Effect of prior sample history on n-hexane sorption in glassy polystyrene microspheres

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The effect of prior swelling or thermal annealing on the kinetics and apparent equilibria of n-hexane vapour sorption at 30°C in submicron diameter polystyrene microspheres was studied at penetrant activities of 0.75 and 0.10. Preswelling with n-hexane at an activity of 0.90 increased both the rate and the apparent equilibrium of subsequent n-hexane sorption at both the lower activities. Conversely, thermal annealing reduced the sorption rate and apparent equilibrium sorption relative to the measured sorption in the 'as-received' sample. Cycling experiments, at the high activity ($p/p^\circ = 0.75$), revealed that the effects of the earlier preswelling or thermal history are effectively erased by the first sorption cycle. In contrast, at the lower activity ($p/p^\circ = 0.10$), the effects of preswelling or thermal annealing decay more gradually consequent to repeated cycling. The observed convergence of the apparent equilibrium penetrant concentration, in all samples, to a single value upon repeated cycling suggests that a true glassy state equilibrium sorption can be approached by conditioning microsphere samples by the particular cycling histories studied in this work.

INTRODUCTION

Transport in glassy polymers

The sorption kinetics of organic vapours in rubbery polymers are often well characterized by Fickian diffusion[1]. Furthermore, the prior sorption and thermal history of the polymer sample does not affect subsequent vapour sorption cycles due to the rapid response of rubbery polymer systems to changes in ambient conditions.

In marked contrast, sorption of organic penetrants in glassy polymers often deviates from Fickian kinetics. Whereas Fickian diffusion is often observed in glassy polymers at low vapour activities[2,3], two stage sorption[4] and Case II transport[5] often predominate at high vapour activities. Reviews of glassy state transport behaviour are given by Park[6], Rogers[7], and others[2,8].

Hopfenberg and Frisch[9] relate observed sorption behaviour to regions of the temperature-activity plane of a polymer/penetrant pair. Vrentas, Jarzebski, and Duda[10] infer that the observed sorption behaviour may also depend upon the characteristic dimension of the polymer sample. Consistent with the notion of Vrentas *et al.*, Enscore, Hopfenberg, and Stannett[11] have reported dimensionally controlled transport kinetics of n-hexane in polystyrene spheres. Specifically, relaxation-controlled (Case II) sorption kinetics were observed in 184 μm diameter polystyrene spheres and primarily Fickian sorption kinetics dominated absorption in 0.534 μm diameter polystyrene spheres under otherwise identical boundary conditions of temperature, penetrant type, and penetrant activity.

History dependent sorption in glassy polymers

In addition to the effects of temperature, penetrant partial pressure, and critical sample dimension on the observed sorption behaviour in glassy polymers, the prior history of the polymer sample can also greatly affect the observed kinetics and equilibria of vapour sorption. Clearly, hysteresis in sorption isotherms represents a history dependent effect[12,13]. Different sorption rates have been observed in samples which have been preoriented[14–16] or, alternatively, annealed[17,18] prior to sorption. Most importantly, an increase in apparent equilibrium uptake, resulting from preswelling of a polymer sample, is typically followed by a decay of sorptivity during repeated cycling[19,20]. Time dependent sorption anomalies are often observed in polymers below their glass transition temperature due to their slow response to changes in the ambient conditions.

Advantages of the microsphere geometry

The microsphere sample geometry offers distinct advantages relative to the more conventional film and fibre sample geometries. The extremely small characteristic dimensions obtainable in spherical samples affords convenient experimental times for exceedingly slow rate processes. Specifically, it is possible to measure diffusion coefficients as low as 10^{-14} cm^2/sec by sorption techniques with microsphere samples[11]. Also, microsphere samples are quite similar in characteristic shape to commercial, as polymerized, polymer resins. This is important if experimental results are to be extended to commercial resins since the size and shape of the polymer sample can strongly influence the observed sorption behaviour[3,11].

EXPERIMENTAL

Materials

Polystyrene microspheres. Emulsion polymerized microspheres of polystyrene were kindly prepared and characterized by The B. F. Goodrich Company Research and Develop-

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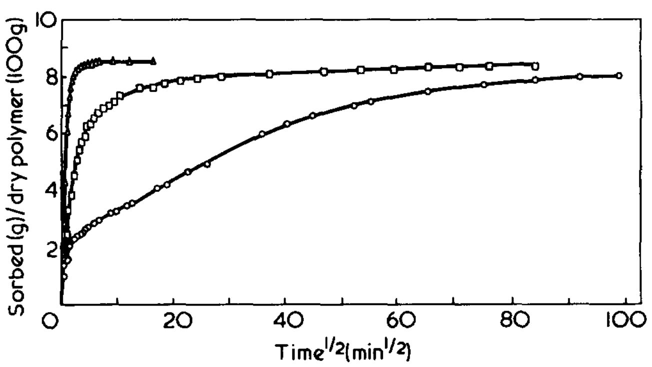

Figure 1 Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.75 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm

ment Center, Brecksville, Ohio. The number-average molecular weight of the polystyrene sample was reported to be 440 000. The mean diameter of this highly monodisperse sample was determined to be 0.534 μm by light scattering using the higher order Tyndall spectrum and 0.533 μm by electron microscopy.

Organic penetrant. Pure (>99 mol %) normal hexane, used as the penetrant in the vapour sorption experiments, was supplied by the Phillips Petroleum Company, Special Products Division, Bartlesville, Oklahoma. The n-hexane was degassed by repeated freeze–thaw cycles under vacuum before admitting the n-hexane into the sorption chamber and related manifolding.

Apparatus and procedure

Thermal annealing. Thermal annealing of the polystyrene samples was carried out by heating the microspheres in a vacuum oven at 79°C for 24h. Annealing below the glass transition temperature of polystyrene was necessary to prevent particle coalescence.

Preswelling. The preswollen samples were prepared by equilibrating the microspheres with a n-hexane vapour at an activity of 0.90 at 15°C. The high activity ensured a large degree of swelling while the low temperature kept the microspheres below their effective T_g, preventing particle coalescence. After one week in contact with the penetrant vapour, the sample chamber was evacuated and the n-hexane was removed from the sample. Following desorption, the sample was stored in a sealed container at 2°C.

Vapour sorption. Vapour sorption experiments were performed using a McBain spring balance system. The vapour sorption system was serviced by a high vacuum line for sample and penetrant degassing and desorption experiments. The temperature of the water-jacketed sorption chamber was controlled to ±0.01°C by water circulated by a constant temperature bath. Helical quartz springs supplied by Worden Quartz Products Inc., Houston, Texas, were used to measure the amount of penetrant sorbed by the polystyrene samples. The springs extended linearly within 2% over the calibrated range and the sensitivity did not vary over the 10° to 50°C temperature range used in this investigation. The extension of the quartz spring was followed by an optical reader supplied by Misco Scientific, Berkeley, California. Desorption kinetics were routinely recorded after the n-hexane had sorbed to equilibrium. A more detailed discussion of the experimental procedure is given by Jacques and Hopfenberg[19,20].

RESULTS AND DISCUSSION

Effect of prior sample history on the kinetics of sorption

The sorption kinetics of n-hexane in preswollen, 'as received', and annealed polystyrene microsphere samples at a n-hexane vapour activity of 0.75 and 30°C are compared in *Figure 1.* The rapid sorption into the preswollen sample and the protracted sorption into the annealed sample demonstrate the strong influence of prior sample history on the kinetics of n-hexane sorption in polystyrene.

The long term slow rise to equilibrium observed in the 'as received' sample and, particularly, in the annealed sample is most likely associated with slow glassy-state relaxation of the polymer, following the initial, rapid Fickian diffusion[4,11,13]. The rapid sorption in the preswollen sample is presumably related to the excess free volume imparted to the sample during preswelling at high (p/p^0 = 0.90) activity. Preswelling and annealing primarily affect the long-term, slow relaxations; the initial, diffusion-controlled sorption rates in all samples are quite similar.

The first cycle desorption kinetics for each sample, at 30°C, are represented in a plot of fractional sorption *versus* the square root of time in *Figure 2.* In contrast to the wide disparity of responses in the first cycle sorption behaviour, the desorption kinetics for the preswollen 'as received', and annealed microsphere samples are essentially identical. Moreover, the comparison of resorption data for these samples, at 30°C and p/p^0 = 0.75, presented in *Figure 3,* reveals essentially identical results for all three samples. Furthermore, the rate and form of the kinetics of resorption for each sample are virtually the same as the first cycle sorption kinetics for the preswollen sample. Apparently, the prior histories of the 'as received' and annealed samples are erased by the first sorption cycle at an activity of 0.75 or by preswelling at an activity of 0.90 and, consequently, these resorbed samples attain a state quite similar to that of the preswollen sample.

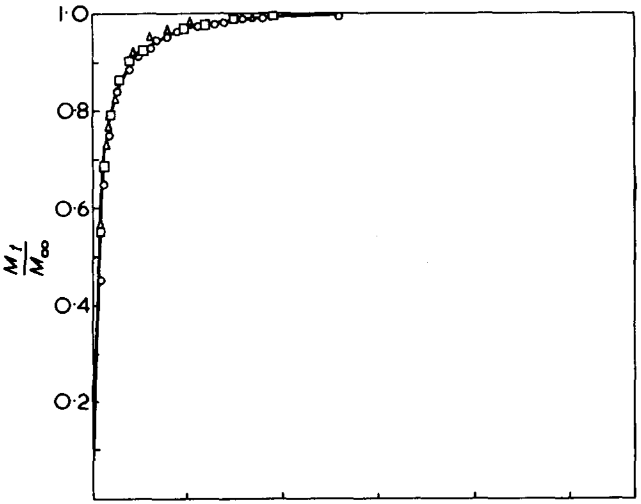

Figure 2 Comparison of n-hexane desorption from preswollen (△), 'as-received' (□), and annealed samples (○) previously equilibrated at p/p^0 = 0.75 and 30°C. Desorption-cycle 1, polystyrene, d = 0.534 μm

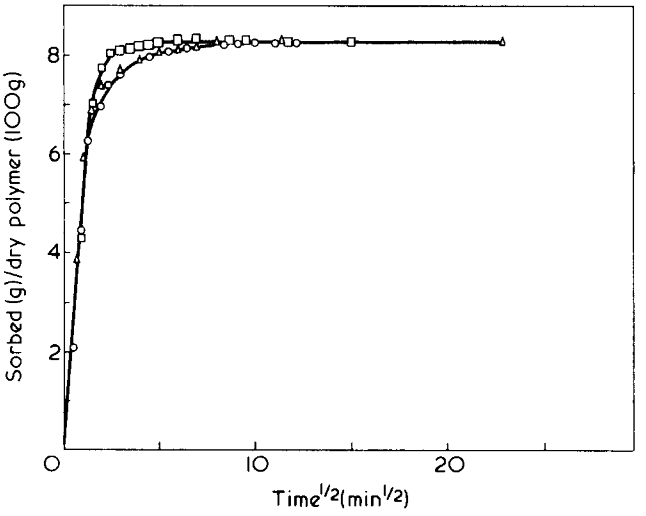

Figure 3 Comparison of n-hexane resorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.75 and 30°C. Sorption-cycle 2, polystyrene, d = 0.534 μm

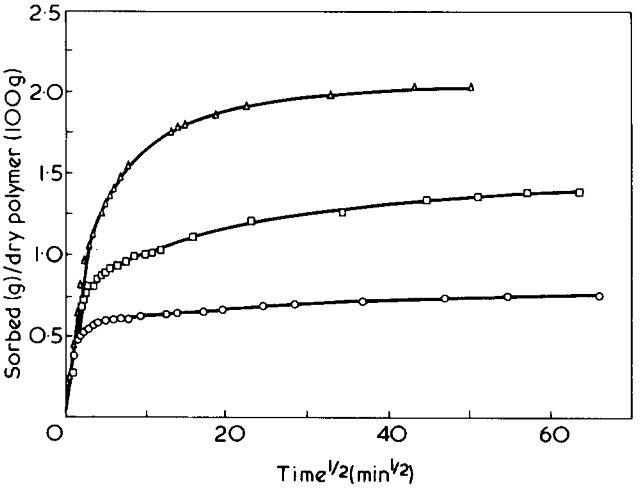

Figure 4 Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.10 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm

A comparison of first cycle low activity sorption data (at an activity of 0.10 and 30°C) is presented for the preswollen, 'as received', and annealed samples in *Figure 4*. Although there is a marked difference in apparent equilibrium sorption among the samples, the form of the kinetics and magnitude of the initial rate of sorption for each sample are similar; each sample exhibits some long term non-Fickian swelling behaviour. The rate of the latter stages of sorption in the preswollen sample is somewhat more rapid than the long term sorption in the 'as received' and annealed samples. Presumably, the volume relaxations associated with the long term drift to an apparent equilibrium have been essentially completed by the high activity preswelling. These effects will be discussed more fully in the discussion of cycling which follows.

Typical sorption–desorption data at the low activity, for the preswollen sample, are shown in *Figure 5*. The desorption kinetics are more rapid than the corresponding sorption kinetics. These comparative results suggest that the long term uptake during sorption is due to non-Fickian swelling and is not related to the particle size distribution of the sample. Berens[3,23] has emphasized that the sorption kinetics into a distribution of spheres would be confounded by an apparent long term drift to the final equilibrium as a consequence of relatively slow sorption into the larger particles. A long term approach to a sorption equilibrium, owing to particle size distribution, would result in a similar slow approach to a desorption equilibrium.

The desorption kinetics represented in *Figure 5* conform to the predictions of Fickian diffusion in a monodisperse array of spheres, therefore, the long term drift to an apparent sorption equilibrium is most likely related to non-Fickian relaxations rather than to particle size distribution effects. Some consolidation must, however, occur during the desorption since the preswollen sample exhibits long term swelling in the subsequent sorption cycles.

The experimental resorption data at an activity of 0.10 are presented for all three samples in *Figure 6*. The 'as received' and preswollen samples exhibit similar resoprtion kinetics although the equilibrium concentrations remain quite different. Furthermore, the resorption kinetics in the preswollen and 'as received' samples are again confounded by long term, presumably relaxation-controlled, swelling.

A comparison of sorption kinetics for four preswollen samples, which were desorbed under vacuum for varying time periods, is presented in *Figure 7* The time required to complete sorption for the preswollen sample becomes more protracted as the time under vacuum or 'penetrant-free time' is increased. The sorption kinetics for the first and third

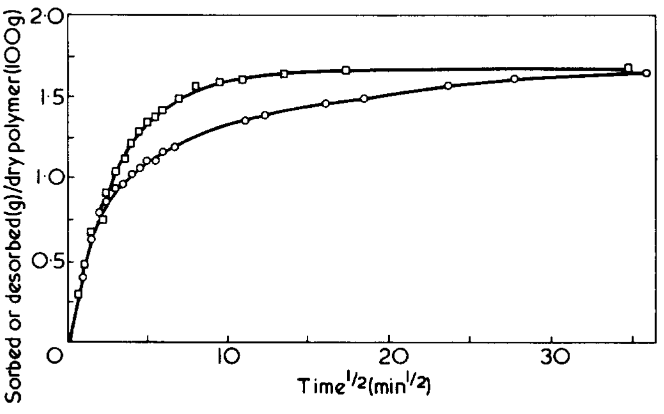

Figure 5 Comparison of n-hexane sorption (○) and desorption kinetics (□) in a preswollen sample at p/p^0 = 0.10 and 30°C. Cycle 3, polystyrene preswollen, d = 0.534 μm

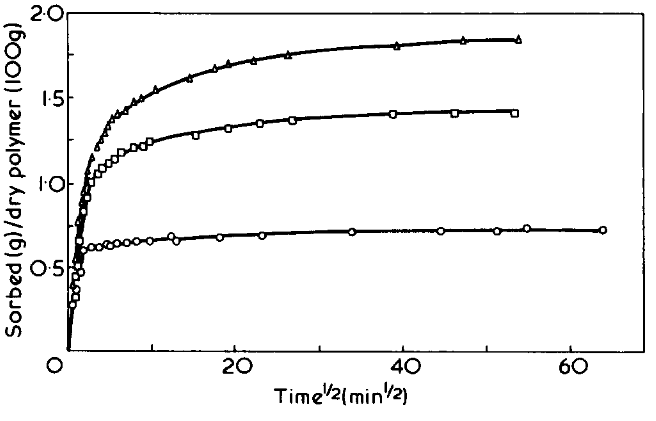

Figure 6 Comparison of n-hexane resorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.10 and 30°C. Sorption-cycle 2, polystyrene, d = 0.534 μm

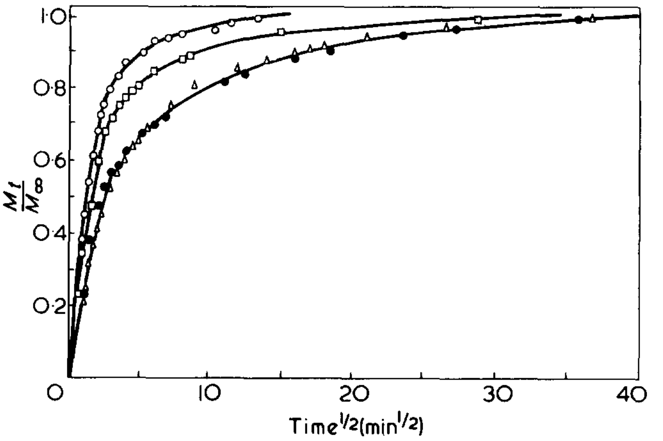

Figure 7 Comparison of n-hexane sorption kinetics in a preswollen sample maintained previously under vacuum at 30°C for various times. Sorption carried out at p/p^0 = 0.10 and 30°C. Sorption kinetics, polystyrene preswollen, d = 0.534 μm. ○, cycle 1, 172 min prior vacuum time; □, cycle 3, 530 min desorb after cycle 2; △, cycle 1, 1125 min prior vacuum time; ●, cycle 3, 1050 min desorb after cycle 2

sorption cycles on preswollen samples, with the same immediate vacuum history, are virtually identical. These data strongly suggest that the immediate prior vacuum history of preswollen samples, and not the number or frequency of sorption cycles, determines the kinetic behaviour during the subsequent sorption cycle.

First and second cycle sorption kinetics, at an activity of 0.10 and 30°C, are presented for the 'as received' sample in *Figure 8*. Although the initial sorption rates are virtually identical, the long term, presumably relaxation controlled sorption of the first cycle is much slower than the approach to an apparent equilibrium in the second cycle. Supposedly, a volume loss occurs during the 1400 min of imposed vacuum (desorption) between cycles 1 and 2. The volume loss during desorption is, presumably, less than the volume expansion caused by the cycle 1 swelling. The penetrant, therefore, encounters a more 'open' sample during the second cycle and more rapid sorption is observed. This interpretation seems consistent with the earlier observations of Berens[19,23] regarding the amount of vinyl chloride monomer sorbed in poly(vinyl chloride). Berens suggested that free volume changes during swelling and deswelling were responsible for changes in subsequent sorption.

The annealed sample exhibits nearly identical sorption kinetics for the first and second cycles (see *Figures 4* and *6*). These data suggest that the kinetics of glassy-state relaxations are extremely slow in this densified polymer sample under these particular swelling conditions.

Effect of prior sample history on apparent equilibrium sorption

The low activity first cycle sorption data, presented in *Figure 4*, reveal a large effect of prior thermal and/or swelling history on the apparent equilibrium sorption. Specifically, the sorption in the preswollen sample is 50% greater than the apparent equilibrium in the 'as received' sample and almost 300% greater than the observed asymptotic sorption in the annealed sample.

The low apparent equilibrium sorption at 30°C in the annealed sample is in remarkable agreement with the apparent equilibrium, determined independently at 90°C in an 'as received' sample at the same relative pressure of n-hexane. Assuming a very low enthalpy of sorption (viz. athermal sorption), consistent with the equilibrium behaviour reported earlier for n-pentane in polystyrene[24], these data suggest that the level of 'frozen-in' free volume in the annealed sample is reduced to the vanishingly small level of 'frozen-in' free volume characteristic of rubbery polymers. Specifically, Berens has suggested that an excess sorption in the glassy state, corresponding phenomenologically to a 'second-mode' of sorption in preexisting 'holes'[25] is eliminated above the T_g[19,23]. Berens based his arguments upon solubility data for vinyl chloride monomer in poly(vinyl chloride) obtained above and below the T_g of poly(vinyl chloride).

Presumably, annealing the polystyrene microspheres in this present study has effectively eliminated the free volume responsible for sorption in excess of the amount sorbed above T_g. Quite consistent with these notions of free volume, the increased sorption in the preswollen sample results presumably from the excess free volume introduced to the sample under these particular conditions of preswelling.

Upon resorption at the low activity (see *Figure 6*) the preswollen sample reaches an apparent equilibrium which is lower than the apparent equilibrium achieved in the first cycle. In contrast, comparing the data of *Figures 4* and *6*, the 'as received' sample sorbs to a higher apparent equilibrium in the second cycle.

As suggested by the data of *Figure 9*, the apparent equilibrium in the preswollen sample is independent of the time the preswollen sample was in contact with the penetrant atmosphere. Specifically, the intriguing results of *Figure 9* indicate that maintaining the polymer sample in an atmosphere of n-hexane at a relative pressure of 0.10 for various time intervals does not affect the amount of sorption achieved in the subsequent cycle. In fact, the amount sorbed after each successive cycle in the preswollen sample appears to decrease regularly with the time interval between sorption cycles rather than the contact time with n-hexane.

In contrast, n-hexane swelling of the 'as received' sample appears to trigger the observed increase in solubility. The increase in apparent equilibrium sorption with cycling for the 'as received' sample was correlated, therefore, with the total time the sample was in contact with n-hexane vapour. The correlations of the amounts sorbed for the cycled pre-

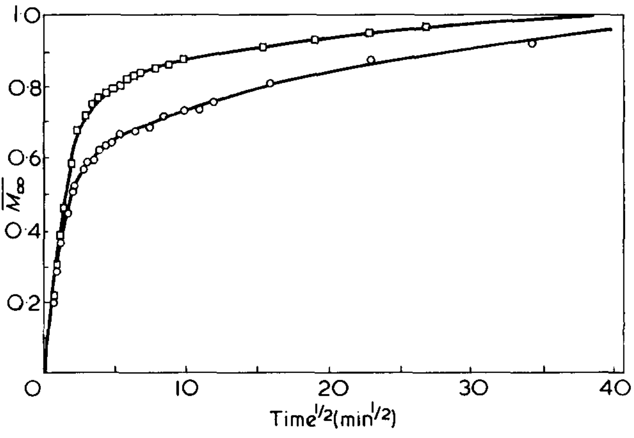

Figure 8 Comparison of n-hexane sorption and resorption kinetics at p/p^0 = 0.10 and 30°C in as 'as-received' sample. ○, cycle 1; □, cycle 2, sorption kinetics, polystyrene 'as-received', d = 0.534 μm, 1400 min desorption between cycles

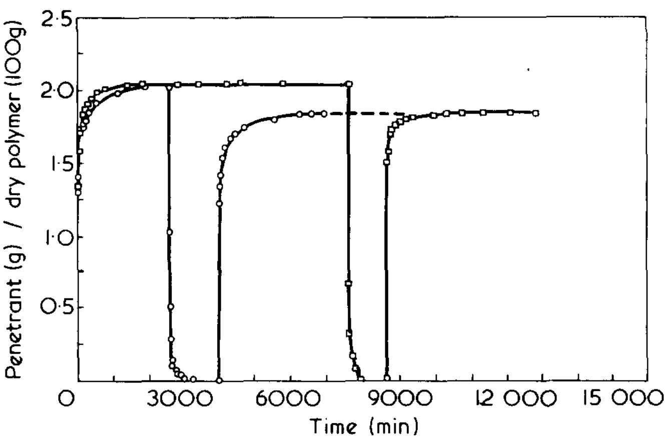

Figure 9 Comparison of n-hexane resorption in preswollen samples, contacted with n-hexane for various time intervals during the preceding sorption cycle. Resorption was carried out at $p/p^0 = 0.10$ and 30°C. ○, sample 1; □, sample 2. Sorption-cycling, polystyrene preswollen $d = 0.534$ μm

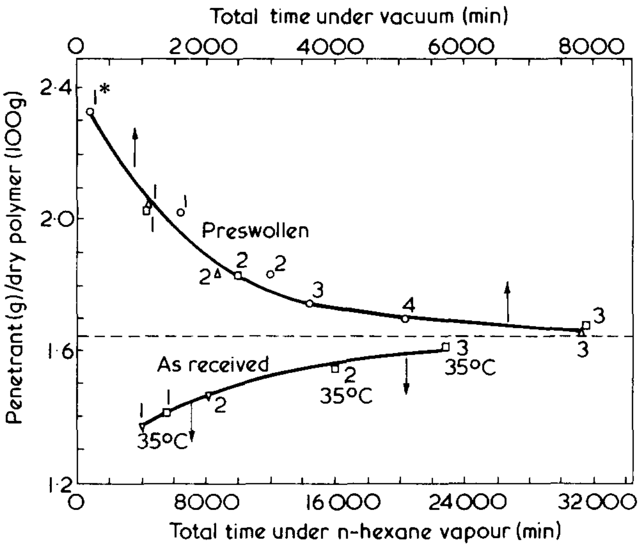

Figure 10 Effect of cycling on the apparent equilibrium sorption of n-hexane at $p/p^0 = 0.75$ and 30°C in preswollen and 'as-received' samples. Sorption-equilibria, polystyrene, $d = 0.534$ μm. * Cycle number

swollen and cycled 'as received' samples with the total time under vacuum and total time under n-hexane contact, respectively, are presented in *Figure 10*. The sorptions for each sample correlate smoothly with the intuitively selected 'time' and the apparent equilibria appear to converge to the same penetrant concentration. This convergence may represent an approach to a true thermodynamic equilibrium for this particular two component glassy state system[26].

The annealed sample sorbs to the same slowly achieved low apparent equilibrium, observed on the first cycle. Apparently, the annealed sample is so densified that only a small degree of essentially 'elastic' swelling (i.e., swelling rapidly lost upon subsequent desorption) occurs at this low activity within the time scale of these arbitrarily patient experiments.

A summary of the first and second cycle sorptions for each sample, at $p/p^0 = 0.75$ and 30°C, is presented in *Figure 11*. The first cycle sorptions are qualitatively consistent with the lower activity results. The preswollen sample exhibits the highest apparent equilibrium concentration and the annealed sample exhibits the lowest apparent equilibrium sorption. Although there is a significant difference in apparent equilibria among the three samples for first cycle sorption at the higher activity, the relative difference in apparent equilibria is smaller than the differences observed at the lower activity.

The resorptions for all samples approach a single limiting value after only one additional cycle at $p/p^0 = 0.75$ and 30°C. Jacques[21] reports that at these conditions of $p/p^0 = 0.75$ and 30°C the T_g of the polymer is depressed to within only a few degrees Centigrade above the experimental temperature of 30°C. Presumably, the increased plasticization associated with the first cycle sorption at $p/p^0 = 0.75$ is responsible for the rapid response of the annealed and 'as received' sample, consistent with the low activity results. The modest decay in apparent equilibrium sorption for the preswollen sample was probably effected during the particular desorption history imposed between cycles. Similar to the lower activity results, a true glassy-state equilibrium is, apparently approached under these particular (and arbitrary) cycling conditions. The similarity between the results obtained by Berens[3,13,19,20,23] with poly(vinyl chloride) and the results reported here with polystyrene suggests that the relaxations associated with these particular annealing, preswelling, and cycling histories are predominantly associated with glassy state processes, *per se*, and do not necessarily relate to the nature of nor change in the crystalline morphology of the poly(vinyl chloride).

CONCLUSIONS

Preswelling at an activity of 0.90 increased both the rate and the amount of subsequent n-hexane sorption at lower activities. Conversely, thermal annealing reduced the rate and amount of sorption relative to the measured sorption in the 'as received' sample. Preswelling and annealing affected the long term, relaxation-controlled approach to equilibrium: initial, diffusion-controlled sorption rates were virtually unaffected by either preswelling or annealing.

Cycling experiments revealed that, at the high activity, ($p/p^0 = 0.75$) the effects of the earlier preswelling or thermal history were effectively erased by the first sorption cycle. In contrast, at the lower activity ($p/p^0 = 0.10$), the effects of preswelling or thermal annealing decay more gradually during repeated cycling.

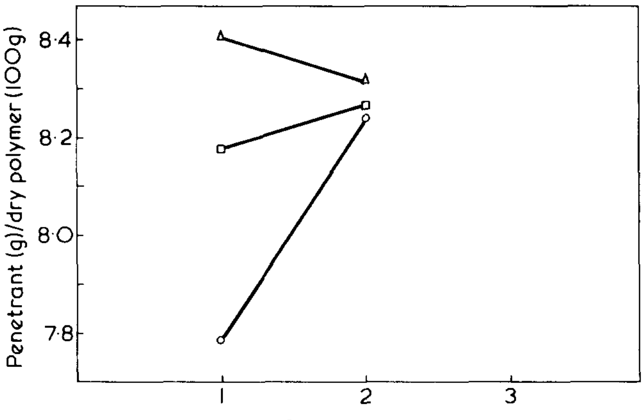

Figure 11 Effect of cycling on the apparent equilibrium sorption of n-hexane at $p/p^0 = 0.75$ and 30°C in preswollen (△), 'as-received' (□), and annealed samples (○)

A systematic decrease in the asymptotic penetrant uptake and rate of sorption was observed in the preswollen sample as the sorption and desorption cycles were continued between vacuum and the low activity ($p/p^0 = 0.10$). This observed monotonic decrease in apparent solubility is probably a consequence of glassy state volume relaxation during the penetrant-free stage of the desorption of the originally preswollen and, therefore, expanded sample.

Conversely, the increase in the asymptotic penetrant uptake and the sorption rate in the 'as received' sample over the course of the multiple sorption cycles at the lower activity appears to be triggered by the repeated swelling of the microspheres by the n-hexane.

The observed convergence of the apparent equilibrium penetrant concentration to a single value upon repeated cycling for all samples at the higher activity suggests that a true glassy state equilibrium sorption can be approached by conditioning microsphere samples by the particular cycling histories studied in this work. Although the sorption in the 'as received' and preswollen samples approached the same level of sorbed penetrant after repeated cycling at low activity, the annealed sample did not respond to this particular cycling history. Presumably, the restorative relaxations, required for the annealed sample to attain the unequivocal equilibrium consequent to low activity cycling, are too slow to take place in the arbitrarily imposed duration of these experiments.

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