

# Polymer Swelling. XV. Swelling and Deswelling Studies of Polystyrene–Liquid Systems in Binary Solutions

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## SYNOPSIS

The specific sorption capacities of poly(styrene-*co*-divinylbenzene) [i.e., (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples for binary solutions of toluene ( $\alpha = 1.98$ )] and a second solvent [i.e., heptane ( $\alpha = <0.01$ ), methanol ( $\alpha = <0.06$ ), acetone ( $\alpha = 0.92$ ) or chloroform ( $\alpha = 3.00$ )] were correlated with the corresponding DVB mole fraction ( $x$ ) in the sorbent polymer samples ( $0.01 < x < 0.11$ ), with the volume fraction ( $z$ ) of toluene in the sorbed binary liquid (which was cycled at least twice from  $z = 0$  to  $z = 1$  and back to  $z = 0$  in increments of 0.1) and with the adsorption parameter ( $\alpha$ ) of the sorbed liquid. These correlations demonstrated that the sorption capacity during the initial transit from  $z = 0$  to 1 reflects the molecular architecture in the original dry state. Once the samples have been swelled to saturation in toluene ( $z = 1$ ), however, the “memory” of the former dry state is erased; thereafter the sorption capacity reflects only the architecture established in the fully swollen state, and the composition of the sorbed solution. The molecular nature of the solvent exchange processes is discussed in the text. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Earlier publications<sup>1,2</sup> from this laboratory, regarding sorption of liquids by poly(styrene-*co*-divinylbenzene) [hereinafter referred to as either poly(Sty-*co*-DVB) or (Sty)<sub>1-x</sub>(DVB)<sub>x</sub>] showed that the specific volume  $S$  (in mL/g) of sorbed liquid at saturation varies linearly with the cube root of the average number ( $\lambda$ ) of backbone carbon atoms between crosslink junctions in the polymer sample as expressed by:

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

Here the slope  $C$  (in mL of adsorbed liquid per gram of polymer) is defined as the relative swelling power of the sorbed liquid,  $\lambda_0$  is the value of  $\lambda$  [i.e.,  $(1 + x)/x$ ] extrapolated to  $S$  equal zero, and the dif-

ference ( $\lambda^{1/3} - \lambda_0^{1/3}$ ) is a dimensionless number defined as the relative “looseness” ( $\Lambda$ ) of the macrostructural architecture of the (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> sample that supports the gel. The molecular nature of this liquid-saturated gel state, however, is understood better when the units for  $S$  and  $C$  of eq. (1) are expressed in molecules per monomer unit of polymer instead of volume of sorbed liquid per gram of polymer. Therefore eq. (1) is rewritten in the form:

$$\Sigma = \alpha\Lambda \quad (2)$$

Here  $\alpha$  is the number of *adsorbed* molecules per *accessible* phenyl group of the (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> sample at liquid saturation, and  $\Sigma$  is the corresponding total number of sorbed molecules. This is an alternative way of expressing sorption capacity of the polymer sample with respect to the sorbed liquid; the units are molecules per phenyl group in the polymer instead of volume per gram of polymer [eq. (1)]. The value of  $\alpha$  for a given test liquid is calculated from the observed  $C$  [eq. (1)] by means of eq. (3).

$$\alpha = 104Cd/M, \quad (3)$$

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where  $d$  and  $M$  are, respectively, the density and formula weight of the adsorbed molecules, and 104 is the formula weight of a monomeric styrene unit.

The values of  $\alpha$ , observed thus far for hundreds of liquids, range from 0 to 3.5 and are reproducible to within  $\pm 0.01$ . Our ongoing studies of swelling in homologous series of liquids  $ZR$ , where  $Z$  is a substituent (such as phenyl or halogen) that has a strong relative affinity for the phenyl groups in the polymer and  $R$  is the rest of the molecule that is varied systematically, show that  $\alpha$  reflects very sensitively the molecular structure of the sorbed liquid  $ZR$ . By this it is meant that it varies directly with the affinity of  $Z$  for the phenyl groups in the polymer and inversely with the magnitude of steric hindrance imposed by the bulkiness of  $R$  (as expected on the basis of well-established principles in physical organic chemistry<sup>1,2</sup>). It was also shown<sup>3</sup> that the Flory-Huggins adsorption parameter,  $\chi$ , for polystyrene-liquid (PS-L) systems varies with the corresponding  $C$  [eq. (2), and therefore also with  $\alpha$ ; eq. (3)] as expressed by eq. (4).

$$\chi_p = 0.49 + 1.01\nu - 0.61\nu C \quad (4)$$

Here  $\nu$  is the volume fraction of polymer in the PS-L system.

The above observations proved to our satisfaction that  $\alpha$  is a parameter of fundamental scientific significance and therefore useful in the elucidation of phenomena in which sorption plays an important role, such as in adsorption and desorption.<sup>4-9</sup> Our time studies, which monitored evaporation (both gravimetrically<sup>4-6</sup> and spectrometrically<sup>7-9</sup>) from microporous composite film samples comprised of liquid-saturated (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> particles (ca. 80% dry weight) enmeshed in poly(tetrafluoroethylene) [PTFE] microfibers,<sup>10,11</sup> showed that the compositions [in molecules of residual adsorbed molecules per phenyl group in the crosslinked PS-L system] that mark sequentially (a) incipient elimination of adsorbed volatile molecules from the PS-L system in its rubbery state (i.e.,  $\alpha'$ ), (b) incipient transition from the rubbery state to the glassy state (i.e.,  $\alpha'_g$ ), and (c) completion of that transition (i.e.,  $\alpha_g$ ) increase with  $\alpha$  [the value at liquid-saturation eq. (3)], as expressed approximately by eqs. (5) to (7).

$$\alpha' = 0.33\Lambda(\alpha + 1) \quad (5)$$

$$\alpha'_g = 0.10\Lambda(\alpha + 1) \quad (6)$$

$$\alpha_g = 0.055(\alpha + 1) \quad (7)$$

The above relationships were used to elucidate

the molecular nature of thermally induced phase separation in polystyrene-liquid (PS-L) systems.<sup>12-14</sup> Kline and Guenet<sup>13</sup> had reported that the average number ( $\bar{\alpha}$ ) of adsorbed molecules per phenyl group of polymer that had undergone thermally induced polymer-polymer association was characteristic of the liquid in that PS-L system. We showed<sup>12</sup> that the  $\bar{\alpha}$ -values reported for the 18 PS-L systems studied by Kline and Guenet vary linearly with the  $\alpha$ -values reported by us for the corresponding PS-L systems. Since  $\alpha$  is the number of adsorbed molecules per phenyl group of solvated polymer before thermally induced phase separation and  $\bar{\alpha}$  is the average number of adsorbed molecules per phenyl group in the polymer fraction ( $y$ ) that had undergone thermally induced polymer-polymer association via expulsion of adsorbed molecules, it was possible for us to show<sup>12</sup> that  $y$  is given approximately by:

$$y = 1 - (\bar{\alpha}/\alpha) \quad (8)$$

It is known<sup>15-19</sup> that self-association of solvated polymer also occurs when a nonsolvent liquid is added to a polymer solution. Such solvent-induced phase separations are used to produce a large fraction of the commercially available polymeric membranes employed in membrane separation technology. This process involves casting a thin film of homogeneous polymeric solution onto a suitable substrate followed by immersion in a nonsolvent bath. It was shown quantitatively by Burghardt et al.<sup>15</sup> Gaides and McHugh,<sup>16</sup> and Tsaiana and McHugh<sup>17</sup> and qualitatively by Chen and Young<sup>18,19</sup> that the ratio ( $r$ ) of the solvent flux (out of the cast film domain) to the nonsolvent flux (into that domain) determines the macrostructure of the film produced thereby, as a result of the various phase transformations that accompany the solvent exchange processes.

It is reasonable to suppose that  $r$  reflects the relative  $\alpha$ -values for the two liquids chosen for such solvent-exchange operations. It was postulated, therefore, that it may be possible to obtain a better understanding of the molecular nature of the solvent-induced physical changes that occur in such processes by monitoring the  $S$  versus  $\lambda^{1/3}$  relationship [eq. (1)] exhibited by a set of (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples as the volume fraction ( $z$ ) of the "good" solvent in the sorbed liquid is decreased incrementally from  $z = 1$  to  $z = 0$ . The purpose of this publication, therefore, is to report the results obtained in such experiments and also the molecular interpretations thereof.

## EXPERIMENTAL

### Materials

The procedure for making microporous composite films, comprised of  $(\text{Sty})_{1-x}(\text{DVB})_x$  particles (>80% by weight) enmeshed in PTFE microfibrils, and the distribution of these particles in the composite films produced thereby (see Figs. 1, 6, 7, and 20 of Reference 1) are described in considerable detail elsewhere.<sup>1,2,10,11</sup> The sets of two component solutions, in which samples of these microporous sheets were allowed to swell to saturation at  $23 \pm 1^\circ\text{C}$ , were prepared by admixing a measured volume of toluene ( $\alpha = 1.98$ ) with a measured volume of a second liquid, such that the volume fraction ( $z$ ) of toluene in the set of test solutions increased from  $z = 0$  to  $z = 1$  in increments of ca. 0.1, and then decreased in like manner from  $z = 1$  to  $z = 0$ . The second liquids were: heptane ( $\alpha = <0.01$ ), methanol ( $\alpha = <0.06$ ), acetone ( $\alpha = 0.92$ ), and chloroform ( $\alpha = 3.00$ ). These liquids were of reagent grade, obtained from commercial sources, and they were used without further purification.

### Swelling to Saturation

The same set of six composite film samples used in earlier studies of  $(\text{Sty})_{1-x}(\text{DVB})_x$  swelling in one-component liquids was used in these studies of swelling to saturation in two-component solutions. The protocol used to establish the volumes [ $S$ , in mL/gram of  $(\text{Sty})_{1-x}(\text{DVB})_x$ ] of sorbed binary liquid at  $23 \pm 1^\circ\text{C}$  by each of the six composite film samples (i.e.,  $x = 0.01, 0.02, 0.03, 0.04, 0.08,$  and  $0.11$ ), was essentially the same as that described in earlier studies,<sup>1-11</sup> with the single modification in these studies that after the dry film samples were allowed to swell to saturation in the initial test solution with  $z = 0$  and then weighed to establish  $S$  at  $z = 0$ , the samples were immersed directly into the next test solution, the  $z$  of which differed from that of the preceding solution only by an increment of ca. 0.1. Not less than 1 h was allowed for the samples to re-establish swelling equilibrium with the " $n$ th" test solution before the samples were reweighed and then transferred to the " $(n + 1)$ th" test solution. Earlier kinetic studies had indicated that resaturation in the next binary solution was usually attained within 20 min. In most cases the samples were cycled at least twice between  $z = 0$  to 1 and back to 0 to ensure reproducibility of the  $S_z$  data at a given level of  $z$ . Only after completion of the study with a given pair of test liquids were the samples "cleaned" in the usual way,<sup>13,14</sup> i.e., by ex-

traction in acetone, evaporation to dryness at ambient conditions, and then drying for an additional hour in an evacuated oven kept at  $100^\circ\text{C}$ . This was done to "erase" all memory effects owing to exposure to previous solvents. The "cleaned" samples were now ready for the next study using a different pair of test liquids.

The compositions of the two-component solutions at a given level of  $z$ , with which the set of six composite film samples was allowed to equilibrate, were corrected to account for sorbed-liquid carryover from the preceding determination. The density ( $d_n$ ) and the average molecular weight ( $M_n$ ) of the sorbed solution, in each sequential determination, were calculated from the  $d$  and  $M$  values of the pure components, assuming that the corresponding  $d_n$  and  $M_n$  values would be a linear combination of the two liquids that comprised these solutions. The sets of  $S_z$ -values obtained at a given level of  $z$  were plotted as a function of  $\lambda^{1/3}$ . The observed changes in the relationships obtained thereby with change in  $z$  from  $z = 0$  to  $z = 1$  and back to  $z = 0$  were interpreted as discussed in the text.

## RESULTS AND DISCUSSIONS

### Swelling in Toluene-Heptane Solutions

The data recorded in these sorption studies of toluene- $n$ -heptane solutions by  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples are collected in Table I. The specific volumes ( $S_{x,z}$ , in mL/g), sorbed by each sample at liquid saturation, were correlated with the corresponding  $\lambda^{1/3}$  and the volume fraction ( $z$ ) of toluene in the sorbed solution as shown in Figures 1 and 2. The former records the data obtained in the first 12 sequential determinations (Table I), in which  $z$  was *increased* from 0 to 1 in increments of about 0.1, and the latter records the data obtained in subsequent determinations, in which  $z$  was *decreased* in like manner from 1 to 0 (sequences  $n = 12$  to 19; Table I). These correlations show that the relationships exhibited by toluene-heptane solutions with  $z > 0.5$  are quite normal, i.e., they are linear, as expressed by eq. (1), and they intersect the abscissa at a common point ( $\lambda^{1/3} = 1.76 \pm 0.03 = \lambda_0^{1/3}$ ); but those exhibited by the solutions with  $z < 0.5$  are abnormal, i.e., they exhibit deviation from the linearity expressed by eq. (2), beginning at some value of  $\lambda^{1/3} > 2.5$ , which varies with  $z$ .

It is assumed that the deviations from linearity, which appear when  $z$  of the sorbed binary solution is less than 0.5, are attributable to self-association

**Table I Sorption of Toluene–Heptane Solutions by (Sty)<sub>1-x</sub>(DVB)<sub>x</sub>**

<i>n</i>	<i>z</i>	<i>d<sub>z</sub></i>	<i>C<sub>z</sub></i>	<i>α<sub>z</sub></i>
0	0.00	0.684	0.00	0.00
1	0.05	0.690	0.01	0.01
2	0.09	0.702	0.08	0.07
3	0.19	0.719	0.36	0.28
4	0.29	0.737	0.59	0.49
5	0.39	0.755	0.89	0.76
6	0.48	0.772	1.16	1.01
7	0.58	0.780	1.40	1.23
8	0.68	0.808	1.61	1.51
9	0.78	0.827	1.83	1.71
10	0.87	0.843	1.92	1.82
11	0.93	0.854	2.02	1.94
12	0.99	0.865	2.05	2.00
13	0.92	0.852	1.98	1.90
14	0.79	0.828	1.87	1.75
15	0.72	0.816	1.68	1.55
16	0.55	0.785	1.35	1.20
17	0.34	0.746	0.96	0.85
18	0.13	0.708	0.76	0.60
19	0.01	0.686	0.64	0.52
20	1.00	0.867	2.03	1.99
21	0.43	0.763	1.17	1.01
22	0.25	0.730	0.81	0.67
23	0.00	0.684	0.66	0.51
a	0.03	0.689	0.01	0.01
b	0.05	0.776	1.23	1.08

*n* = Sequence number.

*z* = Volume fraction of toluene in the sorbed solution.

*d<sub>z</sub>* = Density of sorbed solution with composition *z*.

*C<sub>z</sub>* = Relative swelling power of sorbed solution with composition *z*.

*α<sub>z</sub>* = Number of adsorbed molecules per accessible phenyl group. This was calculated by means of eq. (3), using the formula weight of toluene for that (*M*) of the adsorbed species.

of monomer units in the polymer segments between covalent crosslink junctions. Since microdomains of such self-associated polymer serve as quasi-crosslinkages, the apparent crosslink density is increased from  $1/\lambda$  to  $1/^*\lambda$  (i.e., the value of  $\lambda^{1/3}$  for that sample is decreased accordingly to  $^*\lambda^{1/3}$ ). Thus, the relative “looseness” [i.e.,  $\Lambda = (\lambda^{1/3} - \lambda_0^{1/3})$ ] of the macrostructure decreases, and this causes a commensurate decrease in  $\Sigma$ . Since  $\Sigma$  is the product of  $\alpha$  and  $\Lambda$  [eq. (2)], the magnitude of  $\Delta\Sigma$  induced by a given change in sorbed liquid composition from *z* to (*z* +  $\Delta z$ ) is given by:

$$\Delta\Sigma = \Lambda(\Delta\alpha) + \alpha(\Delta\Lambda) \quad (9)$$

When both *z* and (*z* +  $\Delta z$ ) were at levels that were greater than 0.5,  $\Delta\Sigma$  was given only by  $\Lambda(\Delta\alpha)$  since

$\Delta\Lambda$  under such conditions is zero; but when the initial and/or the final compositions were below 0.5,  $\Delta\Lambda$  as well as  $\Delta\alpha$  was affected by the change in composition, and consequently both terms in eq. (9) contributed to the observed  $\Delta\Sigma$ .

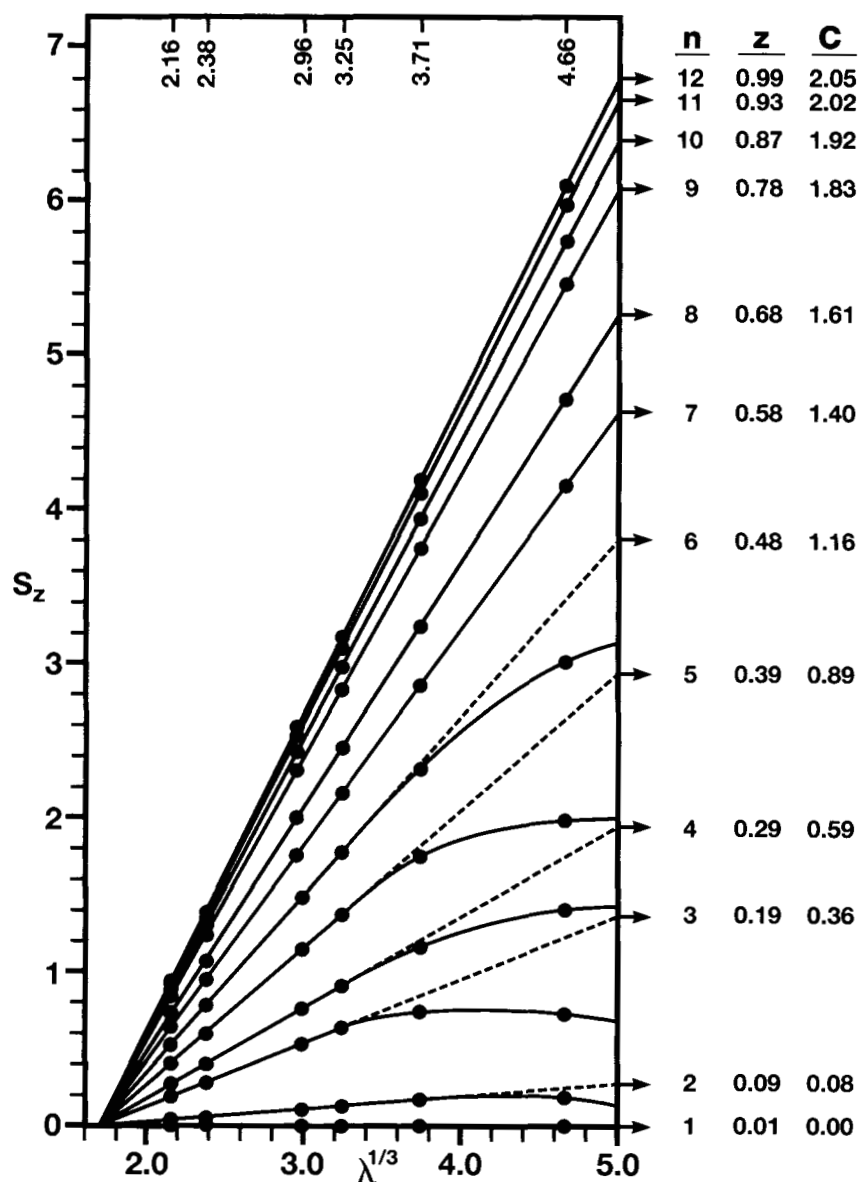
Equation (9) was used earlier<sup>20</sup> to rationalize qualitatively similar sharp alterations in sorption capacity ( $\Delta\Sigma$ ) for a variety of polymer–liquid systems reported by others,<sup>21–23</sup> who induced the observed  $\Delta\Sigma$  for a liquid-saturated gel by a change in temperature, pH, or applied electric field (depending on the system). In those cases, quantitative interpretations were not possible because the  $\alpha$ -values for the sorbed liquids with respect to the sorbent polymers had not been established. In the present cases, however, the  $\alpha$ -values for the sorbed liquids with respect to polystyrene have already been reported by us,<sup>1,2</sup> and consequently it appeared promising that a quantitative molecular interpretation of the observed solvent-induced changes might be possible by appropriate consideration of the data recorded in Figures 1 and 2.

Although the relative solvent power [*C<sub>z</sub>*; eq. (1)] of a sorbed binary liquid having composition *z* > 0.5 is given within  $\pm 0.03$  by the slope of its *S<sub>x,z</sub>* versus  $\lambda^{1/3}$  relationship [eq. (1)], the number ( $\alpha_z$ ) of adsorbed molecules per accessible phenyl group [eq. (3)] does not have the same degree of certainty because the composition of the adsorbed molecules in such systems normally is not the same as that of the sorbed solution. The former reflects not only the composition of the sorbed solution, but also the relative affinities ( $\alpha$ ) of the components of that solution for the phenyl groups of the sorbent polymer. In such cases, the average molecular weight (*M*) of the adsorbed molecules, used in eq. (3) to calculate  $\alpha_z$ , may be a weighted average of the components as expressed by:

$$M^* = z^*M_1 + (1 - z^*)M_2, \quad (10)$$

where  $z^*$  is  $rV_1/(rV_1 + V_2)$ , *r* is a constant that varies with  $\alpha_1/\alpha_2$ , and *V*<sub>1</sub> and *V*<sub>2</sub> are the respective partial volumes of the liquids that comprise the binary solution.

Although the manner in which  $z^*$  varies with *z* is not known with certainty because of the many variables that can affect competitive adsorption from solution, nevertheless, reasonable estimations of *M*<sup>\*</sup> can be made in special circumstances. In those cases that a “good” solvent, such as toluene ( $\alpha = 1.98$ ) is replaced by a “poor” solvent, such as *n*-heptane ( $\alpha = <0.01$ ) or methanol ( $\alpha = <0.06$ ), adsorption partitioning favors the “good” solvent so overwhelm-

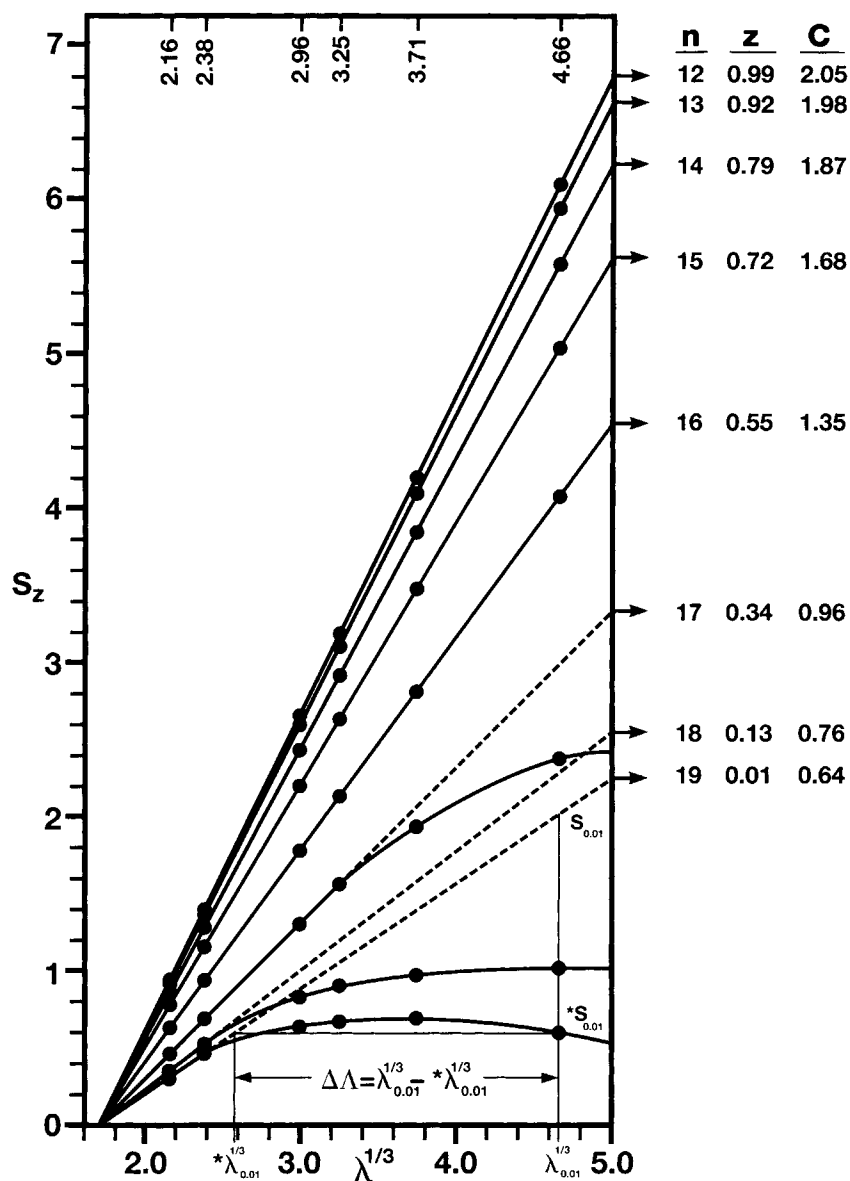


**Figure 1**  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of heptane-toluene solutions: [the toluene volume fractions ( $z$ ) of which were increased from  $z = 0$  to  $z = 1$ ].

ingly that most of the adsorption sites are occupied by molecules of the "good" solvent, even when  $z$  is  $< 0.1$ . That toluene does indeed represent more than 90% of the residual adsorbed molecules, after all of the nonadsorbed molecules had been eliminated by evaporation, was verified<sup>24</sup> by analyses of the liquid-saturated polymer samples that had been extracted in pure *n*-heptane for 2 h and then evaporated until within the transition state compositions, i.e., between  $\alpha'_g$  [eq. (6)] and  $\alpha_g$  [eq. (7)]. This implies that the average molecular weight of the adsorbed species had to be almost that of the "good" solvent, in this case ca. 92 rather than ca. 100. Consequently

this approximate value for  $M$  [eq. (3)] was used in such cases to calculate  $\alpha_z$  at all levels of  $z$  in the sorbed binary solution.

When  $z$  of the sorbed toluene-heptane solution is less than 0.5, determination of  $\alpha_z$  is even more uncertain because deviation from the linearity expressed by eq. (1) is exhibited by one or more of the  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples (Figs. 1 and 2) having the lower values of  $x$  (i.e., higher values of  $\lambda^{1/3}$ ). The magnitude of these deviations appear to increase with decreasing  $x$  of the sorbent sample and with  $z$  of the sorbed binary liquid, presumably in response to the amount of induced polymer self-association.

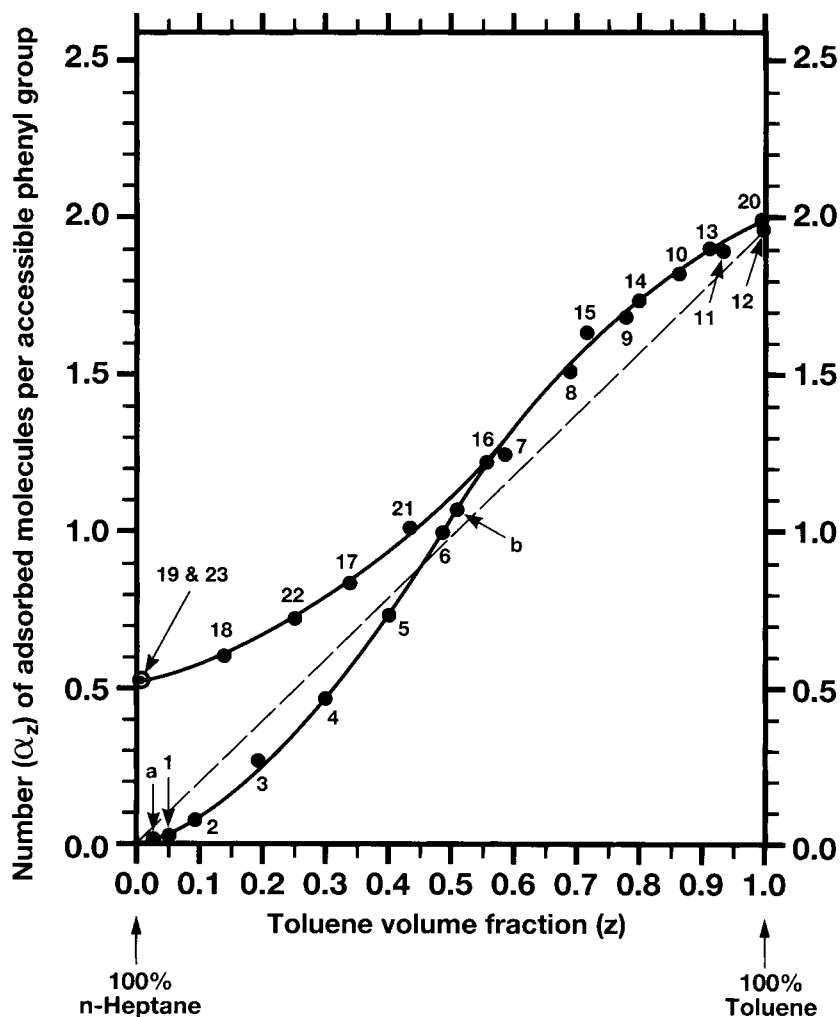


**Figure 2**  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of heptane-toluene solutions: [the toluene volume fractions ( $z$ ) of which were decreased from  $z = 1$  to  $z = 0$ ].

In such cases, the slope for the linear relationship [eq. (1)] that would have been exhibited in the absence of such self-association, which occurred in the  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples having the lower values of  $x$ , is established approximately using only the  $S_{x,z}$ -data points recorded for the samples having the higher values of  $x$ , i.e., the set of points that fall on the dashed "tangent" line drawn through the common point of intersection on the abscissa ( $\lambda^{1/3} = 1.76 \pm 0.03 = \lambda_0^{1/3}$ ) and one or more of the adjacent points, i.e.,  $S_{x,z}$  at  $\lambda^{1/3} = 2.16, 2.38, 2.96$ , and perhaps 3.25 (Figs. 1 and 2). The approximate number ( $\alpha_z$ ) of adsorbed molecules per phenyl group of polymer

that had not yet undergone self-association in sorbed liquid solutions with  $z < 0.5$  is then calculated from the slope of this dashed reference line by means of eq. (1) and the value of  $M^*$ , which was taken to be that of the formula weight of toluene for the reasons stated above.

The manner in which these calculated  $\alpha_z$ -values vary with  $z$  from 0 to 1 and then back to 0 is shown in Figure 3. To make certain of reproducibility of the data recorded after the  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples had been swelled to saturation in toluene, the composition of the sorbed liquid was cycled a second time from  $z = 0$  to 1 and back to 0. The  $\alpha_z$ -values



**Figure 3**  $\alpha_z$  vs.  $z$  plot for sorption of heptane-toluene solutions: [the toluene volume fractions ( $z$ ) of which were cycled from  $z = 0$  to  $z = 1$  and back to  $z = 0$ ].

obtained thereby (sequences  $n = 19$  to  $22$ ) are also recorded in Figure 3, which show that these data points fall nicely on the line defined by the loci of the earlier data (sequences  $n = 12$  to  $19$ ). These point-numbers indicate the numerical sequence in which the  $\alpha_z$ -values were established (Table I).

If one assumes that  $\alpha_z$  [or  $C_z$  from which  $\alpha_z$  was calculated; eq. (3)] reflects only the composition of the sorbed binary liquid, then  $\alpha_z$  should increase linearly with  $z$  from  $\alpha = 0$  (at  $z = 0$ ) to  $\alpha = 1.98$  (at  $z = 1$ ) as indicated in Figure 3 by the dashed straight line that connects these two points. The data recorded therein, however, show clearly that this is not the case. The bottom half of the S-curve, exhibited in the initial ascending mode (sequences  $n = 0$  to  $11$ ) is below the slanted dashed reference line, whereas the top half of this S-curve is above this reference line. The S-curve exhibited in the ensuing

descending mode (sequences  $n = 11$  to  $19$ ), however, is uniformly above the reference line, and it is reproducible in all subsequent transits from 0 to 1 or from 1 to 0 (sequences  $n = 19$  to  $22$ ). These results are consistent with the point of view that the composition of the adsorbed molecules reflect not only the composition of the sorbed liquid but also the relative affinities of the components that comprise that liquid.

In contrast to the results discussed above, the bottom half of the initial S-curve (sequences  $n = 1$  to  $6$ ) is reproducible only when the set of six polymer samples are "cleaned" in acetone, evaporated to dryness in vacuum at  $100^\circ\text{C}$  (i.e., near  $T_g$ ) to restore (statistically) the original macrostructural architecture of the dry polymer, and then reswelled incrementally as indicated in the initial set of heptane-toluene solutions with  $z < 0.6$ . In two additional

experiments, the set of "cleaned" and dried samples were allowed to remain for more than 3 days in binary solutions having  $z = 0.03$  and  $z = 0.5$ . Even under these conditions of prolonged exposure to the sorbed liquid, the  $\alpha_z$ -values obtained thereby fell on the lower half of the initial S-curve as noted by the points marked a and b in Figure 3, which confirms that the observed values are not attributable to an artifact due to diffusion-controlled kinetics, but rather are characteristic of the pseudo-stable equilibrium state, and that they reflect the "memory" of the macrostructural architecture of the polymer in its former dry state, which may not be fully erased until the toluene volume fraction in the sorbed liquid is  $z = 1$ . The  $\alpha_z$ -values collected during subsequent deswelling in toluene/heptane solutions reflect the "memory" of the polymer's macrostructure while saturated in pure toluene ( $z = 1$ ), and this "memory" is retained (or recreated) so long as the system is cycled back and forth between  $z = 0$  and  $z = 1$  for such binary solutions.

We can now consider the concomitant effect on the relative "looseness" ( $\Lambda$ ) of the polymer macrostructure caused by a change in sorbed liquid composition. It was suggested above that the observed difference between the expected specific volume ( $S_{x,z}$ ) of sorbed liquid at composition  $z$ , by a  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample with a given value of  $x$ , and the corresponding observed value ( $*S_{x,z}$ ), i.e.  $\Delta S = (S_{x,z} - *S_{x,z})$ , is attributable to self-association of monomer units in the polymer segments (i.e., between covalent crosslink junctions) and that these quasi-crosslinking microdomains serve to increase the effective crosslink density in that sample, such that  $\Lambda$  decreases accordingly from  $\Lambda_z = (\lambda^{1/3} - \lambda_0^{1/3})$  to  $*\Lambda_z = (*\lambda^{1/3} - \lambda_0^{1/3})$ , where  $*\lambda^{1/3}$  results from the combined contribution of covalent and quasi-crosslinkages. Thus, the change produced thereby, i.e.,  $\Delta\Lambda_z = \Lambda_z - *\Lambda_z$ , is given by the difference  $(\lambda^{1/3} - *\lambda^{1/3})$ . If this is indeed true, then both  $\Delta S$  and  $\Delta\Lambda_z$  should reflect the fraction ( $y$ ) of monomer units that underwent self-association via expulsion of the adsorbed molecules at sorbed-liquid composition  $z$ .

Earlier studies<sup>12</sup> had shown that the magnitude of  $y$  induced in a given polystyrene-liquid (PS-L) system can be established by comparing the number ( $\alpha_z$ ) of adsorbed molecules per phenyl group of completely solvated polymer, i.e., before self-association had occurred, with the corresponding average number ( $\alpha^*$ ) after a significant fraction of that solvated polymer underwent self-association. In such cases,  $\alpha^*$  is the averaged value for the polymer at two levels of solvation as expressed by:

$$\alpha^* = (1 - y)\alpha_z + y\alpha_a \quad (11)$$

Here  $\alpha_z$  is the number of adsorbed molecules per phenyl group in the polymer fraction  $(1 - y)$  that has not yet undergone self-association, and  $\alpha_a$  is the corresponding value in the polymer fraction that has undergone self-association.

This situation is analogous to that reported by Kline and Guenet<sup>13</sup> for his  $\bar{\alpha}$  values, which were determined for the composition of the polymer-rich phase obtained via thermally induced phase separation, as noted in the Introduction. In that case, it was shown<sup>12</sup> that  $\bar{\alpha}$  is given approximately by eq. (8), because  $\alpha_a$  was  $\ll \alpha$ . In this case,  $\alpha_z$  is presumed to be  $> 100\alpha_a$  when  $1 - y$  is  $> 0.1$ . Hence eq. (11) is given approximately by:

$$\alpha^* = (1 - y)\alpha_z \quad (12)$$

and consequently  $y$  for that system is given approximately by:

$$y = 1 - (\alpha^*/\alpha_z), \quad (13)$$

which is the equivalent of eq. (8). Substitution of  $C$  [eqs. (1) and (3)] for the corresponding  $\alpha$  and  $\alpha^*$  in eq. (13), followed by substitution of  $S$  [eq. (1)] for  $C$  gives:

$$\begin{aligned} y &= 1 - (*C_{x,z}/C_z) = 1 - (*S_{x,z}/S_{x,z}) \\ &= (S_{x,z} - *S_{x,z})/S_{x,z} \quad (13a) \end{aligned}$$

where  $C_z$  [i.e.,  $S_{x,z}/\Lambda_x$ ; eq. (1)] is the relative swelling power of the sorbed binary liquid with composition  $z$ , and  $*C_{x,z}$  (i.e.,  $*S_{x,z}/\Lambda_x$ ) is the apparent relative swelling power that reflects the decrease in  $\Lambda_x$  for that  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample owing to the induced self-association, when the composition of the sorbed binary liquid is  $z < 0.5$ .

In such cases, it can be shown geometrically that eq. (13a) is equivalent to eq. (13b) because the relevant data points for each set of PS-L systems, having the same sorbed liquid with composition  $z$ , fall at the corners of two nested right triangles, as illustrated in Figure 2 for the case in which the composition of sorbed liquid is  $z = 0.01$ . The hypotenuse common to both triangles is indicated by the dashed line that passes through the points  $0:1.76$ ,  $*S_{0.01}:*\lambda_{0.01}^{1/3}$  and  $S_{0.01}:\lambda_{0.01}^{1/3}$ ; the side adjacent to both the right angle and the common included angle is indicated by the solid vertical line that passes through the points  $S:\lambda_{0.01}^{1/3}$ ,  $*S:\lambda_{0.01}^{1/3}$ , and  $0:\lambda_{0.01}^{1/3}$ ; the two sides opposite to the common included angle



are the solid lines that connect the points  $*S:\lambda_{0.01}^{1/3}$  and  $*S:\lambda_{0.01}^{1/3}$ , and the points  $0:1.76$  and  $0:\lambda_{0.01}^{1/3}$ .

In such similar right triangles, the ratio of the adjacent sides of the common included angle is equal to the corresponding ratio of the two opposite sides, i.e.:

$$y = (S_{x,z} - *S_{x,z}) / ((S_{x,z} - 0) \\ = (\lambda_x^{1/3} - *\lambda_{x,z}^{1/3}) / (\lambda_x^{1/3} - 1.76) \quad (13b)$$

This means that the values of both  $y$  and the corresponding  $\Delta\Lambda_z = (\lambda_x^{1/3} - *\lambda_{x,z}^{1/3})$  can be established for a given  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample simply by measuring  $S_{x,z}$  and the corresponding difference  $(S_{x,z} - *S_{x,z})$ .

These values of  $y$ , calculated as described above, are correlated in Figure 4 with the volume fraction ( $z$ ) of toluene in the sorbed-liquid, and with the DVB mole fraction ( $x$ ) in the sorbent  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample. These correlations show that both the sorbed liquid composition ( $z_0$ , i.e.,  $z$  at  $y = 0$ ) where polymer self-association first becomes measurable

in a liquid-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample and the ultimate extent of this self-association ( $y_0$ ), attained at  $z = 0$ , vary inversely with  $x$  of the sorbent sample. The correlations of the observed  $y_0$  and  $z_0$  values with  $x$  of the corresponding  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample (inset Fig. 4) imply that addition of  $n$ -heptane to a solution of polystyrene ( $x = 0$ ) in toluene will cause incipient self-association to occur when the toluene volume fraction is decreased from  $z = 1$  to  $z = 0.53$  (at which point  $\alpha_z$  is 1.16; Fig. 3), and that the process of this self-association will be virtually 100% complete (inset Fig. 4) when  $z$  is decreased to zero (at which point  $\alpha_z$  is 0.52; Fig. 3).

Thus, the change ( $\Delta\Sigma$ ) in the total number of sorbed molecules in a binary liquid-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample, caused by a change in composition in that liquid from  $z$  to  $(z + \Delta z)$ , can be established quantitatively by means of eq. (9) using the appropriate data recorded in Figures 3 and 4. Further molecular interpretation of such changes is deferred until the discussion of the results observed in similar studies (Sections B, C, and D, respectively) using methanol, acetone, and chloroform as the second liquids.

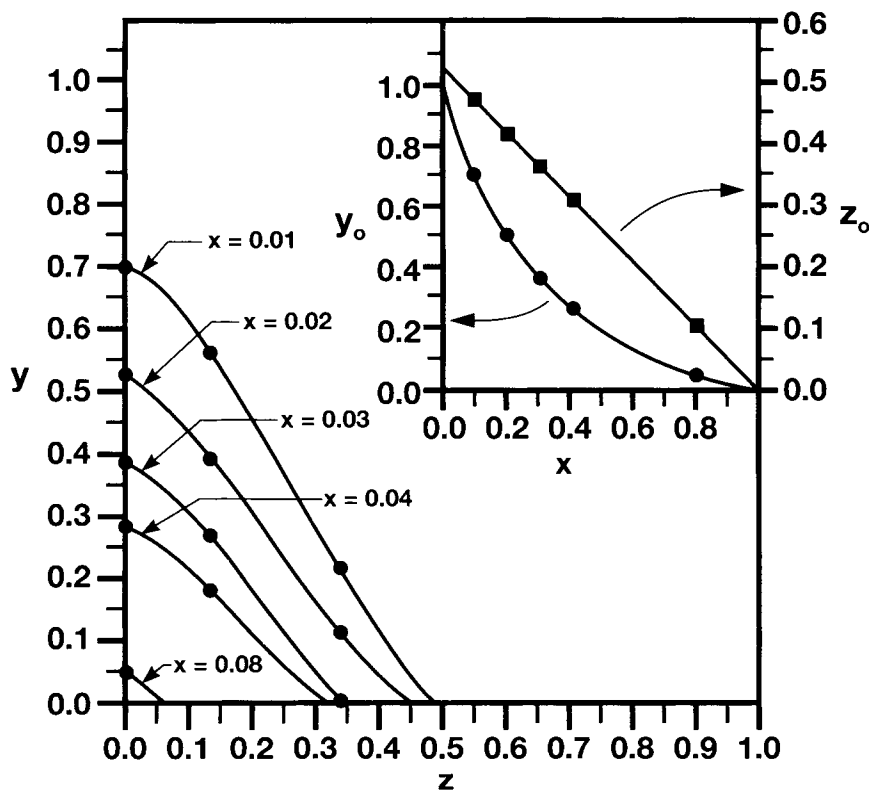


Figure 4 Correlations of  $y$  with  $z$ ; and  $y_0$  and  $z_0$  with  $x$  for sorption of heptane-toluene solution by  $(\text{Sty})_{1-x}(\text{DVB})_x$ .

### Swelling in Toluene–Methanol Solutions

The data recorded in these studies of sorption of toluene–methanol solutions by  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples are collected in Table II. The  $S$ -values are correlated in Figures 5 and 6 with the corresponding  $\lambda^{1/3}$ ; the former shows the relationships established in the ascending mode (sequences 1 to 10; Table II) and the latter shows those established in the descending mode (sequences 11 to 17; Table II). These relationships are qualitatively similar to those (Figs. 1 and 2) noted in the study of toluene– $n$ -heptane sorption using the same set of  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples. Accordingly, the data recorded in Figures 5 and 6 were processed in the same manner as that described above for processing of the data recorded in Figures 1' and 2.

Again the composition of the residual sorbed molecules, after removal of all the non-adsorbed molecules following repeated extractions in methanol over a period of two hours, was found to be > 90% toluene;<sup>24</sup> hence, for the purpose of calculating  $\alpha_z$  by means of eq. (3), the formula weight of toluene was used as the average molecular weight

**Table II Sorption of Toluene–Methanol Solutions by  $(\text{Sty})_{1-x}(\text{DVB})_x$**

$n$	$z$	$d_z$	$C_z$	$\alpha_z$
0	0.00	0.791	0.04	0.03
1	0.05	0.795	0.08	0.07
2	0.10	0.799	0.12	0.11
3	0.19	0.805	0.15	0.14
4	0.29	0.813	0.38	0.34
5	0.48	0.827	0.83	0.77
6	0.67	0.842	1.34	1.27
7	0.78	0.854	1.56	1.50
8	0.88	0.858	1.85	1.80
9	0.94	0.862	1.98	1.93
10	0.99	0.866	2.03	2.00
11	0.85	0.856	1.82	1.76
12	0.59	0.835	1.51	1.42
13	0.26	0.811	1.07	0.91
14	0.18	0.805	0.70	0.65
15	0.47	0.827	1.39	1.30
16	0.25	0.810	1.07	0.98
17	0.00	0.791	0.43	0.39
a	1.00	0.867	2.03	1.99
b	0.75	0.848	1.70	1.63
c	0.35	0.818	1.20	1.11
d	0.10	0.799	0.62	0.56
e	0.00	0.791	0.40	0.36

The symbols  $n$ ,  $z$ ,  $d_z$ ,  $C_z$ , and  $\alpha_z$  are as defined in the footnotes of Table I.

of the adsorbed molecules. The  $\alpha_z$ -values obtained thereby (Table II) are correlated in Figure 7 with the corresponding  $z$  for the sorbed binary liquid. The data points are numbered in the sequence (Table II) in which the set of six  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples were allowed to swell to saturation in the indicated binary solution. The dashed reference line that joins the point  $\alpha_z = 0.06$  at  $z = 0$  to the point  $\alpha_z = 1.98$  at  $z = 1$  (Fig. 7) represents the case for which the composition of the sorbed binary solution is the only factor that affects  $\alpha_z$ . The results show that most of the data collected during the initial transit (i.e., from  $z = 0$  to about 0.88) fall below this reference line, but those collected thereafter fall uniformly above this line.

Again the data recorded in sequences  $n = 1$  to 7 (Fig. 7) are reproducible only when the liquid-swollen  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples are "cleaned" by extraction in acetone followed by evaporation to dryness at 100°C before reswelling in the methanol–toluene solutions as described above. By way of contrast, the pattern defined by the data recorded after the samples had been swelled to saturation in toluene (sequences  $n = 10$  to 17; Table II) was reproducible in all subsequent transits, as verified by the data recorded in sequences  $n = 14$  to 17 and by the data recorded in a second study in which the "cleaned" and dried samples were allowed to swell to saturation first in toluene and then deswelled by incremental addition of methanol (sequences  $n = a$  to  $e$ ; Fig. 7). This indicates that the "memory" of the macrostructure of the toluene-saturated polymer is reflected in the observed  $\alpha_z$ , even when  $z$  is decreased to 0, and that it is retained thereafter so long as the polymer–liquid system is cycled back and forth between  $z = 0$  to  $z = 1$ .

The fraction ( $y$ ) of available solvated monomer units in each of the  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples that had undergone self-association in binary solutions having  $z < 0.8$  was calculated by means of eq. (13b) using the appropriate values for the difference ( $S_{x,z} = *S_{x,z}$ ) as described above. These values of  $y$  are recorded in Figure 8, where they are correlated with the corresponding  $z$  of the sorbed binary solution. These data confirm that both the composition ( $z_0$ ) at incipient polymer self-association, and the ultimate extent ( $y_0$ ) to which this occurs at  $z = 0$ , increase with decreasing  $x$  of the  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample. Extrapolation of these results to  $x = 0$  (inset Fig. 8), shows that a solution of polystyrene in toluene will begin to undergo self-association when the amount of methanol added thereto is enough to decrease  $z$  from 1.0 to ca. 0.9, at which point  $\alpha_z$  is ca. 1.9 (Fig. 7), and that the extent of this self-asso-

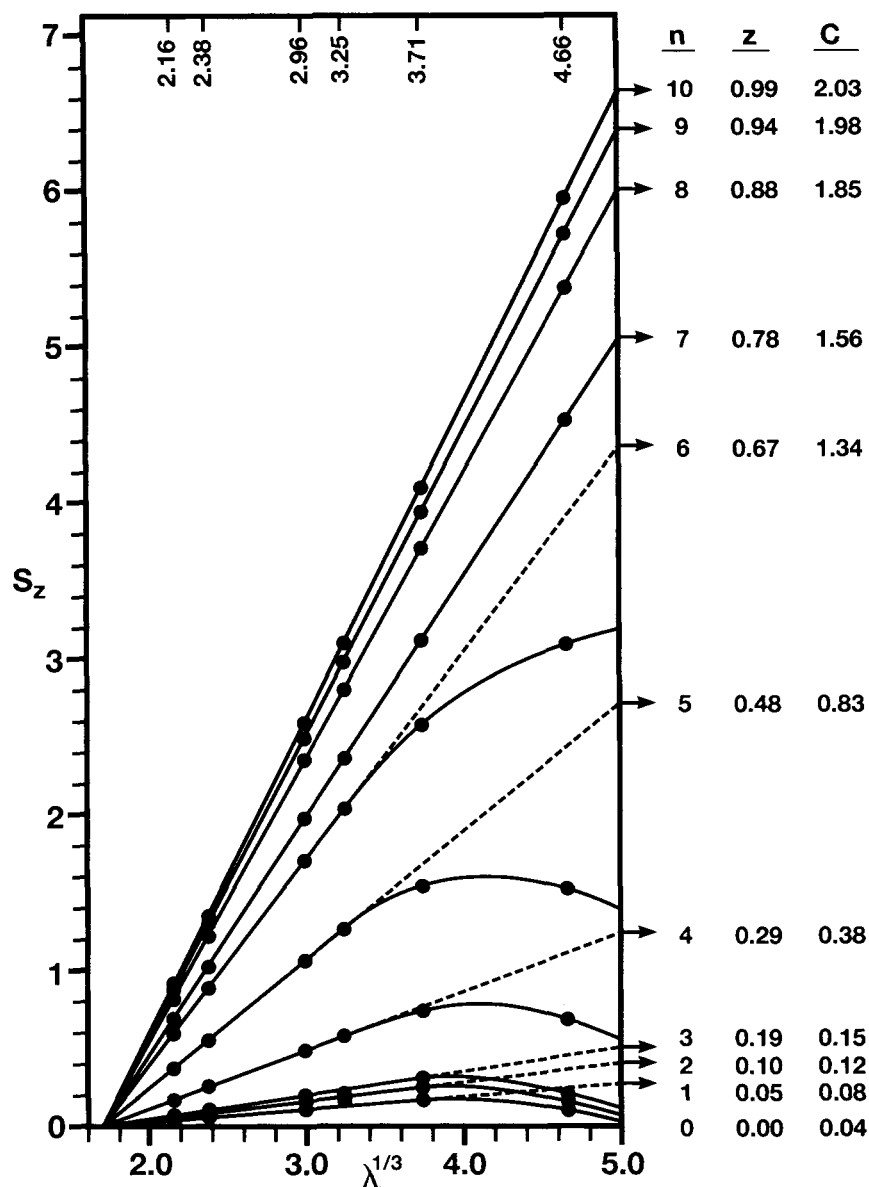


Figure 5  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of methanol-toluene solutions: [the toluene volume fractions ( $z$ ) of which were increased from  $z = 0$  to  $z = 1$ ].

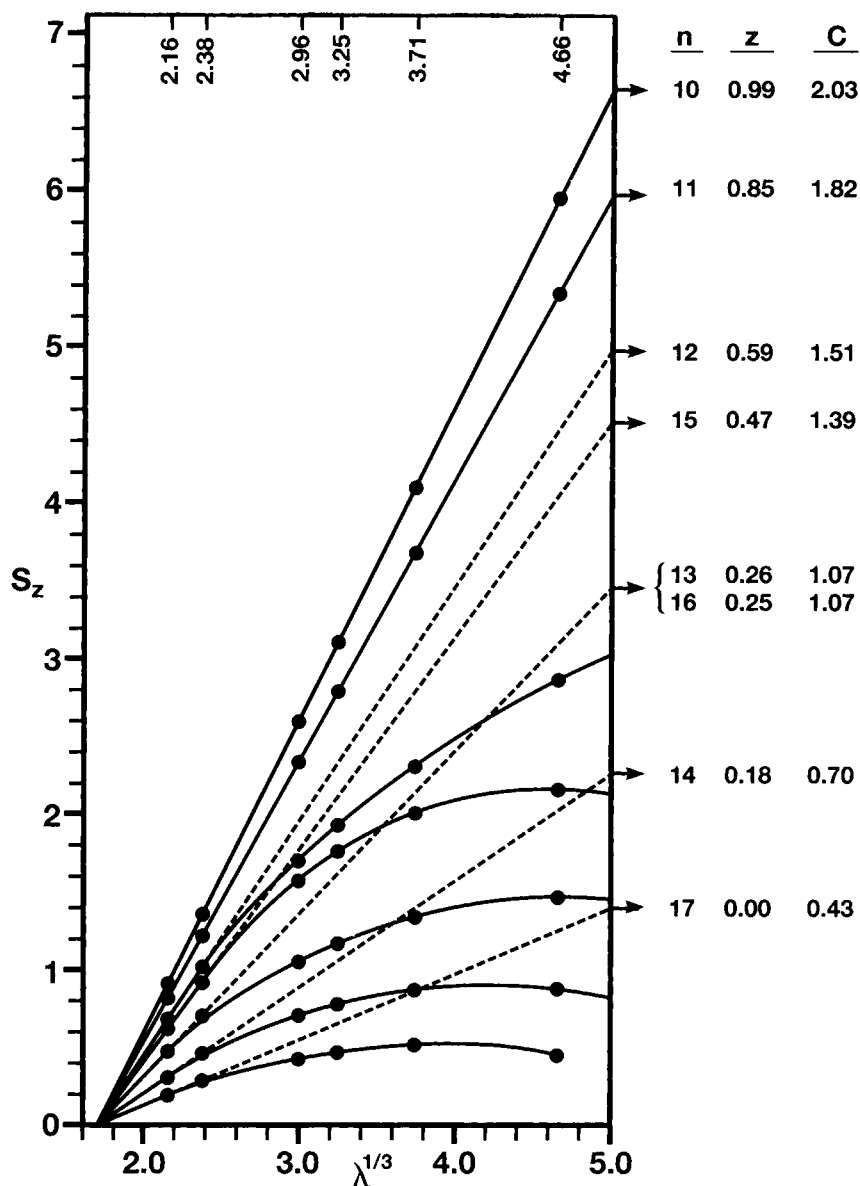
ciation ( $y$ ) at  $z = 0$  is estimated to be ca. 0.8 (inset Fig. 8), at which point  $\alpha_z$  is ca. 0.35 (Fig. 7).

Comparison of these results with the corresponding data established using toluene-heptane solutions (inset Fig. 4) shows that  $z_0$  at a given  $x$  is uniformly greater in the case of toluene-methanol sorption, but that  $y_0$  at a given  $x$  is uniformly greater in the case of toluene-heptane sorption. It appears, therefore, that the results observed in such swelling and deswelling studies will be similar only in a qualitative sense; the exact pattern may be characteristic of the components that comprise the sorbed binary liquid, which will reflect the corresponding set of equilibria

that relate polymer-polymer, solvent-solvent, and solvent-polymer associations in polymer-liquid systems.

### Swelling in Acetone-Toluene Solutions

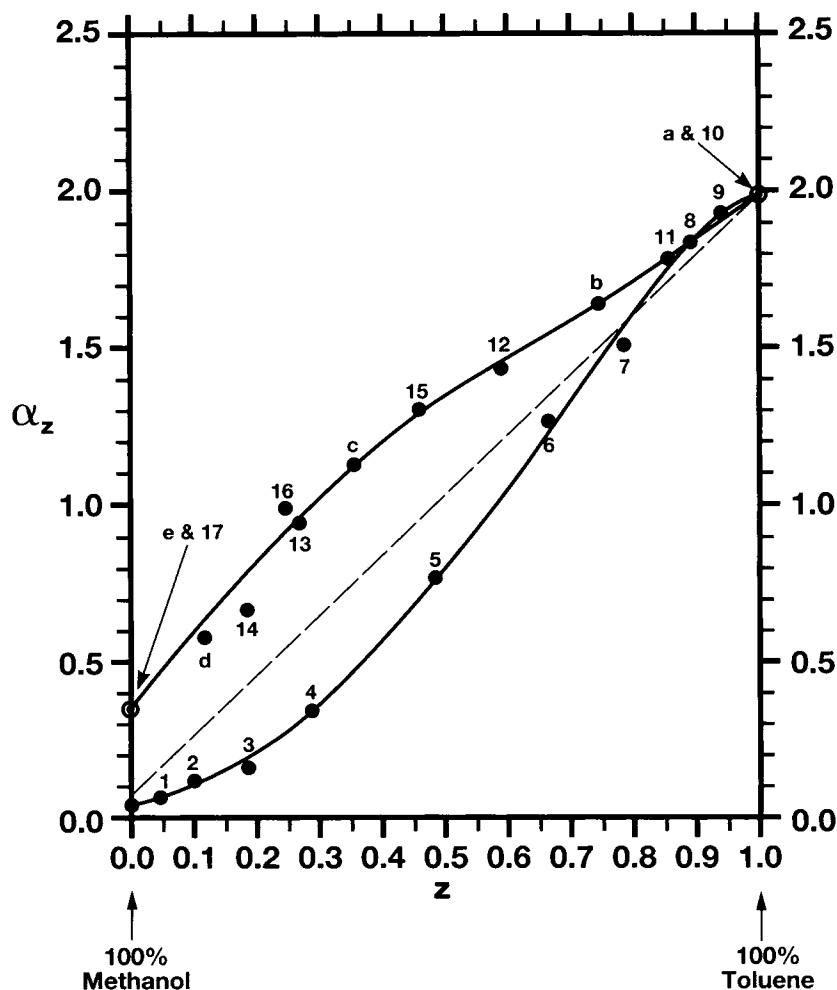
The above studies are examples of deswelling in a second liquid that has a relatively low affinity for polystyrene (the  $\alpha$ -values for heptane and for methanol are, respectively,  $< 0.01$  and  $< 0.06$ ). The present study using acetone as the second liquid is an example of deswelling in a second liquid that has considerably stronger affinity for polystyrene ( $\alpha$



**Figure 6**  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of methanol-toluene solutions: [the toluene volume fractions ( $z$ ) of which were decreased from  $z = 1$  to  $z = 0$ ].

= ca. 0.9) than either heptane or methanol. This study is of particular interest to us because acetone has been used (and continues to be used) as the liquid of choice for "cleaning" the set of  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples before reswelling in the next test liquid. In the course of our ongoing studies of polymer swelling such "cleaning" and reswelling cycles have been repeated more than a thousand times on the same set of composite film samples, and it has been curious to note that the  $\alpha$ -values for acetone, determined gravimetrically immediately after presumably complete elimination of the pre-

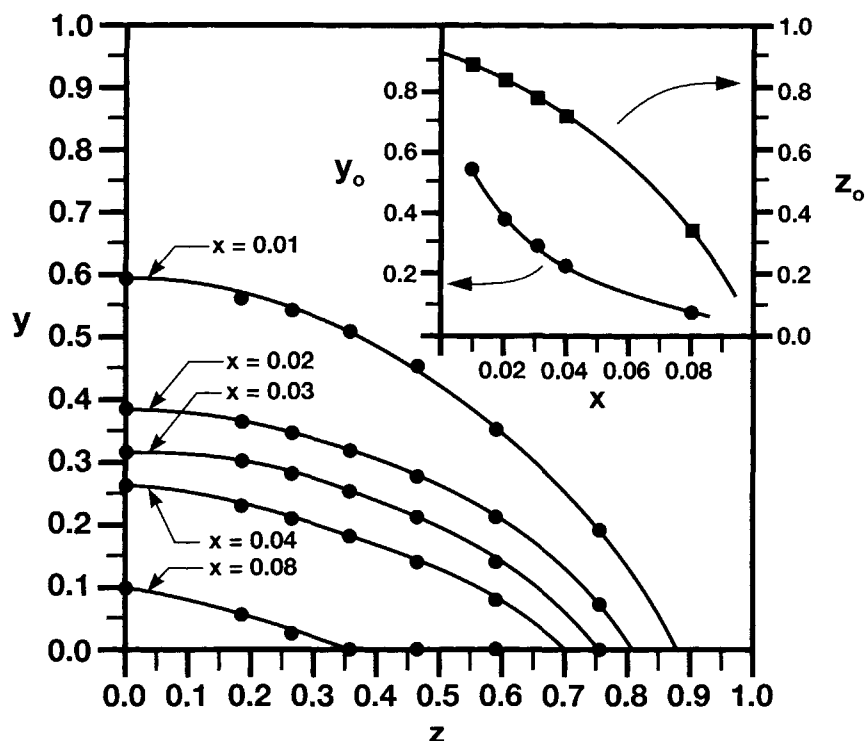
ceding test liquid (by exhaustive extraction in acetone) varied from 0.78 to 1.05, depending on the  $\alpha$  of the test liquid eliminated by the extraction procedure. The higher values were usually recorded after swelling in liquids with  $\alpha > 1.8$ , and the lower values were usually recorded after swelling in liquids with  $\alpha < 0.7$ . The value of  $\alpha = 0.92$  reported for acetone in earlier publications<sup>1-10</sup> represents the average of these values. One of the objectives of this particular study, therefore, was to learn why the  $\alpha$ -value determined for acetone in this way is so dependent on the "memory" of "solvent-past."



**Figure 7**  $\alpha_z$  vs.  $z$  plot for sorption of methanol-toluene solutions: [the toluene volume fractions ( $z$ ) of which were cycled from  $z = 0$  to  $z = 1$  and back to  $z = 0$ ].

All of the  $S$  vs  $\lambda^{1/3}$  plots for swelling  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples in acetone-toluene solutions with  $z > 0.2$  (Figs. 9 and 10) were normal, i.e., they were linear as expressed by eq. (1), and they intercepted the abscissa at  $\lambda_0^{1/3} = 1.76 \pm 0.03$ . Even the corresponding plots for swelling in such binary liquids with  $z < 0.2$  were normal straight line relationships except for the sorption capacity ( $S$ ) values noted for the polymer sample with  $x = 0.01$ , which were always slightly less than that predicted by the best straight line drawn through the common point of intersection on the abscissa and the data points for the other five samples with  $x > 0.01$  (Figs. 9 and 10). The magnitudes of these deviations from linearity appear to increase inversely with  $z$  as noted in Figures 9 and 10. The relative swelling powers [ $C$ ; eq. (1)] noted for each of the sorbed binary liquids are recorded in Table III in the sequence that they were determined.

In these studies the composition of the adsorbed molecules after elimination of the nonadsorbed molecules was  $> 99\%$  acetone, indicating the elimination of the adsorbed toluene molecules was virtually complete during the two hour interval allowed to attain equilibrium swelling at  $z = 0$ . Thus, unlike the two previous studies, the average molecular weight ( $M^*$ ) of the adsorbed species in this case varies appreciably with the composition ( $z$ ) of the sorbed binary solution as expressed in eq. (10). In such cases, it is not possible to determine  $\alpha_z$  directly because the weighted ratio ( $r$ ) in the expression  $z^* = rV_1/(rV_1 + V_2)$ , has not yet been established experimentally. The qualitative way that  $\alpha_z$  varies with  $z$  can be established to a first approximation, however, if one assumes that the value of  $r$  is alternatively 1 or  $\alpha_1/\alpha_2$ , which represent, respectively, the upper and lower limits for the values of  $r$ . Since the magnitude of error introduced at either alter-



**Figure 8** Correlations of  $y$  with  $z$ ; and  $y_0$  and  $z_0$  with  $x$  for sorption of methanol-toluene solution by  $(\text{Sty})_{1-x}(\text{DVB})_x$ .

native value for  $r$  will cause about the same absolute deviation from the "true" values of  $\alpha_z$ , which should be maximal in the range  $0.4 < z < 0.6$ , we chose to use  $r = 1$  to illustrate the qualitative manner that  $\alpha_z$  varies with  $z$ .

These calculated values are correlated in Figure 11 with the corresponding  $z$  of the sorbed acetone-toluene solution. This correlation shows that the  $\alpha_z$ -values exhibited in the initial ascending mode (sequences  $n = 1$  to 8) fall along a curved line that is uniformly above the reference line (i.e., the dashed straight line drawn from  $\alpha_z = 0.8$  at  $z = 0$  to 1.98 at  $z = 1$ ), and those exhibited in the descending mode (sequences  $n = 9$  to 12) fall along a similar curved line, but displaced significantly above the line established for the initial ascending mode. Again the curve exhibited after exposure to pure toluene ( $z = 1$ ) is quite reproducible as indicated by the data collected in sequences  $n = 16$  to 21, which fall nicely on the line established by the  $\alpha_z$ -values recorded for sequences  $n = 8$  to 15 (Fig. 11) as the system was cycled a second time from  $z = 0$  to  $z = 1$  and back to  $z = 0$ . The values recorded in Figure 11 for the solutions for which  $z$  is  $> 0.3$  but  $< 0.7$  may be a little higher than the "true" value because the effect of adsorption partitioning, which favors toluene, was ignored. The error produced by this simplification

is similar to that which would have been observed (but in the opposite sense) if one assumed that  $r$  in eq. (10) was equal to  $\alpha_1/\alpha_2$  instead of 1. In either case, however, the shape of the curve obtained thereby (Fig. 11) is qualitatively correct. It can be amended to make it quantitatively correct at a later date, when the composition of the adsorbed liquid is determined as a function of the composition of the sorbed binary solution. It is believed, however, that these amended results will not change markedly the shape of the curve in the region of relative uncertainty, i.e., between  $z = 0.3$  and  $z = 0.7$ .

The cause of the difference in the  $\alpha_z$ -values (Fig. 11) observed in this study of swelling  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples in acetone, before and after swelling to saturation in pure toluene, is believed to be responsible also for the range in  $\alpha$ -values observed earlier in which the set of six  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples were cleaned by extraction in acetone following swelling to saturation in a test liquid, namely the "memory" of swelling in a "better" solvent.

It was also noted that the  $\alpha$ -values for reswelling in acetone after evaporation of the set of six  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples to apparent dryness depended upon the degree of dryness attained before reswelling in acetone. Thus, if the  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples were dried only to about  $\alpha'$  [eq. (5)] before

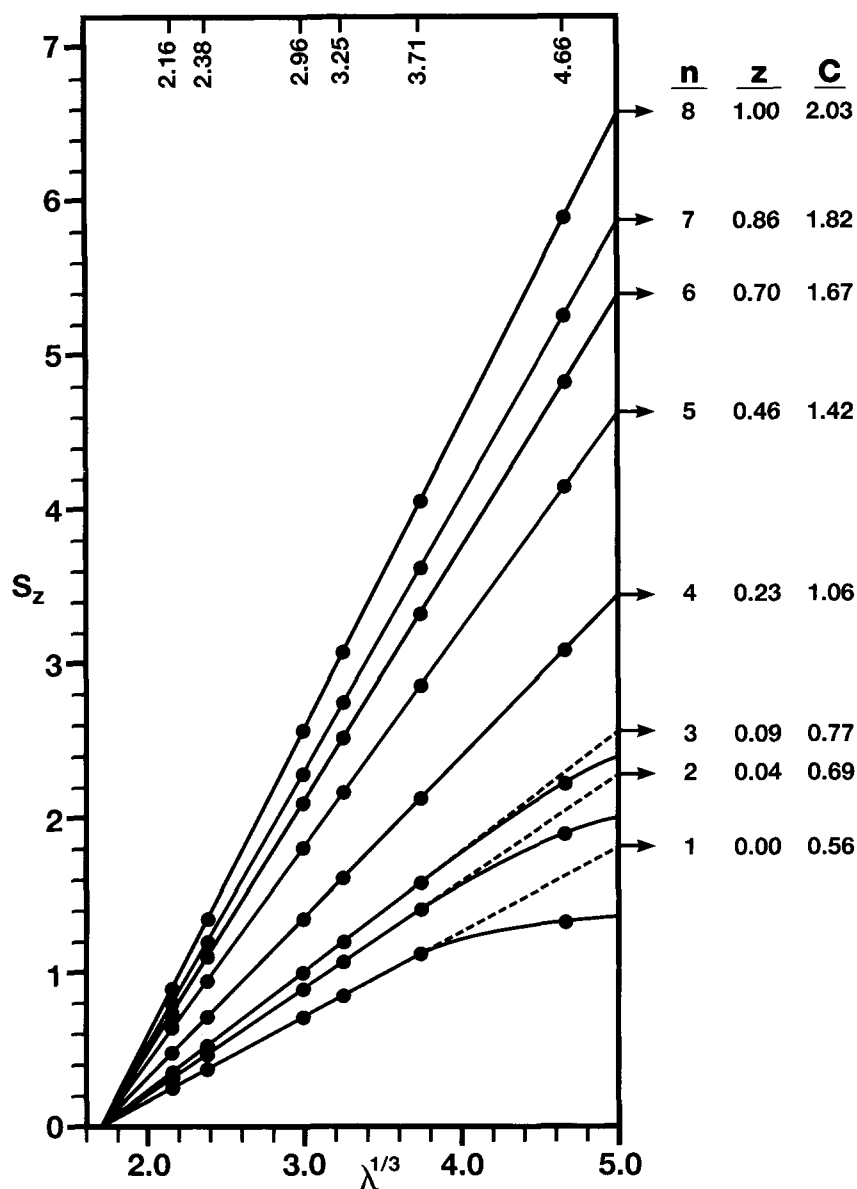


Figure 9  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of acetone-toluene solutions: [the toluene volume fractions ( $z$ ) of which were increased from  $z = 0$  to  $z = 1$ ].

reswelling to saturation in acetone, the  $\alpha$ -value obtained thereby was not decreased significantly ( $\alpha = \text{ca. } 0.95$ ); but if the set of six samples were dried to about  $\alpha_g$  [eq. (7)], the  $\alpha$ -value for acetone observed thereafter was significantly closer to the lower value (i.e., ca. 0.85), and if the samples were evaporated to virtual dryness (i.e., to much below  $\alpha_g$ ) before reswelling in acetone, the  $\alpha$ -value obtained thereby was ca. 0.80. It was inferred from these results that evaporation to virtual dryness serves to "harden" the microdomains of self-associated polymer produced during the time that the poly(styrene)-liquid system is still mobile. Before "hard-

ening," these microdomains are easily resoluted, i.e., the self-association is still "soft," and the system is reversible along the upper path of the  $\alpha_z$  versus  $z$  relationship between  $z = 0$  to  $z = 1$  as shown in Figures 3, 7, and 11. After "hardening" the system follows the lower curve until it crosses the reference line as discussed above.

#### Swelling in Chloroform-Toluene Solutions

In the three preceding studies, the  $\alpha$ -value for the second component was considerably less than that for toluene. In this study, however, the  $\alpha$ -value of

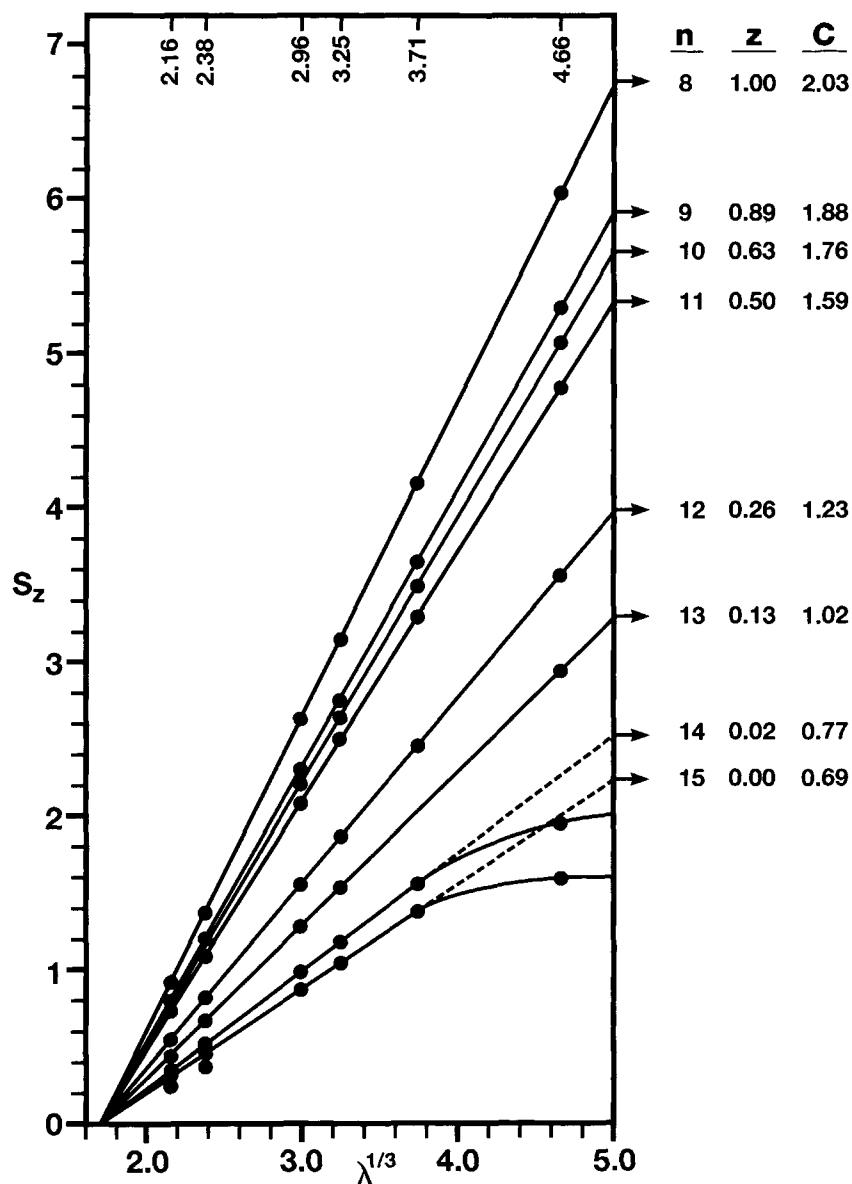


Figure 10  $S_z$  vs.  $\lambda^{1/3}$  plot for sorption of acetone-toluene solutions: [the toluene volume fractions ( $z$ ) of which were decreased from  $z = 1$  to  $z = 0$ ].

the second component is greater than that of toluene. The set of six "cleaned" and dried  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples were swelled to liquid saturation first in chloroform (sequence  $n = 1$ ), then to saturation in toluene-chloroform solutions, the toluene volume fraction ( $z$ ) of which was increased incrementally from  $z = 0$  to 1 (sequences  $n = 1$  to 12; Table IV), and then decreased incrementally from  $z = 1$  to 0 (sequences  $n = 12$  to 22; Table IV), and then re-increased incrementally from  $z = 0$  to 1 (sequences  $n = 22$  to 28; Table IV) to ensure reproducibility of the results observed in sequences  $n = 12$  to 22 (Table IV).

The set of liquid-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples were then "cleaned" by solvent exchange in acetone, followed by evaporation to virtual dryness in a vacuum oven kept at  $100^\circ\text{C}$ . Thereafter these samples were allowed to swell to saturation first in toluene, followed by swelling in toluene-chloroform solutions, the  $z$  of which was decreased incrementally from 1 to 0 (sequences  $a$  to  $i$ ; Table IV), and then increased from 0 to 1 (sequences  $i$  and  $j$ ; Table IV).

All of the  $S$  versus  $\lambda^{1/3}$  plots for the data collected at liquid saturation in the above binary solutions were normal, showing no evidence whatsoever of



**Table III Sorption of Toluene–Acetone Solutions by (Sty)<sub>1-x</sub>(DVB)<sub>x</sub>**

<i>n</i>	<i>z</i>	<i>d<sub>z</sub></i>	<i>M<sub>z</sub></i>	<i>C<sub>z</sub></i>	<i>α<sub>z</sub></i>
1	0.00	0.790	58.1	0.56	0.79
2	0.04	0.793	59.0	0.69	0.96
3	0.09	0.797	61.7	0.77	1.03
4	0.23	0.808	65.9	1.06	1.35
5	0.46	0.825	73.7	1.42	1.65
6	0.70	0.844	81.9	1.67	1.79
7	0.86	0.856	87.3	1.82	1.86
8	1.00	0.867	92.1	2.03	1.99
9	0.84	0.855	86.7	1.88	1.94
10	0.63	0.841	80.2	1.76	1.92
11	0.50	0.819	75.1	1.59	1.80
12	0.26	0.810	66.9	1.23	1.55
13	0.13	0.800	62.5	1.02	1.36
14	0.02	0.792	58.8	0.77	1.08
15	0.00	0.790	58.1	0.69	0.98
16	0.40	0.821	80.1	1.48	1.75
17	0.75	0.847	88.6	1.81	1.92
18	1.00	0.867	92.1	2.03	2.00
19	0.20	0.805	71.9	1.13	1.46
20	0.10	0.798	66.0	0.95	1.30
21	0.00	0.790	58.1	0.70	0.99

The symbols *n*, *z*, *d<sub>z</sub>*, and *C<sub>z</sub>*, are as defined in the footnotes of Table I.

*M<sub>z</sub>* is the estimated average molecular weight of the adsorbed species, assuming that it is a linear combination of the formula weights of the components in the sorbed solution as a function of *z* of that solution.

*α<sub>z</sub>* is the number of adsorbed molecules per accessible phenyl group. This was calculated by means of eq. (3), using the corresponding value of *M<sub>z</sub>* as the average molecular weight of the adsorbed species.

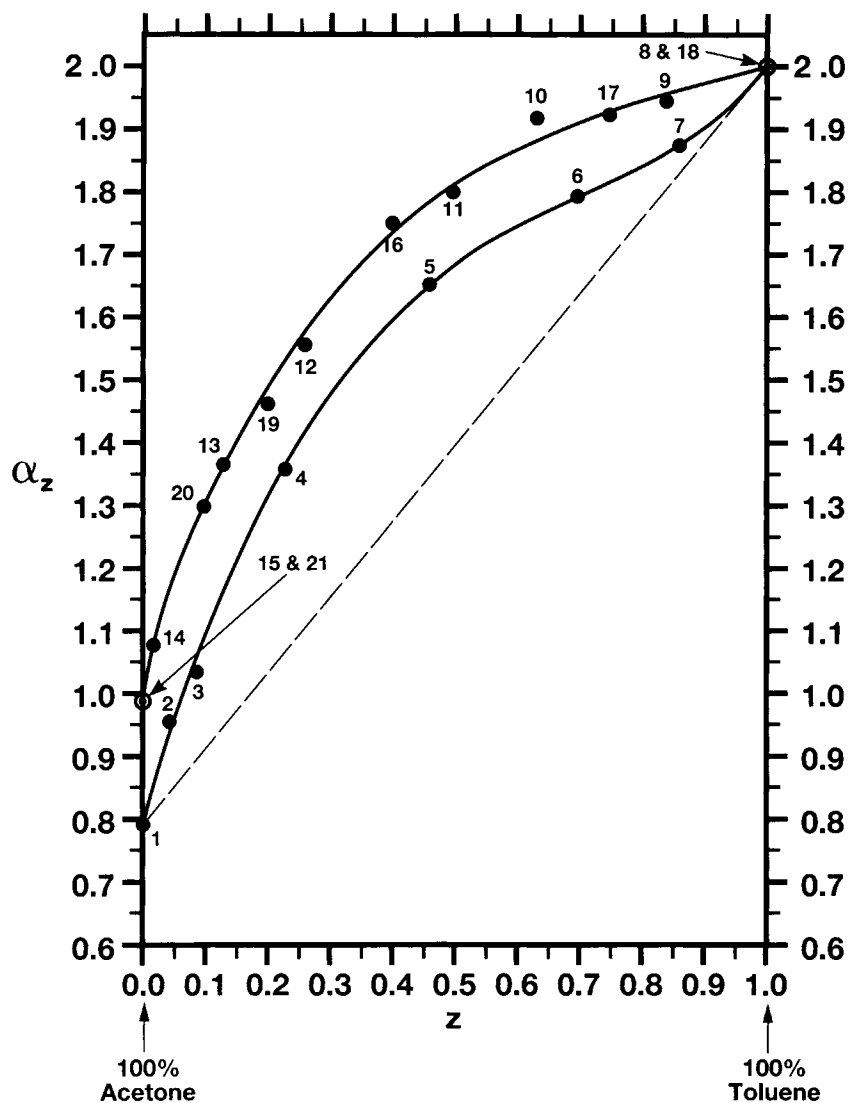
polymer self-association (i.e., all the relationships were linear and they intersected the abscissa at  $\lambda^{1/3} = 1.76 \pm 0.03 = \lambda_0^{1/3}$ ). The relative swelling powers (*C<sub>z</sub>*) deduced from the slopes of these linear relationships [eq. (2)] and the respective adsorption parameters (*α<sub>z</sub>*) calculated therefrom [eq. (3)] are collected in Table IV. Since analyses of the residual adsorbed molecules<sup>24</sup> (after all of the nonadsorbed molecules, at *z* = 0 or 1, were eliminated) indicated the complete absence of the respective complementary component, it was concluded that replacement of the adsorbed complementary component by molecular exchange had gone to completion during the 2-h interval allowed to attain swelling equilibrium at *z* = 1 and at *z* = 0. Consequently, the linear combination of the formula weights of the two components at composition *z* was used once again as the value of the average molecular weight of the adsorbed species to calculate the corresponding *α<sub>z</sub>* by means of eq. (3). These values, established for se-

quences *n* = 1 to 22 and sequences *a* to *j*, are correlated with *z* in Figure 12, which shows that the *α*-values exhibited in the initial transits fall on the reference line drawn from *α<sub>z</sub>* = 3.0 at *z* = 0 (chloroform) to *α<sub>z</sub>* = 1.98 at *z* = 1 (toluene), until the composition of the second component becomes about equal to that of the first. Thereafter, positive deviation from the reference line occurs, such that the *α<sub>z</sub>*-values fall on the solid curved line that is uniformly above the linear dashed reference line.

These results show unequivocally that the relative swelling power of a good liquid becomes significantly better after the samples have been exposed to swelling to saturation in a second good solvent. At first it was assumed that this only reflects improved packing of both adsorbed molecules together on the polymer adsorption sites, thus enhancing the driving force for polymer swelling. It was noted, however, that this effect is not erased even after all of the second solvent has been eliminated by exhaustive extraction in the original solvent for several days. It is suspected, therefore, that the exposure to the second "good" solvent caused the *Λ* of the polymer macrostructure to be increased above that which is normal for swelling in either "good" solvent alone, owing to more efficient "fluffing out" of the polymer segments between covalently crosslinked junctions, i.e., more efficient solvation of the monomer units closest to these junctions, so that the number of accessible monomer units is increased accordingly.

The above reconsideration of the swelling data, about 8 years after they were recorded by Hanson during his 6-month stay in our laboratory, brought to light that we had not yet established whether or not the observed enhancement in *Λ* would be retained if the sorbed toluene–chloroform solution were exchanged incrementally by a liquid, such as acetone, which has a much poorer affinity for the sorbent polymer than does either chloroform or toluene. Accordingly, the enhanced swelling state was re-established using essentially the same set of (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples; these had been used continuously during the interim in our ongoing swelling studies. The samples had just been used to study solvent exchange of formate esters by heptane. These heptane-saturated samples were "cleaned" by continuous extraction in toluene followed by solvent exchange with chloroform until the volume fraction of the latter was *z* = 1. The observed *α*-value at this stage was 3.15, which is a little below that exhibited eight years earlier (3.21; Fig. 12), possibly owing to residual memory effects of the ester–heptane study.

The (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples were then allowed to swell to saturation in a set of chloroform–acetone



**Figure 11**  $\alpha_z$  vs.  $z$  plot for sorption of acetone-toluene solutions: [the toluene volume fractions ( $z$ ) of which were cycled from  $z = 0$  to  $z = 1$  and back to  $z = 0$ ].

solutions, the chloroform volume fraction ( $z$ ) of which was decreased incrementally from  $z = 1$  to 0, then cycled to  $z = 1$  and back to  $z = 0$ . The  $S$  versus  $\lambda^{1/3}$  plots exhibited at each sequential level of  $z$  were similar in form to those exhibited in the corresponding study of deswelling of toluene-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples by addition of acetone in incremental amounts (Fig. 10), i.e., the  $S$  versus  $\lambda^{1/3}$  relationships in the those solutions for which  $z$  was greater than 0.5 were normal, whereas those for which  $z < 0.5$  were abnormal; the latter indicated that a measurable fraction ( $y$ ) of the solvated monomer units in the sample with  $x = 0.01$  had undergone self-association, the magnitude of which varied inversely with  $z$  as shown in the Inset of Figure 13 (the corresponding breakpoint-composition

in the case of toluene-acetone solutions was at  $z = \text{ca. } 0.05$ ; Fig. 10). It was also noted that the  $\lambda_0^{1/3}$  values for these relationships were less than the usual value of  $1.76 \pm 0.03$  as indicated by the swelling data collected in Table V, which also records the corresponding  $z$ ,  $C$ ,  $\alpha$ , and  $y$  values in the sequence that they were determined. This correlation of  $\alpha_z$  with  $z$  (Fig. 13) shows that the memory of the macrostructural architecture established by sequential swelling in toluene and then in chloroform (sequence  $n = 1$ ) prior to incremental addition of acetone (sequences  $n = 2$  to 12) is erased completely at  $z = 0.55$  in the initial transit. The  $\alpha_z$ -values established thereafter form a smooth continuous curve that is uniformly below the dashed straight reference line drawn from  $\alpha = 0.74$  for acetone (at  $z = 0$ ) to  $\alpha = 3.00$  for chlo-

**Table IV Sorption of Chloroform-Toluene Solutions by (Sty)<sub>1-x</sub>(DVB)<sub>x</sub>**

<i>n</i>	<i>z</i>	<i>d<sub>z</sub></i>	<i>M<sub>z</sub></i>	<i>C<sub>z</sub></i>	<i>α<sub>z</sub></i>
1	0.00	1.48	119.4	2.24	2.98
2	0.08	1.43	117.2	2.28	2.88
3	0.16	1.38	115.0	2.26	2.82
4	0.27	1.31	112.0	2.22	2.70
5	0.37	1.25	109.3	2.24	2.66
6	0.47	1.19	106.6	2.23	2.61
7	0.57	1.13	103.8	2.25	2.55
8	0.67	1.06	101.4	2.27	2.47
9	0.77	1.01	98.4	2.27	2.42
10	0.87	0.95	95.6	2.30	2.38
11	0.93	0.91	94.0	2.26	2.28
12	1.00	0.87	92.1	2.25	2.20
13	0.92	0.92	94.3	2.27	2.30
14	0.83	0.97	96.7	2.27	2.37
15	0.72	1.04	99.7	2.25	2.44
16	0.63	1.09	102.2	2.27	2.52
17	0.51	1.17	105.5	2.24	2.58
18	0.42	1.22	107.9	2.26	2.68
19	0.32	1.28	110.7	2.28	2.74
20	0.23	1.34	113.1	2.34	2.88
21	0.13	1.40	115.9	2.36	2.96
22	0.00	1.48	119.4	2.46	3.17
23	0.49	1.18	106.0	2.29	2.65
24	0.65	1.08	101.7	2.26	2.50
25	0.76	1.01	98.7	2.27	2.41
26	0.87	0.95	95.6	2.27	2.35
27	1.00	0.87	92.1	2.25	2.20
a	1.00	0.87	92.1	2.04	2.00
b	0.92	0.92	94.3	2.05	2.07
c	0.81	0.98	97.3	2.06	2.16
d	0.73	1.03	99.5	2.10	2.26
e	0.63	1.09	102.2	2.13	2.36
f	0.53	1.15	104.9	2.17	2.47
g	0.43	1.21	107.7	2.22	2.59
h	0.25	1.33	112.6	2.30	2.83
i	0.00	1.48	119.4	2.45	3.16
j	0.07	1.44	117.5	2.43	3.10
k	0.15	1.39	115.3	2.39	3.00

The symbols *n*, *z*, *d<sub>z</sub>*, *M<sub>z</sub>*, *C<sub>z</sub>*, and *α<sub>z</sub>* are as defined in the footnotes of Table III.

roform (at *z* = 1). These are the *α*-values obtained when acetone-"cleaned" and dried (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples are allowed to reswell in these liquids.

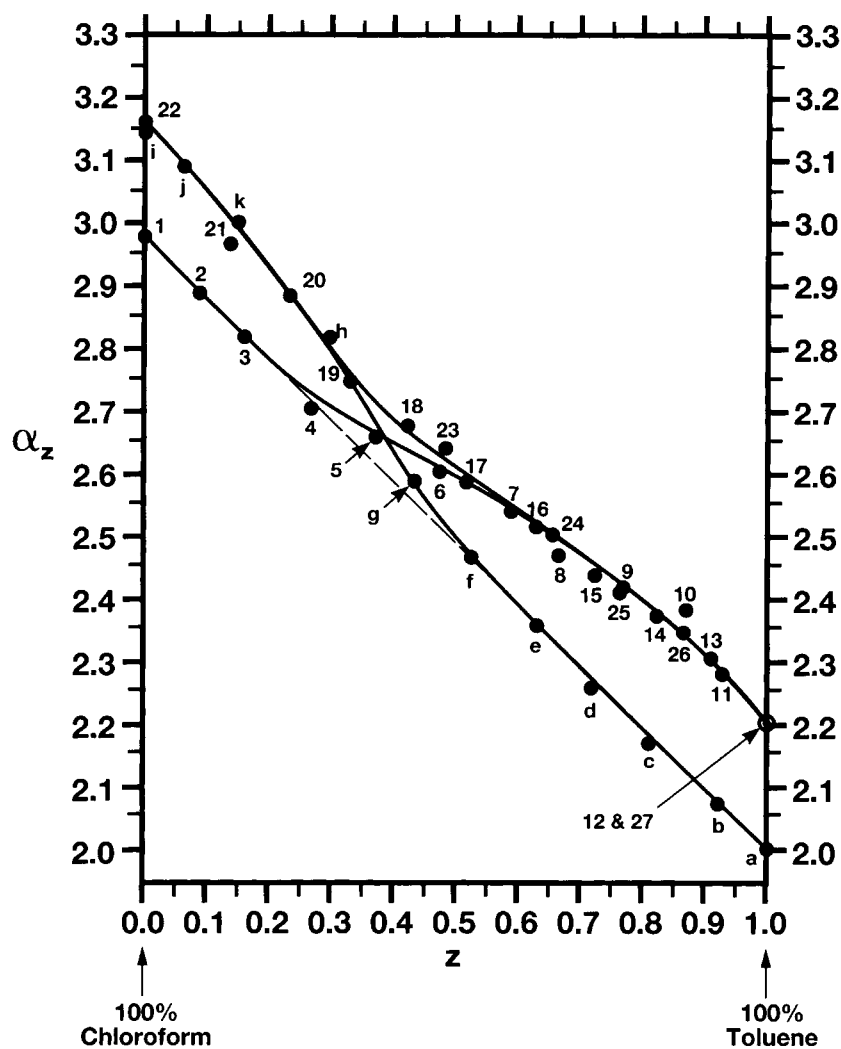
The small negative influence on swelling power found in this case (Fig. 13) is in sharp contrast to the corresponding large positive influence exhibited in the cases wherein toluene-acetone solutions were sorbed by these polymer samples (Fig. 11), which suggests that the mode in which acetone is adsorbed to the polymer may be markedly different in these

two examples. This difference might be attributable to the well-known manner<sup>25</sup> in which chloroform and acetone are associated with one another by hydrogen bonding, i.e., (CH<sub>3</sub>)<sub>2</sub>C=O ··· HCCl<sub>3</sub>. This adduct should adsorb to the phenyl group via one of the three chloro atoms in competition with HCCl<sub>3</sub>, such that the result is a net decrease in *α* for the sorbed binary solution owing to the added bulkiness of the adduct.

## MOLECULAR NATURE OF SWELLING AND DESWELLING

In these studies of polymer swelling and deswelling it is implied tacitly that the equilibrium state for a given PS-L system is determined by three competing modes of molecular association, namely polymer-polymer, polymer-liquid, and liquid-liquid. The observed *α*-value reported for a given polymer-liquid system is a measure of how well polymer-liquid association is favored at room temperature over the other two competing modes. Any perturbation of the equilibrium state expressed by eq. (1), such as a change in temperature or composition of the sorbed liquid, will affect *α* and/or *Λ*, so that *Σ* is changed accordingly as expressed by eq. (9). The induced change in the driving force for polymer swelling, which is proportional to *Δα*, occurs very rapidly since this only involves readjustment of small mobile molecules at the accessible adsorption sites on the polymer segments. The induced change in opposition to polymer swelling, which is proportional to *ΔΛ*, occurs much more slowly because this requires proper molecular alignment of relatively much-slower-moving polymer segments before self-association *via* expulsion of already adsorbed molecules can take place. Experience gained in these swelling and deswelling studies has shown that equilibrium with respect to *α* can occur within a matter of a few minutes, but at least a half hour is required to ensure equilibrium with respect to *Λ*.

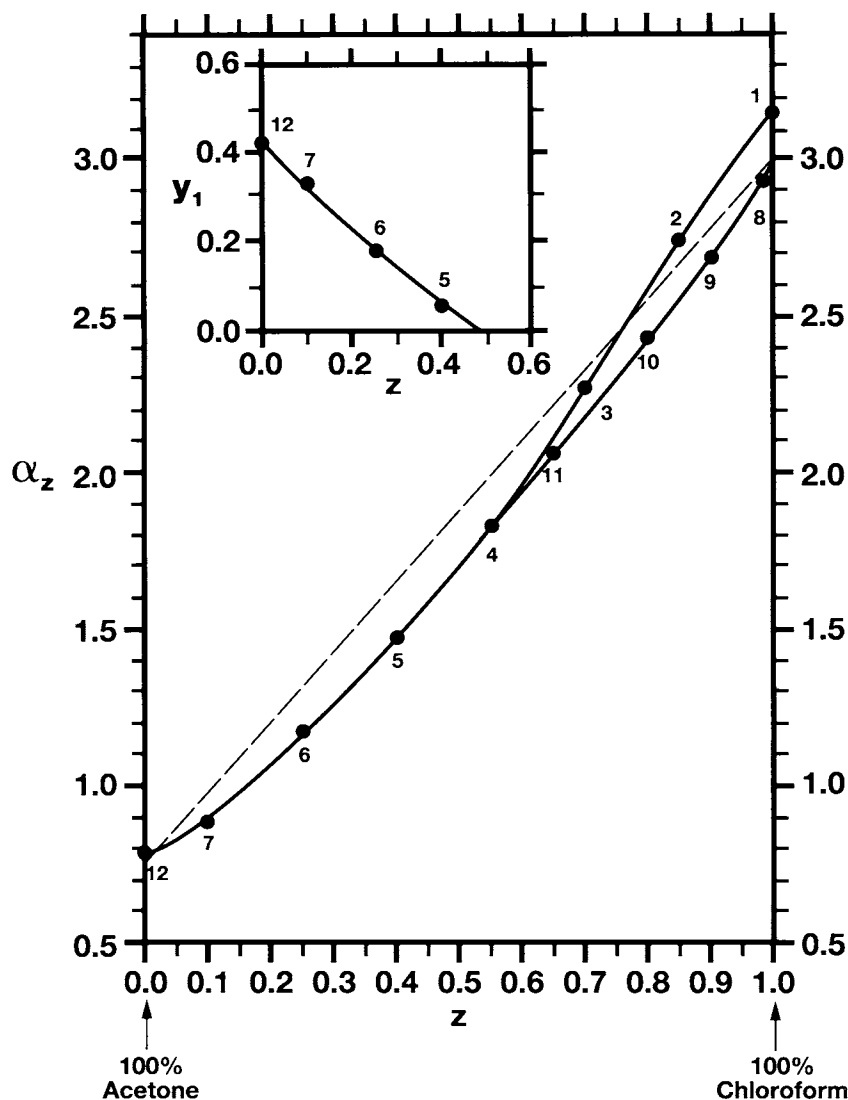
It is believed that the slowest step in this process of self-association may be nucleation thereof, because this requires proper alignment of two or more monomer units in one or more polymer segments, and therefore is very slow even when the thermodynamic conditions strongly favor the associative process. Once such microdomains are created, the growth of that domain proceeds much more rapidly because the necessary alignment of monomer units adjacent to these microdomains is almost in place. Therefore self-association *via* expulsion of the adsorbed molecules becomes highly probable, and con-



**Figure 12**  $\alpha_z$  vs.  $z$  plot for sorption of chloroform-toluene solutions: [ the toluene volume fractions ( $z$ ) of which were cycled from  $z = 0$  to  $z = 1$  and back to  $z = 0$  ].

sequently self-association propagates by “infection” of the adjacent monomer units. The process stops when the tension in the polymer chain, owing to physical restraint by two or more self-associated microdomains, becomes great enough to prevent the necessary freedom of movement needed to attain proper alignment of the adjacent monomer unit. The results observed in earlier studies of thermally induced phase separations<sup>12,13</sup> and also in our studies of solvent-induced phase separations in PS-L systems show that both the fraction ( $y$ ) of polymer that undergoes self-association, and the average number ( $*\lambda$ ) of backbone carbon atoms in the polymer segments between microdomains of self-associated polymer and/or covalent crosslinkages are characteristic of the liquid in that system, and that the macrostructural architecture of the end state is statistically reproducible.

The present studies of deswelling toluene-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples by incremental addition of *n*-heptane or methanol show that the manner in which  $y$  varies with the toluene volume fraction ( $z$ ) in the sorbed binary solution depends not only on the nature of the nonsolvent added thereto, but also on the DVB mole fraction ( $x$ ) in the sorbent polymer. Thus, for a given sorbed binary solution with composition  $z$ , the magnitude of  $y$  varies inversely with  $x$  as noted in Figures 4 and 8. This affects accordingly the composition ( $z_0$ ) where self-association of monomeric units in the polymer segments between covalent crosslink junctions is initiated, and also the extent of this self-association ( $y_0$ ) that is attained at  $z = 0$  (insets in Figs. 4 and 8). Extrapolation of these data to  $x = 0$  identifies the composition  $z$  where a polystyrene-binary-liquid solution will begin to undergo solvent-induced phase



**Figure 13**  $\alpha_z$  vs.  $z$  plot for sorption of acetone–chloroform solutions: [the chloroform volume fractions ( $z$ ) of which were cycled from  $z = 0$  to  $z = 1$  and back to  $z = 0$ ].

separation, owing to the addition of a “poor” solvent, and also the fraction of the monomer units that will be self-associated at  $z = 0$ .

That  $y$  varies with  $x$  of the sorbent  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample follows logically from the conclusion that  $y$  reflects the state where the thermodynamic driving force for self-association in a given polymer–liquid system is matched by the opposing force, owing to physical restraint on segment mobility needed to attain the right configuration for self-association. In the cases that  $x$  is  $> 0$ , part of this restraining force is already provided by the covalent crosslinkages present in the polymer; consequently the magnitude of additional physical restraint, needed to match the driving force for self-association, is decreased accordingly. Thus, the magnitude of ob-

served  $y$  decreases with  $x$  as noted in the insets of Figures 4 and 8.

The data collected in Figures 3 and 7 show that the  $\alpha_z$  versus  $z$  relationships, during the initial transit from  $z = 0$  to  $z = 1$ , reflect the macrostructure of the polymer in its dry state, but after the polymer–liquid system is swelled to saturation in the “good” solvent the relationships in all subsequent transits reflect the macrostructure of the polymer swelled to saturation in that solvent, which is mitigated thereafter by the nature of the second component added to the sorbed solution. It is inferred from these observations that the quasi-crosslinkages created during deswelling by incremental addition of the “poor” solvent are relatively “soft,” i.e., the monomer units in the microdomains of self-associated polymer are

**Table V Sorption of Acetone–Chloroform Solutions by (Sty)<sub>1-x</sub>(DVB)<sub>x</sub>**

<i>n</i>	<i>z</i>	<i>d<sub>z</sub></i>	<i>M<sub>z</sub></i>	$\lambda_0^{1/3}$	<i>C<sub>z</sub></i>	$\alpha_z$
1	1.00	1.492	119.4	1.83	2.43	3.15
2	0.85	1.387	109.3	1.79	2.07	2.74
3	0.70	1.284	101.0	1.70	1.71	2.25
4	0.55	1.177	91.8	1.70	1.37	1.82
5	0.40	1.071	82.6	1.70	1.10	1.49
6	0.25	0.966	73.4	1.60	0.85	1.16
7	0.10	0.861	64.2	1.40	0.63	0.88
8	0.98	1.478	118.2	1.76	2.24	2.92
9	0.90	1.422	113.3	1.75	2.05	2.64
10	0.80	1.352	107.1	1.75	1.84	2.42
11	0.65	1.247	97.9	1.70	1.54	2.03
12	0.00	0.791	58.1	1.55	0.56	0.79

The symbols *n*, *z*, *d<sub>z</sub>*, *M<sub>z</sub>*, *C<sub>z</sub>*, and  $\alpha_z$  are as defined in the footnotes of Table III. The symbol  $\lambda_0^{1/3}$  is as defined in eqs. (1) and (2).

easily solvated within the minimal hour-long interval allowed to re-establish liquid saturation in a binary solution with stronger solvent power.

In contrast the quasi-crosslinkages created via thermally induced phase separation, which are produced very slowly at well below room temperature as described by Kline and Guenet,<sup>13</sup> are relatively “hard,” i.e., they are not eliminated when the system is warmed back to room temperature. In fact, many such thermally induced gel systems remain as such until they are warmed significantly above room temperature (in some cases approaching the *T<sub>g</sub>* of the polymer) in order to “melt” and resolvate the “hard” microdomains of self-associated polymer. When cooled to room temperature, these systems remain as solutions until they are again chilled to well below room temperature in order to renucleate the microdomains of self-associated polymer.

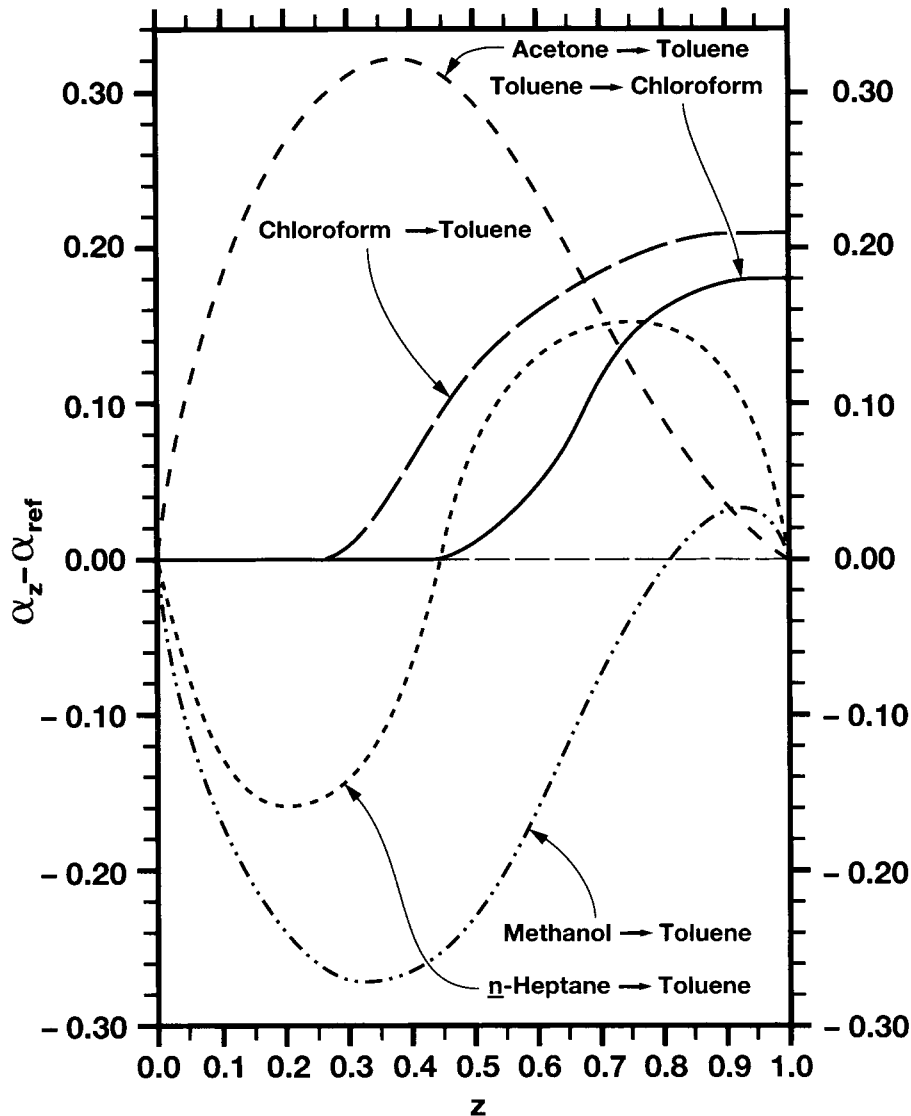
The “soft” quasi-crosslinkages, generated when a liquid-saturated sample of (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> is deswelled by incremental addition of a “poor” solvent, can be “hardened” by evaporation of the “deswelled” system to virtual dryness. Any microdomains of self-associated polymer produced during deswelling, and/or those that are formed during transition of the polymer–liquid system from its rubbery state to its glassy state via evaporation [i.e., from  $\alpha'_g$  eq. (6) to  $\alpha_g$  eq. (7)], are converted to “hard” quasi-crosslinkages as the concentration of residual trapped molecules are decreased from  $\alpha_g$  to zero.<sup>4-9</sup>

The “hardened” macrostructural architecture of the polymer obtained thereby is characteristic of the liquid present during the sequential transitions that occur before the system is rigidified by evaporation to virtual dryness. Consequently the sorption ca-

capacity of the (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> sample, when it is reswelled to liquid saturation, may reflect its “history,” and therefore retain the “memory” of solvent-past, unless the  $\alpha$ -value of the liquid in which the sample is swelled to saturation is at least equal to that of solvent-past.

The sorption data recorded in Figures 1 to 12 for the initial transits from *z* = 0 to *z* = 1 reflect the molecular architecture of acetone-saturated (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> that had been evaporated to virtual dryness before re-exposure to the test liquid solution. In all cases, the  $\alpha_z$  versus *z* relationships established during the initial transits (Figs. 3, 7, 11, and 12), show marked deviation from the corresponding dashed linear reference line, which assumes that the value of  $\alpha_{ref}$  should be a simple linear combination of the  $\alpha$ -values for the components of the sorbed binary solution as a function of *z*. The various types of S-like curves actually observed are consistent with the point of view that  $\alpha_z$  reflects not only the composition (*z*) of the sorbed liquid but also the composition of the adsorbed molecules, which varies with the relative affinities of the components that comprise that liquid for the phenyl groups of the polymer. In order to obtain better insight into the interplay of these two variables, the difference  $\Delta$  (i.e.,  $\alpha_z - \alpha_{ref}$ ), observed during the initial transits in which the dry polymer samples were swelled first in *n*-heptane (Fig. 3), methanol (Fig. 7), acetone (Fig. 11), chloroform (Fig. 12), and toluene (Fig. 12), were plotted as a function of *z* on the same scale with respect to the ordinate  $\Delta$ . This data compilation (Fig. 14) shows that the patterns for  $\Delta$  vs *z* are unique to each type of sorbed binary solution, which presumably reflects how the composition of the sorbed solution interacts with the number ( $\alpha_z$ ) of adsorbed molecules and the respective composition of these adsorbed molecules on the adsorption sites.

Although these patterns are quantitatively unique, they appear to fall qualitatively into three categories. Type I is represented by the patterns exhibited when the (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples were swelled first in a “poor” solvent, the  $\alpha$ -value of which is much less than that of acetone, and then in binary solutions that contain increasing amounts of a “good” solvent, the  $\alpha$ -value of which is much greater than that of acetone. Patterns in this classification (i.e., those for *n*-heptane and for methanol) exhibit sequentially a (negative) minimum and then a (positive) maximum as *z* goes from 0 to 1 (Fig. 14). Type II is represented by the patterns exhibited when the (Sty)<sub>1-x</sub>(DVB)<sub>x</sub> samples are swelled first in a “good” solvent, and then in binary solutions that contain increasing amounts of a second “good” solvent, the  $\alpha$ -value of which is also much greater



**Figure 14** Correlation of  $(\alpha_z - \alpha_{ref})$  with  $z$  for sorbed solutions of A and B. The dry polymer was swelled to saturation in liquid A ( $z = 0$ ), and then solvent exchanged incrementally by solvent B (i.e., the initial transit from  $z = 0$  to  $z = 1$ ).

than that of acetone. The patterns in this classification (i.e., chloroform to which is added toluene, and toluene to which is added chloroform) exhibit no deviation from the reference line until the volume fraction ( $z$ ) of the second "good" solvent is about equal to that of the first. Thereafter  $\Delta$  increases monotonically to an asymptotic limit characteristic of the system (Fig. 14). Type III is represented by the patterns exhibited when the polymer samples are swelled first in acetone and then in binary solutions thereof that contain increasing amounts of a "good" solvent such as toluene. The patterns in this classification show positive  $\Delta$  uniformly over the range from  $z = 0$  to  $z = 1$ , with a maximum occurring at  $z = \text{ca. } 0.3$ .

The negative deviations exhibited in Type I patterns (Fig. 14) are attributable to the "hardened" microdomains of self-associated polymer. These serve as pseudo-crosslinkages and increase accordingly the force in opposition to the driving force for polymer swelling, which varies with  $\alpha_z$ . When the volume fraction  $z$  is high enough to cause solvation of these microdomains, this negative effect on polymer swelling is eliminated and the value of  $\alpha_z$  thereafter is equal to or greater than  $\alpha_{ref}$  (Fig. 14). It is interesting to note that the composition where the effect owing to "hardened" microdomains is eliminated in the initial transit (Figs. 3 and 7) corresponds to the composition where the effect owing to reformation of "soft" microdomains reappears in

subsequent transits (Figs. 4 and 8, respectively). Apparently this marks the composition where polymer-polymer association begins to compete favorably with polymer-solvent association, and it indicates that this critical composition may be characteristic of the system. The positive deviation that follows the negative deviation, exhibited in Type I systems (Fig. 3), is attributed to the combined effects of adsorption partitioning that favors the "good" solvent molecules and the progressive "fluffing-out" of the macrostructural architecture of the polymer to its maximal attainable state at  $z = 1$ .

In Type II systems, the "hardened" quasi-crosslinkages are already eliminated by swelling first in the "good" solvent. Incremental addition of the second "good" solvent causes appropriate molecular interchange of adsorbed molecules in proportion to the molar fraction of the components and the relative affinities of these components for the adsorption sites, such that the value of  $\alpha_z$  is about equal to the corresponding  $\alpha_{ref}$  until  $z$  becomes about equal to 0.5. Thereafter  $\alpha_z$  increases monotonically to its asymptotic limit characteristic of the system. It is believed that this is attributable to an increase in  $\Delta$  owing to synergistically improved solvation of such monomer units adjacent to the covalent crosslinkages, which normally are not accessible when the polymer is swelled in monocomponent liquids.

The uniform positive deviation from  $z = 0$  to  $z = 1$  characteristic of Type III relationships is believed to be attributable to molecular interaction of the components in the sorbed binary solution. It is suspected that association of acetone with toluene affects the geometry of the mode in which acetone is adsorbed to the phenyl groups on the polymer, so that the number of adsorbed molecules is increased markedly even though the amount of added "good" solvent is still small. Continued addition of "good" solvent results in molecular replacement of the adsorbed molecular complexes by those of the "good" solvent which enhances  $\alpha_z$  even further in accordance with the value of  $z$ . Evidence of similar synergistic molecular interactions was noted in other binary solutions of acetone and "poor" solvents, which will be submitted for publication at a later date.

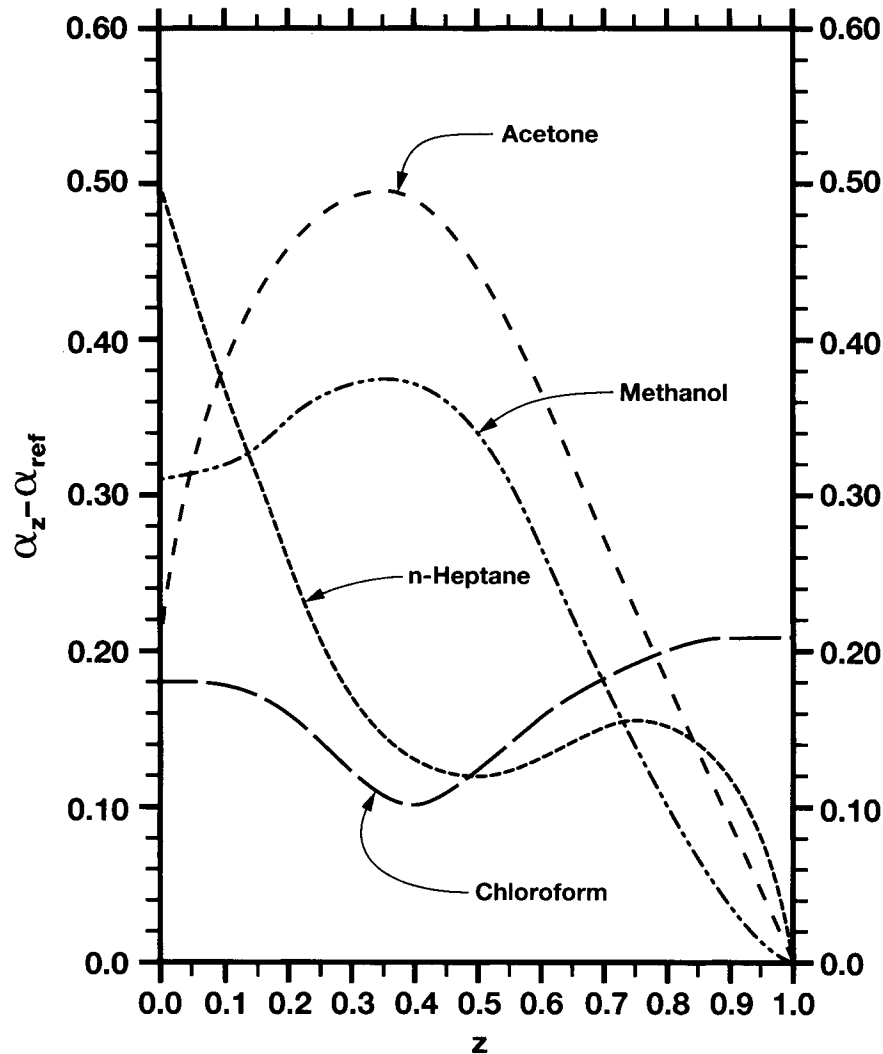
The  $\Delta$  versus  $z$  relationships that were exhibited after the initial transit are recorded in Figure 15. These relationships can also be classified as described above. Type III, represented by sorption of acetone-toluene solutions, is similar to that exhibited in the initial transit (Fig. 14) except that the  $\Delta$ -values in Figure 15 are uniformly greater than the corresponding values in Figure 14. In contrast to the above patterns for Type III, the Type II relationships,

represented by sorption of toluene-chloroform solutions, exhibit a minimum between the asymptotic limits attained at  $z = 0$  and  $z = 1$  (Fig. 15). In this case it is believed that the observed pattern reflects the manner in which the composition of the sorbed liquid exists in equilibrium with the composition of the adsorbed molecules, which varies not only with the composition of the sorbed liquid but also with the relative affinities of the components for the adsorption sites. The product of these two variables is such that the relative solvent power of the binary solutions is minimal at the composition where the volume fractions of the components are about equal. Type I relationships, represented by solutions of toluene with methanol or *n*-heptane (Fig. 15), show a small maximum superimposed on a gradual increase in  $\Delta$  as  $z$  goes from  $z = 1$  to 0. In these cases, virtually all of the adsorption sites are occupied by toluene molecules even when  $z$  is  $< 0.1$  because the  $\alpha$ -value for toluene is so much greater than that for second component. The small maximum superimposed on a gradually changing base line, as noted in Figure 15, may indicate the composition where physical interaction between the components of the sorbed liquid is maximal, but the extent of such interaction is considerably less than that suggested for binary solutions of acetone and toluene.

It is interesting to note the inverse similarity of the patterns exhibited for deswelling of chloroform-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples by solvent exchange, using chloroform-acetone solutions (Fig. 13), with the corresponding patterns exhibited in Figures 14 and 15. In this case (Fig. 13) the "memory" of the "looser"-than-normal macrostructural architecture produced by sequential swelling to saturation in two "good" solvents, toluene and then chloroform, is erased when the molar amount of added "poor" solvent (acetone) becomes about equal to that of the "good" solvent. This result is similar, but in the reverse sense, to that noted in the initial transits that started with dry-polymer, i.e., the "memory" of the "tighter" than normal macrostructural architecture is erased when the molar amount of added "good" solvent becomes about equal to that of the "poor" solvent, as discussed above for Types I, II, and III.

That physical cross-molecular association does occur between species in binary solutions is evidenced in their respective heats of mixing. This can be exothermic or endothermic as noted in relevant examples shown in Table VI, which records in cal/mole the heats of mixing to approximately 1 to 1 molar ratios of the components at 25°C. These values, however, do not fully correlate with the relative





**Figure 15** Correlation of  $(\alpha_z - \alpha_{ref})$  with  $z$  for sorbed solutions of A and B. (in all subsequent transits from  $z = 1$  to  $z = 0$  or from  $z = 0$  to  $z = 1$  following the initial transit shown in Fig. 14).

magnitude of enhanced or depressed  $\alpha$ -values as a function of  $z$  as shown in Figures 3, 7, and 11–15. It is suspected, therefore, that the explanation may be found in the geometry of the complex formed thereby, and how this affects the mode in which the complex is associated with the adsorption site on the polymer, i.e., how well the complex can be accommodated by the molecular structure of the repeat unit.

These observations strongly support the hypothesis first articulated by Fowkes,<sup>26</sup> who suggested in 1984 that the solute in polymer–liquid solutions is not the naked polymer, but rather it is the polymer coated with adsorbed molecules. It follows therefrom that the solubility and other colligative properties of polymer–liquid systems depend not only on the composition of the solvent, but also on the compo-

sition of the adsorbed molecules, which will change with time after immersion in a second solution of a different composition, owing to molecular interchange which does not occur instantaneously as heretofore believed.

In summary, it is proposed that the equilibrium state of a polymer–liquid system at a given temperature is determined by three competing forms of molecular association, namely polymer–liquid, polymer–polymer, and liquid–liquid. When the “good” solvent is added to a  $(\text{Sty})_{1-x}(\text{DVB})_x$ -liquid system, polymer–polymer association is decreased in favor of polymer–liquid association, i.e.,  $\alpha$  and  $\Lambda$  both increase, which causes  $\Sigma$  to increase accordingly as expressed by eq. (9), and to lead eventually to solution if  $x$  is zero. On the other hand, when a “poor” solvent is added to a polymer–liquid solution,

**Table VI** Heats of Mixing to ca. 50% Molar Binary Solutions at ca. 25°C

Component #1	Component #2	$\Delta H$ in Cal/mole
Chloroform	Acetone	-460
Chloroform	Toluene	-157
Acetone	Toluene	+52
<i>n</i> -Heptane	Toluene	+134
Ethanol	Toluene	+145
Methanol	Benzene	+157
Acetone	<i>n</i> -Heptane	+813

Data from ref. 36. G. Beggerow in *Heats of Mixing and Solutions*, Vol 2, K. Shafer, Ed. Springer-Verlag, Berlin-Heidelberg-New York, 1976.

$\alpha$  is decreased within minutes to the value characteristic of the new equilibrium state. If the magnitude of decrease in  $\alpha$  is sufficiently great, then  $\Lambda$  for that sample will also decrease, but this occurs much more slowly owing to the relatively slow movements of polymer molecules. Since the mobility of polystyrene segments between covalent crosslink junctions of liquid-saturated  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples decreases with increasing  $x$ , the fraction of the monomer units in such polymers that can undergo self-association under the same conditions also varies inversely with  $x$ .

## RELEVANCE TO SWELLING STUDIES REPORTED BY OTHERS

### Swelling of Dry Polystyrene Samples made Via Thermal Cooling

It is well known<sup>27</sup> that the specific volume ( $S$ ) of liquid sorbed by a given polymer sample, made via thermal conversion from the rubbery state to the glassy state, attains a maximal value relatively quickly and then decreases relatively slowly thereafter to an asymptotic limit. The times required to attain the maximal value and the subsequent end state varies with the nature of the polymer and physical dimensions of the sample. In the case of polystyrene it was reported by Boyer and Spencer,<sup>28</sup> who used 1-mm slices of extruded polystyrene rods, and later by Smith and Peppas,<sup>29</sup> who used thin films of poly(*Sty-co-DVB*) made via thermal conversion from the rubbery state to the glassy state, that a maximal value of  $S$  is attained within 3 days, but about a month thereafter is required for the value of  $S$  to decrease to its asymptotic limit. This so-called "overshoot" was attributed<sup>27-29</sup> to one or both of two factors, namely (1) solvent extraction of low-molecular-weight polymer and/or unreacted mono-

mer, and (2) an ill-defined "macrostructural relaxation" as described by Vrentas et al.<sup>27</sup> Smith and Peppas reported<sup>29</sup> that the latter factor is more important than the former, and he noted that the magnitude of the "overshoot" varies inversely with the crosslink density in the absorbent polymer.

Kanbour et al.,<sup>30</sup> Titow et al.,<sup>31</sup> and Overbergh et al.<sup>32</sup> observed maxima in sorption curves using crystallizable polymers. They attributed the "overshoot" to postcrystallization induced by the presence of the solvent. Titow et al.<sup>31</sup> demonstrated that "overshoot" is not exhibited if the system is evaporated to dryness and then is reswelled in the same solvent. Presumably, the microdomains of well-organized arrays that serve as pseudo-crosslinkages are retained in the reswelling. In such cases,  $S$  increases monotonically to the asymptotic limit, which is consistent with the above hypothesis.

Vrentas et al.<sup>27</sup> suggested that some form of induced polymer-polymer postassociation, which they defined as "chain-relaxation" must also occur in the case of liquid sorption by noncrystallizable polymers. They demonstrated<sup>27</sup> that "overshoot" is not attributable to postformation of well-ordered microdomains. This was done by means of an experiment similar to that of Titow, i.e., they dried the sample at 120°C, which is well above the glass transition temperature of the pure polymer, and then reswelled the sample at room temperature. The pattern exhibited in the reswelling study was virtually superimposable on that exhibited in the original study, which verified that the original macrostructure was restored by drying the polymer-liquid system at above the glass temperature of the polymer and then cooling the sample to room temperature to attain the glassy state. Unfortunately, the above procedure also eliminated all evidence of polymer "relaxation" in the presence of solvent.

Our studies<sup>1-10</sup> of polymer swelling and subsequent drying, however, indicated that when a PS-L system, at its asymptotic end state, is dried at 23°C to well below the glass transition composition of the polymer at that temperature and then reswelled in the same solvent, no evidence of an overshoot is exhibited. This supports the suggestion of Vrentas et al. that the "overshoot" is attributable to some form of polymer-polymer postassociation, which does not involve well-organized microdomains.

In view of the Results and Discussion recorded above, the observed "overshoot" and subsequent "relaxation" in the presence of sorbed liquid is now amenable to molecular interpretation. It follows from the discussion above regarding polymer in its dry state, that the macrostructural architecture will

reflect the pathway of its formation from its rubbery state (owing either to change in binary composition at a given temperature or to change in thermal energy at a given composition) to its glassy state. When this transition is attained by rapid cooling of the neat polymer, the macrostructure obtained thereby is in its most random possible state, i.e., the number of microdomains of randomly associated monomer units (which have sufficient cohesive strength to serve subsequently as quasi-crosslinkages when the sample is swelled to liquid saturation) will be at its minimal possible value, characteristic of thermally induced rapid rigidification to its glassy state from its rubbery state. When this sample is swelled to saturation in a given test liquid, the number of sorbed molecules,  $\Sigma_{max}$  per functional group of polymer at the maximal point of swelling, is given by the product of  $\alpha$  and  $\Lambda_{max}$  as expressed by eq. (1), where  $\Lambda_{max}$  reflects the macrostructure characteristic of polymer that had been rigidified rapidly by thermal quenching, and therefore in a (dry) state of maximal "looseness." When such a sample is swelled by a liquid, the mobility of the solvated segments (between the minimal number of microdomain that serve as quasi-crosslinkages) results from the aforementioned "looseness," and allows the monomer units that comprise these segments to nucleate microdomains of self-associated polymer. The number and size of these domains increase with time until the restraining force generated thereby matches the driving force for self-association as described above. The magnitude of induced  $\Delta\Lambda$  reflects the fraction ( $y$ ) of available monomer units that undergo self-association, which is characteristic of the solvent as expressed by eq. (14). Thus, the value of  $\Sigma_f$ , attained at the asymptotic limit following the overshoot, becomes:

$$\Sigma_f = \alpha(\Lambda_{max} - \Delta\Lambda) \quad (17)$$

When the polymer-liquid sample at the asymptotic end state is evaporated to dryness at room temperature, the macrostructure of the dry polymer is now characteristic of the liquid from which it was last swelled to saturation. When this polymer is reswelled to saturation in that liquid, the quantity of sorbed molecules [ $\Sigma$ ; eq. (1) or  $S$ ; eq. (2)] increases monotonically to the level expressed by eq. (17), without exhibiting an overshoot.

On the other hand if the polymer-liquid sample at the asymptotic end-state is evaporated to complete dryness at temperatures above  $T_g$  of the polymer and then is cooled to attain the glassy state, the macrostructure of the polymer produced thereby will be characteristic of the thermally induced transition

from the rubbery state to the glassy state, i.e., its effective crosslink density will be relatively low, consequently its sorption capacity will be relatively high initially until the mobility imparted by the then-adsorbed molecules results in polymer self-association to restore the tighter structure characteristic of the polymer-liquid system at saturation.

### Hysteresis-Like Behavior in Swelling and Deswelling in Binary Solutions

O'Kane, Roe, and Sherrington reported<sup>32-34</sup> that the sorption capacity of a  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample for a binary liquid, comprised of a "good solvent" (such as tetrahydrofuran, *p*-dioxane, or pyridine) and a "poor solvent" (such as water or methanol), depends on the sequence in which the solvents are added to the system. He noted that the correlations of the volumes, sorbed by samples of the same crosslinked polymer at liquid saturation, with the volume fraction ( $z$ ) of the "good solvent" in the sorbed binary liquid (the  $z$  of which was varied from 0 to 1) exhibit hysteresis-like patterns, i.e., the relationship exhibited when dry samples of  $(\text{Sty})_{1-x}(\text{DVB})_x$  were allowed to swell to saturation, first in the "poor solvent" and then in test-binary solution, was uniformly below that exhibited when samples of the same dry polymer were allowed to swell to saturation first in a "good solvent" and then in the test binary solutions of the same compositions used in the alternate sequence noted above.

The  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample prepared by Sherrington was characterized only by the volume ratio of divinylbenzene (40 mL) to styrene (60 mL) made to undergo copolymerization, which does not permit one to infer the percentage of DVB (i.e., the value of  $x$ ) incorporated in the polymerized product nor the distribution of DVB needed to estimate the average number of backbone carbon atoms ( $\lambda$ ) in the polymer segments between crosslink junctions. The inverse of the ratios of polymer volumes before ( $V_i$ ) and after ( $V_f$ ) swelling to liquid saturation in tetrahydrofuran (i.e.,  $V_f/V_i = 2.50$ ), acetone (0.78), *p*-dioxane (3.10), and pyridine (2.60) were reported, however, and this enabled us to calculate [by means of eq. (1)] the effective cross-link density [i.e.,  $1/\lambda = x/(1+x)$ ] relative to the results observed for sorption of these same liquids by our set of six  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples. The effective  $x$ -values for Sherrington's sample, calculated by us using the  $V_f/V_i$ -values reported by him, for saturation in *p*-dioxane, pyridine, tetrahydrofuran and acetone are 0.023, 0.027, 0.038, and 0.050, respectively, which is about tenfold less than that (0.37) expected if one assumed that the molar ratio in the copolymer produced

would be the same as the molar ratio of the monomers made to undergo copolymerization.

It was inferred from these results that the macrostructure of the crosslinked polymer prepared by Sherrington may resemble that of a nonhomogeneously crosslinked network of swellable polystyrene segments between "nodules" of nonswellable poly(DVB), i.e., highly crosslinked DVB-rich microdomains interconnected by a multiplicity of poly(styrene) segments.

The above uncertainty of the polymeric macrostructure of his crosslinked sample, however, does not negate his conclusions, namely that the sorption capacity of a given crosslinked polymer sample with respect to a given binary solution depends on its swelling history, as noted in Figures 1 to 11 in ref. 33. In fact, the results reported here in Figures 1, 2, 5, 6, 9, and 10 serve to confirm most of Sherrington's conclusions. When the four sets of  $S$ -values recorded in these figures for sorption by the four  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples with  $x < 0.08$  are correlated with  $z$  from  $z = 0$  to  $z = 1$  and then from  $z = 1$  to  $z = 0$ , as described in the Experimental section, the plots obtained thereby (not shown here) exhibit hysteresis-like patterns, each of which is qualitatively similar to those reported by Sherrington, except that they do not form a closed loop as noted in Figures 1 to 11 in ref. 33. The closed loop is an artifact of the procedure used by Sherrington, because the history of swelling to saturation in his penultimate binary solution was erased by his procedure that required cleaning in acetone and then evaporation to dryness before reswelling to saturation in the test nonsolvent. In all but this final determination, the history was restored by the mode of sequential swelling. If the liquid-swollen penultimate sample had been extracted continuously and thoroughly in fresh nonsolvent, the swelling ratio exhibited by the ultimate sample at  $z = 0$  would have been significantly greater than the swelling ratio exhibited by the initial sample at  $z = 0$ .

In our study, we noted that the initial transit from  $z = 0$  to 1 (i.e., beginning with dry  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples) is reproducible only when the liquid-swollen samples are cleaned in acetone and then evaporated to dryness, before the samples are reswelled sequentially in the set of binary test solutions, the  $z$  of which is increased monotonically from 0 to 1, because the sorption capacity reflects the memory of the polymeric macrostructure in its dry state until this memory is "erased" by swelling to saturation in a good solvent. Thereafter the sorption capacity reflects the memory of the polymeric macrostructure at liquid saturation in the better solvent, such that the pathway exhibited during the second transit

from  $z = 1$  to 0 is reproducible in all subsequent transits, so long as the PS-L system continues to be cycled between the compositional extremes for the test-set of binary solutions, as noted here in Figures 3, 7, 11, and 12.

It is believed that the molecular interpretation of the induced change in sorption capacity noted in our studies may also apply qualitatively to those observed by Sherrington, i.e., the magnitude of change in sorption capacity of a given sample caused by a given change in binary composition by addition of water in incremental amounts is the net effect of two contributions, namely the induced change [ $\Delta\alpha$ ; eq. (9)] in the number (and composition) of adsorbed molecules per accessible phenyl group in the  $(\text{Sty})_{1-x}(\text{DVB})_x$  sample at liquid saturation in the respective binary solutions, and the induced change [ $\Delta\Delta$ ; eq. (9)] in the relative "looseness" of the polymer macrostructure. Unfortunately it is not possible to ascertain the relative contributions of these two effects in Sherrington's study, because aliquot samples from a single batch of crosslinked polymer were used throughout his study, whereas a set of  $(\text{Sty})_{1-x}(\text{DVB})_x$  samples, with known values of  $x$ , is needed to deduce the relative contributions of the two effects.

Such studies of swelling to saturation in tetrahydrofuran, *p*-dioxane, acetone, and pyridine and subsequent cycling between these water-soluble organic liquids and pure water have been completed in our laboratories. The results obtained thereby are consistent with the above point of view; the details of these studies will be published at a later date after we have had an opportunity to describe how the adsorption parameters for homologous series of ethers and ketones vary with the systematic modification of the molecular structures within each of these functional classifications. This kind of information is needed in order to present a clear understanding of the molecular nature of water-induced polymer-polymer association in solutions of polystyrene in organic liquids that are readily soluble in water.

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