Table II
Extrapolated Estimates of θ_c from the Partition Function

n	$k = 0$	1	2	3
4	0.05565			
5	0.06586	0.1067		
6	0.07249	0.1057	0.1037	
7	0.07713	0.1050	0.1033	0.1029
8	0.08058	0.1047	0.1037	0.1043
9	0.08324	0.1045	0.1040	0.1046

timates obtained in this manner from the moments are displayed in Table I, and those from the partition function in Table II. The $k = 0$ columns contain the actual θ_c values for the chains.

The extrapolated θ_c estimates from the partition function apparently settle down very quickly and suggest a final value $\theta_c = 0.104$. The estimates yielded by the moments, however, are still drifting slowly, and it is only the linear extrapolant which seems to improve with increasing p. The higher order extrapolants for the moments (*i.e.*, the $k = 2$ and 3 columns of Table I) suggest the possibility that the extrapolated θ_c values ought really to increase with p. This would mean that the linear extrapolations for $p = 6$ and perhaps even $p = 8$ in Figure 1 are premature. On the other hand, it must be remembered that higher order extrapolants increasingly reflect the behavior of shorter chains where the end effects are more significant. The net result is that the slow convergence of the extrapolants prevents reliable estimation of θ_c for the infinite chain moments; this is very different from the partition function analysis (Table II) where consistent estimates are obtained for all orders of extrapolation.

It appears likely that the final θ_c estimates will lie within the range approximately 0.15–0.18, which is well separated from that of the partition function. But on the basis of this analysis alone the problem of whether the different moments of the infinite chain have the same θ_c or, if this is not the case, the p dependence of θ_c, cannot be resolved.

These results reflect the obvious. For short chains a quantity such as the end-point distribution function (and its moments) is far more sensitive to a variation in chain length than the thermodynamic quantities. The latter depend only on the total number of nearest-neighbor pairs, and not on the manner in which they are distributed along the chain. The end-point distribution does in a sense reflect the distribution of nearest-neighbor pairs and, consequently, longer chains are needed for the limiting behavior to become apparent.

We conclude with a comparison with θ_c estimates obtained from Monte Carlo studies.[6] The θ_c for the partition function, essentially obtained by fitting the Monte Carlo data to the limiting form of (4), was found to be slightly greater than 0.1, close to our extrapolated estimate of 0.104. The estimate $\theta_c = 0.14$ was obtained from the Monte Carlo data on the second moment of the end-point distribution by searching for that value of θ for which the data best fitted the limiting form of (3); *i.e.*, $R_n^2(\theta_c) \sim n$, where $\gamma = 1 -$ the Markovian value. It could be argued that the Neville table for $p = 2$ is converging to a limit in the vicinity of 0.14, but this is by no means certain.

Summary

The results obtained by the exact enumeration method suggest that there exists an extended temperature interval over which different properties of the model polymer chain adopt the values appropriate to the random, no-reversal chain. However, the analysis is unable to determine whether the different moments of the end-point distribution share the same θ temperature in the infinite chain limit. The apparent lack of a unique θ point (as defined by eq 3 and 4) should not come as a surprise—it would perhaps be more surprising if the cancellation of the effects of excluded volume and attractive interaction on different properties were to occur at exactly the same temperature. Studies of polymer chains on other lattices and, possibly, chains with other kinds of interactions, may well provide further insight into the nature of the θ region.

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Thermodynamic Properties of Moderately Concentrated Solutions of Poly(dimethylsiloxane) in *n*-Alkanes

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ABSTRACT: The interaction parameter χ for solutions of poly(dimethylsiloxane) (PDMS) in *n*-alkanes has been determined through osmotic pressure measurements over the concentration range of 5–30 wt %. The free volume theory derived by Delmas and his coworkers fairly well explains the dependence of χ_1, which is the extrapolated value of χ to zero concentration, on temperature and the chain length of solvent. However, the agreement between lower critical solution temperatures estimated by the theory and the observed ones is poor for the solutions of PDMS in comparison with that for the solutions of polyisobutylene in *n*-alkanes. For the solutions of PDMS in *n*-octane and *n*-nonane, the temperature and concentration dependency of χ was examined by the aid of Flory's theory. A method for the derivation of the parameters in his theory was proposed. A good agreement of the theory with the experiment was obtained by the method proposed for the solution of PDMS in *n*-nonane.

Recently, free volume theories of polymer solution thermodynamics have attracted the notice of many investigators, since they semiquantitatively explain various phenomena which have not been interpreted by the traditional theories. Patterson and his coworkers applied Prigogine's theory[2a] to polymer solutions and discussed the lower critical solution temperature.[2b,3] Flory also proposed a free volume theory[4,5] which yields somewhat different

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Table I
Osmotic Pressure and Interaction Parameter χ

Solvent	Temp (°C)	w_2	φ_2	π (g cm^{-2})	χ
n-Hexane	20	0.0489	0.0380	31.5	0.420
		0.0529	0.0412	36.8	0.420
		0.0652	0.0508	57.8	0.416
		0.0652	0.0509	58.7	0.415
		0.0787	0.0615	82.9	0.420
		0.0957	0.0752	133	0.414
		0.1193	0.0942	217	0.414
		0.1397	0.1109	300	0.419
		0.1600	0.1276	424	0.417
		0.1708	0.1366	508	0.414
		0.1921	0.1544	665	0.418
		0.2282	0.1851	1034	0.417
	50	0.0845	0.0662	88.3	0.435
		0.1194	0.0943	187	0.438
		0.1431	0.1137	297	0.434
		0.1602	0.1278	358	0.444
n-Heptane	35	0.0793	0.0601	77.5	0.414
		0.1005	0.0766	132	0.411
		0.1238	0.0950	214	0.409
		0.1377	0.1060	276	0.407
		0.1623	0.1258	401	0.409
		0.1824	0.1421	534	0.408
		0.1985	0.1554	653	0.410
		0.2143	0.1685	784	0.412
		0.2374	0.1878	1019	0.413
		0.2492	0.1977	1146	0.415
	50	0.0793	0.0601	72.2	0.426
		0.0964	0.0733	105	0.430
		0.1231	0.0943	187	0.427
		0.1346	0.1035	226	0.429
		0.1603	0.1240	344	0.429
		0.1809	0.1407	470	0.427
		0.2117	0.1661	686	0.431
n-Octane	20	0.0745	0.0573	51.6	0.435
		0.0956	0.0738	92.4	0.429
		0.1336	0.1042	198	0.429
		0.1515	0.1186	263	0.430
		0.1776	0.1400	376	0.434
		0.1894	0.1498	444	0.434
		0.2181	0.1738	629	0.436
		0.2296	0.1835	725	0.436
		0.2539	0.2042	921	0.441
		0.2646	0.2134	1044	0.440
n-Octane	35	0.0756	0.0580	63.6	0.419
		0.0975	0.0753	110	0.418
		0.1164	0.0904	162	0.418
		0.1341	0.1046	220	0.421
		0.1540	0.1206	299	0.423
		0.1726	0.1359	388	0.425
		0.1912	0.1512	483	0.430
		0.2132	0.1696	635	0.431
		0.2320	0.1854	762	0.437
		0.2498	0.2006	964	0.432
		0.2521	0.2026	940	0.440
		0.2883	0.2339	1383	0.439
	50	0.0768	0.0590	69.0	0.416
		0.0982	0.0758	121	0.412
		0.1169	0.0907	180	0.410
		0.1341	0.1045	245	0.410
		0.1512	0.1183	324	0.410
		0.1761	0.1387	463	0.412
		0.1922	0.1520	559	0.415
		0.2151	0.1712	726	0.419
		0.2240	0.1787	801	0.421
		0.2376	0.1902	933	0.421
		0.2478	0.1988	1031	0.423
n-Nonane	20	0.0963	0.0755	65.0	0.460
		0.1191	0.0939	114	0.454
		0.1393	0.1103	175	0.447
		0.1590	0.1266	242	0.447
		0.1809	0.1448	333	0.448
		0.1994	0.1603	428	0.449
		0.2214	0.1789	551	0.452
		0.2390	0.1940	673	0.453
		0.2574	0.2099	809	0.457
		0.2656	0.2170	878	0.458
	50	0.0991	0.0745	100	0.421
		0.1189	0.0899	150	0.421
		0.1406	0.1070	217	0.423
		0.1554	0.1187	274	0.423
		0.1796	0.1382	377	0.427
		0.1982	0.1533	470	0.431
		0.2300	0.1795	684	0.433
		0.2567	0.2019	898	0.437
		0.2681	0.2116	983	0.442

expressions from Prigogine's theory and explained the negative volume change on mixing in polymer solutions and the concentration dependence of the interaction parameter χ.[6-14] It was shown from the osmotic pressure measurements for the solutions of polyisobutylene in *n*-alkanes that the temperature dependence of χ_1 had the same tendency as predicted by Flory's theory.[15]

These theories were essentially developed to explain the thermodynamical phenomena in nonpolar systems. They have not been modified for taking account of the dipolar effects in polar systems of polymer solutions, though Prigogine[2a] extended his theory to polar solutions composed of small molecules only. It is interesting to investigate the applicability of these theories to polar systems of polymer solutions.

The interaction parameter χ can be deduced through osmotic pressure measurements in moderately concentrated solutions by use of the relation

$$\pi \bar{V}_1/RT = -[\ln (1 - \varphi_2) + (1 - 1/r_2)\varphi_2 + \chi\varphi_2^2] \quad (1)$$

where π is osmotic pressure, $\bar{V}_1$ is the partial molar volume of solvent, R is the gas constant, T is temperature, and r_2 is the number of segments in a polymer molecule. The segment fraction of polymer φ_2 is defined by[7]

$$\varphi_2 = x_2V_2^*/(x_1V_1^* + x_2V_2^*) \quad (2)$$

where x is the mole fraction and V^* is the characteristic volume, or the core volume. The subscripts 1 and 2 denote quantities for solvent and polymer, respectively. According to Flory's theory[4] the characteristic volume V^* of each component is determined by

$$(V/V^*)^{1/3} = 1 + \alpha T/3(1 + \alpha T) \quad (3)$$

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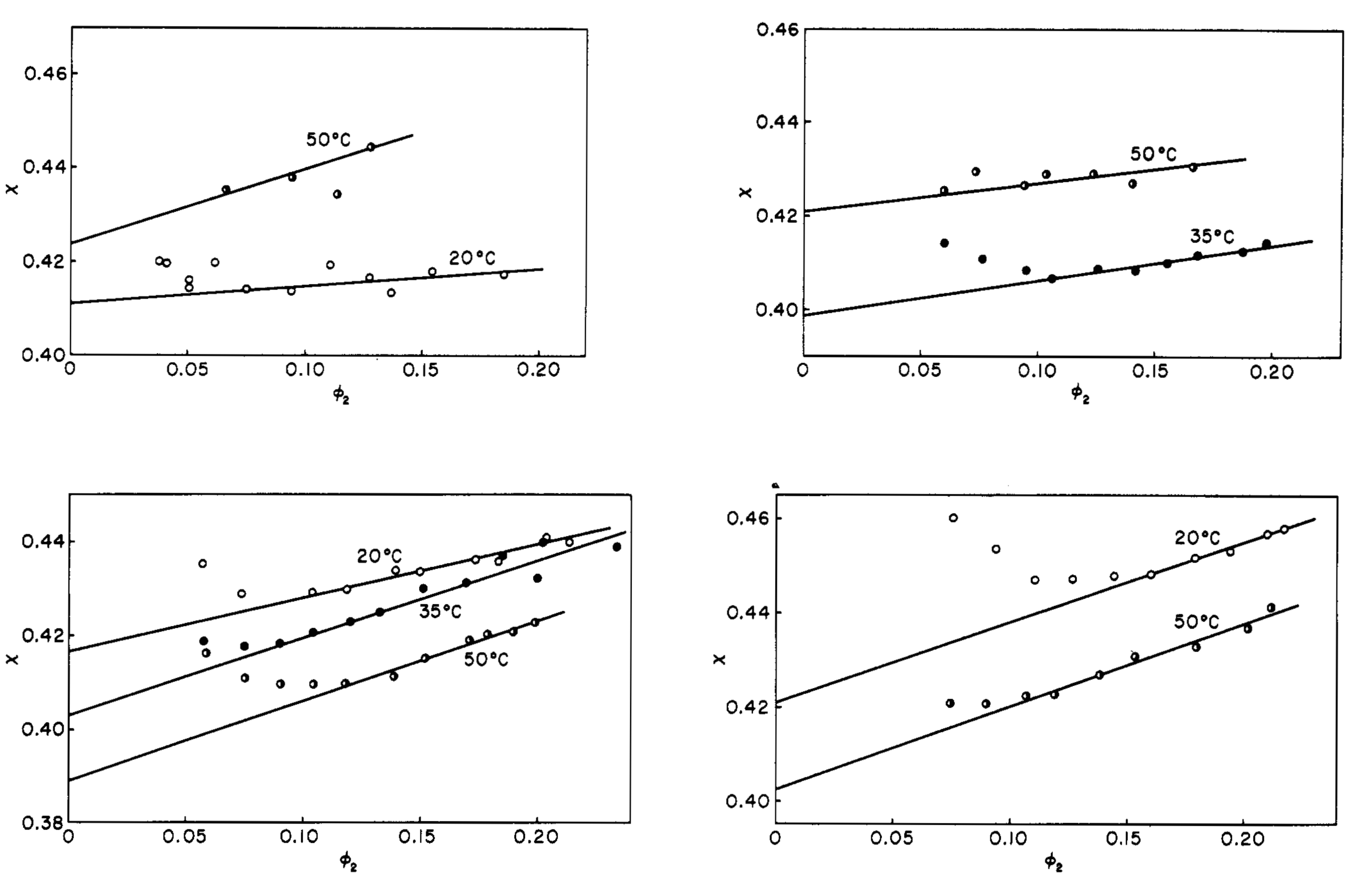

Figure 1. Plots of the interaction parameter χ against the segment fraction of polymer φ_2: (a, top left) PDMS solution in *n*-hexane, (b, top right) PDMS solution in *n*-heptane, (c, bottom left) PDMS solution in *n*-octane, (d, bottom right) PDMS solution in *n*-nonane. Temperatures used for measurements are indicated.

where V and α are the molar volume and the thermal expansion coefficient of the component, respectively.

The value of the cohesive energy density of poly(dimethylsiloxane) (PDMS) is similar to that of polyisobutylene (PIB)[16] and both PDMS and PIB dissolve well in *n*-alkanes. Contributions of dipolar interactions to the parameter χ are expected to be brought out by comparing the results of PDMS with those of PIB, since the former is polar and the latter is nonpolar. In the present work, the temperature and concentration dependence of χ for the solutions of PDMS in *n*-alkanes (polar solution systems) was studied through high-pressure osmometry over a wide range of concentration of about 5–30 wt % and compared with the results obtained for the solutions of PIB in *n*-alkanes (nonpolar solution systems) on the basis of the free volume theory.

Experimental Section

Two samples were prepared from commercial PDMS (Shinetsu Chemical Co., Japan, product KF96H) by means of solution fractionation (coacervation fractionation) at room temperature with benzene and methanol as solvent and nonsolvent, respectively. Number-average molecular weights of the samples determined with a Mechrolab Model 501 high-speed membrane osmometer were 1.37×10^5 and 1.44×10^5. Reagent grade *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane were refluxed over sodium and then fractionally distilled.

Osmotic pressures for the solutions of PDMS in *n*-alkanes were measured at the several temperatures in the concentration range of about 5–30 wt %. Details of the osmometer used for high osmotic pressure measurements were described elsewhere.[17] The temperature was controlled within ±0.01° using a thermostatted water bath. The concentrations of the solutions were determined by the evaporation of the known amount of the solution to dryness and the weighing of the residual polymer.

Results and Discussions

By use of eq 2 and 3, values of the segment fraction of PDMS (φ_2) were calculated from the concentration measured in weight fraction w_2 with the aid of the density data for PDMS[18] and *n*-alkanes.[19] Values of the interaction parameter χ were obtained by means of eq 1 with the observed data of the osmotic pressure and the segment fraction. In this calculation r_2 in eq 1 was put equal to V_2^*/V_1^*. Values for w_2, φ_2, π, and χ are given in Table I.

The χ values in the range of high concentrations vary linearly with φ_2 for all solutions as shown by full lines in Figure 1. It seems to be preferable to approximate the concentration dependence of χ by

$$\chi = \chi_1 + \chi_2\varphi_2 \qquad (4)$$

in the moderately concentrated region. The values of χ_1 defined in eq 4 are presented in Table II. Deviations from the full lines in the region of lower concentration are owing to the nonuniformity in the distribution of polymer segments in this region. Fixman[20] and Yamakawa[21] treated theoretically the thermodynamic properties of the polymer solution in the low concentration range by an application of a distribution-function method with consideration of the expansion of polymer chains and derived the

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Table II
χ_1 at Various Temperatures

Solvent	Temp (°C)	χ_1
n-Hexane	20	0.411
	50	0.424
n-Heptane	35	0.399
	50	0.421
n-Octane	20	0.417
	35	0.403
	50	0.389
n-Nonane	20	0.421
	50	0.403

relations of the osmotic pressure to concentration. Similar behavior of the osmotic pressure in the low concentration range has been found for most of the polymer–solvent systems studied by means of the high pressure osmometry and has been explained with their theories.[17,22-24]

For the *n*-hexane solution χ slightly increases between 20 and 50°. By considering the small positive value of mixing enthalpy at 25°,[25] it is much probable that the change of χ with temperature is inconsistent with the result of the calorimetry. The temperature dependency of χ is compatible with the calorimetric results for the *n*-octane and *n*-nonane solutions where the mixing enthalpy is observed to be rather large value at 25°.[25] The behavior of χ to the change of temperature for the *n*-heptane solution is out of accord with the result of the mixing enthalpy measured at 25°.[25] It will be found, however, through the detailed inspection of Figure 2 shown later that the χ_1 values at 35 and 50° for the *n*-heptane solution are fairly good results for showing the relation of χ_1 with temperature and the chain length of solvents.

At first, discussions will be made mainly on the parameter χ_1 extrapolated to zero concentration from the concentration range where the linear relation of eq 4 holds. Delmas, Patterson, and Somcynsky[2b] related χ_1 for solutions of polymer in a series of homologous solvents to temperature and the chain length of solvent r_1 by the equation

$$R\chi_1 = a(r_1/T) + b(T/r_1) \qquad (5)$$

where a and b are molecular parameters. For a series of *n*-alkanes, r_1 is defined by[2b]

$$r_1 = (n + 1)/2 \qquad (6)$$

where n is the number of carbon atoms in a *n*-alkane molecule. Equation 5 indicates that χ_1 first decreases with an increase of T/r_1 and then increases after passing through the minimum value of $2(ab)^{1/2}/R$ at $T/r_1 = (a/b)^{1/2}$. On substitution of $\chi_1 = \frac{1}{2}$ at the Θ or Flory temperature into eq 5, the following relation

$$T/r_1 = [R + (R^2 - 16ab)^{1/2}]/4b \qquad (7)$$

are obtained for a given r_1. The smaller value of T corresponds to the upper critical solution temperature (ucst) and the larger one to the lower critical solution temperature (lcst).

The plot of $\chi_1(T/r_1)$ against $(T/r_1)^2$ is shown in Figure 2 and is expressed by a linear relation as expected from eq 5. Values of a and b are calculated from the slope and the intersect of the linear line shown in Figure 2 and are presented in Table III, in which the results obtained from measurements of mixing enthalpy by Delmas *et al.*,[25] are also included. It should be noticed that the difference between the values from the osmotic pressure measurement and those from the mixing enthalpy measurement is larger than that obtained for the solutions of PIB in *n*-alkanes.[15] As described above, χ_1 has the minimum value of $2(ab)^{1/2}/R$ at $T/r_1 = (a/b)^{1/2}$. The minimum estimated from the values of a and b in the present work is 0.41, while it is 1.02 for the data of mixing enthalpy. Since the value of χ_1 in polymer solutions must be less than $\frac{1}{2}$ or nearly so, the present values of a and b are more reasonable than those obtained by the measurements of mixing enthalpy.

Table III
Molecular Parameters a and b in eq 5

Method	a (J mol^{-1})	$b \times 10^2$ (J deg^{-2} mol^{-1})
Osmometry	117	2.4
ΔH_M^{∞} [a]	430	5.1

[a] Data of Delmas, Patterson, and Böhme.

Values of lcst estimated with the values of a and b in this study for the solutions of PDMS in *n*-alkanes are compared with experimental points by Patterson *et al.*[3] in Figure 3. The full line represents the estimated lcst and the open circles are for the observed ones. The results of the PIB-*n*-alkane systems are also given in Figure 3 for comparison. The dashed line represents the estimated lcst with values of a and b by Okazawa and Kaneko[15] and the filled circles are for the experimental values of lcst by Patterson *et al.*[3] It is recognized that the discrepancy between the estimated values of lcst and the experimental points for PDMS solutions is a little larger than that for PIB solutions.

Flory derived relationships

$$\chi_1 = (p_1{*}V_1{*}/RT\tilde{v}_1)[(s_2/s_1)^2(X_{12}/p_1{*}) + A^2\alpha_1T/2] \qquad (8)$$

for the temperature dependence of χ_1[4,5] and

$$\Delta H_M^{\infty} = (p_1{*}v_2{*}/\tilde{v}_1)[(s_2/s_1)(X_{12}/p_1{*}) + (\tilde{v}_1/\tilde{v}_2 - 1)(p_2{*}/p_1{*}) - A\alpha_1T] \qquad (9)$$

for the mixing enthalpy to infinite dilution.[14] The quantity A is given by

$$A = (1 - T_1{*}/T_2{*})(p_2{*}/p_1{*}) - (s_2/s_1)(X_{12}/p_1{*}) \qquad (10)$$

where $p*$, $v*$, and $T*$ are the characteristic parameters of pressure, specific volume, and temperature, respectively. Three characteristic parameters $p*$, $v*$, and $T*$ and the reduced volume $\tilde{v}$ can be estimated through the data of the thermal expansion coefficient, the thermal pressure coefficient defined by $(\partial p/\partial T)_v$, and the specific volume. Several methods have been attempted on determination of s_1/s_2, which is the ratio of surface areas per segment for solvent and polymer, and the exchange enthalpy parameter X_{12}. The value of s_1/s_2 was estimated with the aid of molecular models[7] or from the crystallographic data.[6] Morimoto[26] calculated s_1/s_2 on the basis of the van der Waals volume of the segments. X_{12} was determined from the experiment on the excess volume[7] or from the observed data for the mixing enthalpy.[8-12] Okazawa and Kaneko[15] estimated s_1/s_2 for the solution of PIB in *n*-hep-

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Table IV
Parameters at 25° Calculated by Means of Various Methods

Method	s_1/s_2	X_{12} (J cm^{-3})	$\chi_{1,0}$ (Q_{12} = 0)	Q_{12} (J cm^{-3} deg^{-1})	$\chi_{1,\text{exp}}$	$\chi_{H;1}$	$\chi_{S;1}$	ΔH_M^∞ (J g^{-1})	No. of Curves
				PDMS–*n*-Octane					
Experimental					0.412	0.278	0.134	2.56[a]	
I	2.04	6.82	0.091	−0.0869		0.073	0.339	2.56	1
II	2.04	31.0	0.312	−0.0270		0.396	0.016	13.0	2
III	2.04	22.2	0.231	−0.0491		0.278	0.134	9.20	3
IV	1.05	3.51	0.153	−0.0186		0.157	0.255	2.56	4
IV	1.56	5.22	0.111	−0.0479		0.100	0.312	2.56	5
V	0.62	2.06	0.243	−0.0042		0.278	0.134	2.56	6
I′	1.20	4.01	0.137	−0.0257		0.136	0.276	2.56	7
				PDMS–*n*-Nonane					
Experimental					0.418	0.183	0.235	3.37[a]	
I	2.00	8.01	0.105	−0.0735		0.112	0.306	3.37	1
II	2.00	25.7	0.297	−0.0283		0.381	0.037	11.1	2
III	2.00	12.7	0.155	−0.0616		0.183	0.235	5.38	3
IV	1.06	4.24	0.185	−0.0153		0.219	0.199	3.37	4
IV	1.63	6.54	0.125	−0.0459		0.139	0.279	3.37	5
V	1.26	5.03	0.158	−0.0240		0.183	0.235	3.37	6

[a] Data of Delmas, Patterson, and Böhme.

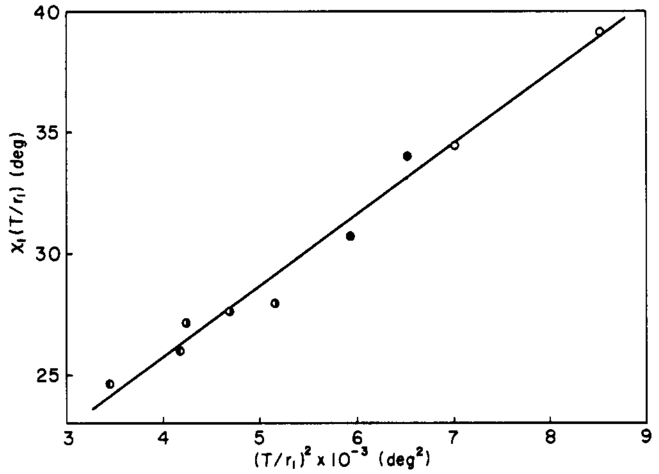

Figure 2. Plots of $\chi_1(T/r_1)$ against $(T/r_1)^2$ for solutions of PDMS: (○) *n*-hexane, (●) *n*-heptane, (◑) *n*-octane, and (◐) *n*-nonane.

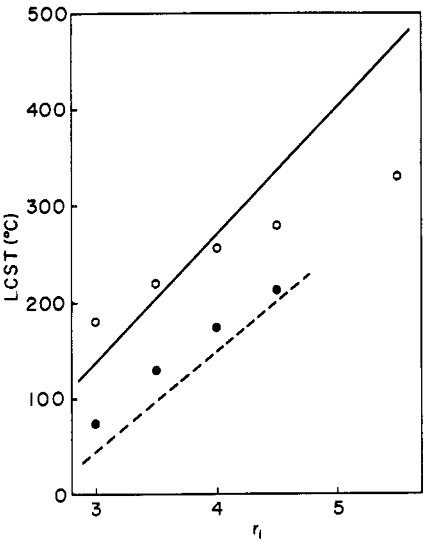

Figure 3. Plots of lcst against the chain length of solvent r_1 for solutions of PDMS and PIB in *n*-alkanes. Theoretical relationships are shown by the full curve for PDMS and the dotted one for PIB. Symbols ○ and ● represent experimental values for solutions of PDMS and PIB,[3] respectively.

tane by using eq 9 with the experimental ΔH_M^∞ value and a relationship

$$X_{12} = p_1^*[1 - (s_1/s_2)^{1/2}(p_2^*/p_1^*)^{1/2}]^2 \qquad (11)$$

derived from the geometric mean rule.[4] According to their procedure the values of s_1/s_2 and X_{12} are estimated from only thermodynamic data without use of any molecular model. However, the geometric mean rule is not always fitted to all solution systems.[27,28] Another procedure is to use the theoretical relation

$$\chi_{H;1} = (p_1^*V_1^*/RT\tilde{v}_1)(1 + \alpha_1 T) \times [(s_2/s_1)^2(X_{12}/p_1^*) - 2(A\alpha_1 T)^2/3] \qquad (12)$$

for the enthalpy term in χ_1.[14] Both s_1/s_2 and X_{12} can be determined from eq 9 and 12 by the aid of experimental results of the mixing enthalpy and of the observed value of $\chi_{H;1} = -T(\partial\chi_1/\partial T)$. In this procedure there is also a merit that s_1/s_2 and X_{12} are evaluated from only thermodynamic data.

The temperature dependence of χ_1 was examined for the solutions of PDMS in *n*-octane and *n*-nonane by the aid of the values of s_1/s_2 and X_{12} evaluated through the several methods described above. Method I: the values estimated by Morimoto[26] were adopted for s_1/s_2 and the values of X_{12} were determined from eq 9 with the aid of the experimental results for ΔH_M^∞ at 25° by Delmas *et al.*[25] Method II: the values of s_1/s_2 were those by Morimoto and X_{12} was calculated from eq 11. Method III: the empirical values of $\chi_{H;1}$ were derived from the temperature dependence of χ_1 to be 0.278 for the *n*-octane solution and 0.183 for the *n*-nonane solution at 25°. X_{12} was evaluated from eq 12 with the values of s_1/s_2 by Morimoto and the empirical values of $\chi_{H;1}$. Two roots were obtained for X_{12} in this case, but larger ones (5.59 × 10^3 J cm^{-3} for the *n*-octane solution and 6.41 × 10^3 J cm^{-3} for the *n*-nonane solution) are too large to be regarded in comparison with those derived from other methods. Method IV: according to the method by Okazawa and Kaneko, a pair of roots for both s_1/s_2 and X_{12} were calculated on the basis of the observed data of ΔH_M^∞ by Delmas *et al.* through the use of eq 9 and 11. Method V: this method is to be proposed in the present study. From eq 9 and 12

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(27) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, 87 1838 (1965).
(28) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, 88, 2887 (1966).

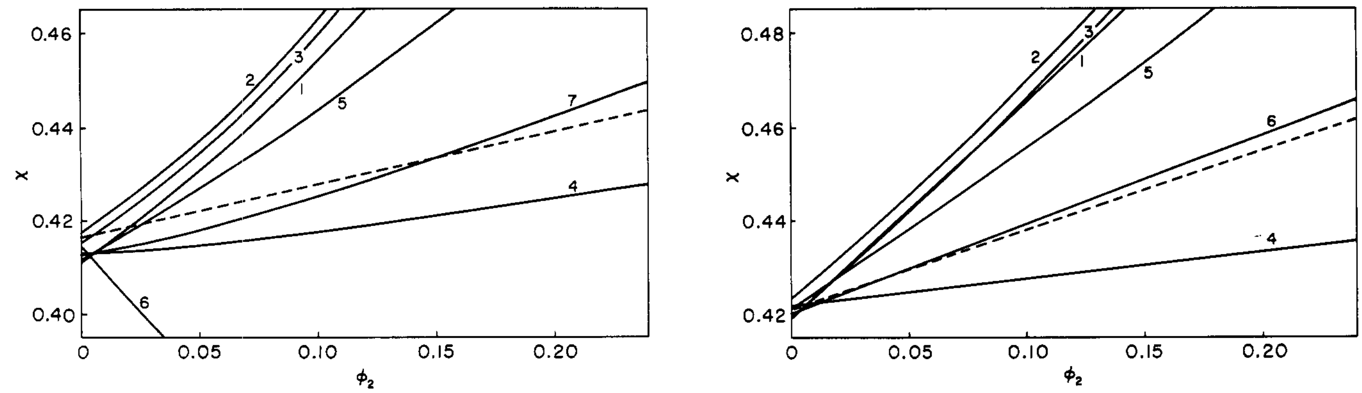

Figure 4. χ as a function of φ_2 at 20°: (a, left) PDMS in *n*-octane and (b, right) PDMS in *n*-nonane. Theoretical results obtained from eq 13 are shown by the full curves. Numbers on curves denote the method of evaluation for the parameters, as presented in Table IV. Experimental results are shown by the dotted curves.

s_1/s_2 and X_{12} were evaluated by the aid of the experimental data for both ΔH_M^∞ and $\chi_{H;1}$ at 25°.

The results for s_1/s_2 and X_{12} are listed in the second and third columns of Table IV, respectively. χ_1 was calculated as a function of temperature for each method by using eq 8. The corresponding values at 25° are expressed by $\chi_{1,0}$ (Subscript 0 stands for $Q_{12} = 0$, in which Q_{12} is the exchange entropy parameter described later.) and presented in the fourth column. The empirical values of χ_1 at 25° were found to be 0.412 and 0.418 for the *n*-octane and *n*-nonane solutions, respectively, by interpolation from the observed data at 20, 35, and 50°. These values are distinguished by $\chi_{1,\mathrm{exp}}$ from $\chi_{1,0}$ and listed in the sixth column. The calculated values of $\chi_{H;1}$ and ΔH_M^∞ at 25° from eq 9 and 12 are also given in the seventh and ninth columns, respectively. In all of calculations above, s_1/s_2 and X_{12} were treated as constants independent on temperature. The so-called equation-of-state parameters for *n*-octane, *n*-nonane,[19] and PDMS[29] were cited from the literature except p_1^* for *n*-nonane. The values of p_1^* for *n*-nonane were calculated from eq 17 of ref 19.

In either *n*-octane or *n*-nonane solution, a disagreement of the calculated values of χ_1 with the experiment is, on the whole, found as seen in Table IV. The calculated χ_1 corresponding to each method decreases with increasing temperature and the overall behavior is consistent with the experimental result. The discrepancy between the χ_1 values calculated by method IV and the experiment is larger for PDMS in *n*-octane and *n*-nonane than for PIB in *n*-heptane.[15] The values of s_1/s_2 obtained by method V for PDMS in *n*-octane is too small. Since chain ends contribute on the mean surface area of the segment more effectively in solvent than in polymer, it naturally follows that s_1/s_2 must be larger than unity.

According to Flory, the discrepancy between the calculated and the observed values of χ_1 is attributable to the presence of exchange entropy represented in terms of the parameter Q_{12}.[7,11,30] The exchange entropy is introduced into the theory through replacing X_{12} in eq 8 with the exchange interaction parameter $\bar{X}_{12}$ which is defined by[14]

$$\bar{X}_{12} = X_{12} - \tilde{v}_1 T Q_{12}$$

The difference of the experimental from the calculated values of χ_1 is given by the relation

$$\chi_{1,\mathrm{exp}} - \chi_{1,0} = -V_1^* Q_{12}(s_2/s_1)^2/R$$

The values of Q_{12} at 25° determined from the relation are presented in the fifth column of Table IV. The values of $\chi_{S;1} = \chi_{1,\mathrm{exp}} - \chi_{H;1}$, in which $\chi_{S;1}$ is the entropy term of χ_1, are given in the eighth column.

Secondly, the concentration dependence of χ were examined on the basis of s_1/s_2, X_{12}, and the exchange entropy parameter Q_{12}. The parameter χ at 20° was calculated from the following theoretical relation[4,5] as a function of the segment fraction φ_2

$$\chi = (p_1^* V_1^*/RT\varphi_2^2)\{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + (V_1^* \bar{X}_{12}/\tilde{v}RT)(\theta_2/\varphi_2)^2 \quad (13)$$

where

$$\bar{X}_{12} = X_{12} - \tilde{v}TQ_{12} \quad (14)$$

and

$$\theta_2 = \varphi_2/[s_1/s_2 + (1 - s_1/s_2)\varphi_2] \quad (15)$$

The reduced volume of solution, $\tilde{v}$, is determined by the equation of state at zero pressure

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (16)$$

where $\tilde{T}$ is the reduced temperature. The characteristic temperature for solution, T^*, is given by

$$T^* = (\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 X_{12}\theta_2)/(\varphi_1 p_1^*/T_1^* + \varphi_2 p_2^*/T_2^*) \quad (17)$$

The results are shown by full curves in Figure 4 with the dotted curves for the experimental ones. The numbers denoted on the curves represent different ways of calculation and are shown in the last column of Table IV. It is apparent that the value of s_1/s_2 has a large influence on the concentration dependence of χ. It is recognized from Figure 4b for PDMS in *n*-nonane that curve 6 calculated by method V with the experimental values of $\chi_{H;1}$ and ΔH_M^∞ is in good agreement with the experiment. This fact indicates that method V gives preferable values for parameters s_1/s_2, X_{12} and Q_{12}, at least for the PDMS-*n*-nonane system. The values of χ_1 calculated with the same values of s_1/s_2, X_{12}, and Q_{12} well reproduce the observed temperature dependence of χ_1, as shown in Figure 5b. The other methods could not reproduce the experimental values for $\chi_{H;1}$ and/or ΔH_M^∞. In PDMS-chlorobenzene system the values of s_1/s_2, X_{12}, and Q_{12}, which are determined to conform to the observed concentration dependence of χ, well reproduce the experimental results of $\chi_{H;1}$ and ΔH_M^∞ simultaneously.[14] This fact gives support to the usefulness of method V.

For the solution of PDMS in *n*-octane shown in Figure 4a, curves 1–6 all fail to agree with the experiment. The

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(29) H. Shih and P. J. Flory, *Macromolecules*, 5, 758 (1972).

(30) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, 89, 6822 (1967).

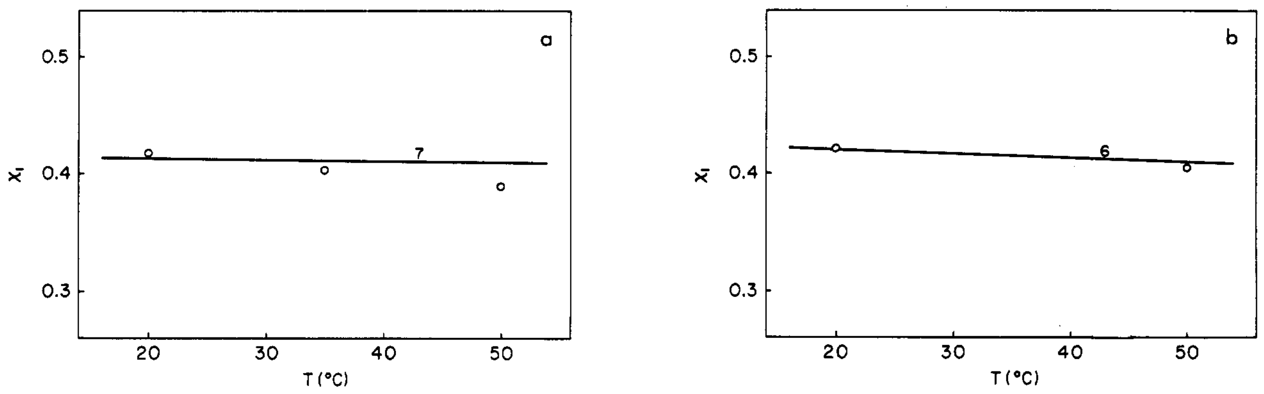

Figure 5. χ_1 as a function of T: (a) PDMS in *n*-octane and (b) PDMS in *n*-nonane. Theoretical results obtained from eq 8 with the aid of X_{12} are shown by the full curves. Numbers on curves denote the method of evaluation for the parameters, as presented in Table IV. Experimental results are shown by open circles.

slope of curve 6 calculated by method V is negative because of the excessive smallness of the value of s_1/s_2. By considering that the experimental curve lies between curve 4 with $s_1/s_2 = 1.05$ and curve 5 with $s_1/s_2 = 1.56$ and that s_1/s_2 should be larger than unity, the values of χ were calculated with an assumed value of $s_1/s_2 = 1.20$ and the experimental value of ΔH_M^∞ (2.56 J g^{-1}). This method is denoted as method I′ because of similarity to method I. The calculated values of χ shown by curve 7 in Figure 4a fairly well agree with experiment. Curve 7 in Figure 5a calculated by use of method I′ also reproduces the experimental result of the temperature dependence of χ_1. The values of the parameters used in the calculations are listed in Table IV. The calculated $\chi_{H;1}$ is about half of the experimental value and is smaller than the empirical one in the *n*-nonane solution. The contribution of the term of free volume difference to $\chi_{H;1}$ is generally small in these solutions. $\chi_{H;1}$ should be smaller for the *n*-octane solution than for the *n*-nonane solution on the basis of the calorimetric results of ΔH_M^∞.[25] Therefore, for the *n*-octane solution the $\chi_{H;1}$ calculated by means of method I′ is considered to be rather reasonable value. The failure of method V for PDMS-*n*-octane system is probably caused by an overestimation in the experimental determination of $\chi_{H;1}$.

The values of $\chi_{S;1}$ obtained by method I′ for the *n*-octane solution and by method V for the *n*-nonane solution are large in comparison with those of $\chi_{H;1}$. The large values of $\chi_{S;1}$ arise principally from the term of $-V_1^*Q_{12} \times (s_2/s_1)^2/R$ including Q_{12} as above mentioned. The deviation of $\chi_{1,\mathrm{exp}}$ from $\chi_{1,0}$ may be really owing to entropy contribution, in view of the fact that such large deviations for the solutions of PDMS in *n*-alkanes are well explained by use of the parameter Q_{12}. It is suggested that the large entropy "deficit" for the solutions of PDMS in benzene, cyclohexane, and chlorobenzene is due to the easy fit of solvent molecule to polymer because of the irregularity of the PDMS chain.[14] According to the similar consideration, the value of $\chi_{S;1}$ should be larger for the solution in the shorter chain solvent, *n*-octane, than for the solution in the longer chain solvent, *n*-nonane. The value of $\chi_{S;1}$ by method I′ for the *n*-octane solution is in conformity with this requisite. The detailed discussions on $\chi_{S;1}$ or Q_{12} must be still postponed until the parameter Q_{12} is examined for the wide variety of polymer solution systems.

Conclusion

The deviation of the theoretical lcst from the experiment for the solutions of PDMS in *n*-alkanes is somewhat larger than for the solutions of PIB in *n*-alkanes. PDMS is a polar polymer and its segment has a definite magnitude of dipole moment. Since the interaction parameter χ represents the nature of the interaction between segments of solvent and solute, it must be naturally affected by the polarity of PDMS segment. Nevertheless, no theoretical treatment for lcst has taken the dipolar interactions into consideration. The dipolar interaction may be one of causes of the relatively large discrepancy between the experimental results and the theoretical estimations in lcst for PDMS solutions.

Flory's theory seems to be successful for the polar system, the solution of PDMS in *n*-nonane and also effective for the solution of PDMS in *n*-octane. In the theory of Flory the main part of the discrepancy between the theory and the experiment is considered to be improved by the introduction of the exchange entropy. Success of Flory's theory may be due to the fact that the polar effect is included implicitly in the exchange entropy as well as in the intermolecular energy. It is greatly expected to make clear the effect of the dipolar interactions in the free volume theory.

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