degrees of freedom for mixtures gives agreement with the experimental values of χ, and in addition, agreement of values of calculated V^E/V^0 with experimental ones is also improved to some extent.[23] The latter is further improved by taking into account the difference in the size of core volume per segment of both components and by assuming eq 16 and 17 for PDMS–solvent systems. The parameter c_{12} seems to reflect the characteristics of each system. Its value could be evaluated from data obtained by the method of Ogino et al. described above.[24,29]

It is hoped that this parameter and the combining rule of volume for mixtures can be further investigated by the systematic accumulation of thermodynamic data for mixtures, and that the evaluation of the parameters from the properties of pure components may become possible.

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Conformational Characteristics of Poly(vinyl fluoride), Poly(fluoromethylene), and Poly(trifluoroethylene)

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ABSTRACT: Conformational energy estimates are employed to determine the conformational characteristics of poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PTF_3). Effects of stereoconfiguration and, in the case of PVF and PTF_3, the presence of head-to-head:tail-to-tail (H-H:T-T) defect structures are considered. Rotational isomeric state models are developed for these polymers and used to calculate their unperturbed dimensions, dipole moments, and conformational entropies. The calculated results are compared to corresponding values found for poly(vinylidene fluoride), poly(tetrafluoroethylene), and polyethylene, and the equilibrium flexibilities of PVF, PFM, and PTF_3 are discussed on this basis.

During the course of our studies concerning the ^{13}C NMR chemical shifts of vinyl polymers we became interested in understanding the ^{13}C chemical shifts observed in the fluorinated polymers poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVF_2), poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PTF_3). We have demonstrated in hydrocarbon polymers, such as poly(propylene),[1,2] ethylene–propylene copolymers,[3,4] polystyrene,[5] etc., and in a chlorine-substituted vinyl polymer [poly(vinyl chloride)[6]], that the chemical shift of a given carbon atom depends on the frequency with which it is involved in three bond gauche or γ interactions[7-11] with other carbon or chlorine atoms.

Each γ interaction produces an upfield chemical shift on the order of 3-5 ppm. Enumeration of the number and kind of γ interactions involving a given carbon atom permits[11] a determination of its relative ^{13}C chemical shift. Bond rotation probabilities obtained from the rotational isomeric state (RIS) model[12,13] of a polymer chain lead to just such an accounting of possible γ interactions.

With knowledge of the conformational characteristics of these polymers it was possible to understand their stereosequence-dependent ^{13}C chemical shifts. Before the same approach can be attempted for fluorinated polymers, we must possess information concerning their conformational characteristics.

The conformational characteristics of PTFE[14] and PVF_2[15] have been determined through approximate potential energy estimates[16] and checked against experimentally determined unperturbed dimensions[17,18] and dipole moments.[14] However, neither PVF nor PFM nor PTF_3 have been studied from a conformational point of view. Such a study is described in this report, where the conformational energies of PVF, PFM, and PTF_3 chain fragments of various stereosequence are calculated, and where the possibility of head-to-head:tail-to-tail (H-H:T-T) addition of monomer units in PVF and PTF_3 is permitted and considered. From the conformational energies, RIS models are developed, and the conformationally sensitive properties $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$, i.e., the mean-square unperturbed dimensions and dipole moments, and the conformational entropies, S_c, are calculated.

Conformational Energy Calculations

Portions of PVF (PTF_3) and PFM chains whose conformations depend on one or both of two neighboring bond rotation angles are illustrated in Figure 1. For PVF

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