Polymer Swelling, 13: Correlation of Flory–Huggins Interaction Parameter, X, with Molecular Structure in Polystyrene–Liquid Systems

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SYNOPSIS

It is shown that the Flory–Huggins interaction parameters (X), for polystyrene–liquid systems, reported by others, vary linearly with the readily and precisely determinable relative swelling power (C) of the selfsame liquid, determined in this laboratory using poly (styrene-co-divinylbenzene) as the sorbent polymer. This simple gravimetric method appears to be the most suitable for the determination of X values of polystyrene–liquid systems over the full range of polymer volume fractions. Accordingly, the C values already determined by this method were used to calculate numerous X values for polystyrene–liquid systems not yet reported in the literature. The data obtained thereby show that X reflects sensitively the molecular structure of the liquid.

INTRODUCTION

It is well known[1-3] that the Flory–Huggins interaction parameter (X) characterizes intermolecular interaction energetics, which in turn affect the colligative properties of polymer–liquid (P–L) systems. This parameter is a measure of the change in chemical potential of the liquid in going from the pure state (μ_1^0) to the solution state (μ_1), which varies with temperature (T) and volume fraction (v) of the polymer as given[3] approximately by

$$X = \frac{(\mu_1 - \mu_1^0)}{RTv^2}$$
$$- \frac{[\ln(1 - v) + v(1 - V_1^0/V^0)]}{v^2} \quad (1)$$

where V_1^0/V^0 is the ratio of molar volumes for liquid and polymer. Thus X is related thermodynamically to the physical properties of the corresponding P–L systems through the difference $(\mu_1 - \mu_1^0)$. Some of the more common of these relationships involve osmotic pressure, vapor sorption, and gas-liquid chromatography. Osmotic pressure is used primarily for measuring X at levels of $v < 0.5$, whereas vapor sorption is used more often for measuring X at levels of $v > 0.5$, and gas-liquid chromatography is used to measure X at levels of v close to 1.0.

The precision for measuring X by any of these methods, however, leaves much to be desired. At levels of v less than 0.4, it is at best ± 0.01, and thereafter it decreases monotonically with v such that at $v > 0.8$ it is sometimes only about ± 1 in the *first* significant figure. Such limited precision allows one to predict only that a liquid is a relatively "good solvent" $(X < 0.3)$ or a "poor solvent" $(X > 0.8)$ for a given polymer,[3] but it does not enable one to establish meaningful correlations of X with the molecular structures of the two components that comprise the respective P–L systems, despite the belief based on intuition that such relationships must exist.

Recently we reported[4-15] that it is possible to determine the number, α, of adsorbed molecules per *accessible* phenyl group of poly (styrene-co-divinylbenzene) [hereafter referred to as either poly (Sty-co-DVB) or $(Sty)_{1-x}(DVB)_x$] at liquid saturation (or in solution when x is zero), based on the volume of sorbed liquid (ZR) per gram of polymer, where Z is a substituent with relatively strong affinity for the phenyl groups in the polymer and R is the rest of the molecule. Our sorption studies, using homol-

ogous series of liquids ZR (in which Z was kept constant and R was varied systematically), showed that α increases with the affinity of Z for the phenyl groups in poly(Sty-co-DVB) and decreases with the "bulkiness" of R in accordance with expectation based on simple physical-organic theories. We noted too that α, which ranges from ca. 3.3 to 0 for polystyrene–liquid systems, reflects even the smallest structural modifications in sorbed aromatic[4-10] or aliphatic[10-15] molecules. Since α can be determined with a precision of ±0.01, it was well worth the effort required to test whether or not this adsorption parameter correlates meaningfully with χ. If this proved to be the case, then the good correlations with molecular structure noted with α for polystyrene–liquid systems would be equally valid for χ at the same T and v.

As reported earlier, α is calculated from the experimentally determined relative swelling power, C [in volume of adsorbed liquid per unit weight of poly(Sty-co-DVB) at liquid-saturation] by means of Eq (2).

$$\alpha = 104Cd/M \qquad (2)$$

where d and M are the density and formula weight, respectively, of the sorbed liquid, and 104 is the formula weight of styrene. The relative swelling power is defined by the slope of the linear relationship obtained when the volume, S, per unit weight of $(Sty)_{1-x}(DVB)_x$ at liquid saturation is plotted versus the cube root of the average number (λ) of backbone carbon atoms between crosslink junctions, i.e.,

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) \qquad (3)$$

where λ is approximately equal to x when x is less than 0.1, and $1/\lambda_0$ is the crosslink density above which S is virtually zero.

Earlier publications[9-15] from this laboratory reported that α (and C from which α is derived) correlates meaningfully with the Hildebrand solubility parameter δ (within the limits that δ is valid, i.e., in the absence of specific solute–solvent interactions), and that α has relevance as well for the phenomena of polymer drying[16-19] and gel formation from polymer–liquid solutions.[14,20] We also showed[16] that the driving force in polymer swelling is the difference in free energy between the adsorbed and nonadsorbed molecules. Since the sorbed molecules in the liquid-saturated gel that are not immobilized by adsorption are in exchange equilibrium with those that are so adsorbed, the above observation is equivalent to saying that this driving force is proportional to

the difference in chemical potential between the liquid in its pure state (μ_1^0) and that (μ_1) in the gelled state. Since χ also varies with this difference [Eq. (1)], it is reasonable to suspect that χ at a given temperature and polymer volume fraction v may vary linearly with C. The purpose of this article is to report the results of such attempted correlations.

RESULTS AND DISCUSSION

Reconsideration of Reported χ Values

A large database of χ values for P–L systems has already been compiled by Orwoll[1] as part of his 1976 review (with 128 references). He classified these data (Tables III to XXII of Ref. 1) according to polymer (P), liquid (L), volume fraction (v) of that polymer in the P–L system, and the temperature (T) at which the measurements were made. The type of measurement and the reference to the original literature are also listed.

In view of the known uncertainty associated with measuring χ, it is clear that some of these data may in fact be in serious error. The identification of these unreliable data, however, is difficult without a good criterion for adjudicating data reliability. I postulated that such adjudication might be possible on the basis of self-consistency with a suitable mathematical relationship of χ as a function of v, provided that such a relation could be established empirically on the basis of data already published. In this endeavor only those χ values that were determined at 25 ± 5°C were considered because the ultimate purpose of this exercise was the correlation of χ values with the C value for the corresponding liquids, which had been determined at 23 ± 1°C.

Figures 1 and 2 of Ref. 1 show that χ varies with v, but definitely not in the manner predicted by Flory's equation-of-state theory (calculated data represented by the solid lines in Figs. 1 and 2 of Ref. 1). It is implied in these two figures that the relationship is represented better by the curved dotted lines that pass through the highest values in the range of data reported at a given level of v. I believe (for reasons soon to be presented) that even the dotted lines do not represent correctly the corresponding relationships of χ with v for the two P–L systems considered (namely, polyisobutylene–benzene and polystyrene–methyl ethyl ketone).

Initially, the Flory–Huggins theory[1-3] considered χ to be independent of v because the apparent explicit dependence on v as indicated in Eq. (1) appeared to be canceled by the implicit dependence on

v contained in the associate terms. This proved to be an unsatisfactory representation of how χ varies with v, however, and Flory suggested later[21] that the dependence of χ on v might be expressed better by a power series:

$$\chi = \chi_0 + \chi_1 v + \chi_2 v^2 + \cdots \qquad (4)$$

In fact, Flory noted (Fig. 111 of Ref. 3) that for the P–L systems polydimethylsiloxane–benzene, polystyrene–methyl ethyl ketone, polystyrene–toluene, and rubber–benzene, χ appears to vary linearly with v from $v = 0.2$ to $v = 0.8$, which suggests that for these P–L systems the third term of Eq. (4) may already be too small to contribute significantly. Flory cautioned, however, that these examples may represent exceptions rather than the rule.

In order to determine which is the exception and which is the rule, every case in which χ was reported at two or more levels of v for a given P–L system at $25 \pm 5°C$ was gleaned from the data compiled by Orwoll in Tables III–XXII of Ref. 1 (many of these data are also shown in Table 3 of Ref. 2). Each of these sets of data were then plotted as a function of v. These correlations (Fig. 1) show that in almost every case χ appears to vary linearly with v from 0 to 1 despite the usual scatter in the data at a given level of v, especially for values of v greater than 0.5. In those cases that the liquid is a "poor" solvent for the polymer, χ increases with v, indicating that the polymer would prefer to associate with itself rather than with molecules of solvent. In those cases that the liquid is a "good" solvent for the polymer, χ decreases with v, indicating that the polymer would prefer to associate with molecules of solvent rather than with itself. It follows, therefore, that for P–L systems in which the tendency for self-association is about equal to that for association with the sorbed liquid, χ–v relationships should exhibit essentially zero slope.

As stated above, Figures 1 and 2 of Ref. 1 show that χ varies with v, but the dotted lines therein imply that the relationships are not linear for these two P–L systems. It is obvious from the pattern of the data points that the range of χ values at a given level of v is narrow (ca. ±0.01) for levels of v that are less than 0.4, but that this range increases with the difference ($v = 0.4$) such that it approaches ±0.1 χ units at $v = 1$. It is also obvious that the dotted line favors the upper range of the data at a given level of v and virtually ignores the data at the lower end of the range. Moreover the data at a given level of v appear not to have a normal distribution, but rather a bimodal distribution, i.e., the data appear
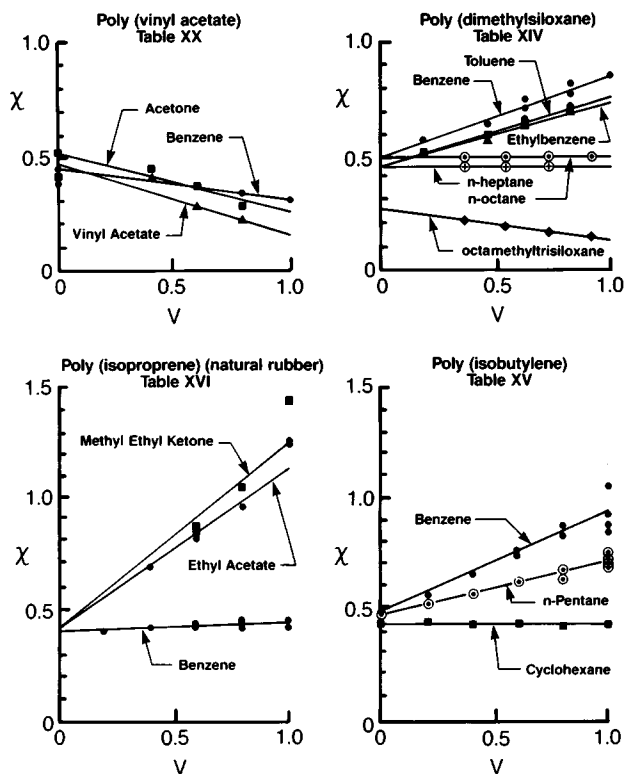

Figure 1 Correlation of χ for P–L systems at ca. 25°C with the corresponding volume fraction (v) of the polymer in that system. The data for doing so are taken from Tables XIV, XV, XVI, and XX in Ref. 1.

to bunch at the top and bottom ends of the range for each level of v greater than 0.4.

Consequently, it seemed quite probable that these results might be amenable to an alternative interpretation. Accordingly, the data recorded in Figures 1 and 2 of Ref. 1 are replotted here in Figure 2, which shows bifurcated relationships that begin to separate at about $v = 0.4$. The χ values that represent the data at the bottom of the range for a given level of v greater than 0.4 (these were determined either by vapor-pressure measurements above the solution, represented here by circles, or by retention volume measurements in gas-liquid chromatography, represented here by squares) fall along a line that appears to be a linear extension of the straight line established by the χ values for v less than 0.5 (determined by osmotic pressure measurements, represented here by triangles). The χ values (circles) that represent the upper limits of the data at a given level of v greater than 0.5 fall along a straight line of greater slope that intersects the lower line at ca. $v = 0.5$. In view of the consistency of the apparent linear relationship noted for other P–L systems (Fig.
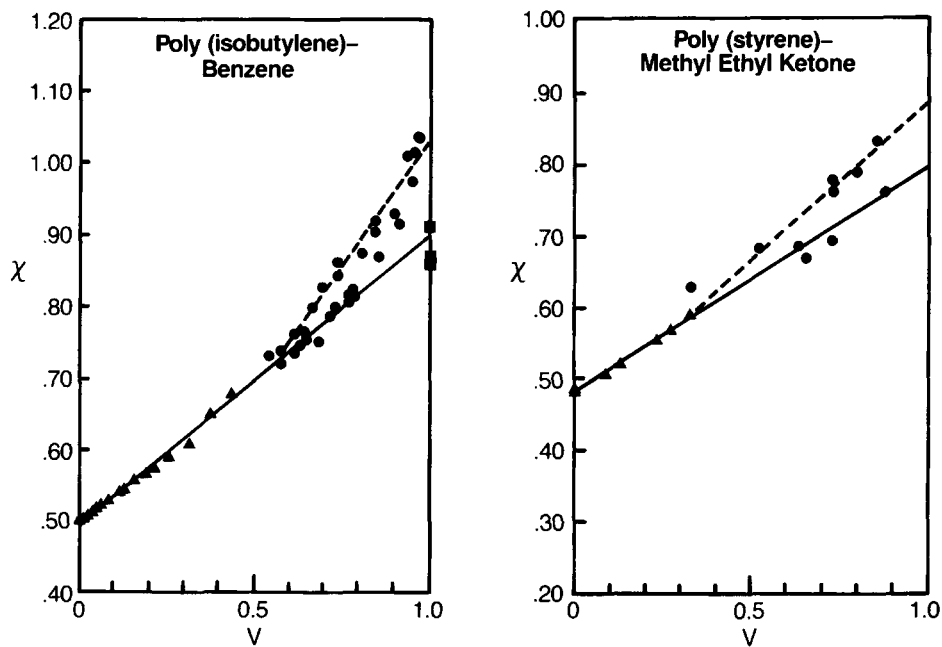
Figure 2 Correlation of χ with the volume fraction (v) reported for poly(isobutylene)–benzene and polystyrene–methyl ethyl acetate systems at 25°C. The data for doing so are taken from Figs. 1 and 2 in Ref. 1. The triangles represent data determined by osmotic pressure measurement, the circles represent data determined by vapor pressure above the solution measurements, and the squares represent data determined by volume retension measurements in gas-liquid chromatography.

1), the "true" relationship of χ vs. v at 25°C for the polyisobutylene–benzene system (Fig. 2) is taken, tentatively, to be the straight line that passes through the points at (χ = ca. 0.49; v = 0) and at (χ = ca. 0.90; v = 1), and that for polystyrene–methyl ethyl ketone system (Fig. 2) is taken, tentatively, to be the straight line that passes through the points at χ = ca. 0.48, v = 0 and at χ = ca. 0.82, v = 1.

Thus most of the correlations collected in Figures 1 and 2 (and those in Fig. 3, shortly to be discussed) for systems of a given polymer with various liquids show convergence at v = 0 to a common point somewhere between χ = 0.4 and 0.5. This is consistent with theories proposed by Flory, who pointed out (Chapter XII and XIII of Ref. 3) that for a system at its theta-temperature, χ at v = 0 is $\frac{1}{2}$, but at temperatures below the theta-temperature χ deviates from $\frac{1}{2}$ by a small amount that depends on the system, primarily the polymeric component. This is usually the case as indicated by Table I, which records the average χ at v = 0 and 25 ± 5°C calculated for each classification of the P–L systems, based on the polymer, as noted in Tables III to XXII of Ref. 1. These data (χ ± σ, where χ is the average of N χ

values at v = 0 reported for a given classification in Ref. 1, and σ is the standard deviation from this average) show that χ at v = 0 is typically (10 out of

Table I   Average Interaction Parameter (χ) at v = 0 and T = 25 ± 5°C[a]

Table[b]	Polymer	N[c]	χ[d] ($\pm\sigma$[e])
III	Cellulose acetate	10	0.35 ± 0.07
VI	Cellulose nitrate	12	0.16 ± 0.10
IX	Poly(o-chlorostyrene)	3	0.48 ± 0.01
X	Poly(p-chlorostyrene)	3	0.47 ± 0.02
XIV	Polydimethylsiloxane	3	0.47 ± 0.03
XV	Polyisobutylene	8	0.47 ± 0.03
XVI	Polyisoprene	1	0.40
XVII	Polymethylmethacrylate	15	0.48 ± 0.03
XVIII	Polypropylene	2	0.46 ± 0.06
XIX	Polystyrene	18	0.48 ± 0.03
XX	Polyvinyl acetate	8	0.41 ± 0.02
XXI	Polyvinyl chloride	3	0.38 ± 0.13

[a] Calculated from data compiled by Orwoll in Ref. 1.
[b] Table: refers to table number as given by Orwoll in Ref. 1.
[c] N is the number of χ values at v = 0 and T = 25 ± 5°C used to calculate χ ± σ.
[d] χ is the average value of the interaction parameter.
[e] σ is the standard deviation from the average.

12 classifications) between 0.38 and 0.48, with the norm at 0.47 ± 0.01 (7 out of 12 classifications), the standard deviations usually being less than 0.04. In the single case of cellulose nitrate–liquid systems, however, X was 0.16 ± 0.10; this example shows that exceptions do exist for reasons not yet understood.

If the observed average value of X at $v = 0$ for a given polymer and set of liquids is close to 0.5 and the standard deviation for that set of systems is less than ±0.05, as is the case for the polystyrenes and for the acrylates, then it is reasonable to expect that other extrapolations of X to $v = 0$, which have not yet been reported, may also fall within the range established using the reported data. It is assumed that this is true for polystyrene–liquid systems (X at $v = 0$ and 25 ± 5°C being 0.48 ± 0.03; Table I). It is reasonable to expect, therefore, that all correlations of X with v for these systems might converge to a common point of intersection at $v = 0$, somewhere within the range $X = 0.45$ to 0.51.

Examination of Table XIX of Ref. 1 shows that there are five polystyrene–liquid systems for which

X at 25 ± 5°C are recorded at two or more levels of v greater than 0. These data are recorded in Figure 3 (indicated by the filled circles), which shows that the lines drawn through these points do indeed converge at $v = 0$ to a common point of intersection at $X = 0.48 ± 0.01$, which is well within the expected range stated above. The above results confirm that for all practical purposes X varies linearly with v, implying that extrapolation of X to $v = 1$ is justified.

These linear relationships now afford a useful criterion for adjudicating the reliability of data reported for these polystyrene–liquid systems; i.e., those data that deviate from the linear relationship, established using the bulk of the data for that P–L system, may be discarded with reasonable justification. Thus, the value of $X = 0.52$ for the polystyrene–chloroform system at $v = 0.2$ is so far off the line established by the other four X values at $v = 0.4$, 0.6, and 0.8 and the common point of intersection at $v = 0$ (i.e., $X = 0.477 - 0.394v$, the square of the correlation coefficient of which is $r^2 = 0.997$) that this point must be considered to be highly suspect
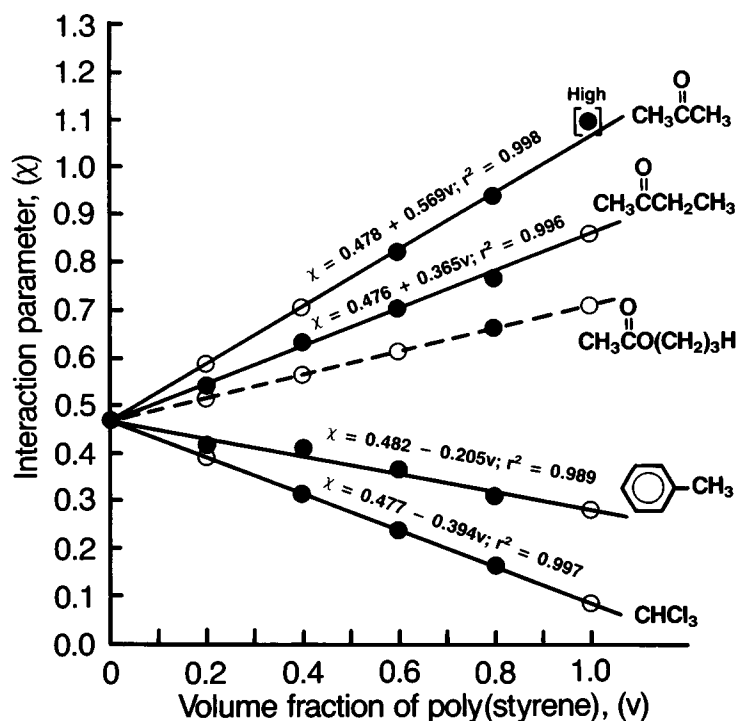
Figure 3 Correlation of X for polystyrene–liquid systems at 25°C with the volume fraction (v) of polymer in the system. The filled circles represent experimentally determined data recorded in Table XIX of Ref. 1. The empty circles represent estimations by interpolation or extrapolation of the linear relationships established on the basis of the experimental data shown. The X datum for acetone at $v = 1$ is placed in brackets to indicate that this point seems too high, and therefore it was not included in the data set used to establish by linear regression the equation shown for this linear relationship.

(i.e., errant) and, therefore, is not recorded in Figure 3 for the sake of clarity of presentation. Similarly, $X = 1.1$ reported for acetone at $v = 1$ is significantly above the line established by the other three data points at $v = 0.0$, 0.6, and 0.8 (i.e., $X = 0.478 + 0.569v$; $r^2 = 0.998$). This wayward point, however, is not as far off the line of reference as that noted above for chloroform, and therefore it is recorded in Figure 3 along with the more reliable data; it is placed in brackets, however, to emphasize that it may be inconsistent with the relationship established by the other data.

The three X values reported for polystyrene-(n-propyl acetate) at $v = 0.4$, 0.6, and 0.8 present a challenge to this criterion for adjudication of validity of data because all three values are reported to be 0.66, which is highly improbable; two of these values must be incorrect, but which two? Since only the

data reported for X at $v = 0.8$ is consistent with other correlations (to be presented shortly), this value was accepted tentatively in preference to the other two. The line drawn through this data point at $v = 0.8$ and the averaged data point at $v = 0$ is dashed to emphasize the arbitrary manner in which it was here chosen.

In view of the apparent general validity that X for polystyrene–liquid and other P–L systems increase linearly with v from 0 to 1, as indicated in Figures 1–3, it follows that those values of X at levels of v for polystyrene–liquid systems not yet established by experiment might be estimated with reasonable confidence by interpolation and extrapolation to X at $v = 1.0$. These estimated values are indicated in Figure 3 by empty circles. Those that were determined experimentally are indicated by filled circles. This entire set of self-consistent data can
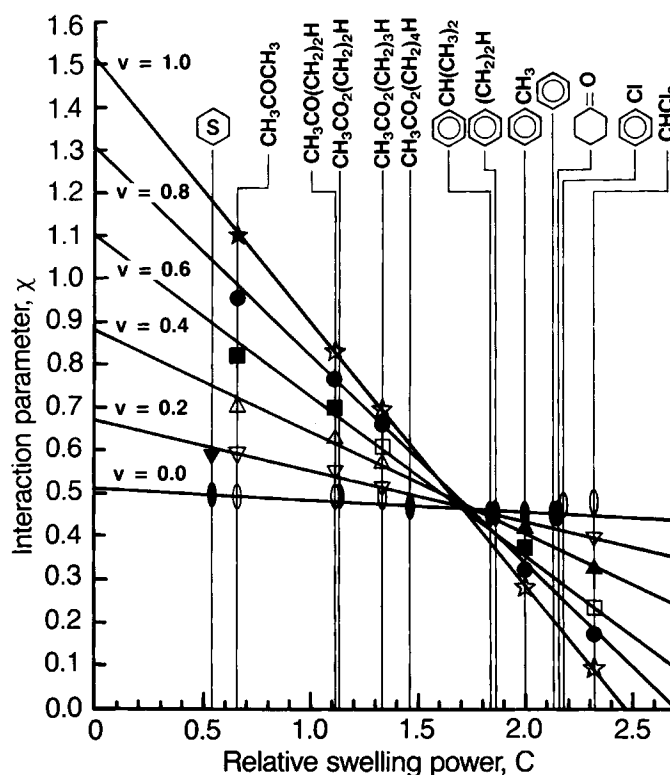
Figure 4   Correlation of the Flory–Huggins interaction parameter for polystyrene–liquid systems at 25°C with the relative swelling power (C) of the corresponding liquid at 23°C as a function of the volume fraction (v) of the polymer in the system. The X data at v = 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0 are represented, respectively, by the following symbols: star, circle, square, triangle pointing upward, triangle pointing downward, and narrow oval. The X data determined experimentally are represented by the filled symbols, whereas those obtained by interpolation or by extrapolation as noted in Figure 3 are represented by the corresponding empty symbols.

Table II Summary of Regression Analysis Data for $X = X_0 - AC$ **[Eq. (5)]**

v^a	0.0	0.2	0.4	0.6	0.8	1.0
$X_0{}^b$	0.51	0.67	0.80	1.08	1.30	[1.51]
A^b	0.03	0.12	0.24	0.36	0.49	[0.61]
N^c	13	7	5	5	5	5
$r^{2\,d}$	0.574	0.965	0.993	0.996	0.998	0.996

^{a} v is the volume fraction of polymer in the liquid polystyrene system.
^{b} X_0 and A as defined in Eq. (5).
^{c} N is the number of data points used to establish Eq. (5).
^{d} r^2 is the square of the correlation coefficient to the line of best fit [Fig. 4; Eq. (5)] through the set of N data points for liquid–polymer systems with a given v.

now be used to test correlatability with the respective set of swelling power data (C) for the corresponding liquids, which are known[4–15] to reflect meaningfully the molecular structure of the liquid (as stated in the Introduction).

Correlation of X with C for Polystyrene–Liquid Systems

Only the 29 X values reported in Table XIX of Ref. 1 that were measured at $25 \pm 5°C$ were considered for this correlation. Three of these were discarded because of obvious inconsistency with the rest of the data as discussed above. The remaining set of 26 usable data were combined with the 10 X values deduced by interpolation and extrapolation (Fig. 3). The data comprised of the union of the above two sets of data are correlated graphically in Figure 4 with the corresponding relative swelling powers, C, which were determined at 23°C in 3M Laboratories.[4–15] The data established experimentally by others (Table XIX and Fig. 2 of Ref. 1) are represented in Figure 4 by filled symbols, whereas those obtained by interpolation or extrapolation (as noted in Fig. 3) are represented in Figure 4 by the corresponding empty symbols.

These correlations (Fig. 4) show that X at a given v varies with C in accordance with Eq. (5).

$$X = X_0 - AC \tag{5}$$

The square of the correlation coefficients, r^2, for the line of best fit through each set of N data points at a given level of v (Fig. 4) are collected in Table II, along with the corresponding parameters X_0 and A, where X_0 at a given level of v is the corresponding value of X at C equal to zero.

The data collected in Table II show that both X_0 and A increase with v from 0 to 0.8. The respective

correlations of X_0 and A with v (Fig. 5) show linear relationships as expressed by Eqs. (6) and (7).

$$X_0 = 0.49 + 1.01v \tag{6}$$

$$A = 0.012 + 0.59v \tag{7}$$
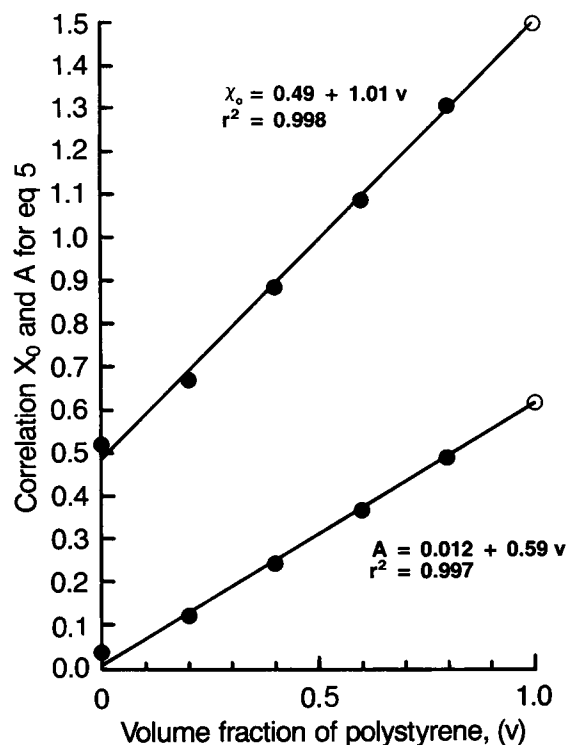
Figure 5 Correlation of parameters X_0 and A, established for polystyrene–liquid systems as a function of C and v [Eq. (5)], with v. The filled circles represent the data established in Fig. 4 for v ranging from 0 to 0.8 in increments of 0.2, and the empty circles represent the corresponding estimated data, established by extrapolation of the line of best fit (through the data represented by filled circles) to $v = 1$.

Table III   Correlation of X_1 for Polystyrene–Liquid Systems with the Corresponding Relative Swelling Power (C) and Adsorption Parameter (α) of the Liquid[a]

A. Monosubstituted Derivatives of Benzene; C_6H_5R				
R	Ref.[b]	C	α	X_1
Cl	10	2.18	2.23	0.170
H	10	2.14	2.50	0.195
Br	10	2.06	2.04	0.243
F	10	1.98	2.19	0.292
I	10	1.88	1.75	0.353
CH_3	10	2.01	1.98	0.268
CCl_3	10	2.00	1.66	0.280
CF_3	10	0.71	0.59	1.07
$N(CH_3)_2$	10	2.25	1.84	0.128
OCH_3	10	2.00	1.92	0.280
$COCH_3$	10	1.88	1.68	0.353
NO_2	10	1.57	1.14	0.542
NH_2	10	1.49	1.70	0.591
CH_2OH	10	0.82	0.83	1.00
CH_2Cl	10	2.39	2.16	0.042
$CH_2O_2CCH_3$	10	1.94	1.26	0.317
$CH_2OCH_2CH_3$	10	1.85	1.34	0.371
$CH_2C_6H_5$	10	2.07	1.29	0.237
H	10	2.14	2.50	0.195
CH_3	10	2.01	1.98	0.280
CH_2CH_3	10	1.84	1.55	0.378
$(CH_2)_3H$	10	1.78	1.33	0.414
$(CH_2)_4H$	10	1.69	1.13	0.469
$(CH_2)_5H$	10	1.53	0.93	0.567
$(CH_2)_6H$	10	1.45	0.80	0.616
$(CH_2)_7H$	10	1.30	0.66	0.707
$(CH_2)_8H$	10	1.07	0.50	0.847
$(CH_2)_9H$	10	0.92	0.40	0.94
$(CH_2)_{10}H$	10	0.70	0.30	1.1
$CH(CH_3)_2$	15	1.65	1.23	0.494
$C(CH_3)_3$	15	1.47	0.99	0.603
$CH(CH_3)CH_2CH_3$	15	1.69	1.13	0.469
$C(CH_3)_2CH_2CH_3$	15	1.48	0.91	0.597
$CH_2CH(CH_3)_2$	15	1.62	1.07	0.512
$CH(CH_2)_5$ (cyclohexyl)	15	1.80	1.11	0.402

B. Disubstituted Derivatives of Benzene				
Liquid Compound	Ref.	C	α	X_1
Tetrahydronaphthalene	10	2.22	1.69	0.146
o-Xylene	10	2.02	1.74	0.268
m-Xylene	10	1.80	1.53	0.402
p-Xylene	10	1.73	1.46	0.445
o-Chlorotoluene	10	1.99	1.77	0.286
m-Chlorotoluene	10	1.91	1.68	0.335
p-Chlorotoluene	10	1.81	1.59	0.396
o-Dichlorobenzene	10	1.95	1.80	0.311
m-Dichlorobenzene	10	2.05	1.87	0.250

Table III   *(Continued)*

C. Mono-halosubstituted-alkanes; ZR					
Z	R	Ref.	C	α	χ_1
I	CH_3	11	2.08	3.47	0.231
I	CH_2CH_3	11	2.03	2.64	0.262
I	$(CH_2)_3H$	11	2.03	2.17	0.262
I	$(CH_2)_4H$	11	1.94	1.78	0.317
I	$(CH_2)_5H$	11	1.82	1.45	0.390
I	$(CH_2)_6H$	11	1.72	1.22	0.451
I	$(CH_2)_7H$	11	1.57	1.00	0.542
I	$(CH_2)_8H$	11	1.36	0.78	0.570
I	$(CH_2)_9H$	11	1.90	0.67	0.829
I	$(CH_2)_{10}H$	11	0.89	0.43	0.96
I	$(CH_2)_{11}H$	11	0.57	0.26	1.2
I	$(CH_2)_{12}H$	11	0.35	0.15	1.3
I	$CH(CH_3)_2$	15	1.85	1.91	0.372
I	$C(CH_3)_3$	15	1.63	1.43	0.506
I	$CH(CH_3)CH_2CH_3$	15	1.85	1.67	0.372
I	$CH_2CH_2CH(CH_3)_2$	15	1.83	1.65	0.384
I	$CH(CH_2)_5$ (cyclohexyl)	15	1.78	1.43	0.414
Br	CH_3	13	1.34	2.72	0.683
Br	CH_2CH_3	13	1.62	2.26	0.512
Br	$(CH_2)_3H$	13	1.79	2.05	0.408
Br	$(CH_2)_4H$	13	1.73	1.68	0.445
Br	$(CH_2)_5H$	13	1.67	1.44	0.481
Br	$(CH_2)_6H$	13	1.64	1.22	0.500
Br	$(CH_2)_7H$	13	1.60	1.06	0.524
Br	$(CH_2)_8H$	13	1.46	0.87	0.609
Br	$(CH_2)_9H$	13	1.31	0.71	0.701
Br	$(CH_2)_{10}H$	13	1.06	0.53	0.853
Br	$(CH_2)_{11}H$	13	0.87	0.41	0.97
Br	$(CH_2)_{12}H$	13	0.64	0.28	1.1
Br	$CH(CH_3)_2$	15	1.65	1.83	0.494
Br	$C(CH_3)_3$	15	1.49	1.34	0.890
Br	$CH(CH_3)CH_2CH_3$	15	1.65	1.57	0.494
Br	$CH(CH_3)CH_2CH_2CH_3$	15	1.58	1.30	0.536
Br	$C(CH_3)_2CH_2CH_3$	15	1.56	1.27	0.548
Br	$CH(CH_2CH_3)CH_2CH_3$	15	1.63	1.37	0.506
Br	$CH_2CH(CH_3)_2$	15	1.57	1.59	0.542
Br	$CH_2CH_2CH(CH_3)_2$	15	1.46	1.26	0.609
Br	$CH(CH_2)_4$ (cyclopentyl)	15	1.97	1.91	0.298
Br	$CH(CH_2)_5$ (cyclohexyl)	15	1.92	1.62	0.329
Br	$CH(CH_2)_6$ (cycloheptyl)	15	1.96	1.49	0.304
Br	$C(CH_3)(CH_2)_5$ (cyclohexyl)	15	1.83	1.37	0.394
Cl	CH_3	12	1.70	3.21	0.463
Cl	CH_2CH_3	12	1.54	2.23	0.551
Cl	$(CH_2)_3H$	12	1.63	1.94	0.506
Cl	$(CH_2)_4H$	12	1.42	1.55	0.634
Cl	$(CH_2)_5H$	12	1.50	1.29	0.585
Cl	$(CH_2)_6H$	12	1.37	1.04	0.664
Cl	$(CH_2)_7H$	12	1.42	0.96	0.634
Cl	$(CH_2)_8H$	12	1.27	0.78	0.725
Cl	$(CH_2)_9H$	12	1.03	0.57	0.872
Cl	$(CH_2)_{10}H$	12	0.85	0.44	0.98

Table III (*Continued*)

C. Mono-halosubstituted-alkanes; ZR

Z	R	Ref.	C	α	χ_1
Cl	$(CH_2)_{11}H$	12	0.60	0.29	1.1
Cl	$(CH_2)_{12}H$	12	0.40	0.18	1.3
Cl	$CH(CH_3)_2$	15	1.26	1.44	0.731
Cl	$C(CH_3)_3$	15	0.98	0.94	0.90
Cl	$CH(CH_3)CH_2CH_3$	15	1.28	1.25	0.719
Cl	$C(CH_3)_2CH_2CH_3$	15	1.00	0.84	0.89
Cl	$C(CH_3)(CH_2CH_3)_2$	15	1.05	0.80	0.86
Cl	$CH_2CH(CH_3)_2$	15	1.35	1.34	0.677
Cl	$CH(CH_2)_4$ (cyclopentyl)	15	1.95	1.95	0.311
Cl	$CH(CH_2)_5$ (cyclohexyl)	15	1.89	1.66	0.347

D. Multihalo-substituted Alkanes

Halocarbon	Ref.	C	α	χ_1
CH_2Cl_2	10	1.99	3.27	0.286
$CHCl_3$	10	2.32	2.99	0.085
CCl_4	10	1.97	2.14	0.298
CH_3CHCl_2	10	1.68	2.10	0.475
$ClCH_2CH_2Cl$	10	1.79	2.39	0.408
$ClCH_2CHCl_2$	10	2.04	2.28	0.256
$Cl_2CHCHCl_2$	10	2.29	2.28	0.103
$Cl(CH_2)_4Cl$	10	1.78	1.70	0.414
$Br(CH_2)_4Br$	10	1.82	1.58	0.390

E. Aliphatic Ketones; RCOR'

R	R'	Ref.	C	α	χ_1
CH_3	CH_3	10	0.65	0.91	1.10
CH_3	CH_2CH_3	10	1.11	1.28	0.823
CH_3	$(CH_2)_3H$	10	1.37	1.35	0.664
CH_3	$(CH_2)_5H$	10	1.47	1.09	0.603
CH_3	$(CH_2)_6H$	10	1.31	0.87	0.701
CH_3CH_2	CH_2CH_3	10	1.52	1.50	0.573
CH_3CH_2	$(CH_2)_7H$	10	1.04	0.57	0.866
$H(CH_2)_3$	$(CH_2)_3H$	10	1.36	1.01	0.670

F. Aliphatic Acetate Esters: CH_3CO_2R

R	Ref.	C	α	χ_1
CH_3	10	0.86	1.13	0.98
CH_2CH_3	10	1.13	1.20	0.810
$(CH_2)_3H$	10	1.33	1.20	0.689
$(CH_2)_4H$	10	1.46	1.16	0.609

Table III (*Continued*)

G. Aliphatic and Alicyclic Ethers

Ether	Ref.	C	α	X_1
$(CH_3CH_2)_2O$	10	0.64	0.64	1.1
$[H(CH_2)_4]_2O$	10	0.51	0.30	1.2
$[H(CH_2)_6]_2O$	10	0.41	0.18	1.3
Tetrahydrofuran	10	2.00	2.57	0.280

H. Aliphatic and Alicyclic Hydrocarbons

Hydrocarbon	Ref.	C	α	X_1
$H(CH_2)_nH$, n is 5 to 10	10	0	0	1.5
Cyclohexane	10	0.53	0.51	1.2
Cyclohexene	10	1.47	1.50	0.60
trans-decalin	10	0.44	0.29	1.2
cis-decalin	10	1.00	0.90	0.89

I. Aliphatic Alcohols

Alcohol	Ref.	C	α	X_1
$H(CH_2)_nOH$, n is 1 to 6	10	0	0	1.5
Cyclohexanol	10	0.47	0.47	1.2

J. Miscellaneous Liquids

Liquid	Ref.	C	α	X_1
CS_2	14	1.95	3.37	0.310
Pyridine	10	1.63	2.11	0.506
$Cl_2C{=}CCl_2$	10	1.96	2.02	0.304

[a] The X_1 values given refer to polystyrene–liquid systems that have a polymer volume fraction (v) equal to 1.0. The X values for the corresponding systems with v less than 1 are given by

$$X_v = 0.49 + v(X_1 - 0.49)$$

[b] References are to the original literature.

The square of the correlation coefficient with respect to the line of best fit through each set of five data points used to establish Eqs. (6) and (7) are 0.998 and 0.997, respectively. Extrapolation of these relationships to $v = 1$ (empty circles in Fig. 5) give values of X_0 and A equal to 1.51 and 0.61, respectively. These data are also included in Table II for the sake of completeness. They are placed in brackets, however, to emphasize that they were obtained by extrapolation not by direct correlation of X with C.

It is obvious that A at $v = 0$ in Figure 5 is too high, and in view of the very poor r^2 observed for Eq. (5) at $v = 0$ (Table II), I considered it justified to do the regression analysis without including this data point. In so doing, the intercept at $v = 0$ for Eq. (7) decreases to 0.005, the regression constant (i.e., the slope) increases to 0.615 and r^2 increases to 0.9996. This is strong evidence that the line should in fact pass through the origin. Indeed such a line having a regression constant equal to 0.610 has $r^2 = 0.9997$, which is indistinguishable from the above.

The resulting equation [Eq. (8)] is preferred, therefore, over Eq. (7).

$$A = 0.610v \qquad (8)$$

Direct substitution of Eqs. (6) and (8) into Eq. (5) gives

$$X = 0.49 + 1.01v - 0.610vC \qquad (9)$$

The value of X at $v = 0$, predicted by Eq. (9), is 0.49, which is well within the range expected on the basis of the calculated average X value at $v = 0$ using the 18 reported values for polystyrene–liquid systems (Table I).

Since C reflects very sensitively[5-15] the molecular structure of the liquid sorbed by poly(Sty-co-DVB), it follows that X for the corresponding polystyrene–liquid system at a given level of v must also reflect in like manner the molecular structure of that liquid as expressed by Eq. (9). This equation (represented in Fig. 4) shows clearly that for polystyrene–liquid systems, X is most sensitive to the molecular structure of the liquid at $v = 1$, and least sensitive at $v = 0$. Accordingly, the more than 100 C values reported[5-13] thus far from this laboratory were used to calculate X_1 for the corresponding polystyrene–liquid system at $v = 1$ by means of Eq. (10), i.e., Eq. (9) when $v = 1$.

$$X_1 = 1.50 - 0.61C \qquad (10)$$

Since almost all of these X values at $v = 1$ have not yet been reported in the literature, they are collected here in Table III for easy reference and subsequent further testing with experimentally determined data, when and if such data become available. The corresponding X_v values, at any other level of $v < 1$, can be calculated by the interested reader using the X_1 values reported in Table III and Eq. (11), which is obtained from Eqs. (9) and (10) by direct substitution.

$$X_v = 0.49 + v(X_1 - 0.49) \qquad (11)$$

As noted in the Introduction, the molecular nature of the adsorption process is seen better on the basis of α [the number of adsorbed molecules per accessible phenyl group of poly(Sty-co-DVB) at liquid saturation] than it is on the basis of C, because C is proportional to the product of α and the respective molar volume of the sorbed liquid [Eq. (2)].

The relationship [Eq. (12)] of X with α is obtained by direct substitution of Eq. (2) into Eq. (9).

$$X = 1.50 - 0.00587(M/d)\alpha \qquad (12)$$

where M and d are the formula weight and density of the sorbed liquid. The α data derived from the corresponding observed C are also recorded in Table III to show how X varies with α within a given classification of liquids based on functionality.

Previous publications from this laboratory (summarized in the Introduction) have reported in detail how α is affected by the molecular structure of the sorbed liquid. The interplay of electronic and steric factors that affect α is discussed in Ref. 10 for the case of aromatic liquids, and in Refs. 11–13 for the homologous series of liquids of the type $Z(CH_2)_nH$, where Z is a phenyl or halogen substituent and n is 0 to 12.

This linear correlation of X with C [Eqs. (9) and (10)], which is related to α by Eq. (2), strengthens the conclusion that α and C are also parameters of fundamental scientific value, and therefore potentially useful not only in the treatment of polymer swelling[5-15] and drying,[16-19] but also in the understanding of other phenomena in which molecular-scale adsorption plays an important role, such as chromatography, membrane permeation, and the theta-temperature of polymer–liquid systems. Such applications will be considered more fully in subsequent publications.

It is hoped that the relationship established by this correlation of X with C, which shows that X for P–L systems is most sensitive to molecular structure of the sorbed liquid at $v = 1$, will stimulate interest in improving the accuracy for measuring X at $v = 1$. At this time, gas-liquid chromatography is the only method for so doing, but its reproducibility appears to suffer from the occurrence of phenomena such as interfacial adsorption. The precision of this method, however, needs to be improved by a factor of at least 10 to permit meaningful correlation with molecular structure.

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