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Vapor–liquid equilibria for binary solutions of arborescent and linear polystyrenes

J.G. Lieu[a,b], J.M. Prausnitz[a,b,*], M. Gauthier[c]

[a]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[b]Chemical Engineering Department, University of California, Berkeley, CA 94720-1462, USA
[c]Department of Chemistry, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

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Abstract

Vapor–liquid-equilibrium (VLE) data are reported for binary mixtures of arborescent polystyrene or linear polystyrene dissolved in chloroform, toluene, or cyclohexane in the range 50–70°C. Using a classic gravimetric-sorption method, the amount of solvent absorbed by the polymer was measured as a function of solvent vapor pressure. VLE data are compared to osmotic second-virial-coefficient data for similar arborescent and linear polystyrenes. Solvent activity depends on the arborescent polystyrene generation number in cyclohexane solutions but similar dependence on arborescent polystyrene generation number is not observed for polymers dissolved in chloroform or toluene. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Vapour–liquid-equilibrium data; Osmotic second-virial-coefficient data; Arborescent polystyrene generation number

1. Introduction

The synthesis and study of polymers with highly branched, well-defined architectures have become the topics of growing interest in recent years. Dendrimers are an important class of macromolecules; synthetic methods have become available to control precisely their structure, molecular weight, and surface chemistry. Dendrimers are characterized by a central core with multiple “arms” radiating outwards to form increasingly packed “shells” or “generations” [1].

In general, dendrimer building blocks are low-molecular-weight molecules; many steps are required to produce a material of high molecular weight. To reduce the number of steps, Gauthier and Möller developed a synthetic “graft-on-graft” technique using polymers as building blocks [2]. Through this technique, arborescent polymers of high molecular weight can be obtained in fewer steps than those required for traditional dendritic growth.

A promising application of these polymers is in the formation of ultrathin films. Sheiko et al. [3] demonstrated that monomolecular films of uniform thickness can be obtained from arborescent polystyrenes. The thickness of monolayer film depends on the molecular weight and branching density of the polymer.

This work reports binary vapor–liquid-equilibrium (VLE) data for arborescent or linear polystyrenes in chloroform at 50°C, toluene at 70°C, and cyclohexane at 70°C. VLE data are compared to osmotic second virial coefficients reported by Gauthier et al. [4] for similar arborescent polystyrenes in toluene and cyclohexane.

2. Experimental

2.1. Materials

Solvents were degassed with a standard freeze–thaw procedure described by Panayiotou and Vera [5] and used without further purification. Table 1 gives solvent properties.

The arborescent polymers used in the investigation were synthesized by repeatedly grafting a linear polystyrene core with polystyrene side chains. The initial grafting reactions yielded a comb polymer designated as generation zero (S05-0); the generation one polymer (S05-1) is twice grafted, and so on. The core polymer and the side chains grafted in each reaction had a molecular weight around 5000 g/mol. Gauthier et al. [2,6,7] described the methods for synthesizing and characterizing these samples.

Two linear polystyrene samples of different molecular weights were also investigated. A sample with molecular

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[*] Corresponding author. Tel.: +1-510-642-3592; fax: +1-510-642-4778.

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Table 1
Solvent properties

Solvent	Supplier	Purity (%)
Chloroform	Fisher Scientific	99.9
Toluene	Fisher Scientific	99.9
Cyclohexane	Fisher Scientific	99.96

weight 1.75×10^4 g/mol was investigated in chloroform; a sample with molecular weight 5.0×10^4 g/mol was investigated in toluene and in cyclohexane.

For subsequent calculations, all polymers are assumed to have a specific gravity of unity. Tables 2 and 3 give the polymer properties.

2.2. Apparatus

VLE data were collected using a gravimetric-sorption method previously described by several authors (see, for example, Gupta and Prausnitz [8]). Fig. 1 shows a schematic diagram of the apparatus. The entire system is submerged in an isothermal water or air bath maintained at ±0.3°C.

Each glass chamber contains one aluminum pan suspended from a quartz spring (Ruska Instruments Corp., Houston, TX). The calibrated springs have a sensitivity of about 1 mg/mm and a maximum load of 250 mg. Within this range, the elongation of each spring is linear with respect to change in mass.

A cathetometer (Wild, Heerbrugg, Switzerland) is used to measure the extension of the springs and the mercury levels of the manometer.

2.3. Experimental procedure

Polymer samples of known mass (10–20 mg) are placed into previously weighed aluminum pans. The system is then vacuum-dried for 12–24 h to remove residual moisture and solvent. After obtaining the mass of dry polymer, solvent is introduced by opening and then closing the valve between the solvent flask and the evacuated glass chambers.

The system is allowed to equilibrate anywhere from 12 h to a few days after each solvent injection. Equilibrium is assumed when measurements in spring length do not change more than ±0.05 mm over a 12 h period.

As the polymer is nonvolatile, the total pressure is equal to the vapor pressure of solvent above the polymer solution. As experimental pressures are low (less than 0.7 bar), the solvent vapor is considered to be an ideal gas. Solvent activity a_1 is given by the ratio of the measured pressure to the pure-solvent saturation pressure at system temperature.

Table 2
Linear-polystyrene properties

Polymer	Supplier	M_w (g/mol)	M_w/M_n
Linear polystyrene[a]	Pressure Chemical Company	1.75×10^4	<1.06
Linear polystyrene[b]	Pressure Chemical Company	5.0×10^4	<1.06

[a] VLE data obtained in chloroform.

[b] VLE data obtained in toluene and cyclohexane.

Table 3
Arborescent-polystyrene properties

Polymer	Generation number	M_w[a] (g/mol)	M_w/M_n[b]
S05-0	0	6.7×10^4	1.07
S05-1	1	8.7×10^5	1.07
S05-3	3	9.0×10^7	1.15

[a] Absolute weight-average molecular weight from light-scattering measurements.

[b] Apparent polydispersity index from SEC analysis of the graft polymers.

The vernier scale on the cathetometer allows measurements to be made to the nearest 0.05 mm; therefore, pressure and mass readings have a precision of 0.1 Torr and 0.1 mg, respectively. Uncertainty in solvent activity is

Table 4
Vapor–liquid-equilibrium data for S05-1, S05-3 and linear polystyrene. w_1(POLY) = solvent weight fraction in the liquid phase with polymer “POLY”; “linear” refers to linear polystyrene; $a_1 = P/P_1^{sat}$ = solvent activity; P = vapor pressure in Torr; P_1^{sat} = pure-solvent saturation pressure (calculated from equations suggested by Daubert and Danner [15]) in Torr

Solvent: Chloroform; $T = 50$°C; $P_1^{sat} = 526$ Torr

w_1(linear[a])	a_1	w_1(S05-1)	w_1(S05-3)	a_1
0.043	0.088	0.138	0.139	0.279
0.160	0.327	0.190	0.184	0.369
0.288	0.541	0.351	0.349	0.627
0.378	0.673	0.453	0.449	0.760
0.468	0.782	0.541	0.538	0.855
0.544	0.859			

Solvent: Toluene; $T = 70$°C; $P_1^{sat} = 204$ Torr

w_1(linear[b])	w_1(S05-1)	w_1(S05-3)	a_1
0.020	0.020	0.027	0.066
0.048	0.041	0.048	0.180
0.082	0.078	0.076	0.294
0.116	0.110	0.108	0.403
0.155	0.142	0.146	0.506
0.188	0.177	0.181	0.594
0.244	0.232	0.235	0.691
0.307	0.293	0.303	0.785
0.404	0.379	0.398	0.855

Solvent: Cyclohexane; $T = 70$°C; $P_1^{sat} = 544$ Torr

w_1(linear[b])	w_1(S05-1)	w_1(S05-3)	a_1
0.024	0.025	0.020	0.348
0.046	0.052	0.036	0.468
0.077	0.081	0.060	0.612
0.099	0.106	0.078	0.724
0.108	0.114	0.093	0.803
0.115	0.129	0.100	0.852

[a] $M_w = 1.75 \times 10^4$ g/mol.

[b] $M_w = 5.0 \times 10^4$ g/mol.

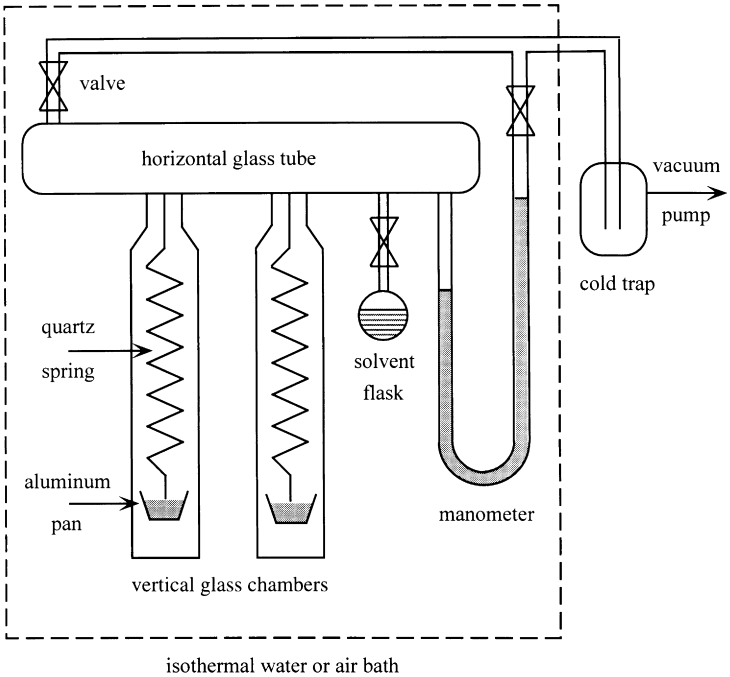

Fig. 1. Experimental apparatus for vapor–liquid-equilibrium measurements.

1–2% above $a_1 = 0.1$ and 2–4% below $a_1 = 0.1$. Solvent weight fraction w_1 uncertainty is 2–5% above $w_1 = 0.5$ and 5–15% below $w_1 = 0.5$.

Reliability of the apparatus and experimental procedure were established by reproducing published experimental VLE data for polystyrene in chloroform [9].

3. Results and discussion

Table 4 present VLE data for S05-1, S05-3 and linear polystyrene. Figs. 2–4 show solvent activity a_1 as a function of solvent segment fraction Φ_1.

Fig. 2 shows solvent activities for solutions of S05-1, S05-3 and linear polystyrene in chloroform; there is no significant difference in solvent absorption among the polymers. Fig. 3 shows results for S05-1, S05-3 and linear polystyrene in toluene. Again, solvent-activity data for the polymers do not differ significantly. However, Fig. 4 shows considerable differences for solvent absorption in cyclohexane; S05-1 absorbs the most cyclohexane, followed by linear polystyrene and then by S05-3.

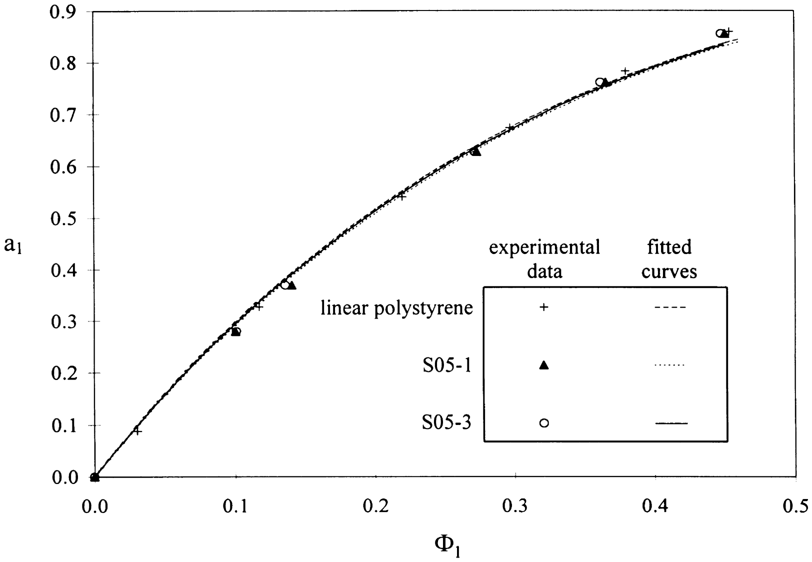

Fig. 2. Solvent activities for binary solutions of S05-1, S05-3 and linear polystyrene in chloroform at 50°C; fitted curves calculated with the Flory–Huggins equation; linear polystyrene with $M_w = 17\ 500$ g/mol.

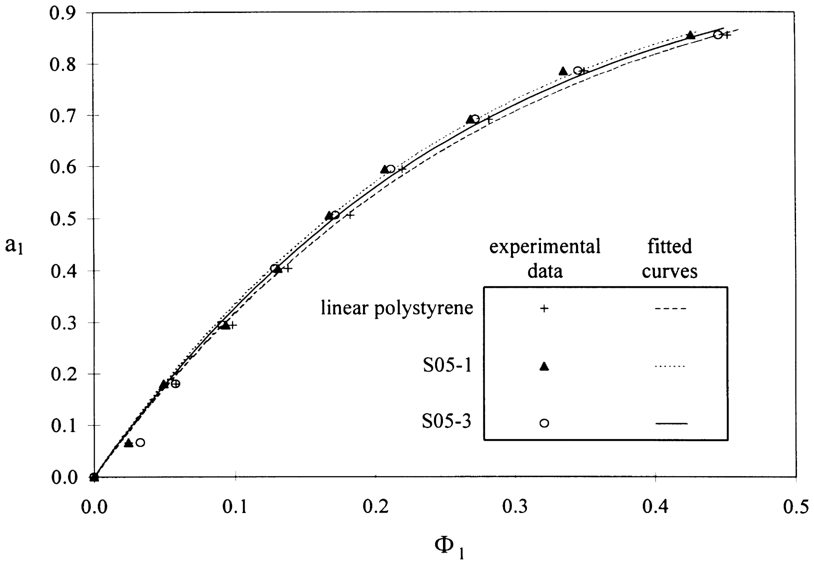

Fig. 3. Solvent activities for binary solutions of S05-1, S05-3 and linear polystyrene in toluene at 70°C; fitted curves calculated with the Flory–Huggins equation; linear polystyrene with $M_w = 50\ 000$ g/mol.

The data are fitted using the Flory–Huggins equation [10]. The activity of the solvent is given by

$$\ln a_1 = \ln \Phi_1 + \left(1 - \frac{r_1}{r_2}\right)\Phi_2 + \chi_{FH}\Phi_2^2. \quad (1)$$

Solvent and polymer segment fractions, Φ_1 and Φ_2, are defined by

$$\Phi_2 = 1 - \Phi_1 = \frac{r_2 N_2}{r_1 N_1 + r_2 N_2}, \quad (2)$$

where N_1 and N_2 are the number of molecules and r_1 and r_2 are the number of segments per molecule of solvent and polymer respectively. We set r_1 equal to unity and calculate r_2 by

$$r_2 = \frac{M_2}{M_1}\frac{\rho_1}{\rho_2} = \frac{\text{molar volume of polymer}}{\text{molar volume of solvent}}, \quad (3)$$

where M_1 and M_2 are molecular weights and ρ_1 and ρ_2 are mass densities of solvent and polymer, respectively. The dimensionless Flory–Huggins parameter χ_{FH} characterizes the solvent–polymer interaction energy; the lower this parameter, the stronger the attraction between solvent and polymer. Table 5 gives fitted χ_{FH} values.

The Flory parameters in Table 5 indicate that the polymers interact most favorably with chloroform (low χ_{FH}) and least favorably with cyclohexane (high χ_{FH}). Fig. 5 shows

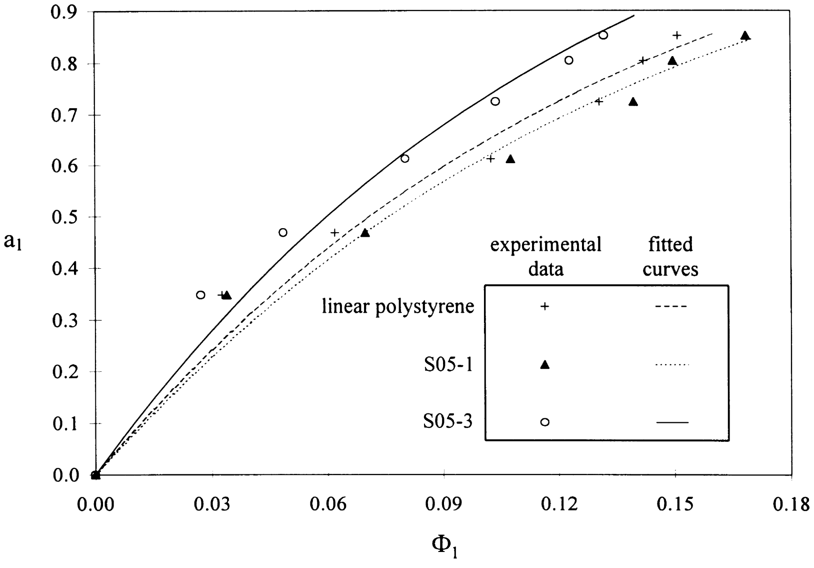

Fig. 4. Solvent activities for binary solutions of S05-1, S05-3 and linear polystyrene in cyclohexane at 70°C; fitted curves calculated with the Flory–Huggins equation; linear polystyrene with $M_w = 50\ 000$ g/mol.

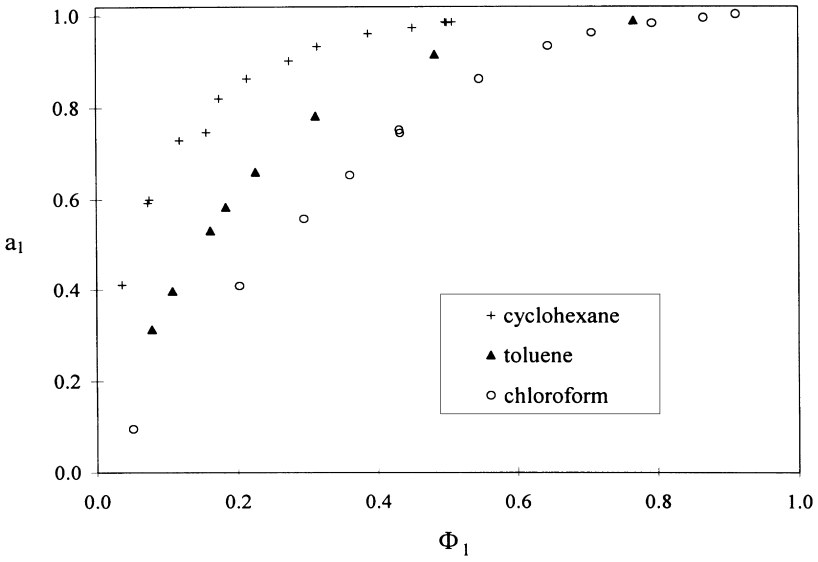

Fig. 5. Solvent activity data for binary solutions of: Linear polystyrene with $M_n = 290\ 000$ g/mol in chloroform at $T = 50$°C from Bawn et al. [9]; linear polystyrene with $M_n = 10\ 300$ g/mol in toluene at $T = 48.5$°C from Tait et al. [11]; linear polystyrene with $M_n = 25\ 100$ g/mol in cyclohexane at $T = 44$°C from Krigbaum et al. [12].

that our results are consistent with those in the literature for linear polystyrene in chloroform, toluene, and cyclohexane.

Figs. 2 and 3 show that the Flory–Huggins theory gives a good fit for the polymers in chloroform and toluene, respectively. Fig. 4, however, shows that the calculated VLE for the polymers in cyclohexane are not reproduced with the same accuracy.

With rising generation number, the branching density of arborescent polystyrene increases and the resulting molecular structure is expected to stiffen and approach that of a hard sphere in semi-dilute solution owing to steric crowding [13]. This stiffening suggests that solvent power may show a significant dependence on generation number.

From light-scattering measurements, Gauthier et al. [4] reported the dependence of osmotic second virial coefficients A_2 on temperature for arborescent and linear polystyrenes in toluene and in cyclohexane in the range 25–65°C. As the data cover a reasonable temperature range, A_2 can be split into contributions from enthalpy ($A_{2,H}$) and entropy ($A_{2,S}$). For S05-0 and S05-1, Gauthier et al. report that $A_{2,S}$ is positive and decreases with rising generation number when dissolved in toluene or cyclohexane; $A_{2,H}$ is negative and changes insignificantly in toluene, but decreases in magnitude with rising generation number in cyclohexane. The variation of $A_{2,H}$ and $A_{2,S}$ supports our conjecture that a decrease in solvent power (lower A_2) with rising generation number is due to steric factors (lower $A_{2,S}$); increased molecular stiffness inhibits penetration of solvent into the polymer.

To compare our Flory parameters with osmotic second virial coefficients, we use the relation [14]

$$\chi_{FH} = 0.5 - \nu_1 \rho_2^2 A_2 \tag{4}$$

where ν_1 is the molar volume of the solvent and ρ_2 is the polymer mass density. The dependence of A_2 on temperature is linear for S05-0, S05-1 and for linear polystyrene. Table 6 shows A_2 linearly extrapolated to 70° and Table 7 shows χ_{FH} calculated by Eq. (4).

As shown in Tables 5 and 7, χ_{FH} obtained from VLE in toluene and cyclohexane do not agree well with χ_{FH} calculated from A_2. Disagreement is probably due to very different concentration regimes used for data acquisition. Our Flory parameters are obtained from solvent-activity data for concentrated polymer solutions, whereas osmotic

Table 5
Flory–Huggins interaction parameters

Solvent	T (°C)	χ_{FH}		
		Linear polystyrene	S05-1	S05-3
Chloroform	50	0.238[a]	0.207	0.219
Toluene	70	0.318[b]	0.382	0.353
Cyclohexane	70	1.187[b]	1.123	1.337

[a] $M_w = 1.75 \times 10^4$ g/mol.
[b] $M_w = 5.0 \times 10^4$ g/mol.

Table 6
Osmotic second virial coefficients for S05-1, S05-3 and linear polystyrene from Gauthier et al. [4]; A_2 extrapolated to 70°C

Solvent	A_2 (cm^3 mol/g^2)		
	Linear polystyrene[a]	S05-0	S05-1
Toluene	7.78×10^{-4}	3.14×10^{-4}	3.48×10^{-5}
Cyclohexane	1.77×10^{-4}	1.31×10^{-4}	1.32×10^{-5}

[a] $M_w = 7.3 \times 10^4$ g/mol.

Table 7
Flory parameters calculated from osmotic second virial coefficients for S05-1, S05-3 and linear polystyrene; A_2 extrapolated to 70°C

Solvent	$\chi_{FH} = 0.5 - \nu_1\rho_2^2 A_2$		
	Linear polystyrene[a]	S05-0	S05-1
Toluene	0.413	0.465	0.496
Cyclohexane	0.480	0.485	0.498

[a] $M_w = 7.3 \times 10^4$ g/mol.

second virial coefficients are obtained from light-scattering data for highly dilute polymer solutions.

Qualitatively, our VLE data indicate that solvent absorption depends on polymer generation number in cyclohexane, but not in chloroform or toluene. A possible explanation is that for binary mixtures of arborescent polystyrenes, entropic contributions are of similar magnitude in the solvents used here. The quality of the solvents may then be primarily a function of the enthalpic contributions. For example, chloroform and toluene are good solvents for arborescent polystyrene and favorable polymer–solvent interactions may result from favorable enthalpic contributions with relatively small entropic contributions. Cyclohexane, however, is a poor solvent for arborescent polystyrene, perhaps because the enthalpic contribution is low. As the entropic contribution in cyclohexane may be significant, VLE results for polymers in cyclohexane depend on generation number.

4. Conclusions

Osmotic second virial coefficients indicate that for arborescent polystyrene, solvent–polymer interaction depends on generation number. VLE data for solutions of arborescent polystyrenes in cyclohexane also show dependence on generation number; however, similar dependence of solvent absorption on generation number is not observed when the solvent is chloroform or toluene. Conclusions from osmotic-second-virial-coefficient data are not necessarily inconsistent with those obtained from VLE data because the former pertain to very dilute solutions whereas the later pertain to highly concentrated polymer solutions.

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