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Swelling Equilibria of Mixed Solvent/Poly(dimethylsiloxane) Systems

Jin Sung Yoo, Sung Jun Kim, and Joong So Choi*

Department of Chemical Engineering, Institute of New Technology, Kwangwoon University, 447-1, Wolgyedong,
Nowonku, Seoul 139-701, Korea

The hydroxyl-terminated poly(dimethylsiloxane) (PDMS) was used to measure swelling equilibria for solvent(1)/PDMS(2) and solvent(1)/solvent(2)/PDMS(3) systems. PDMSs were vulcanized to prepare four compounds (PDMS-35, PDMS-40, PDMS-45, and PDMS-50) having different hardness. The swelling ratios of the binary and the ternary systems were measured and supplied at various temperatures from 303.15 K to 318.15 K. They were used to describe the swelling abilities of the cross-linked PDMS absorbing mixed solvents into the polymers. A Flory−Huggins model was combined with three different expressions to describe swelling equilibria of the binary and the ternary systems. The experimental swelling equilibria data were correlated with the models to estimate the Flory−Huggins (FH) interaction energy parameters and the average molecular weights of chains between the cross-linked PDMS. The swelling behaviors of the cross-linked PDMSs were described by the FH interaction energy parameters.

Introduction

It is well-known that cross-linked polymers absorb solvent when immersed. However, they have the property to return to the previous form when the absorbed solvents are slowly volatilized from the polymer in the atmosphere. Measurement and estimation of the absorption ability of the cross-linked polymers in mixed solvents are important for many polymer applications, e.g., packaging materials, controlled drug release, plastic pipes, etc. A cross-linked PDMS in particular is often used as a solid phase in extraction techniques such as solid-phase microextraction, which is being used a great deal in trace and headspace analysis. And, the cross-linked PDMS has been widely used in many industrial fields because of its flexibility and heat-resistant and cold-resistant properties. Therefore, we chose it to apply its swelling properties to some industries.

Neuburger and Eichinger (1988) have worked out the vapor sorption techniques to determine the amounts of solvents absorbed into the cross-linked polymers by using an electronic balance in a vacuum atmosphere. Badiger et al. (1994) have also developed new techniques to measure the swelling ability of supersolvent gels in situ conditions. A gravimetric method has been also used by many researchers because it was an economic and convenient one that had a similar error of measurement in comparison with their techniques. On the other hand, few models have been proposed to describe the swelling equilibria of a cross-linked polymeric network. Some models were based on a polymer scaling theory (Daoud et al., 1986; Geissler et al., 1989), and others were based on an osmotic theory between solvent and polymer (Horkay et al., 1991; Vink, 1983). However, the most common theory was that of the Flory and Rehner (1943a,b), which was based on polymer swelling.

In this work, we used a gravimetric method to measure the swelling equilibria for solvent(1)/PDMS(2) and solvent(1)/solvent(2)/PDMS(3) systems. The experimental data were correlated with swelling models that were combined with the free energy due to mixing and that due to elastic deformation. The Flory−Huggins expression (1953) was used to describe the free energy due to mixing, and three different expressions were combined to describe the free energy due to elastic deformation in the swollen PDMS. Those three expressions were models based on the Gaussian distribution (Flory, 1953; James and Guth, 1943) or non-Gaussian distribution (Wall and White, 1974) of the chain lengths of polymers. The Flory−Huggins interaction parameters and the average molecular weights between backbone of PDMS were estimated for the solvent(1)/PDMS(2) and solvent(1)/solvent(2)/PDMS(3) systems (McKenna, 1990). They were used to describe the swelling behaviors of cross-linked PDMS.

Experimental Section

Procedure. The PDMSs were the hydroxyl-terminated products of General Electrics Co. The solvents were special grades and used without further purification. The apparatus that measured the swelling equilibria consisted of a constant temperature water bath with thermostat and the Erlenmeyer sample flasks corked in order to prevent a volatilization of solvent. The bath was equipped with a precise temperature controller, which was able to adjust temperature within the accuracy of ±0.01 °C. The PDMSs were kneaded with the cross-linker (2,4-dichlorobenzoyl peroxide) and vulcanized twice in the drying oven. The first and second vulcanization temperatures were 142.5 °C/h and 205.4 °C/h, respectively. The vulcanized PDMSs were cut into the size 20 mm (width) × 10 mm (length) × 1.5 mm (thickness) in order to measure the swelling abilities in the single solvent or mixed solvents. The swelling ratios for the binary and the ternary systems were measured over the various time intervals by the typical method (Mark, 1964). The samples were weighed prior to the initiation of swelling and immersed perfectly in the various solvents at constant temperature. The samples were removed from the flasks and weighed at 30-min intervals until swelling equilibrium was achieved. Swell-

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* To whom correspondence should be addressed.

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Table 1. Measured Densities of Solvents and Polymers

materials	303.15 K	308.15 K	313.15 K	318.15 K
chloroform	1.4560	1.4531	1.4459	1.4370
trichloroethylene	1.4401	1.4320	1.4280	1.4221
cyclohexane	0.7780	0.7740	0.7700	0.7660
diisopropyl ether	0.7170	0.7130	0.7060	0.7040
n-Hexane	0.6630	0.6600	0.6550	0.6500
n-Heptane	0.6820	0.6800	0.6770	0.6730
toluene	0.8670	0.8630	0.8590	0.8570
chlorobenzene	1.1010	1.0981	1.0910	1.0890
benzene	0.8730	0.8690	0.8650	0.8610
methyl isobutyl ketone	0.7930	0.7910	0.7880	0.7850
methyl ethyl ketone	0.7990	0.7960	0.7920	0.7870
acetone	0.7870	0.7840	0.7799	0.7729
ethanol	0.8080	0.8019	0.7980	0.7960
PDMS-35[a]	1.1115	1.1115	1.1115	1.1115
PDMS-40[a]	1.1345	1.1345	1.1345	1.1345
PDMS-45[a]	1.1293	1.1293	1.1293	1.1293
PDMS-50[a]	1.1507	1.1507	1.1507	1.1507

[a] Hardness.

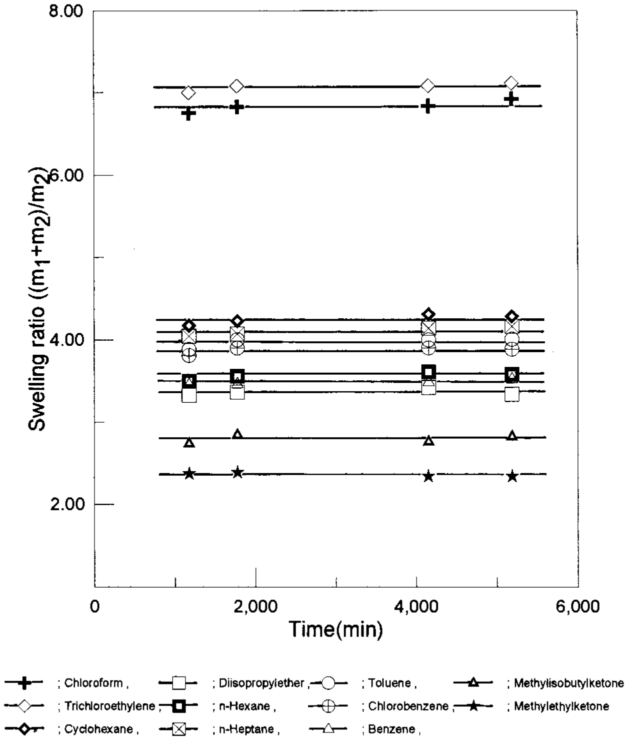

Figure 1. Swelling ratios for solvent(1)/PDMS-35(2) systems at 318.15 K.

ing equilibrium was considered to be achieved when the samples had a constant weight after being immersed in the solvents. Once equilibrium was established at the experimental temperatures, the samples were weighed at 12-h intervals.

In the binary systems, the above swelling ratios were used to determine the volume fractions of each component on swelling equilibria by using eq 1 at each temperature

$$\phi_i = \frac{m_i/\rho_i}{\sum_j m_j/\rho_j} = \frac{v_i}{\sum_j v_j} \tag{1}$$

where ρ_i, m_i, and v_i are densities, masses, and volumes of each component *i*.

In the ternary systems, it was assumed that each solvent absorbed into the PDMS network was equilibriated with remaining solvents in the flask. The compositions of each solvent absorbed into the PDMS were obtained from gas chromatography (GC-14B, SHIMADZU Co.) analyses of the remaining mixed solvents in the flasks. The compositions of remaining mixed solvents were replaced as those of solvents in the swollen PDMS network and converted into the volume fractions of each component. The densities of the solvents and the cross-linked PDMSs used to determine the volume fractions were measured by a typical pycnometer at each temperature and are listed in Table 1. The average of three measurements for each sample was taken for data evaluation, and the experimental error was ±0.005 g/cm^3.

Swelling Equilibria Data of Binary Systems. The solvents used for the solvent(1)/PDMS(2) systems were hydrocarbon substitutes (chloroform, trichloroethylene, cyclohexane), ether (diisopropyl ether), saturated hydrocarbons (*n*-hexane, *n*-heptane), aromatics (toluene, chlorobenzene, benzene), and ketones (methyl isobutyl ketone, methyl ethyl ketone). The PDMSs were classified as four kinds of compounds (PDMS-35, PDMS-40, PDMS-45, PDMS-50) according to the hardness. The swelling ratios were measured at various temperatures from 303.15 K to 318.15 K, and a representative result is shown in Figure 1 for the solvent(1)/PDMS-35(2) systems at 318.15 K. Other systems were shown to behave in a similar way. The volume fractions of the binary systems on swelling equilibria are listed in Tables 2 and 3. The volume fractions of PDMS of Table 2 for the benzene(1)/PDMS(2) system were compared with the literature values (Andray et al., 1980; Mark and Sullivan, 1977) to test the accuracy of the experimental data and are shown in Figure 2. The errors introduced were certainly negligible because they were well within the limits of experimental error as shown in Figure 2.

Swelling Equilibria Data of Ternary Systems. To measure the swelling ability of the PDMSs in mixed solvents, *n*-hexane was chosen as a suitable solvent, giving the swelling ratio of more than 3.0 as shown in Figure 1. The measurements of swelling ratios for *n*-hexane(1)/acetone(2)/PDMS(3) and *n*-hexane(1)/ethanol(2)/PDMS(3) systems were performed by increasing the concentration of the acetone (or ethanol) at 10 vol % intervals in the mixed solvents. The swelling ratios of *n*-hexane(1)/acetone(2)/PDMS(3) systems at 303.15 K are representatively shown in Figure 3. The volume fractions of each component for the ternary systems obtained from GC analyses are tabulated in Tables 2 and 3. The experimental errors introduced may come from the precision of GC. But, they were certainly negligible because not only were averages taken over three times but also swelling ratios measured on the descending temperature were shown to be similar to those obtained from the ascending cycle.

Results and Discussion

Swelling of Cross-linked PDMS. Cross-linked PDMS has a property to adjust swelling when immersed in a mixed solvent with a good solvent and a poor solvent. Representative Figure 3 describes those swelling behaviors of *n*-hexane(1)/acetone(2)/PDMS(3) systems. As shown in Figure 3, the swelling ratios of the systems in equilibrium continuously increase up to a maximum until the *n*-hexane content reaches 90% and start to decrease gradually with further addition of *n*-hexane (the concentration of acetone influenced contrarily) and did not have constant equilibrium values in the concentration range below approximately 50 vol % of *n*-hexane. The swelling ratios of *n*-hexane(1)/ethanol(2)/PDMS(3) systems showed a similar tendency. These swelling behaviors have been often de-

Table 2. Experimental Volume Fractions on Swelling Equilibria of *n*-Hexane(1)/Acetone(2)/PDMS(3) Systems

n-hexane(1)/ acetone(2)	303.15 K			308.15 K			313.15 K			318.15 K		
	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3
PDMS-35												
100:0	0.833		0.167	0.826		0.174	0.818		0.182	0.814		0.186
80:20	0.665	0.166	0.169	0.666	0.166	0.168	0.665	0.166	0.169	0.662	0.166	0.172
60:40	0.481	0.320	0.199	0.490	0.327	0.183	0.498	0.332	0.170	0.494	0.330	0.176
40:60	0.281	0.421	0.298	0.296	0.444	0.260	0.288	0.431	0.281	0.300	0.450	0.250
20:80	0.104	0.417	0.479	0.107	0.429	0.464	0.101	0.404	0.505	0.119	0.477	0.596
PDMS-40												
100:0	0.828		0.172	0.823		0.177	0.813		0.187	0.794		0.206
80:20	0.648	0.162	0.190	0.661	0.165	0.174	0.665	0.166	0.169	0.665	0.166	0.169
60:40	0.460	0.307	0.233	0.484	0.323	0.193	0.490	0.327	0.183	0.493	0.328	0.179
40:60	0.269	0.403	0.328	0.271	0.407	0.322	0.291	0.437	0.272	0.301	0.452	0.247
20:80	0.093	0.372	0.535	0.091	0.363	0.546	0.110	0.440	0.450	0.108	0.432	0.460
PDMS-45												
100:0	0.801		0.199	0.797		0.203	0.799		0.201	0.798		0.202
80:20	0.637	0.159	0.204	0.630	0.157	0.213	0.618	0.154	0.228	0.623	0.156	0.221
60:40	0.464	0.309	0.227	0.451	0.301	0.248	0.449	0.299	0.252	0.452	0.302	0.246
40:60	0.268	0.401	0.331	0.255	0.383	0.362	0.263	0.395	0.342	0.278	0.417	0.305
20:80	0.093	0.371	0.536	0.091	0.365	0.544	0.095	0.380	0.525	0.115	0.461	0.424
PDMS-50												
100:0	0.770		0.230	0.784		0.216	0.772		0.228	0.772		0.228
80:20	0.629	0.157	0.214	0.360	0.158	0.482	0.629	0.157	0.214	0.637	0.159	0.204
60:40	0.459	0.306	0.235	0.461	0.307	0.232	0.465	0.310	0.225	0.468	0.312	0.220
40:60	0.269	0.399	0.332	0.273	0.409	0.318	0.269	0.403	0.328	0.288	0.432	0.280
20:80	0.096	0.383	0.521	0.097	0.389	0.514	0.094	0.376	0.530	0.118	0.471	0.411

Table 3. Experimental Volume Fractions on Swelling Equilibria of *n*-Hexane(1)/Ethanol(2)/PDMS(3) Systems

n-hexane(1)/ ethanol(2)	303.15 K			308.15 K			313.15 K			318.15 K		
	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3
PDMS-35												
100:0	0.833		0.167	0.826		0.174	0.818		0.182	0.814		0.186
80:20	0.653	0.163	0.184	0.661	0.165	0.174	0.673	0.168	0.159	0.650	0.163	0.187
60:40	0.436	0.291	0.273	0.421	0.281	0.298	0.397	0.265	0.338	0.438	0.292	0.270
40:60	0.190	0.190	0.620	0.164	0.246	0.590	0.137	0.205	0.658	0.202	0.304	0.494
20:80	0.043	0.171	0.786	0.029	0.116	0.855	0.031	0.120	0.849	0.043	0.172	0.785
PDMS-40												
100:0	0.828		0.172	0.823		0.177	0.813		0.187	0.794		0.206
80:20	0.627	0.157	0.530	0.642	0.161	0.197	0.646	0.162	0.192	0.641	0.160	0.199
60:40	0.416	0.277	0.861	0.413	0.275	0.312	0.402	0.268	0.330	0.426	0.284	0.290
40:60	0.161	0.242	0.597	0.124	0.186	0.690	0.140	0.210	0.650	0.207	0.310	0.517
20:80	0.032	0.128	0.840	0.029	0.114	0.857	0.031	0.122	0.847	0.041	0.165	0.794
PDMS-45												
100:0	0.801		0.199	0.797		0.203	0.799		0.201	0.796		0.204
80:20	0.629	0.157	0.214	0.638	0.160	0.202	0.603	0.151	0.246	0.609	0.152	0.543
60:40	0.417	0.278	0.305	0.404	0.269	0.327	0.387	0.258	0.355	0.410	0.274	0.316
40:60	0.188	0.281	0.531	0.140	0.211	0.649	0.150	0.225	0.625	0.214	0.322	0.464
20:80	0.039	0.158	0.803	0.033	0.132	0.835	0.024	0.097	0.879	0.052	0.210	0.738
PDMS-50												
100:0	0.770		0.230	0.784		0.216	0.772		0.228	0.772		0.228
80:20	0.618	0.155	0.227	0.649	0.162	0.189	0.607	0.152	0.241	0.619	0.155	0.226
60:40	0.239	0.159	0.602	0.396	0.264	0.340	0.360	0.240	0.400	0.412	0.275	0.313
40:60	0.270	0.404	0.326	0.156	0.234	0.610	0.122	0.183	0.695	0.211	0.317	0.472
20:80	0.029	0.115	0.856	0.025	0.101	0.874	0.014	0.054	0.932	0.051	0.203	0.746

scribed by the phase transitions (Amiya et al., 1987) in deforming polymeric networks. Whereas phase transitions in chemically cross-linked networks have been well understood, the presence of phase transitions in physically cross-linked networks (e.g., hydrogen-bonded networks) has gained attention recently (Ilmain et al., 1991). The PDMSs used in this work were hydroxyl-terminated products and were physically cross-linked by forming hydrogen-bonded networks. The networks of polymers that have physical cross-links are weak and can be reversibly disrupted by imposing a deformation due to the excessive solvents against the cross-linked polymers. Few researchers have described the disruption as a phase transition which was formed from the breakage of some of the physical cross-links in the polymer due to deformation but restabilized reversibly in the other atomsphere. Amiya et al. (1987) observed the reentrant volume-phase transitions of the physically cross-linked polymers in the methanol−water mixtures when the solvent compositions were systematically varied. Badiger et al. (1994) also described the behaviors that the physical origin of the decreased swelling ratios formed from the breakage of some of the physical cross-links in the network due to deformation. In this work, the slight phase transitions shown in Figure 3 appeared in the presence of only below about 50 vol % of *n*-hexane but reversibly restabilized by maintaining the constant equilibrium values near about 10 vol % of *n*-hexane because the PDMSs were physically cross-linked. We would like to recommend that the physically cross-linked PDMSs having a concentration range of only more than 50 vol % of *n*-hexane in the *n*-hexane(1)/acetone(2)/PDMS(3) and *n*-hexane(1)/ethanol(2)/PDMS(3) systems

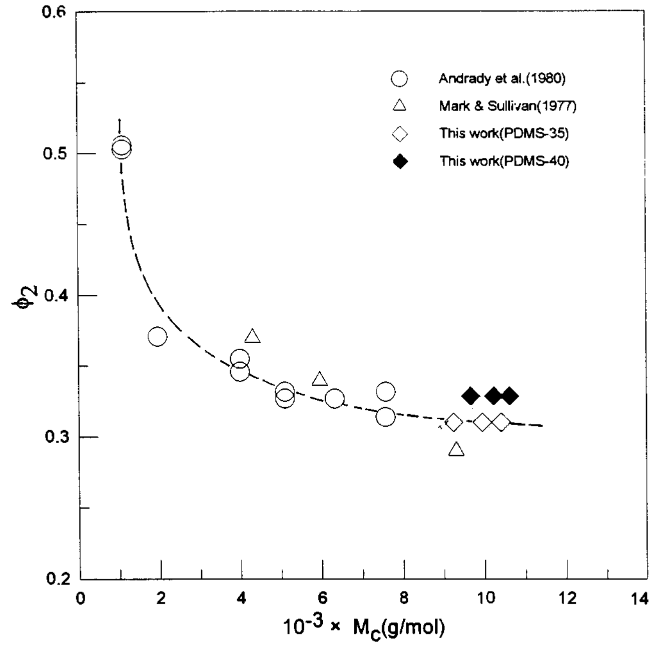

Figure 2. Comparison of experimental volume fractions with those of references according to average molecular weight between cross-links for the benzene(1)/PDMS(2) system at 298.15 K. Dotted line: least-squares values of references.

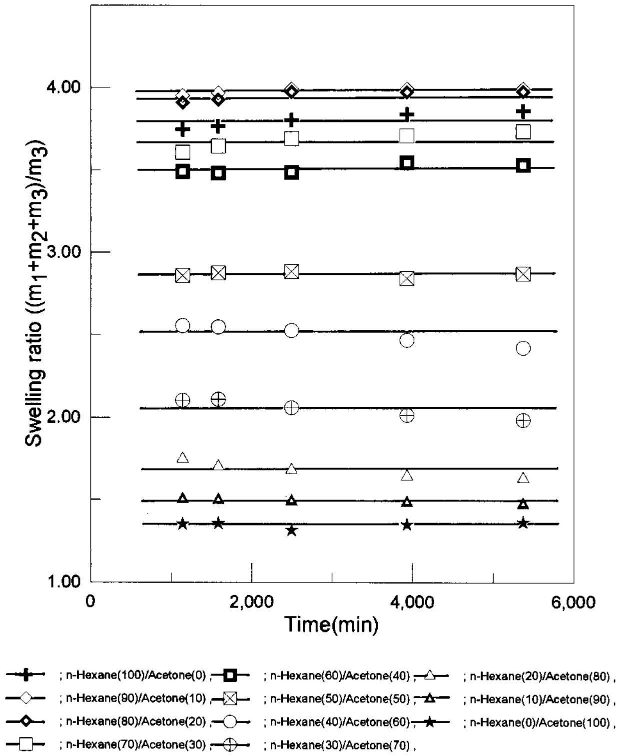

Figure 3. Swelling ratios for *n*-hexane(1)/acetone(2)/PDMS-35-(3) systems at 303.15 K.

should be applied to the relevant industries. Therefore, it might be considered that the results could be generalized for different physically cross-linked polymers.

Expression of Swelling Equilibria. The swelling model (Flory, 1953) to express swelling equilibria consists of the sum of the Gibbs free energy changes of the solvent in the bulk phase and the elastic deformation of the polymer network. This equation can be also used to determine the chemical potential changes. One term in the equation is associated with a chemical potential change due to mixing, and the other term is relevant to elastic deformation induced by an expansion of network structure. Therefore, when cross-linked polymers were swelled in the mixed solvent at constant temperature and pressure, the relation between the change of chemical potential and the Gibbs free energy for component *i* could be thermodynamically represented as follows (Flory and Rehner, 1943a,b):

$$\Delta\mu_{i,\mathrm{mix}} + \Delta\mu_{i,\mathrm{el}} = \frac{\partial(\Delta G_{\mathrm{mix}})}{\partial n_i} + \frac{\partial(\Delta G_{\mathrm{el}})}{\partial n_i} \tag{2}$$

Equation 2 could be represented as eq 3, indicating the swelling equilibria of the cross-linked polymers.

$$\Delta\mu_{i,\mathrm{mix}} + \Delta\mu_{i,\mathrm{el}} = \frac{\partial}{\partial n_i}(\Delta G_{\mathrm{mix}} + \Delta G_{\mathrm{el}}) = 0 \tag{3}$$

In this work, the Flory–Huggins expression (Flory, 1953) was used to describe the free energy of mixing. The resulting expression of the chemical potential change of component *i* for the solvent(1)/solvent(2)/PDMS(3) systems was given as the next equation (Flory, 1953)

$$\Delta\mu_{i,\mathrm{mix}} = \frac{\partial(\Delta G_{\mathrm{mix}})}{\partial n_i} = RT[\ln \phi_i + (1-\phi_i) + \chi_i\,(1-\phi_i)^2] \tag{4}$$

$$\chi_i = \sum_{i \neq j} \chi_{ij}, \quad \chi_{ij} = \chi_{ji} \tag{5}$$

where ϕ_i is the volume fraction of component *i* and χ_i and χ_{ij} are the Flory–Huggins interaction parameters of component i and between components *i* and *j*, respectively.

Three kinds of expressions were used to describe the free energy of elastic deformation. Flory (1953) suggested that the chemical potential change was due to elastic deformation. It was based on the Gaussian chain length distribution, and the final expression for the solvent(1)/solvent(2)/PDMS(3) systems is given as the next equation

$$\Delta\mu_{i,\mathrm{el}} = RT\left[\frac{V_i}{v_3 M_c}\left(1 - \frac{2M_c}{M}\right)\left(\phi_3^{\,1/3} - \frac{\phi_3}{2}\right)\right] \tag{6}$$

James and Guth (1943) proposed another expression named as the “phantom network” that could account for network of the idealized flexible chains and the volume-filling properties of the “rubber-like” network. The resulting expression for the chemical potential change due to elastic deformation, as it applied to polymer swelling, is given as next equation (Flory, 1979)

$$\Delta\mu_{i,\mathrm{el}} = RT\left[\frac{V_i}{2v_3 M_c}\left(1 - \frac{2M_c}{M}\right)\phi_3^{\,1/3}\right] \tag{7}$$

Equation 7 was also based on the Gaussian chain length probability distribution, but Wall and White (1974) proposed the expression that was based on the non-Gaussian distribution. It is given by

$$\Delta\mu_{i,\mathrm{el}} = RT\left[\frac{V_i}{v_3 M_c}\left(1 - \frac{2M_c}{M}\right)\left(\frac{5}{3}\phi_3^{\,1/3} - \frac{7}{6}\phi_3\right)\right] \tag{8}$$

Equations 6–8 have the common term $1 - [(2M_c)/M]$ that accounts for dangling chains, or the deviation of the real network from a perfect network (Flory, 1953) where no dangling chains are present for a perfect network (i.e., $2M_c/M$). In eqs 6–8, V_i was the molar volume of solvent *i* and

Table 4. The Flory−Huggins Interaction Parameters and the Average Molecular Weights of the Chains between Cross-linked PDMSs Estimated by Flory−Huggins and Gaussian Distribution-Flory Model for Solvent(1)/PDMS(2) Systems

	303.15 K		308.15 K		313.15 K		318.15 K	
solvents	χ_{12}	M_c	χ_{12}	M_c	χ_{12}	M_c	χ_{12}	M_c
			poly(dimethylsiloxane)-35					
chloroform	0.4849	9848.7	0.1304	3603.6	0.0475	5474.8	0.3544	5834.5
trichloroethylene	0.4544	9544.3	0.3603	8602.5	0.3351	8351.4	0.4262	9262.3
cyclohexane	0.1909	6909.0	0.0652	5651.9	0.0812	5811.7	0.0998	5998.2
diisopropyl ether	0.1512	6512.0	0.0488	5488.1	0.0909	5909.1	0.3555	8555.4
n-Hexane	0.0518	5517.9	0.0809	5808.7	0.0840	5840.1	0.1479	6479.2
n-Heptane	0.0587	5587.1	0.2920	7919.8	0.0546	5546.1	0.1559	6558.9
toluene	0.3955	8955.3	0.2168	7168.2	0.1873	6872.6	0.3814	8814.4
chlorobenzene	0.5149	10148.8	0.4512	9511.6	0.4407	9406.2	0.5291	10291.0
benzene	0.4950	9950.0	0.4236	9236.1	0.4435	9434.9	0.4447	9446.7
methyl isobutyl ketone	0.5231	10231.1	0.5251	10250.6	0.5304	10303.7	0.5638	10638.1
methyl ethyl ketone	0.6633	11632.5	0.6446	11446.3	0.6919	11919.3	0.6144	11143.7
			poly(dimethylsiloxane)-40					
chloroform	0.5224	10244.4	0.4374	9373.5	0.3334	8334.3	0.2501	7500.8
trichloroethylene	0.5181	10180.9	0.5165	10165.3	0.5100	10099.6	0.4526	9526.4
cyclohexane	0.3463	8463.1	0.1064	6064.4	0.0915	5914.5	0.0702	5702.4
diisopropyl ether	0.0709	5708.7	0.0530	5529.6	0.3116	8116.3	0.0903	5902.9
n-Hexane	0.0399	5399.0	0.0967	5967.3	0.0739	5738.7	0.0866	5866.5
n-Heptane	0.2682	7681.6	0.1770	6770.4	0.0231	5231.4	0.0594	5594.1
toluene	0.5094	10094.4	0.4363	9362.5	0.3925	8924.9	0.3460	8459.5
chlorobenzene	0.6045	11044.5	0.5671	10670.9	0.5279	10278.8	0.4827	9827.3
benzene	0.5226	10226.0	0.4697	9696.8	0.4761	9761.3	0.3857	8857.0
methyl isobutyl ketone	0.6371	11371.3	0.6137	11136.7	0.5775	10775.0	0.4946	9946.0
methyl ethyl ketone	0.7463	12462.6	0.7058	12058.0	0.6792	11792.3	0.5913	10913.2
			Poly(dimethylsiloxane)-45					
chloroform	0.5107	10107.3	0.2714	7713.6	0.3702	8701.7	0.3361	8361.0
trichloroethylene	0.4752	9751.8	0.3992	8992.1	0.4283	9283.2	0.4088	9087.7
cyclohexane	0.3952	8951.8	0.1465	6464.8	0.2650	7650.2	0.1480	6480.3
diisopropyl ether	0.3266	8266.0	0.0146	5146.4	0.0487	5486.6	0.0004	5004.3
n-Hexane	0.2558	7558.1	0.0967	5967.2	0.0730	5730.2	0.0789	5788.6
n-Heptane	0.2682	7682.4	0.0948	5948.3	0.1083	6082.8	0.0714	5714.0
toluene	0.4561	9651.4	0.4047	9047.0	0.4050	9050.0	0.4009	9009.0
chlorobenzene	0.5313	10314.6	0.5008	10008.3	0.4901	9901.3	0.4316	9316.1
benzene	0.4472	9472.3	0.4306	9306.0	0.3682	8682.1	0.4132	9131.8
methyl isobutyl ketone	0.5640	10639.7	0.5453	10452.8	0.5778	10777.6	0.5698	10697.6
methyl ethyl ketone	0.6448	11447.7	0.6111	11110.7	0.6360	11359.6	0.6134	11133.8
			poly(dimethylsiloxane)-50					
chloroform	0.5292	10292.1	0.3889	8899.0	0.4888	9887.8	0.3910	8909.7
trichloroethylene	0.5056	10055.8	0.4477	9478.0	0.5249	10249.2	0.4474	9474.3
cyclohexane	0.3967	8975.9	0.2246	7246.2	0.2417	7417.0	0.2014	7014.3
diisopropyl ether	0.3848	8847.5	0.1920	6919.5	0.2333	7333.3	0.1877	6876.9
n-Hexane	0.3524	8524.1	0.2625	7624.6	0.1475	6475.1	0.2375	7374.9
n-Heptane	0.3296	8295.6	0.2070	7070.3	0.1081	6081.2	0.1861	6860.8
toluene	0.4904	9903.7	0.4448	9447.7	0.4353	9353.0	0.4364	9364.3
chlorobenzene	0.5774	10774.0	0.5541	10540.8	0.5410	10410.1	0.4913	9913.4
benzene	0.5163	10162.5	0.4881	9880.8	0.4590	9590.3	0.4694	9693.9
methyl isobutyl ketone	0.5792	10791.5	0.5694	10693.7	0.5646	10646.2	0.5562	10562.3
methyl ethyl ketone	0.6524	11524.3	0.6487	11486.6	0.6334	11334.1	0.6260	11259.6

v_3 the specific volume of PDMS, M_c the average molecular weight of the chains between cross-links, and ϕ_3 the volume fraction of polymer in the swollen network.

Calculation of Swelling Equilibria. When the solvent(1)/PDMS(2) or solvent(1)/solvent(2)/PDMS(3) systems reached swelling equilibria, the chemical potential change of solvent in the polymeric network was given by eq 3. The model was combined with the chemical potential changes of solvent due to mixing and elastic deformation on the swelling equilibria, and the form is given as next equation

$$\ln \phi_i + (1 - \phi_i) + \chi_i(1 - \phi_i)^2 + \Delta\mu_{i,\mathrm{el}} = 0 \qquad (9)$$

where some equation of the three expressions (eqs 6−8) for the chemical potential change due to elastic deformation could be substituted for $\Delta\mu_{i,\mathrm{el}}$. The experimental volume fractions of the solvent(1)/PDMS(2) and solvent(1)/solvent(2)/PDMS(3) systems in Tables 2 and 3 were correlated with eq 9 to estimate the Flory−Huggins interaction parameters between *i* and *j* components and the average molecular weight of chains dangling between two backbones of the cross-linked PDMSs. The representative results estimated by eqs 4 and 6 for the solvent(1)/PDMS(2) systems are shown in Table 4. The results estimated by other models also had the same tendency. As shown in Table 4, the average molecular weights of chains between cross-links were widely varied according to the species of solvents. The variations of the average molecular weights proved that the PDMSs used in this work were physically cross-linked ones by forming the hydrogen-bonded network. The Flory−Huggins interaction parameters of the *n*-hexane(1)/PDMS(2) systems among the solvent(1)/PDMS(2) systems were arbitrarily chosen and extended to reestimate the Flory−Huggins interaction parameters between good solvent(1)−poor solvent(2) and poor solvent(2)-PDMS(3) components for *n*-hexane(1)/acetone(2)/PDMS(3) and *n*-hexane(1)/ethanol(2)/PDMS(3) systems. The results estimated by eqs 4 and 6 are representatively plotted on Figure 4

Table 5. Average Deviations between the Experimental Volume Fractions and Those of PDMSs Calculated by Each Model for Solvent(1)/PDMS(2) Systems[e]

	FH−GF[a,b]				FH−PN[c]				FH−NG[d]			
polymers	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K
PDMS-35	0.20	0.83	1.03	0.32	0.03	0.15	0.12	0.04	1.70	3.24	2.95	1.48
PDMS-40	0.14	0.20	0.48	0.36	0.02	0.12	0.09	0.04	1.17	1.39	2.09	2.36
PDMS-45	0.14	0.29	0.33	0.21	0.04	0.15	0.07	0.02	0.49	1.96	1.61	2.00
PDMS-50	0.05	0.26	0.35	0.34	0.04	0.03	0.04	0.03	0.26	1.02	1.24	1.24
average	0.13	0.40	0.55	0.31	0.03	0.11	0.08	0.03	0.91	1.90	1.97	1.77

[a] FH: Flory−Huggins model defined as in eqs 4 and 5. [b] GF: Gaussian distribution-Flory model defined as in eq 6. [c] PN: Phantom-Network model defined as in eq 7. [d] NG: Non-Gaussian model defined as in eq 8. [e] Average deviation (%) = $(1/N)\sum_i |(\phi_{i,\mathrm{cal}} - \phi_{i,\mathrm{exp}})/\phi_{i,\mathrm{exp}}| \times 100$.

Table 6. Average Deviations between the Experimental Volume Fractions and Those Calculated by Each Model for *n*-Hexane(1)/Acetone(2) (or Ethanol(2))/PDMS(3) Systems

	303.15 K			308.15 K			313.15 K			318.15 K		
polymers	FH−GF	FH−PN	FH−NG	FH−GF	FH−PN	FH−NG	FH−GF	FH−PN	FH−NG	FH−GF	FH−PN	FH−NG
						n-Hexane(1)/Acetone(2)/PDMS(3)						
PDMS-35	1.88	1.88	1.88	1.72	1.72	1.72	1.50	1.50	1.50	0.89	0.89	0.89
PDMS-40	2.56	2.56	2.56	2.43	2.43	2.43	2.13	2.13	2.13	1.12	1.12	1.12
PDMS-45	1.78	1.78	1.78	2.45	2.45	2.45	2.67	2.67	2.67	2.27	2.27	2.27
PDMS-50	2.01	2.01	2.01	3.04	3.04	3.04	2.53	2.53	2.53	3.27	3.27	3.27
average	2.06	2.06	2.06	2.41	2.41	2.41	2.21	2.21	2.21	1.89	1.89	1.89
						n-Hexane(1)/ethanol(2)/PDMS(3)						
PDMS-35	2.36	2.36	2.36	3.16	3.16	3.16	3.12	3.12	3.12	3.07	3.07	3.07
PDMS-40	1.77	1.77	1.77	3.25	3.25	3.25	2.02	2.02	2.02	2.39	2.39	2.39
PDMS-45	2.12	2.12	2.12	2.53	2.53	2.53	1.73	1.73	1.73	1.10	1.10	1.10
PDMS-50	2.18	2.18	2.18	2.79	2.79	2.79	3.30	3.30	3.30	2.92	2.92	2.92
average	2.11	2.11	2.11	2.93	2.93	2.93	2.54	2.54	2.54	2.37	2.37	2.37

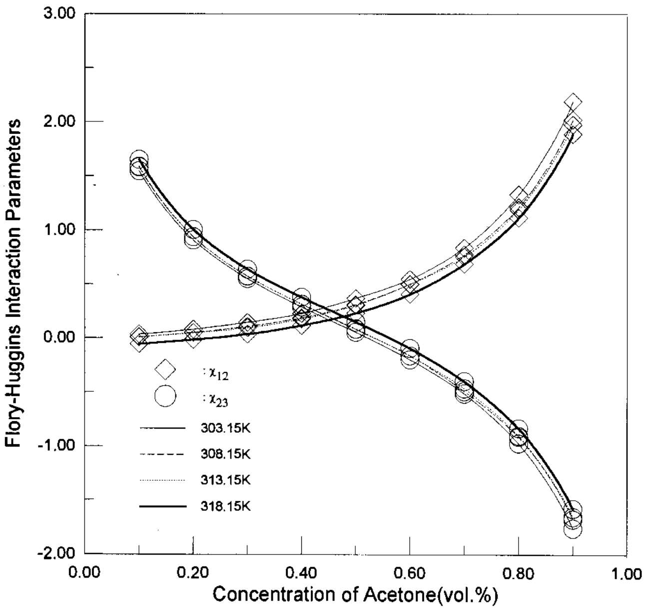

Figure 4. Dependence of concentration of solvent and temperature on Flory−Huggins interaction parameters for the *n*-hexane(1)/acetone(2)/PDMS-35(3) system.

with the concentration changes of acetone for the *n*-hexane(1)/acetone(2)/PDMS-35(3) system. They gave us the information for describing the interactions between 1−2 and 2−3 components at the swelling equilibria of mixed solvent/PDMS systems. As shown in Figure 4, χ_{12} was nonlinearly increased and χ_{23} decreased as the concentrations of acetone were increased. Besides, χ_{12} was slightly decreased and χ_{23} oppositely increased as the temperatures were increased. The interaction energies between 2−3 pairs were larger than 1−2 pairs when the concentrations of the poor solvent (acetone) in the *n*-hexane(1)/acetone(2)/PDMS-35(3) system were below approximate 40 vol %, but reversed when those were over approximate 50 vol %. Other ternary systems also had a similar tendency. The $\chi_{23} > \chi_{12}$ meant that the PDMS-35 showed a good swelling by accompanying the swelling ratios of Figure 3 below approximately 50 vol % of poor solvent and a poor swelling inthe case of $\chi_{23} < \chi_1$ over approximately 50 vol % of poor solvent. The *n*-hexane(1)/ethanol(2)/PDMS(3) systems could be described in the same way as the *n*-hexane(1)/acetone(2)/PDMS(3) systems. Therefore, its results would be generalized for different systems as well as PDMS systems. The average deviations between the experimental and the calculated volume fractions are shown in Tables 5 and 6 for the binary and ternary systems, respectively. The calculated volume fractions were in good agreement with the experimental data, and the average deviations were 0.13% to 0.55% for the FH-GF, 0.03% to 0.11% for the FH−PN, and 0.91% to 1.97% for the FH−NG models for the binary systems. The calculated values for the ternary systems agreed well with the experimental data showing almost the same errors of 1.89% to 2.41% for the *n*-hexane(1)/acetone(2)/PDMS(3) and 2.11% to 2.93% for the *n*-hexane(1)/ethanol(2)/PDMS(3) systems. The mathematical algorithm used to calculate the swelling equilibria was the Marquardt's method (Marquardt, 1963), and the volume fractions of PDMSs were calculated by minimizing the objective function $(\phi_i^{\mathrm{cal}} - \phi_i^{\mathrm{exp}})$. In the above calculations, the term $1 - [(2M_c)/M]$ in eqs 6−8 was taken to be unity, which was equivalent to assuming $2M_c/M \ll 1$.

Conclusions

The swelling ratios were repeatedly measured for the binary and ternary systems at 303.15 K to 318.15 K. Binary systems consist of 11 solvents and 4 PDMSs. The ternary systems were *n*-hexane(1)/acetone(2)/PDMS(3) and *n*-hexane(1)/ethanol(2)/PDMS(3). The swelling ratios of *n*-hexane(1)/acetone(2)/PDMS(3) systems were continuously increased and showed a maximum at about 90% *n*-hexane content. Further addition of *n*-hexane decreased gradually the swelling ratios. The swelling ratios for *n*-hexane(1)/acetone(2)/PDMS(3) systems showed slight phase transition when the concentrations of acetone in the mixed solvent were below about 50 vol %. The swelling ratios of *n*-hexane(1)/ethanol(2)/PDMS(3) systems also showed a similar tendency. The phenomena of slight phase transitions were caused by an excessive good solvent (*n*-hexane) against the cross-linked PDMSs. It meant that the breakage of chains of physically cross-linked PDMSs were responsible for the phase transitions.

On the other hand, three kinds of models were introduced to describe the swelling equilibria for the solvent(1)/PDMS(2) and solvent(1)/solvent(2)/PDMS(3) systems. The experimental volume fractions of binary systems were correlated with the models to estimate the Flory−Huggins interaction parameters and the average molecular weights of the chains between cross-links of PDMSs. The average molecular weights of the chains between cross-links were widely varied because the PDMSs were physically cross-linked by forming the hydrogen-bonded network. The binary interaction parameters were extended to reestimate the other Flory−Huggins interaction parameters between good solvent(1)−poor solvent(2) and poor solvent(2)−PDMS(3) for the ternary systems. The reestimated Flory−Huggins interaction parameters could be used to verify the swelling abilities of cross-linked PDMS. The volume fractions calculated were in good agreement with the binary experimental data showing the average errors of 0.13% to 0.55% for the FH-GF, 0.03% to 0.11% for the FH−PN, and 0.91% to 1.97% for the FH−NG models. Those values for the ternary systems agreed well with the experimental data showing errors of 1.89% to 2.41% for the *n*-hexane(1)/acetone(2)/PDMS(3) and 2.11% to 2.93% for the *n*-hexane(1)/ethanol(2)/PDMS(3) systems.

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