

Polymer Drying. IX. Effect of History on the Kinetics of Evaporation from Poly(styrene-co-divinylbenzene)–Liquid Systems in the Rubbery and Glassy States

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SYNOPSIS

In these time studies of evaporation from liquid-saturated microporous composite film samples, comprised of poly(styrene-co-divinylbenzene) particles enmeshed in poly(tetrafluoroethylene) microfibers, the samples were preswelled to saturation in a good solvent, such as toluene, which was then replaced via solvent exchange in excess test liquid before the start of the time study that monitored the residual weight (W_t) of sorbed liquid to virtual dryness. The patterns of change with time (i.e., W_t vs. t and $\text{Log } W_t$ vs. t) obtained thereby were compared with the corresponding time studies already reported for evaporation from equivalent polystyrene–liquid (PS–L) systems that did not have a history of preswelling in a better solvent. These comparisons show that the history of the sample in its liquid-saturated gel state can affect markedly the kinetics of desorption from the PS–L system in its glassy state, and also during the interval of transition from the rubbery state to the glassy state, as discussed in the text. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the first¹ of this set of three companion articles we reported that the sorption capacity [S , in mL of sorbed liquid per gram of sorbent polymer (eq. (1) of ref. 1), or alternatively Σ , in sorbed molecules per functional group of polymer sample (eq. (2) of ref. 1)] of a polymer, with respect to a given test liquid, is increased significantly when that sample is preswelled to saturation in a good solvent and then solvent-exchanged in excess of the test liquid. Examples of such studies, using poly(styrene-co-divinylbenzene) [hereinafter referred to either as poly(Sty-co-DVB) or $(\text{Sty})_{1-x}(\text{DVB})_x$] as the sorbent polymer that was preswelled to saturation in toluene and then solvent-exchanged for methanol, acetone, or chloroform, are recorded in Figures 1 through 11 of ref. 1.

We suggested,¹ without supporting evidence, that this improved sorption capacity might be attributable to “memory” effects, carried over from the preswelling to saturation in a suitable good solvent, namely adsorption partitioning that favors the better solvent. If true, then it should be possible to obtain supporting evidence for such memory effects by monitoring the kinetics of evaporation, which is known to reflect the nature of the adsorbed molecules as the polystyrene-liquid (PS–L) system evaporates from saturation to virtual dryness.^{2–12} Such observations should differ meaningfully from those already reported for time studies that had monitored evaporation from the corresponding PS–L system lacking an immediate history of exposure to toluene. Evidence of adsorption retentivity favoring the better solvent could be deduced from the observed differences, and perhaps further supported by analytical data establishing the composition of residual adsorbed molecules after the PS–L system had evaporated to the composition that marks the start of the glassy state.

The purpose of this publication, therefore, is to report the results of such comparisons and the conclusions derived therefrom.

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EXPERIMENTAL

Multireplicated Time Studies of Evaporation from (Sty)_{1-x}(DVB)_x Samples

The procedures for making microporous composite films comprised of (Sty)_{1-x}(DVB)_x particles (> 80% by weight) enmeshed in PTFE microfibers (see Figs. 1, 6, 7, and 20 of ref. 9) are described in considerable detail elsewhere.⁹⁻¹² The protocol used to establish the volumes [S , in mL per gram of (Sty)_{1-x}(DVB)_x] of sorbed liquid at ($23 \pm 1^\circ\text{C}$) by each of the six composite film samples (i.e., $x = 0.01, 0.02, 0.03, 0.04, 0.08, \text{ and } 0.11$), was essentially the same as that described previously.⁹⁻¹² After the set of six polymer samples were swelled to saturation in toluene ($\alpha = 1.98$, in molecules per accessible phenyl group in a PS-L system at liquid saturation), they were solvent-exchanged "to saturation" in one of the test liquids [i.e., *n*-heptane ($\alpha \leq 0.01$), methanol ($\alpha \leq 0.06$), acetone ($\alpha = 0.92$), or chloroform ($\alpha = 3.00$)], the amount being such that contamination by desorbed toluene was less than 0.1%. They were then extracted in fresh test liquid for at least 2 h to ensure that all of the nonadsorbed toluene molecules had been eliminated.

The kinetics of evaporation of test liquid from each of the above set of six composite film samples was established by monitoring simultaneously the respective weights (W_t) of residual sorbed liquid, as described in the Experimental section of ref. 3. No attempt was made, however, to preclude sample shrinkage, despite that it is known to complicate the kinetics of evaporation from the rubbery state.^{2,3} The number (α_t) of residual sorbed molecules per phenyl group of polymer was calculated from the corresponding observed W_t by means of eq. (1).

$$\alpha_t = (104/M)W_t, \quad (1)$$

where 104 is the formula weight of a styrene monomer unit, and M is the formula weight of the sorbed liquid. The values of α_t (or the corresponding Log α_t -value) obtained thereby were then correlated with t as described in earlier publications.³⁻⁸ The replicated evaporation-to-dryness patterns obtained for this set of six PS-L systems were compared with those reported earlier³ for evaporation from the same liquid-saturated samples when they had not been exposed temporarily to toluene before starting the time study, in order to identify differences that might be attributed to the "memory" of presaturation in toluene.

These kinetic studies were terminated 24 h after α_t became equal to α_g (the composition that marks completion of transition from the rubbery to the glassy state) in order to establish the composition of the residual adsorbed molecules. To this end, the six composite film samples were placed together at one end of an evacuated closed system that was heated to 110°C for about 3 h. The residual molecules desorbed therefrom were collected at the other end of the closed system, which was kept at liquid nitrogen temperature. The composition of the condensate was then analyzed by means of a gas-chromatography apparatus fitted with a 30 meter DB-5 capillary column that was connected to a mass spectrometric detector. The molecular fraction of toluene in the condensate was thus a measure of its affinity for polystyrene relative to that of the test liquid with which the set of six (Sty)_{1-x}(DVB)_x samples had been re-equilibrated before starting the time-studies of evaporation.

Individual Time Studies of Evaporation Excluding Sample Shrinkage

A microporous composite film sample (about 0.3 mm thick, 3 cm wide, and 4.5 cm long weighing about 1.5 g), comprising of (Sty)_{1-x}(DVB)_x particles (> 80% by weight), enmeshed in PTFE microfibers, was swelled to saturation in toluene. The liquid-saturated film sample obtained thereby was then exposed to saturation in ample test-liquid (*n*-heptane, methanol, acetone, or chloroform) such as to become contaminated by no more than 0.1% desorbed toluene. The sample was then exposed to fresh test-liquid for at least 2 h to ensure elimination of all of the sorbed toluene molecules that had not been immobilized by adsorption. Shrinkage of the liquid-saturated film sample during drying was prevented by "sandwiching" it between two stainless steel screens. The "sandwich" was held together by four binder clamps, which also served as a vertical stand (see Fig. 1 of ref. 4a) so that evaporation could occur simultaneously from both sides of that sample. The weight of residual sorbed liquid was monitored by means of an electronic balance that enabled one to record the data automatically to within ± 0.1 mg at predetermined time intervals without disturbing the system as it evaporated to virtual dryness, as described in the Experimental of ref. 4a.

One to five days after α_t became equal to the composition that marks completion of the rubber-to-glass transition interval (i.e., α_g), the time study of evaporation was terminated and the composition of

the residual trapped molecules was determined as described above for the multireplicated time studies of evaporation from six $(\text{Sty})_{1-x}(\text{DVB})_x$ samples simultaneously (which had been carried out about six years earlier, in 1984). The mole fraction (ϕ) of toluene in the volatile condensate, was correlated with the time (τ) that the sample, saturated with test solution that contained no more than 0.1% accumulated toluene, had been exposed to fresh (toluene free) test-liquid before starting the time study of evaporation to dryness.

RESULTS AND DISCUSSION

The PS-L systems, considered in this set of time studies that were monitored from saturation to virtual dryness, had histories of solvent exchange at liquid saturation that could be classified in one of two categories; those in which the solvent exchange caused polymer-polymer association, and those in which it did not. The first category is represented by toluene ($\alpha = 1.98$) saturated PS-L systems that were solvent exchanged by a very poor solvent, such as *n*-heptane ($\alpha \leq 0.01$) or methanol ($\alpha \leq 0.06$), which are known to cause liquid-induced phase separation of polystyrene solutions in toluene.¹³ The kinetics of evaporation from systems of the first category is considered in the following section, and that from systems in the other category is considered in the section thereafter.

Evaporation from Polymer-Polymer Associated Systems

n-Heptane-Induced Polymer-Polymer Associated Systems

We reported^{1,2} that little if any *n*-heptane is absorbed by the poly(*Sty-co-DVB*) particles enmeshed in the six microporous composite film samples that were used to establish the relative swelling power of the test liquid, even when these samples had been immersed in that liquid for several days at room temperature, and despite that the void volume surrounding the enmeshed particles was filled with wetting liquid within seconds after contact owing to capillary action (see Fig. 8 of ref. 9). The residual weights (W_t) of *n*-heptane, sorbed in the interstices of these microporous composite films, were monitored simultaneously. When the α_t values [which were calculated from the corresponding W_t -data by

means of eq. (1)] were plotted as a function of time, it was noted that the kinetics of evaporation follow zero order from saturation to virtual dryness, i.e., to $\alpha_t = 0$, as expressed by eq. (2)

$$\alpha_t = \alpha_0 - rt \quad (2)$$

Here α_0 is the average number of residual sorbed molecules per phenyl group in the polymer particles enmeshed in the composite film sample at the start of the time study ($t = 0$), and r is the zero-order rate constant in molecules eliminated per phenyl group per minute.

In all six time studies, α_t decreased from about $\alpha_t = 1$ to 0 within 10 minutes in accordance with eq. (2), which verified that little if any of the *n*-heptane that had been sorbed into the void space surrounding the enmeshed particles had been absorbed by the particles. A representative example of *n*-heptane evaporation from a liquid-saturated microporous composite membrane is recorded in Figure 2 of ref. 2.

In contrast to the above results, the time studies of *n*-heptane evaporations from each of the same six liquid-saturated microporous film samples, after they had been cycled to saturation in toluene and then back to *n*-heptane as noted in Figures 1 to 4 of ref. 1, showed that the kinetics of evaporation follow zero-order only until α_t decreases to about 0.2, which requires less than 10 minutes. Thereafter the rate of evaporation decreases sharply such that α_t was > 0.06 even after $t = 24$ hours. The six evaporation patterns, exhibited after the sharp deviation from zero-order kinetics, resembled those for elimination of residual molecules from a PS-L system in its glassy state. We inferred from this observation that the PS-L systems, obtained via *n*-heptane-induced polymer-polymer association, may have undergone transition to the glassy state *before the start* of evaporation to dryness, and that as a result a measurable amount of residual volatile molecules was still present in the PS-L system even after it was evaporated to apparent dryness at 23°C.

These time studies were terminated at $t = 24$ hours in order to permit collection and identification of the residual molecules after the system had attained the glassy state as described in the Experimental section. The results obtained thereby showed that the condensate, collected from $\alpha_t = \text{ca. } 0.06$ to 0.03, was a mixture of toluene and *n*-heptane. We noted in repeat studies that the mole fraction (ϕ) of toluene in this mixture varied with the time (τ) that the sample (which had been deswelled "to sat-

Table I Correlation of the Time (τ) of Extraction with the Mole-Fraction (ϕ) of Residual Toluene

τ (in hours)	0.5	2	24	48	72
ϕ	0.55	0.33	0.05	0.02	0.01

uration" in *n*-heptane that was contaminated by not more than 0.1% desorbed toluene), was exposed to fresh *n*-heptane before the start of the time study. The data collected in Table I show that ϕ decreases monotonically with τ from $\phi = 0.55$ at $\tau = 0.5$ hrs to $\phi = 0.01$ at $\tau = 72$ h, which means that replacement of entrapped toluene by *n*-heptane *via* solvent exchange does indeed occur, albeit at a relatively slow rate. It was inferred from these results that adsorption-partitioning favors toluene ($\alpha = 1.98$) overwhelmingly over *n*-heptane ($\alpha \leq 0.01$) such that the mole fraction of toluene (ϕ) adsorbed to the polymer may be as high as $\phi \geq 0.9$, even though the toluene volume fraction (z) in the sorbed liquid, with which the adsorbed molecules are presumably in equilibrium, may be as low as $z \leq 0.01$.

Additional evidence that supports this adsorption-partitioning hypothesis was obtained in another experiment, in which the mole fraction (ca. 0.002) of methylcyclohexane (b.p. 101°C) added to the sorbed *n*-heptane solution (b.p. 98°C) that had replaced completely the presorbed toluene, was compared to the mole fraction (0.08) of methylcyclohexane in the residual adsorbed molecules remaining after that PS-L system was evaporated to the glassy

state. These "before and after" adsorption compositions (0.002 *vs* 0.08) show that the methylcyclohexane mole fraction adsorbed to the polymer was about 40-fold greater than the corresponding fraction in the non-adsorbed molecules that comprise the sorbed liquid. The boiling points of these two liquids differ by only 3°C, and thus, differential evaporation is negligible. Therefore, the observed enrichment must be attributable to the greater affinity of methylcyclohexane ($\alpha = 0.32$) for polystyrene relative to that of *n*-heptane ($\alpha \leq 0.01$).

The above multireplicated time studies of evaporation were carried out under conditions that did not preclude sample shrinkage, which the latter is known^{2,3} to complicate, if not obfuscate, the kinetics that infer sequential changes in macro-molecular architecture during evaporation from a PS-L in its rubbery state. Therefore, equivalent time studies were carried out subsequently¹⁴ under conditions that did preclude sample shrinkage to provide firm evidence concerning the possibility that most of the associated polymer, produced via *n*-heptane-induced polymer-polymer association (Figs. 1 to 4 of ref. 1), may have undergone the transition from the rubbery to the glassy state before the start of the time-study.

Accordingly a set of four (Sty)_{1-x}(DVB)_x composite film samples (Table II) were swelled to saturation in toluene and then deswelled "to saturation" in enough *n*-heptane to contain < 0.1% desorbed toluene at the end state. The samples were extracted with fresh *n*-heptane for an additional two days [to ensure removal of at least 98% of the adsorbed toluene molecules that were present at $\tau = 0$ (Table I)] before starting the time study of evapo-

Table II Evaporation Turn *n*-Heptane-Saturated (Sty)_{1-x}(DVB)_x Samples Under Conditions that Preclude Sample Shrinkage

#	x	w	τ	α'	α_g	α_t	ϕ_t	Log k_0	m
1	0.02	1.8901	72	0.353	0.140	0.041	0.006	0.75	0.69
2	0.02	1.8878	48	0.241	0.116	0.060	0.020	0.32	0.61
3	0.02	1.3100	48	0.228	0.139	0.052	0.021	0.32	0.78
4	0.08	1.7684	72	0.221	0.115	0.042	0.005	0.32	0.69
Ref	0.01 to 0.11	ca. 1.0	—			ca. 0.03	1.0	-0.31	0.76

= identification run-number of the time study.

x = DVB mole fraction in the sorbent sample.

w = weight in grams of the composite sample (20% by weight PTFE).

τ = time in hours of extraction before starting the time-study.

α' = α_t at the completion of the interval for elimination of non-adsorbed molecules. In these studies $\alpha' = 0.26 \pm 0.05$.

α_g = α_t at the completion of the transition from the rubbery state to the glassy state. In these studies $\alpha_g = 0.13 \pm 0.01$.

α_t = α_t at termination of the time-study.

ϕ_t = mole fraction of toluene in the residual sorbed molecules at the termination of the time-study.

Log k_0 = Intercept for eq. (4) at $i = 0$. In these studies it is 0.32 ± 0.04 (ignoring Run No. 1).

m = decrementation constant in eq. (4). In these studies it is 0.69 ± 0.06 .

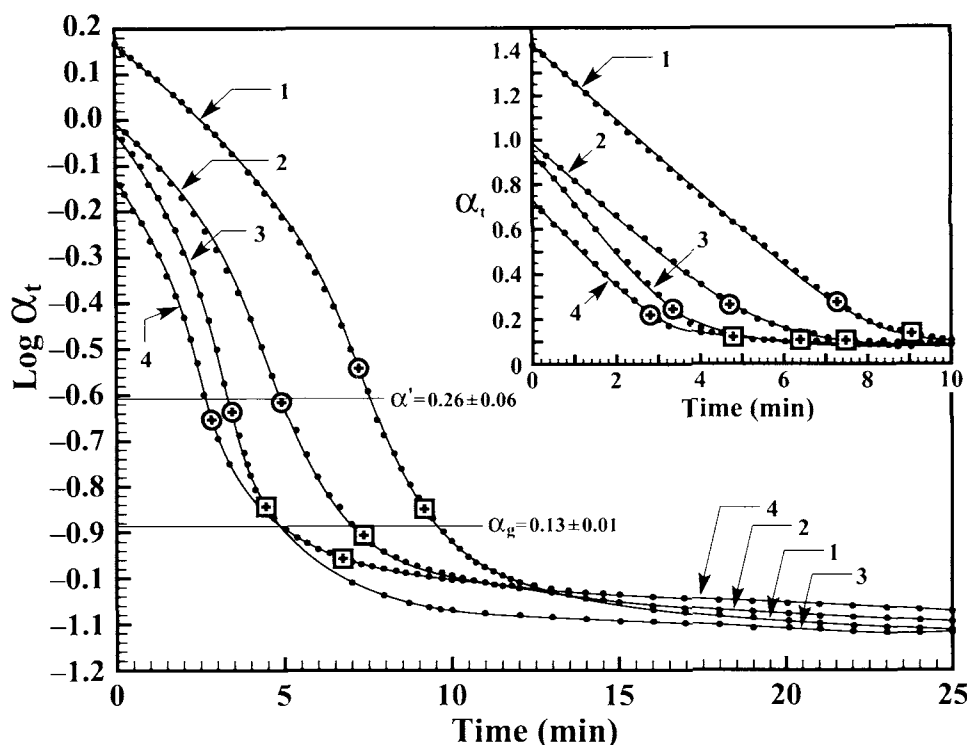


Figure 1 Correlations of α_t and $\text{Log } \alpha_t$ with time (in minutes) for evaporation from *n*-HEPTANE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples that had been swelled to saturation in toluene and then solvent exchanged by *n*-heptane.

ration as described in the Experimental section. The α_t -data (in molecules of *n*-heptane per phenyl group of polymer), collected during only the first 25 minutes of these time studies (which were continued for an additional 5 to 138 h) are recorded in Figure 1. It is seen that in each case (a) the kinetics of evaporation follows zero-order until the weight of the residual sorbed molecules is about 10% of that at liquid saturation, and (b) thereafter the pattern for evaporation resembles those for elimination of residual trapped molecules from a PS-L system in its glassy state, i.e., α_t is given by a linear combination of exponential decay functions,⁴⁻⁹ which represent the sum of the contributions to the overall rate of elimination from *n* (not more than six) populations of trapped molecules, as expressed by eq. (3).

$$\alpha_t = \alpha_g \sum_{i=1}^n f_i e^{-k_i t} \quad (3)$$

Here α_g is the composition that marks the start of the glassy state, k_i is the rate constant for decay of the *i*th population, f_i is the fraction of α_g (i.e., $\alpha_{i,g}/\alpha_g$) trapped in the *i*th population, and *i* is the identification number of the population in the order of decreasing rate k_i .

Equation (3) implies that the nature of the glassy state, produced *via* evaporation of a PS-L system to apparent dryness, can be characterized by the values for the constants α_g , f_i , k_i , and *i*. The value of α_g (Table II; see also Table 8 of ref. 15, the third in this set of three companion articles) is determined from the first in the set of data points that define the kinetics for elimination from the population having the fastest decay rate ($i = 1$), after sequential subtractions of contributions from the other populations starting with the one having the slowest decay rate (i.e., $i = n$), as has been described previously.^{4a} Each of the set of four α_g -values (0.13 ± 0.01) is marked in Figure 1 by a cross in a square (\boxtimes).

The data collected in Table II of ref. 14 also show that incipient elimination of adsorbed molecules (α') occurred at $\alpha_t = 0.26 \pm 0.06$. This set of α' -values are marked by a cross in a circle (\oplus) in both the α_t vs. *t* and the $\text{Log } \alpha_t$ vs. *t* plots recorded in Figure 1. The difference ($\alpha' - \alpha_g$) represents the total loss in weight owing to evaporation of sorbed volatile molecules from both the fraction (ψ) of the PS-L system that is still in its rubbery state and the fraction ($1 - \psi$) already converted to the glassy state, during the interval that ψ decreased from ψ' at α' to 0 at α_g . Because the differences ($\alpha' - \alpha_g$), noted in Figure

1, are relatively small (i.e., $\Delta\alpha = \text{ca. } 0.13$), it is suspected that value of ψ and α' in these cases is < 0.1 ; i.e., most of the polymer in the PS-L system that underwent *n*-heptane-induced polymer-polymer association (see Fig. 4 of ref. 1) had already undergone transition to the glassy state before α_i had decreased to α' (and perhaps even before the start of the evaporation). Continued evaporation caused ψ to decrease from ca 0.1 to α' to 0 at α_g , at which point the residual molecules are trapped in *n* (not greater than 6) different glassy molecular environments, such that $(\sum \alpha_{i,g}) = \alpha_g$, where α_i is the portion of α_g in the *i*th population.

We showed^{4,9} that the logarithms of the rate constants k_i , for decay of each population in a given

set of populations, decrease incrementally with *i* in accordance with eq. (4).

$$\text{Log } k_i = \text{Log } k_0 - mi, \quad (4)$$

Here $\text{Log } k_0$ and *m* are constants characteristic of the system. In the case of toluene-saturated polystyrene systems (bold straight line in Fig. 2), the values of these constants are $-0.31 \pm 0.02\sigma$ and $0.76 \pm 0.01\sigma$, respectively.^{3,4} This reference line was used as the basis for comparison with the corresponding sets of k_i -values observed for elimination of *n*-heptane from PS-L systems that had been exposed temporarily to toluene (time studies 1 to 4 in Fig. 1). The data collected in these four time studies are

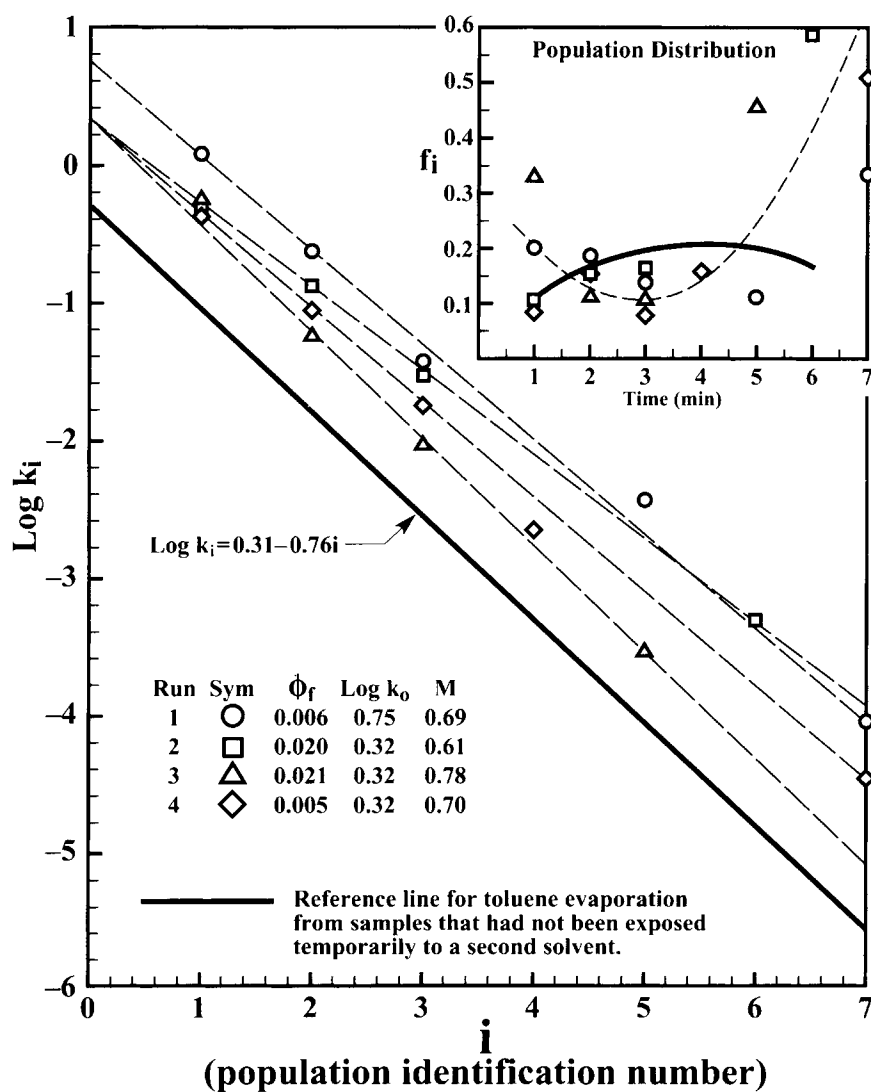


Figure 2 Correlations of $\text{Log } k_i$ and f_i with *i* for evaporation from *n*-HEPTANE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples (Fig. 1) that had been swelled to saturation in toluene and then solvent exchanged by *n*-heptane.

recorded in Figure 2, where they are identified by the symbols \circ for #1, \square for #2, \triangle for #3, and \diamond for #4. The average decrementation constant [m ; eq. (3)] for the four *n*-heptane relationships is $m = 0.69 \pm 0.06$ and the corresponding average intercept at $i = 0$ is $\text{Log } k_0 \pm 0.32 \pm 0.004\sigma$ (Table II; this average does not include the value recorded for run #1 because it is more than twice that of the values for each of the other three and it is far outside the variance in this average). This average value of m is virtually within experimental reproducibility of the average m for toluene, but the average $\text{Log } k_0$ value is well above the average $\text{Log } k_0$ for toluene. These observations are interpreted to mean that the molecular architecture of the polymeric "cage" for an entrapped "guest" molecule in the polymeric inclusion complex⁸ is essentially the same in both cases, and that the difference between the observed k_0 -values reflects the relative ease with which *n*-heptane and toluene molecules can escape from such "cage"-like structures (see Figs. 12 and 13 of ref 8). It is presumed that the molecular architecture of a polymeric inclusion complex will vary with the nature of the solvent chosen to preswell the polymer before *n*-heptane-induced polymer-polymer association. This assumption, however, has not yet been verified by experiment.

The history of the PS-L system prior to evaporation-induced transition to a glassy state can also affect the distribution of the fractions ($f_i = \alpha_{i,g}/\alpha_g$) of entrapped molecules at α_g . Unlike the $\text{Log } k_i$ vs i relationship [eq. (4); Fig. 2], however, f_i does not vary monotonically with i . Such correlations (Figs. 9 to 11 of ref. 3) usually show maximal f_i -values averaging 0.23 (but ranging from 0.1 to 0.4) at $i = 3$ or 4, minimal f_i -values averaging 0.10 (but ranging from 0.05 to 0.2) at $i = 1$ and 6 and intermediary f_i -values averaging 0.16 (but ranging from 0.10 to 0.3) at $i = 2$ and 5. The large variance in the f_i data for a given population created during the transition interval was presumed to be attributable to unknown factors that affect the poorly understood transition from the rubbery state of a PS-L system to a glassy state. The average f_i distribution pattern, exhibited by about 20 PS-L systems exposed only to toluene before the start of evaporation to dryness, is shown in the inset of Figure 2 (the bold line that is concave downward). The corresponding f_i data for the four PS-L systems, which were deswelled "to saturation" in *n*-heptane before the start of the time study, are also recorded in the inset of Figure 2, which show typical large variances in the f_i data. Nevertheless, an unusually skewed f_i distribution in favor of populations with the much slower decay rates (namely

$i = 5$ or 6 or even 7) is unmistakable as indicated by the dashed line through the combined data sets, which implies a concave upward relationship of f_i to i , such that f_i may be minimal at $i = 3$ instead of maximal.

The above results show clearly that the kinetics of evaporation from a PS-L system that had undergone *n*-heptane-induced polymer-polymer association is affected by the history of that sample prior to the start of the time study. It is presumed that this may also be true for other PS-L systems produced via liquid-induced phase separation. The manner in which it is affected, however, depends on the liquid chosen to induce phase separation, as indicated in the following subsections.

Methanol-Induced Polymer-Polymer-Associated Systems

The results observed in our swelling and deswelling studies using six PS-L systems that were cycled from saturation in methanol to saturation in toluene and back to methanol are recorded in Figures 5 to 8 in ref. 1. These results are qualitatively similar to the corresponding studies observed using *n*-heptane, which are recorded in Figures 1 to 4 in ref. 1. Both studies show that more than 50% of the solvated polymer underwent liquid-induced polymer-polymer association as the volume fraction (z) of toluene in the sorbed binary solution was decreased incrementally from $z = 1$ to $z = 0$. The proportion of the PS-L system that underwent polymer-polymer association varied inversely with the cross-link density (i.e., inversely with x in the $(\text{Sty})_{1-x}(\text{DVB})_x$ sample).

The kinetics of methanol evaporation from each of the six liquid swollen samples, which were monitored before and after temporary saturation in toluene as described in the Experimental section, were also qualitatively similar to the results noted in the studies of *n*-heptane evaporation, i.e., before temporary exposure to toluene, the kinetics of evaporation followed zero-order [eq. (1)] from the start of the time study at $W_t = \text{ca } 1.0$ (in grams of sorbed molecules per gram of polymer) to virtual dryness, which in the case of methanol evaporation was attained within 20 minutes. After temporary exposure to toluene, the kinetics of methanol evaporation followed zero-order only down to $W_t = \text{ca } 0.3$. Thereafter the rate of evaporation decreased sharply, and the kinetics with respect to residual W_t was similar to that for elimination of adsorbed molecules from a PS-L system undergoing evaporation-induced transition from its rubbery to a glassy state, such

that W_t did not decrease below 0.02 even after 24 h, at which point the time studies were terminated to permit collection and analysis of the residual adsorbed molecules, as described previously. The analytical data obtained thereby showed that the mole fraction (ϕ_f) of toluene in the residual adsorbate at termination was $\phi_f = 0.99$. It was again noted, however, that ϕ_f varies with the time (τ) that the set of six methanol-saturated samples were post-extracted continuously in fresh methanol; in this case ϕ decreased from 0.99 at $\tau = 2$ hrs to 0.01 at $\tau = 2$ days. In these runs sample shrinkage was permitted to occur.

As above, additional time studies were carried out six years later on individual samples under conditions that precluded sample shrinkage, as described in the Experimental section.¹⁴ Accordingly four composite film samples (Table III), comprised of $(\text{Sty})_{1-x}(\text{DVB})_x$ particles (80% by weight) enmeshed in PTFE microfibers, were swelled to saturation in toluene and then deswelled "to saturation" in methanol, the volume of which was such that the amount of desorbed toluene at the end state was not more than 0.1%. Three of the four samples were then extracted in fresh methanol for only 2 h (Runs No. 1, 3, and 4; Table III) to ensure minimal elimination of residual adsorbed toluene molecules, and only one (Run No. 2) was extracted in fresh methanol for an additional 48 h to ensure elimination of almost all of the residual adsorbed toluene. The kinetics of methanol evaporation from each of these samples was monitored at 23°C from saturation to virtual dryness over 1 to 5 days at which point the time-study was terminated to permit determination of ϕ_f at the final data point as described in the Experimental section.

Most of the W_t data recorded in these time-studies were not converted to the corresponding α_t -values by means of eq. (1) because the residual sorbed molecules that were eliminated below $W_t = W'$ contained an unknown small amount of toluene, the mole fraction (ϕ_t) of which increased as W_t decreased to zero. Since the formula weight of methanol (32) is about one-third of that for toluene (92), the corresponding true α_t would be significantly less than the calculated value (based on M in eq. (1) having the value for methanol) by the magnitude of ϕ_t for the residual sorbed molecules at the corresponding W_t . The W_t data for the first 100 min of these time studies are recorded in Figure 3; in addition the values of W_t at W' , W'_g , and W_g are recorded in Table III (see also Table 3 of ref. 15). The approximate α_t -values (see above caveat) for the corresponding average values of W_t at W' , W'_g and

W_g are recorded in Figure 3 for the sake of convenience in following the nature of the elimination relative to those reported in the other time studies. These data (Table III) show that incipient elimination of adsorbed molecules (W') occurred at $W_t = 0.48 \pm 0.12$ (i.e., $\alpha' = \text{ca. } 1.6$). The respective W'_t -values are marked by a cross in a circle (\oplus) in both the W_t vs. t and the $\text{Log } W_t$ vs. t plots for each of the four time studies recorded in Figure 3. The corresponding W_g -values ($W_t = 0.017 \pm 0.006$; i.e., $\alpha_g = \text{ca. } 0.06$) are marked in Figure 3 by a cross in a diamond (\diamond).

The respective differences [$(\alpha' - \alpha_g) = \Delta\alpha$] represent the sum of the molecules eliminated from both the fraction (ψ) of the PS-L system not yet converted to a glassy state and the complementary fraction ($1 - \psi$) already converted to the glassy state, during the interval that ψ decreased from ψ' at α' to 0 at α_g . In these cases of methanol evaporation, the magnitude of such differences is about $\Delta\alpha = 1.5$, which is considerably greater than that ($\Delta\alpha = 0.13$) noted for *n*-heptane evaporation. Indeed, it approaches the magnitude of $\Delta\alpha$ noted in PS-L systems that do not have a history of liquid-induced polymer-polymer association. We inferred from this observation that ψ' at α' , in the case of methanol evaporation, is close to unity. In the case of *n*-heptane evaporation, ψ' at α' is < 0.1 , i.e., most of the PS-L system involved in liquid-induced phase separation in the case of *n*-heptane underwent transition to a glassy state before the system had evaporated to $W_t = W'$, whereas in the case of methanol most of the associated polymer was still in its rubbery state.

The pattern of methanol evaporation, exhibited during the subsequent interval required for α_t to decrease from α' to α_g (Fig. 3), is also consistent with this point of view. The kinetics, during the first part of the interval, was first-order, owing to elimination of adsorbed molecules from the PS-L system in its rubbery state; whereas the kinetics during the second part, beginning at $\alpha_t = \alpha'_g$, gave the appearance of changing continuously. This results from evaporation-induced transition from its rubbery state to a glassy state, during which ψ is presumed to decrease from unity at $\alpha_t = \alpha'_g$ to 0 at $\alpha_t = \alpha_g$. The data of Table III show that the value of W_t at incipient transition to the glassy state (W'_g), which was signaled by a sharp decrease in the instantaneous rate of change in $\text{Log } W_t$ (Fig. 3), was $W'_g = 0.185 \pm 0.002\sigma$ (i.e., $\alpha'_g = \text{ca. } 0.60$). In the calculation of this average, the W'_g -value observed in Run No. 1 was omitted because it is almost twice that of each of the other three, and it is far outside of the variance

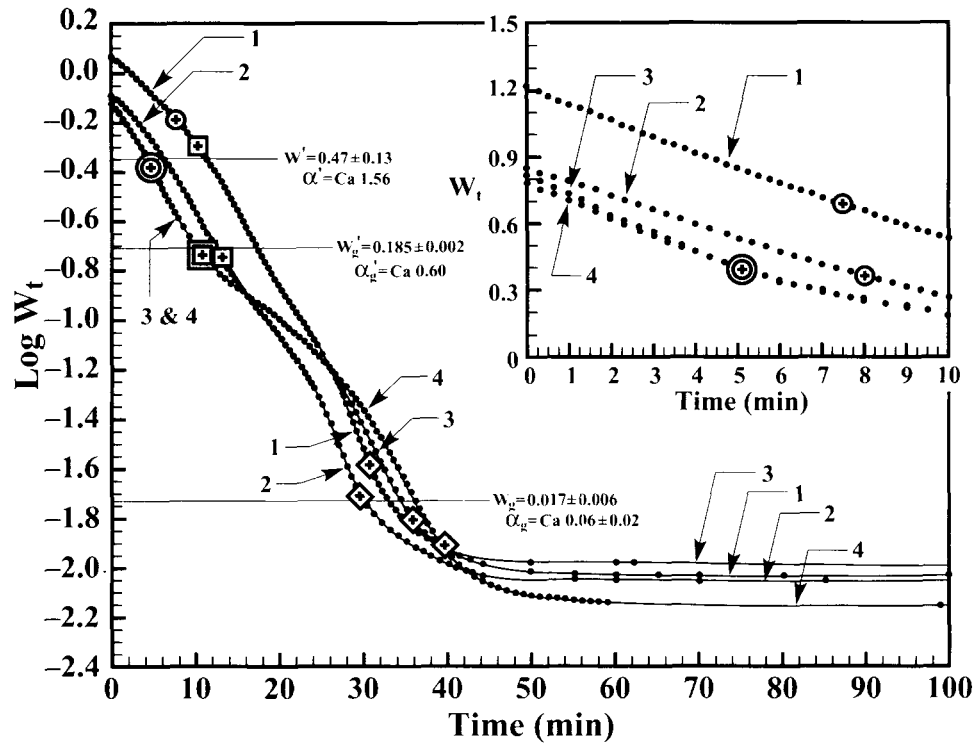


Figure 3 Correlations of W_t and $\text{Log } W_t$ with time (in minutes) for evaporation from METHANOL-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples that had been swelled to saturation in toluene and then solvent exchanged by methanol.

noted for these data. The respective W'_g -values for each of the four time studies of evaporation, however, are marked in Figure 3 by a cross in a square (\boxtimes).

The interval of first-order kinetics for elimination of methanol molecules exhibited between W' and

W'_g (Fig. 3) is consistent with the usual patterns for elimination of adsorbed molecules from the rubbery state of PS-L systems before incipient transition to the glassy state (W'_g), but the pattern exhibited subsequently between W'_g and W_g (Fig. 3) is anomalous. The patterns exhibited during the in-

Table III Evaporation from Methanol-Saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ Samples that had been Presaturated in Toluene and then Solvent Exchanged by Methanol

#	x	w	τ in hrs	W_0	W'	W'_g	W_g	W_f	ϕ_f
1	0.02	1.8868	2	1.2216	0.692	0.513	0.0251	0.0092	0.99
2	0.02	1.8734	48	0.8577	0.182	0.182	0.0203	0.0090	< 0.01
3	0.02	1.2943	2	0.8397	0.413	0.186	0.0133	0.0088	0.99
4	0.08	1.5319	2	0.7906	0.414	0.186	0.0107	0.0063	0.99

#, x , w , τ , and ϕ_f are as defined in Table II.

W_0 Initial weight of sorbed liquid in grams per gram of polymer sample.

W' Weight of residual sorbed molecules per gram of polymer sample at incipient elimination of adsorbed molecules from the PS-L system in its rubbery state. $W' = 0.48 \pm 0.12$ ($\alpha' = \text{ca. } 1.56$).

W'_g Weight of residual sorbed molecules per gram of polymer sample at incipient transition from the rubbery state to the glassy state. $W'_g = 0.185 \pm 0.02$ (excluding run No 1) ($\alpha'_g = \text{ca. } 0.60$).

W_g Weight of residual sorbed molecules per gram of polymer sample at the completion of the transition to the glassy state. $W_g = 0.017 \pm 0.006$ ($\alpha_g = \text{ca. } 0.06$).

W_f Weight of residual sorbed molecules per gram of polymer sample at the termination of the time study.

In this study, $\alpha_t = 3.25 W_t$ [see eq. (1)].

terval of evaporation-induced transition from the rubbery to the glassy state of PS-L systems that had not been exposed temporarily to a second liquid, are usually concave upwards (see Fig. 2 of ref. 8), owing to a continuously decreasing rate of evaporation from the PS-L system, which reflects the corresponding decrease in ψ from 1 at $W_t = W'_g$ to 0 at $W_t = W_g$. The patterns exhibited during these intervals of evaporation-induced transition, in the case of methanol evaporation from PS-L systems that had been exposed temporarily to toluene (Fig. 3), are concave downward. This means that although the rate of elimination was decreasing as expected during the first part of the evaporation-induced transition interval, it changed (uncharacteristically) to *increasing* during the second part of that interval. Presumably this anomalous behavior is attributable in some way to the history of temporary exposure to toluene.

The constants α_g , f_i , k_i , and i that characterize evaporation of residual toluene molecules from a PS-L system in a glassy state [as expressed by eq. (3)] differ for PS-L systems exposed only to toluene from those exposed to methanol-toluene solutions. Thus, α_g for the latter system is $0.143 \pm 0.02\sigma$ (Table 2 in ref. 4a), whereas that for the former system is ca. 0.06 (Fig. 3 and Table III), which surprisingly resembles that expected for PS-L systems that had been swelled to saturation in a relatively poor solvent (i.e., one with α ca. 0.09) rather than one swelled to saturation in a relatively good solvent, such as toluene ($\alpha = 1.98$), despite that toluene was the major component ($\phi = 0.99$) of the residual molecules trapped in the glassy state in the "two-hour" samples of Table III.

Similarly, as shown in Figure 4, the sets of k_i -values observed for decay of the molecular populations trapped in the glassy state of the above two types of PS-L systems differ significantly. The average k_i -values, observed in more than twenty time studies of toluene evaporation from PS-L systems that had been swelled to saturation only in toluene,⁴⁻¹⁰ fall on the bold straight line drawn in Figure 4 [eq. (4) the constants $\text{Log } k_0$ and m of which are $-0.31 \pm 0.02\sigma$ and $0.76 \pm 0.01\sigma$, respectively]. In contrast, the set of k_i -values observed for the present set of four time studies of evaporation from PS-L systems that had been swelled to saturation in toluene and then solvent-exchanged by methanol (Table III; Fig. 4) fall along a line that is uniformly above the reference line, i.e., the $\text{Log } k_0$ and m constants that quantify eq. (4) for the methanol-treated systems are 0.3 and 0.85, respectively (Fig. 4). This is interpreted to mean that the rate

of escape of entrapped toluene molecules (Runs No. 1, 3, and 4; Table III) from the "cages" created in the presence of methanol-toluene solution is about 4 times faster than that from the corresponding "cages" created in the presence of toluene alone.

It is interesting to note that the set of k_i -values for the escape of methanol molecules, which had replaced the former caged inhabitants (i.e., toluene molecules) by solvent exchange (Run No. 2; Table III), fall within experimental reproducibility on the line that represents the $\text{Log } k_i$ vs. i relationship (Fig. 4) established by the toluene data (Runs No. 1, 3, and 4). It is inferred from this observation that the architecture of the "cage," self-assembled during liquid-induced polymer-polymer association, shrinks uniformly, during evaporation-induced transition to the glassy state, to conform to the shape and "bulkiness" of the "guest" molecule entrapped therein.

This may also be true in the case of *n*-heptane-induced polymer-polymer association, discussed above. The progressive increase in the range of k_i -values at a given i as i increases, observed in the case of *n*-heptane (Fig. 2) relative to that noted in the case of methanol (Fig. 4), might reflect the corresponding extents to which the respective self-associated polymer had undergone transition to its glassy state before the start of the evaporation to dryness.

The fractional (f_i) distribution of the entrapped populations at $\alpha_t = \alpha_g$, over the range of populations $i = 1$ to n , is also affected markedly by the history of the PS-L system, as noted earlier in the case of *n*-heptane (inset of Fig. 2) and now in the case of methanol (inset of Fig. 4). The average distribution of entrapped molecules obtained when a PS-L system is saturated with toluene and then evaporated to dryness is indicated by the bold curved line having a maximal f_i -value of ca. 0.20 at $i = 3$ to 5. By way of contrast, the distribution of entrapped molecules obtained in this methanol-exchanged set of four time-studies of evaporation, show a minimal value of $f_i =$ ca. 0.02 at $i = 3$, and maximal values of $f_i \geq 0.4$ at $i = 1$ and 6, as indicated by the U-shaped dashed line that passes through the band of f_i -data points recorded in the inset of Figure 4.

We inferred from these results (insets in Figs. 2 and 4) that the "cage"-like structures of the "guest-host" complexes having designations $i > 4$ may have been formed while the macromolecular "host" component of the PS-L system still had the necessary mobility to adjust to the shape and size of the "guest" molecule, much in the manner that the coils of a boa-constrictor conform to the shape and size of its

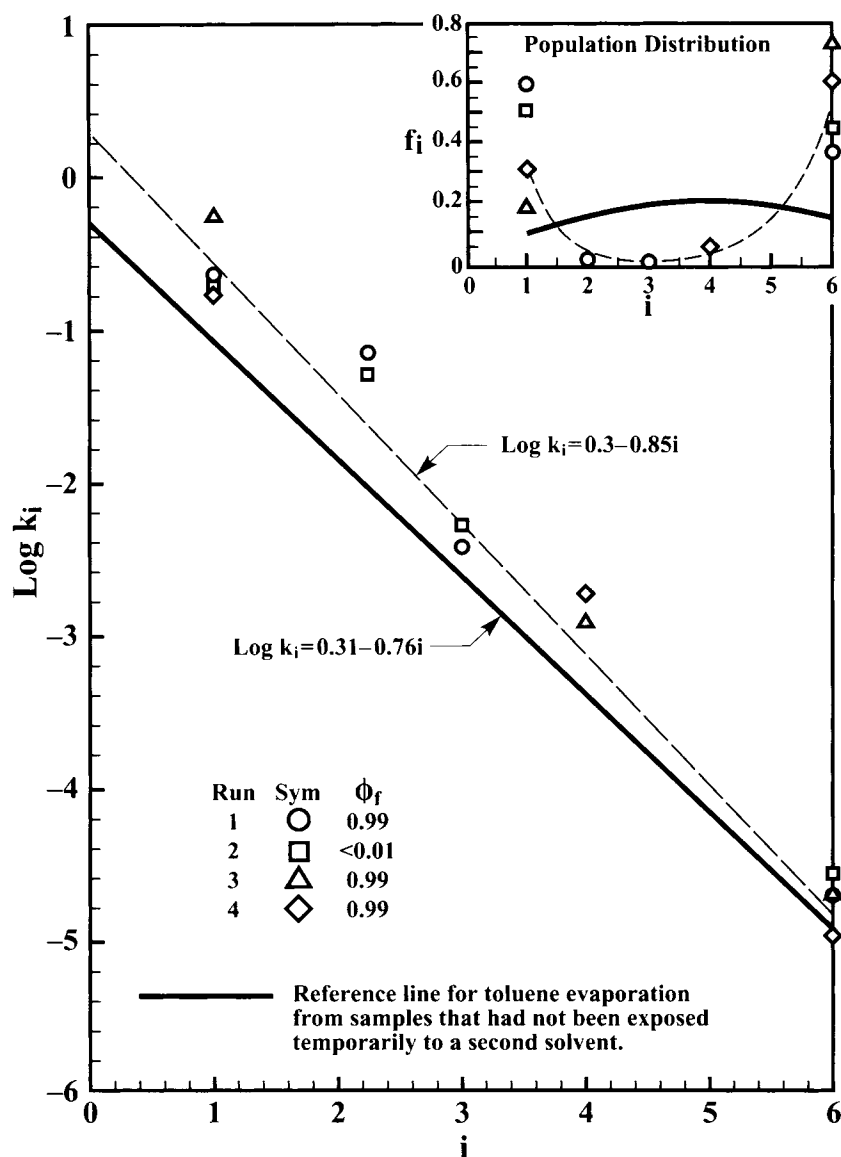


Figure 4 Correlations of $\text{Log } k_i$ and f_i with i for evaporation from METHANOL-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples (Fig. 3) that had been swelled to saturation in toluene and then solvent exchanged by methanol.

prey. This relatively "loose" architecture of the "host" polymer, which was self-assembled around the "guest" nucleus, tightens subsequently to a rigid assembly as the PS-L system undergoes evaporation-induced transition to a glassy state, in which the polymeric inclusion complexes, produced during liquid-induced polymer-polymer association, are distributed randomly.

Others¹⁶ who studied thermally induced phase separations from polymer solutions have shown that "host"-polymer-"guest"-molecule complexes are indeed formed, when polymer solutions are cooled to well below room temperature. Apparently seg-

ments of the solvated polymer produce microdomains of self-associated polymer that contain entrapped adsorbed molecules. These microdomains serve as quasi-crosslinkages which impart physical integrity to the liquid-saturated gel structure. Guenet¹⁷ showed that, in the cases of solvated isotactic polymer, these microdomains of self-associated polymer resemble liquid-crystalline assemblies, which are comprised initially of solvated polymer segments in the form of structured helices that are "supported" by entrapped solvent molecules. He showed that the ratio ($\bar{\alpha}$) of these entrapped molecules to polymer repeat units is characteristic of

the solvent-polymer solution that had been caused to undergo thermally induced gel formation. We noted¹⁸ that the $\bar{\alpha}$ -values reported by Guenet for 18 PS-L systems correlate linearly with the α -values reported by us for the corresponding cross-linked forms of these PS-L systems at liquid saturation.

Evaporations from Nonassociated PS-L Systems

The results reported above show that when a PS-L system is pre-swelled to saturation in toluene and then deswelled by solvent exchange "to saturation" in a much "poorer" solvent, such as *n*-heptane or methanol, which cause liquid-induced polymer-polymer association, the kinetics of evaporation to dryness thereafter is qualitatively different from that exhibited by the same PS-L system that was not preswelled to saturation in toluene. This section reports the results of experiments that were designed to test whether or not the same is true when a toluene-saturated (Sty)_{1-x}(DVB)_x sample is solvent-exchanged in like manner but by a solvent that has much greater affinity for polystyrene than *n*-heptane or methanol, and therefore does not cause the liquid-induced polymer-polymer association observed in the aforementioned cases. Acetone and chloroform are two solvents that are suitable for such a test.

The kinetic data observed for evaporation from the set of six liquid-swollen (Sty)_{1-x}(DVB)_x samples, under conditions that did not preclude sample shrinkage during the transition interval, failed to provide evidence of carryover effects from the toluene-saturated gel state, despite the history effects were clearly manifested in the studies of (Sty)_{1-x}(DVB)_x swelling in acetone-toluene solutions (see Figs. 9 to 11 in ref. 1) and in chloroform-toluene solutions (see Fig. 12 in ref. 1). The evaporation-to-dryness patterns obtained thereby appeared to be essentially the same as those reported earlier for acetone and for chloroform evaporations (Figs. 3 and 2, respectively, in ref. 3) from the liquid-saturated (Sty)_{1-x}(DVB)_x samples that had *not* been preswelled to saturation in toluene. Moreover, gas chromatographic analysis of the residual adsorbed molecules, after the PS-L systems had attained a glassy state, indicated that all of the adsorbed toluene molecules had been replaced *via* solvent exchange before the start of their respective time studies, contrary to the findings when *n*-heptane or methanol was used to replace toluene.

Similar negative results also were noted for toluene evaporation from the set of six (Sty)_{1-x}(DVB)_x samples that had been preswelled to saturation in

chloroform and then solvent-exchanged by toluene. The evaporation patterns obtained thereby under the above conditions were essentially the same as those reported for toluene evaporation from the same set of six samples that had not been exposed temporarily to chloroform (Fig. 1 of ref. 3). Again, analysis of the adsorbed molecules remaining at the termination of the time studies indicated that all of the adsorbed chloroform molecules had been replaced by toluene molecules before the start of evaporation to dryness.

Positive results were indeed obtained, however, when elimination of volatile test molecules was monitored carefully under conditions that precluded sample shrinkage during the evaporation-induced transition from the rubbery state to the glassy state. There was evidence of "memory" effects carried over from the binary liquid-swollen gel state in each case, as outlined in the following subsections.

Acetone Systems

The desorption pattern exhibited during the transition interval of this time study (Fig. 5), was concave downward, i.e., the instantaneous rate of change in $\text{Log } \alpha_t$ was increasing with time in the manner observed in the study of methanol evaporation (Fig. 3) from the same poly(Sty-co-DVB) sample that had been exposed temporarily to swelling in toluene. By way of contrast, the pattern of evaporation from an acetone-saturated (Sty)_{1-x}(DVB)_x sample that had *not* been subjected to preswelling in toluene is usually concave upward to form a curve with continuously decreasing slope that joins smoothly to the data for desorption from the glassy state, as noted in Figure 2 of ref. 4a. The values observed for α_t at α' , α'_g , and α_g (Table IV) at $t = 3.5, 6.0,$ and 22.5 minutes respectively (Fig. 5) do agree reasonably well with the corresponding average values (Table IV) observed for acetone evaporations from liquid-saturated samples that had not been preswelled in toluene.

The kinetics of evaporation from this PS-L sample in its glassy state, as expressed by eq. (7), was unmistakably different from those that had not been preswelled in toluene. Thus, the linear $\text{Log } k_i$ vs. i relationship [eq. (4)] for decay of the molecular populations trapped in the glassy state of the PS-L system in this experiment (Fig. 6; Table IV) is uniformly below and almost parallel to that (indicated by the bold straight line in Fig. 6) established for elimination of residual acetone molecules trapped in the glassy state of PS-L systems that had *not*

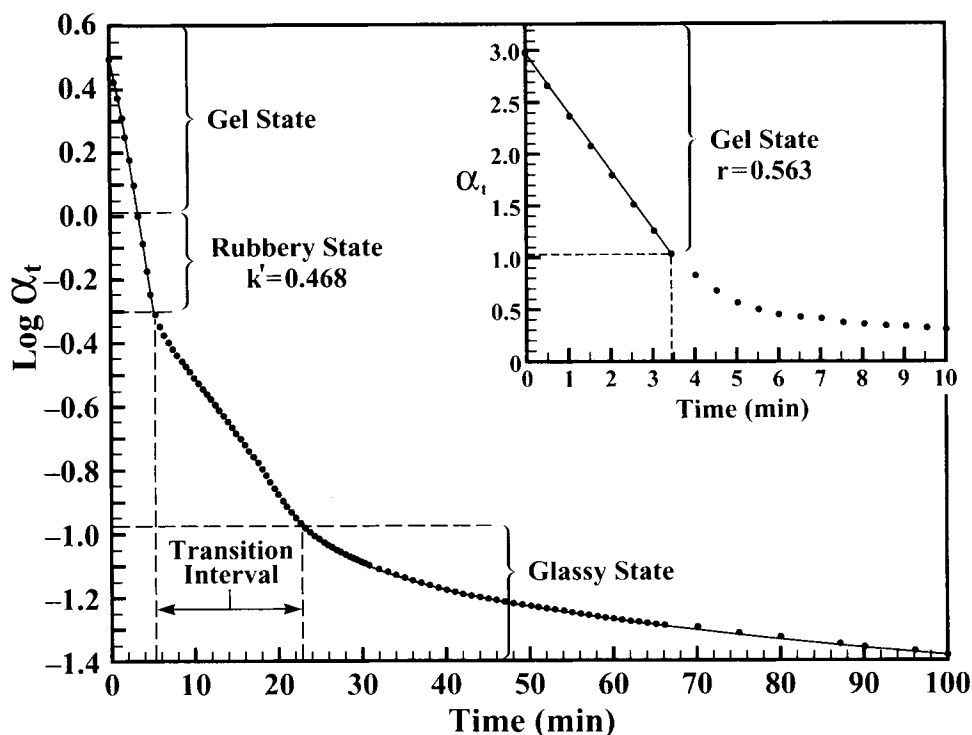


Figure 5 Correlations of α_t and $\text{Log } \alpha_t$ with time (in minutes) for evaporation from an ACETONE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample that had been swelled to saturation in toluene and then solvent exchanged by acetone.

been preswelled in toluene (Table IV; see also Fig. 8 of ref. 4a). The observed difference in the respective $\text{Log } k_0$ values recorded in Table 4 imply that the rate of escape of acetone molecules from the cage structures, self-assembled in the presence of acetone-toluene solutions, is about half that for es-

cape from the corresponding cage structures, which had been self-assembled in the presence of pure acetone.

The population distribution pattern (f_i vs. i ; inset of Fig. 6) appears to indicate a slight shift in favor of the populations with slower decay rates (i.e., i

Table IV Comparison of α' , α'_g , and α_g -Values for Evaporation from Acetone-, Chloroform-, and Toluene-Saturated $(\text{Sty})_{0.98}(\text{DVB})_{0.02}$ Samples Before and After Preswelling Temporarily in a Second Good Solvent

Test Liquid	Preswell History	α'	α'_g	α_g	$\text{Log } k_0$	m
Acetone	none ^a	1.16	0.35	0.10	0.45	0.74
Acetone	Toluene	1.03	0.50	0.11	0.20	0.75
CHCl_3	none ^a	2.57	0.78	0.22	0.25	0.75
CHCl_3	Toluene	2.68	0.81	0.26	0.20	0.73
Toluene	none ^a	1.87	0.58	0.16	-0.31	0.76
Toluene	CHCl_3	1.53	0.58	0.13	-0.45	0.84

^a Data in this row are the averages of the respective quantities reported in earlier publications.³⁻⁵

History: Solvent in which the sample was preswelled temporarily

α' The composition that marks incipient elimination of adsorbed molecules (eq. (5) of ref. 1).

α'_g The composition that marks incipient transition from the rubbery to the glassy state (eq. (6) of ref. 1).

α_g The composition that marks the completion of the transition. (eq. (6) of ref. 1).

$\text{Log } k_0$ and m are the constants for eq. (4).

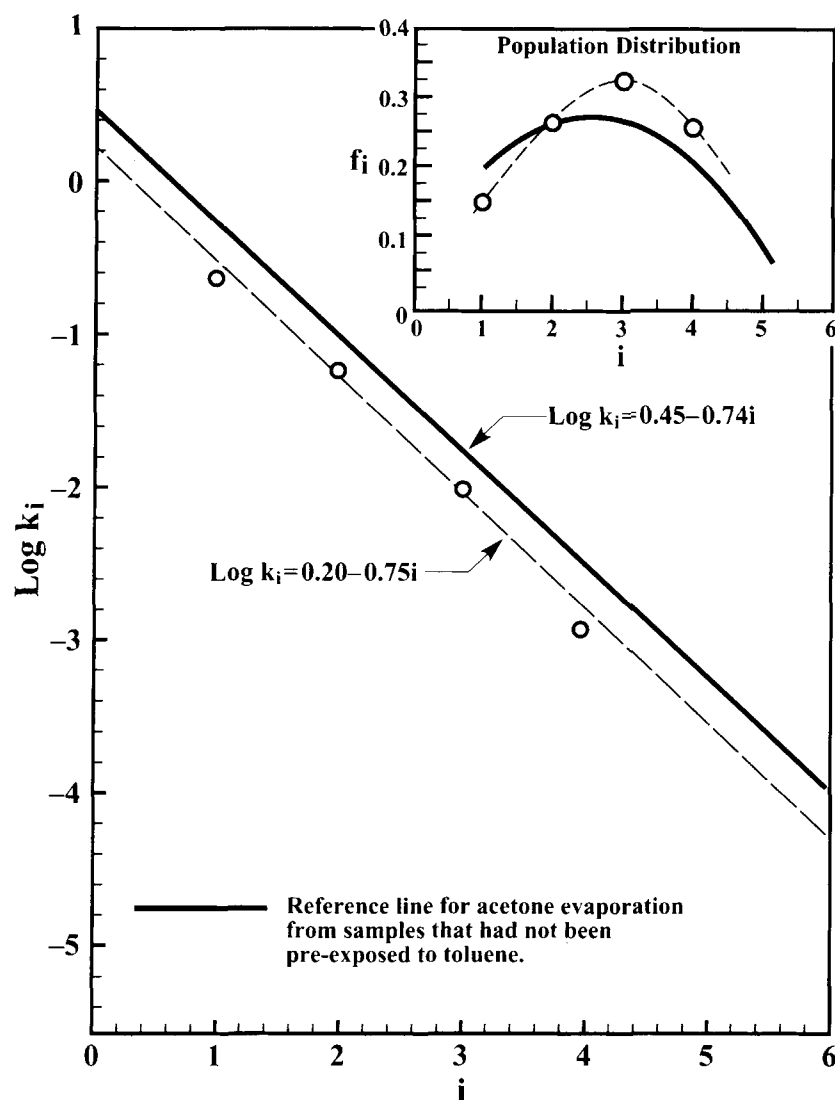


Figure 6 Correlations of $\text{Log } k_i$ and f_i with i for evaporation from an ACETONE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample (Fig. 5) that had been swelled to saturation in toluene and then solvent exchanged by acetone.

> 2). This conclusion may not be justified, however, in view of the large variances from the average f_i data points for a given population observed in the sets of multireplicated time studies, as already discussed.

The difference in the pattern exhibited during the transition interval (Fig. 5 vs. Fig. 2 of ref. 2a) and that noted in the $\text{Log } k_i$ vs. i relationships, recorded here in Figure 6, is attributed to the "memory" of this PS-L system in its liquid-saturated gel state, even when virtually all of the toluene used to preswell the system to saturation had been eliminated via solvent exchange in acetone before the start of the evaporation to dryness.

Chloroform Systems

The desorption pattern, exhibited during the transition interval of this time study (Fig. 7), was slightly concave downward, whereas the corresponding patterns, exhibited during the transition intervals of evaporation from chloroform-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples that had *not* been subjected to preswelling in toluene, are usually slightly concave upward to form a curve with continuously decreasing slope that joins smoothly to the data for desorption from the glassy state as noted in Figure 3 of ref. 4a. The values observed for α_i at α' , α'_g , and α_g (Table IV) at = 6.5, 11.0, and 28.0 minutes, respectively

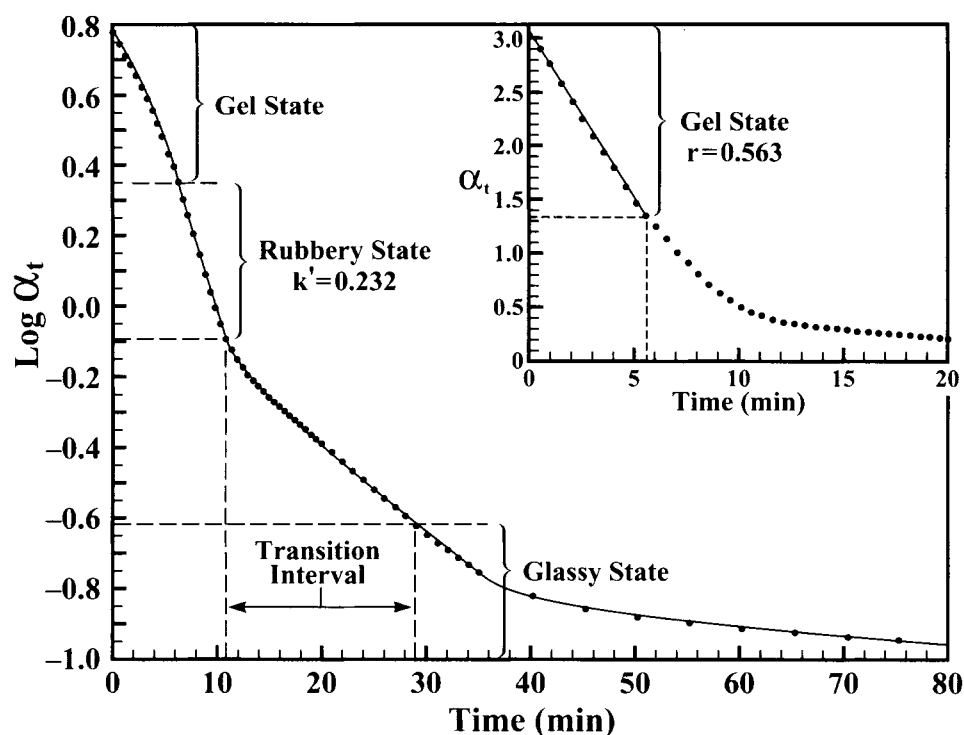


Figure 7 Correlations of α_t and $\text{Log } \alpha_t$ with time (in minutes) for evaporation from a CHLOROFORM-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample that had been swelled to saturation in toluene and then solvent exchanged by chloroform.

(Fig. 7), however, agree reasonably well with the corresponding average values (Table IV) observed for chloroform evaporations from liquid-saturated samples that had not been preswelled in toluene.

The kinetics of evaporation from this PS-L system in its glassy state, as expressed by eq. (7), was essentially the same as that exhibited by such PS-L systems that had *not* been preswelled to saturation in toluene. Thus, the linear $\text{Log } k_i$ vs. i relationship [eq. (4)] for decay of the molecular populations trapped in the glassy state of the PS-L system in this experiment (Fig. 8; Table IV) is essentially the same as that (indicated by the bold straight line in Fig. 8) established for elimination of residual chloroform molecules trapped in the glassy state of PS-L systems that had *not* been preswelled in toluene (Table IV; see also Fig. 8 of ref. 4a).

Moreover, the population distribution pattern (f_i vs. i ; inset of Fig. 8) also appears to be essentially the same as the average distribution pattern (bold curved line in the inset of Fig. 8) for systems that were not preswelled in toluene. This conclusion may not be justified, however, in view of the large variances from the average f_i data points observed in multireplicated time studies, as already discussed.

It is concluded that solvent exchange of toluene

($\alpha = 1.98$) by chloroform ($\alpha = 3.00$) served to erase most if not all "memory" of preswelling in toluene, presumably because the affinity of chloroform for polystyrene is greater than that of toluene.

Toluene Systems

In this study, the $(\text{Sty})_{1-x}(\text{DVB})_x$ sample was preswelled to saturation in chloroform and then deswelled "to saturation" in toluene before starting the time-study of evaporation to dryness. The desorption pattern exhibited during the transition interval of this time study (Fig. 9) is essentially the same as those exhibited during this interval of evaporation from toluene-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ samples that had *not* been subjected to preswelling in toluene (see Fig. 4 of ref. 4a). Moreover, the values observed for α_t at α' , α'_g , and α_g (Table IV) at $t = 26$, 42, and 146 minutes, respectively (Fig. 9), agree reasonably well with the corresponding average values (Table IV) observed for toluene evaporations from liquid-saturated samples that had not been preswelled in chloroform.

The kinetics of evaporation from this PS-L system in its glassy state, however, was *not* the same as that exhibited by systems that did not have a

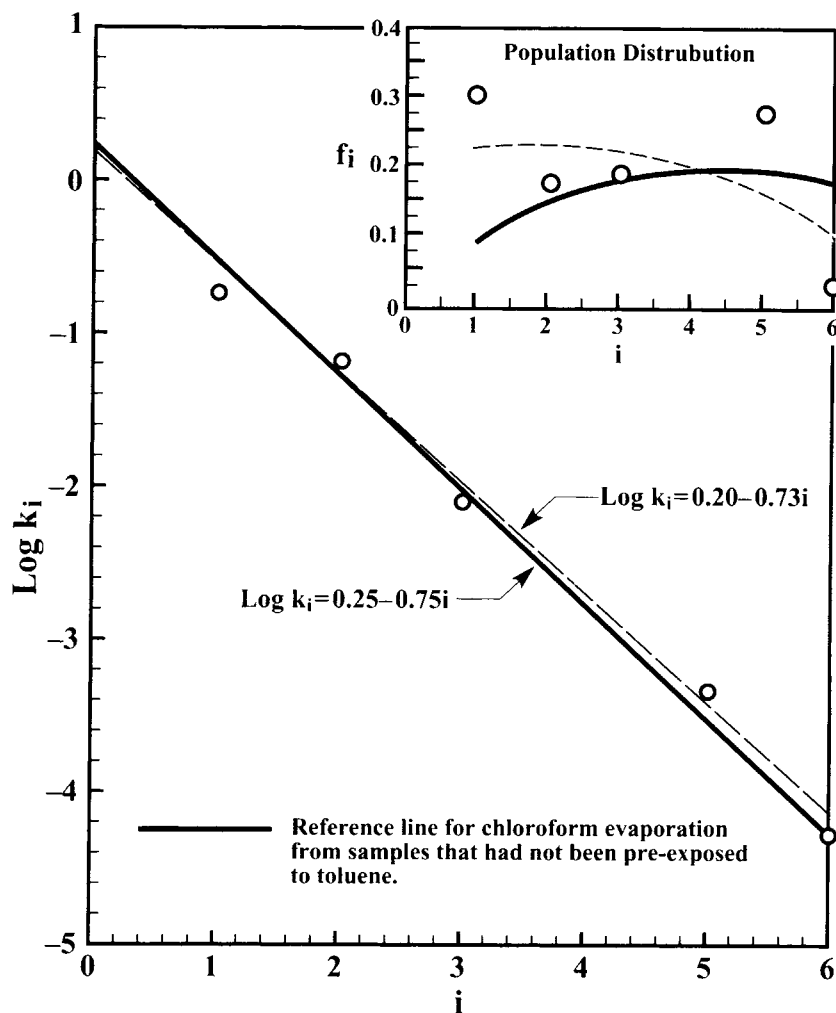


Figure 8 Correlations of $\text{Log } k_i$ and f_i with i for evaporation from CHLOROFORM-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample (Fig. 7) that had been saturated with toluene and then solvent exchanged by chloroform.

history of preswelling in a solvent that had an α -value greater than that for toluene. Thus, the linear $\text{Log } k_i$ vs. i relationship [eq. (4)] for decay of the molecular populations trapped in the glassy state of the PS-L system in this experiment (Fig. 10 and Table IV) is uniformly below that (indicated by the bold straight line in Fig. 10) established for elimination of residual toluene molecules trapped in the glassy state of PS-L systems that had not been preswelled in chloroform (Table IV; see also Fig. 8 of ref. 4a). The slope of the line of best fit to the $\text{Log } k_i$ -values (dashed line in Fig. 10) for the present time study ($m = 0.84$) is more negative than that for the reference line ($m = 0.76$), and the observed difference in the respective $\text{Log } k_0$ values recorded in Table IV imply that the rate of escape of toluene molecules from the cage structures, self-assembled

in the presence of toluene-chloroform solutions, is about two-thirds that for escape from the corresponding cage structures, self-assembled in the presence of pure toluene.

The population distribution pattern (f_i vs. i ; inset of Fig. 10) appears to indicate a strong shift in favor of the populations with slower decay rates (i.e., $i > 2$), even in view of the large variances from the average f_i data points observed in the sets of multireplicated time studies, as already discussed. That difference in the pattern exhibited in the $\text{Log } k_i$ vs. i relationship and the corresponding population distribution pattern (Fig. 10) are believed to reflect the "memory" of this PS-L system when preswelled to saturation in chloroform, despite that virtually all of the chloroform molecules had been eliminated via solvent exchange in toluene before the start of

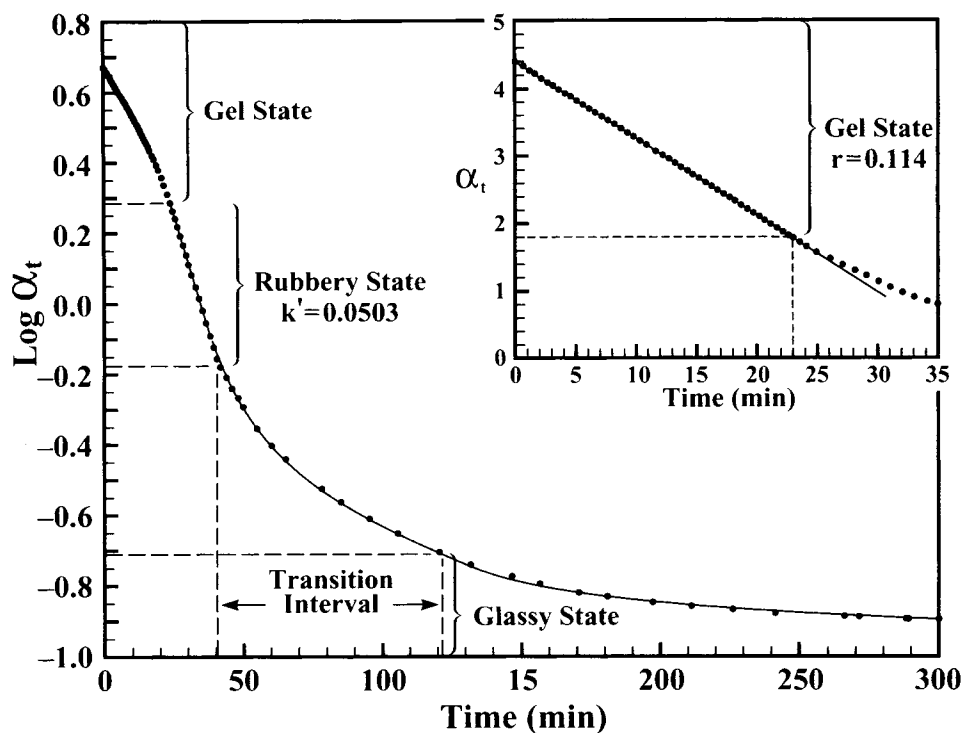


Figure 9 Correlations of α_t and $\text{Log } \alpha_t$ with time (in minutes) for evaporation from a TOLUENE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample that had been swelled to saturation in chloroform and then solvent exchanged by toluene.

evaporation to dryness. This observation, and the failure to observe a “memory” effect in the system that was swelled to saturation first in toluene and then in chloroform, led us to conclude that “memory of solvent-past” can be erased when the liquid-saturated sample is solvent-exchanged in a liquid that has even greater affinity for the polymer.

To test this possibility $(\text{Sty})_{1-x}(\text{DVB})_x$ samples were swelled first in acetone and then solvent-exchanged by swelling to saturation in toluene before starting the time study of evaporation to dryness. In every case, the pattern of evaporation during the transition interval, the values of α_t at α' , α'_g , and α_g , the $\log k_i$ vs. i relationship and the population distribution pattern (f_i vs. i) were essentially the same as those for toluene evaporation from PS-L liquid systems that had been exposed only to toluene.

SUMMARY AND CONCLUSIONS

The molecular nature of the changes in the macromolecular architecture that occur as the liquid in a PS-L system is exchanged incrementally by a second liquid is elucidated in the first of this set of three companion papers. When this exchange involves replacement of a liquid that has strong affinity

(i.e., $\alpha \geq 1.9$) for polystyrene by one that has weak affinity (i.e., $\alpha \leq 0.1$), a significant fraction of the polymer in that PS-L system undergoes liquid-induced polymer-polymer association, the amount of which is characteristic of the system, as noted in Figures 4 and 8 of ref. 1. The present publication reports that the kinetics for evaporation of such a system from liquid-saturation to virtual dryness reflects its history in the liquid-saturated state, which permits one to establish the approximate degree to which the self-associated polymer underwent transition from its rubbery to a glassy state, while it was still in the presence of excess liquid. The kinetics of desorption from the rubbery and glassy states reflect not only the composition of residual trapped molecules (which includes the original sorbed species) but also the molecular architecture of the “host” polymer that formed around the entrapped “guest” molecule during liquid-induced polymer-polymer association, and subsequently during evaporation-induced transition to a glassy state of that portion of the PS-L system that had not initially been converted to the glassy state.

When solvent exchange in a PS-L system at saturation involves exchange of a good solvent (i.e., $\alpha = \text{ca. } 2$ or 3) by another good solvent, the α of which

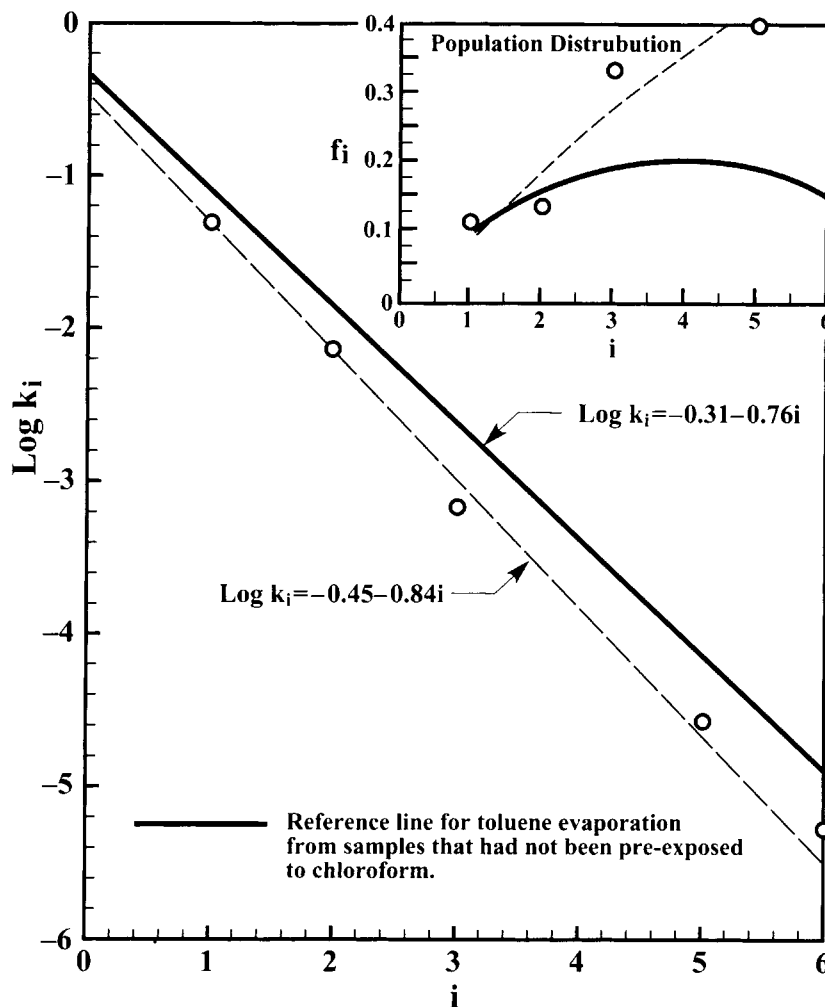


Figure 10 Correlations of $\text{Log } k_i$ and f_i with i for evaporation from a TOLUENE-saturated $(\text{Sty})_{1-x}(\text{DVB})_x$ sample (Fig. 9) that had been saturated with chloroform and then solvent exchanged by toluene.

is only a unit lower (i.e., $\alpha = \text{ca. } 1$ or 2 , respectively), the PS-L system does not undergo liquid-induced polymer-polymer association. Nevertheless the "memory" of swelling to saturation in the better solvent is retained in the liquid-saturated state established with the poorer solvent, as noted in Figures 11 and 12 of ref. 1. Also, the kinetics of evaporation to dryness reflects the "memory" of liquid-saturation in the better solvent, especially after onset of the interval for transition from the rubbery state to a glassy state, despite that the original adsorbed molecules had already been exchanged completely by those of the test liquid before the start of the time-study.

It was inferred from these observations that the kinetics of elimination of residual molecules trapped

in the glassy state, as expressed by eq. (7), may reflect the pattern of desorption during the transition interval, which in turn may be influenced by the history of the sample in its liquid-saturated state. The physical properties of a polymeric film, produced via solvent casting and subsequent evaporation to dryness, are markedly dependent upon the macromolecular architecture and the residual composition produced thereby (which change continuously with time in storage). It is important, therefore, that the molecular nature of evaporation-induced transition from the rubbery state to the glassy state be elucidated, in order to learn how this transition affects the physical properties of the product. This information should lead to better reproducibility and improved physical properties of film

products produced by solvent-casting procedures. It was decided, therefore, to examine more closely the kinetics of evaporation during the transition interval in the hope of gaining this needed understanding. The results observed in this aspect of our ongoing investigation is the subject of the third report¹⁵ in this set.

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