The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders. II. *n*-Propane Sorption in Polystyrene

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Synopsis

Both the rate and apparent equilibrium of propane sorption in glassy polystyrene were increased after swelling the polymer by exposure to a highly sorbing vapor. Cyclic sorption experiments revealed that the increase in rate and apparent equilibrium of sorption due to the preswelling treatment decayed only during vacuum aging. The presence of low levels of propane in the polymer during aging, however, appeared to arrest the decay in sorption capacity. These composite results, taken in conjunction with the results of previous work in our laboratory, suggest that the component of the total sorption which resides in nonequilibrium, distended interchain gaps retards the chain motions which otherwise lead to consolidation of the dilated glass.

INTRODUCTION

Unlike sorption in polymers about their glass transition temperature, the kinetics and apparent equilibria of small molecule sorption in glassy polymers are affected by the history of the polymer sample.[1–18] In part I of this series, Connelly et al.[8] investigated the effect of aging previously dilated PMMA microspheres in the presence of low activities of various penetrants on the subsequent sorption capacity of the preswollen polymer for the respective penetrant. Their work was motivated by the similar previous studies of Berens[1–5] for the vinyl chloride monomer/poly(vinyl chloride) system, and Enscore et al.[6,7] for the *n*-hexane/polystyrene system.

The results reported by Connelly et al.[8] for the time and history dependence of *n*-propanol sorption in preswollen PMMA were entirely consistent with those of Berens[1–5] and Enscore et al.[6,7] The kinetics and apparent equilibrium of low activity *n*-propanol sorption were increased by the preswelling treatment, which consisted of equilibrating the polymer with high activity methanol vapor followed by the rapid desorption of the methanol. The increased sorption levels were stable as long as the polymer was maintained in contact with the *n*-propanol, but decayed during vacuum aging, and approached the apparent equilibrium sorption level measured in untreated

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polymer. The presence of low levels of *n*-propanol in the polymer during aging, however, arrested the decay in sorption capacity. Presumably, the chain motions responsible for the consolidative relaxations, which otherwise take place in the absence of penetrant, were retarded by the interspersion of penetrant within molecular scale gaps which characterize the distended, out-of-equilibrium chain segments.

These phenomena, though also observed for the *n*-hexane/polystyrene system, are not universal. Strikingly different behavior was reported in Part I of this series of papers[8] for the single case of low pressure methanol sorption in preswollen and, therefore, dilated PMMA. An initial rapid rise to a peak sorption level in the preswollen sample was observed, followed by a decline in sorption in the *presence* of methanol which was essentially identical to the decline in sorption level which occurred under vacuum in cyclic sorption experiments. The presence of methanol during aging appeared, therefore, to have no effect on the consolidative relaxations.

Intermediate behavior, between completely arrested relaxations and completely unaffected relaxations, was also reported in the earlier paper[8] for the aging of PMMA in the continuous presence of ethanol and water. In these systems, the sorption level in preswollen PMMA also rose to a peak and then declined during aging in the continuous presence of the penetrant, but more slowly than samples in contact with methanol or samples maintained under vacuum.

Although there was insufficient information at hand to determine unequivocally the reason for the difference in the sorption behavior of PMMA aged in the presence of the three homologous lower alcohols and water, it appeared that differences in the molecular dimensions of the penetrants might be principally important in determining the course of aging in the presence of an aging penetrant. To test this hypothesis, and to extend the polystyrene work to include smaller probes, the kinetics and equilibria of propane sorption in submicron microspheres of as-received polystyrene, preswollen polystyrene, and preswollen polystyrene, aged in the presence of propane, were investigated in this work.

EXPERIMENTAL

Polymer Samples

Emulsion-polymerized, polystyrene microspheres were kindly provided and characterized by the B. F. Goodrich Co. Research and Development Center, Brecksville, OH. The number-average molecular weight of the polymer was reported as 440,000, and the T_g was determined from DSC measurements to be 108°C. The average diameter of the monodisperse microspheres was determined to be 0.533 μm by electron microscopy and 0.534 μm by light scattering using the higher order Tyndall spectrum. Because of their extremely small characteristic dimension, the approach to diffusive equilibrium in microspheres is orders of magnitude faster than in thin films or fibers. This allows for rapid experimentation and the convenient use of organic penetrants with penetrant diffusivities as low as 10^{-17} (cm^2/s).[19] Furthermore, the approach to diffusive equilibrium often occurs before significant relaxation is apparent, thereby permitting convenient and unequivocal separation of the diffusion and relaxation kinetics.[20]

Penetrants

Instrument Grade propane (99.99 mol% pure) was used in the propane sorption experiments and *n*-hexane (99 mol%) was used as a preswelling penetrant. Prior to use, the *n*-hexane was subjected to two freeze–thaw cycles to remove dissolved gases.

Preswelling

Preswollen polystyrene samples were prepared by exposing the polymer to 0.90 activity *n*-hexane at 15°C for 2 weeks. These conditions ensured a large degree of swelling without particle coalescence. After 2 weeks in contact with the preswelling vapor, the mass uptake of *n*-hexane by the polystyrene was 10.75 g/100 g polystyrene. At the end of the preswelling period, the sample was exposed to vacuum for 4 days to remove the *n*-hexane from the sample. At this temperature approximately 26 h were required to desorb the *n*-hexane. The additional desorption time ensured that essentially all *n*-hexane was removed. Following the preswelling, samples were stored in a sealed container at −15°C.

Another set of experiments was performed with samples preswollen by exposure to propane at 700 mm Hg and 30°C, followed by exposure to vacuum for approximately 30 min. This preswelling was performed in the sorption system and resulted in a mass uptake of 1.07 g propane/100 g polymer. These samples will be referred to as propane-preswollen in this article to distinguish them from the *n*-hexane-preswollen samples described above.

Sorption Measurements

Gas sorption measurements were performed using a Cahn RG electrobalance. The balance was enclosed in a glass vacuum system with service lines to a penetrant source, a reservoir bulb, an MKS type 221A pressure transducer with a sensitivity of 0.01 mm Hg, and a vacuum service capable of achieving vacuum pressures of 10^{-4} mm Hg. The temperature of the reservoir bulb and electrobalance were maintained within ±0.1°C of the set point by enclosing them in a thermostatted plywood box. The output of the electrobalance was recorded using a strip chart recorder. The microbalance was calibrated for a recorder readout of 1.0 mg full scale, and, at this setting, a sensitivity of 5 μg could be discerned.

Prior to the start of a sorption measurement, polymer samples were placed in balance pans, weighed, and suspended from the microbalance. The glassware was then reassembled, the penetrant source was isolated from the remainder of the system, and the system was slowly evacuated. The time under vacuum was recorded for preswollen samples, and as-received samples were exposed to vacuum for a period of at least 12 h.

To start a run, the glass vacuum bottle containing the microbalance and sample was isolated from the system, and the line to the vacuum service was closed. The reservior bulb and connecting lines were then pressurized with

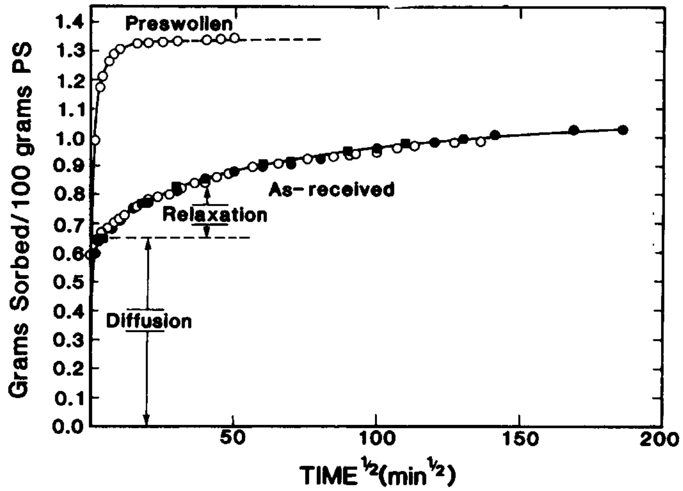

Fig. 1. Propane sorption in polystyrene at 700 mm Hg and 30°C. Comparison of the rate and extent of propane sorption in as-received and *n*-hexane-preswollen polystyrene: (○) interval sorption, $P = 600 \rightarrow 700$ torr; (●) integral sorption, $P = 0 \rightarrow 700$ torr; (■) integral sorption, $P = 0 \rightarrow 700$ torr; $T = 30°\text{C}$, $d = 0.534$ μm.

propane to an empirically determined value that would give the desired pressure when the stopcock to the microbalance was opened. After allowing the pressure and temperature to stabilize, the stopcock to the microbalance was opened and the timer started. The first data point was generally taken after about 6–9 s of sorption, and measurements continued until an apparent equilibrium was reached. Following a sorption run, the sample was exposed to vacuum and the desorption monitored. Cyclic sorption sorption experiments with alternating exposure to propane and vacuum were performed without removing the polymer samples from the sorption system.

A more detailed discussion of the sorption apparatus and procedure is given by Fechter.[21]

RESULTS AND DISCUSSION

Sorption Kinetics in As-Received Polystyrene

The time dependence of propane sorption at 700 mm Hg and 30°C in polystyrene is shown in the lower experimental curve of Figure 1. The data are plotted against square root time. This was not done to imply that the kinetics are Fickian, but rather to condense the abscissa. In fact, the sorption kinetics are non-Fickian and appear to be two stage as described in the classic work of Bagely and Long for the acetone/cellulose acetate system.[22] A very rapid, predominately diffusion-controlled uptake of approximately 0.65 g/100 g polymer is followed by a protracted relaxation-controlled uptake of approximately 0.3 g/100 g polymer, resulting in an apparent equilibrium uptake of 1.07 g/100 g polymer. As shown by the dotted line in the figure, the time scale of diffusion controlled uptake is much shorter than the time scale of relaxation-controlled sorption. Non-Fickian, two-stage sorption kinetics were also observed at all other propane pressures studied.

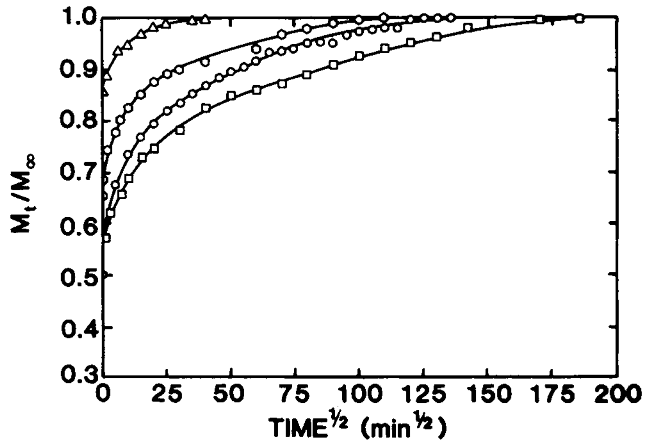

Fig. 2. Comparison of the normalized kinetics of propane sorption in as-received polystyrene at various propane pressures. Final pressure (mm Hg): (△) 150 mm Hg; (○) 350 mm Hg; (o) 550 mm Hg; (□) 700 mm Hg. $T = 30°C$, $d = 0.534$ μm.

The normalized kinetics of propane sorption at various pressures in polystyrene are shown in Figure 2, in which M_t is the amount of propane sorbed at time t and M_∞ is the amount sorbed at apparent equilibrium. Clearly, as the propane activity increases, the non-Fickian nature of the sorption kinetics becomes more pronounced as evidenced by an increased contribution of relaxation-controlled sorption, which produces the slow drift towards equilibrium. The relaxations, which lead to the slow increase in sorption level, are probably initiated by stresses created in the polymer by the presence of sorbed penetrant. Presumably, these stresses lead to a rearrangement and increase in the excess volume of the polymer involving large scale, and therefore slow, segmental motion of the polymer chain.[20] As the penetrant concentration is increased, due to an increase in penetrant activity, the stresses generated within the polymer also increase, resulting in an increase in the amount of relaxation-controlled sorption observed. The effect of penetrant pressure on the sorption kinetics is consistent with the notions of Hopfenberg and Frisch[23] and Vrentas et al.[24] concerning the systematic change in behavior associated with sorption in polymeric glasses at temperature and penetrant activity vary.

Sorption Kinetics in Preswollen Polystyrene

The time dependence of propane sorption at 700 mm Hg and 30°C in polystyrene microspheres, which have been previously dilated by preswelling with *n*-hexane vapor, is compared with the sorption kinetics of propane at the same temperature and final pressure in as-received polystyrene in Figure 1. Both the rate of sorption and the apparent equilibrium uptake of propane are increased by the preswelling treatment. This was true at all activities studied.

The rapid sorption into the preswollen sample, compared to the protracted process in the as-received sample, demonstrates the strong influence of prior sample history on the kinetics of propane sorption in polystyrene. Similar results have been reported for sorption of *n*-hexane in preswollen polystyrene by Enscore et al.[7] and for sorption of lower alcohols in PMMA by Connelly

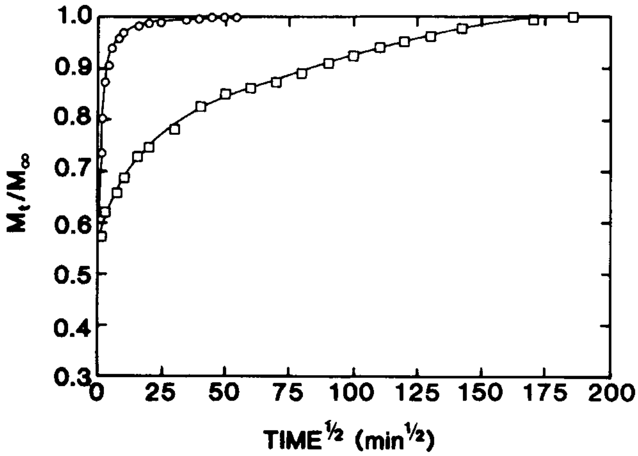

Fig. 3. Comparison of the normalized kinetics of propane sorption in as-received (□) and *n*-hexane-preswollen polystyrene (○); $T = 30°$ C; $P = 700$ mm Hg; $d = 0.534$ μm.

et al.[8] The large difference in the rates of sorption into these two samples is emphasized in Figure 3, in which the data of Figure 1 are presented as a plot of fractional sorption vs. the square root of time. The differences in shape of the two curves indicate that long-term relaxation processes play a much lesser role for propane sorption in the preswollen sample at 700 mm Hg and 30°C. Specifically, at the conditions studied, 90% of the apparent equilibrium uptake in the preswollen sample was complete in the first 15 min of the experiment, while approximately 6 days were required to reach the same fractional uptake in the as-received polystyrene.

The consolidation of the preswollen sample is presumably much slower than either the diffusive addition or diffusive removal of the swelling penetrant. Resorption into the distended sample is then quite rapid since most of the penetrant-induced, long-term relaxations which control the later stages of sorption in the as-received sample have already taken place during preswelling. Although long-term relaxations control a smaller fraction of the sorption of propane in *n*-hexane-preswollen polystyrene than in the as-received sample, their effect is not negligible. The time scale of the long-term response at 700 mm Hg shown in Figure 4 is much longer than the characteristic time associated with the approach to Fickian equilibrium, even using a conservative estimate of 10^{-12} cm^2/s for the diffusivity. This value is an order of magnitude smaller than the value of 10^{-11} cm^2/s reported by Barrie et al.[25] Apparently, at the higher pressures studied, long-term relaxations control the later stages of sorption in the *n*-hexane-preswollen samples, and the contribution of this non-Fickian component becomes more important as the penetrant activity is increased.

The kinetics of a subsequent propane sorption experiment are expected to depend on the prior history of the preswollen sample and, therefore, upon the time a preswollen sample is exposed to vacuum following the preswelling treatment but prior to the propane sorption. The kinetics of sorption of propane at 700 mm Hg and 30°C in six *n*-hexane-preswollen samples with systematically different histories are shown in Figure 5. As expected, the

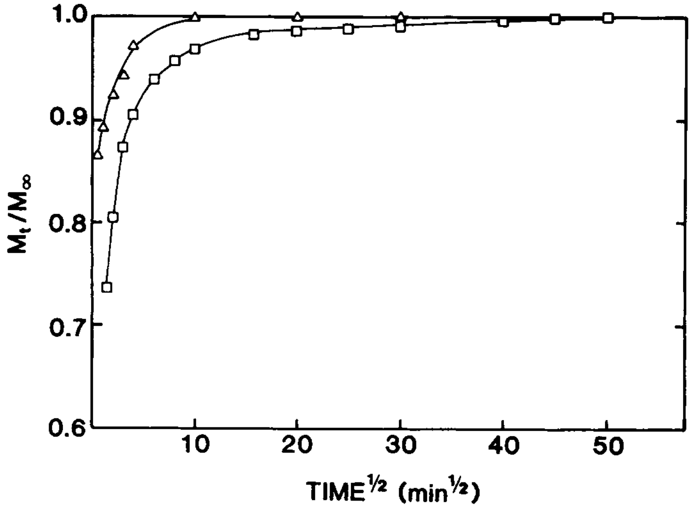

Fig. 4. Comparison of the normalized kinetics of propane sorption in *n*-hexane-preswollen polystyrene at propane pressures of 50 (△) and 700 mm Hg (□). T = 30°C, d = 0.534 μm.

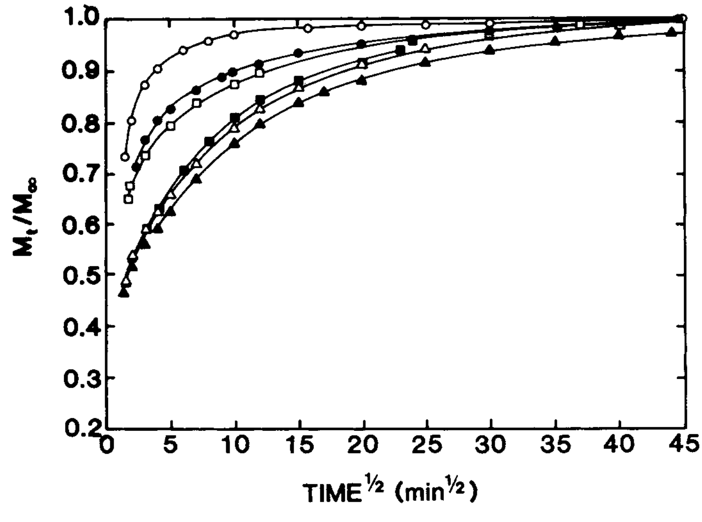

Fig. 5. The normalized kinetics of propane sorption in *n*-hexane-preswollen polystyrene after various prior vacuum times. P = 700 mm Hg, T = 30°C, d = 0.534 μm.

Symbol	Immediate prior vacuum time (min)	M_∞ (g/100 g)
○	62	1.345
●	2,653	1.206
□	3,282	1.171
■	11,300	1.103
△	20,300	1.081
▲	29,920	1.075

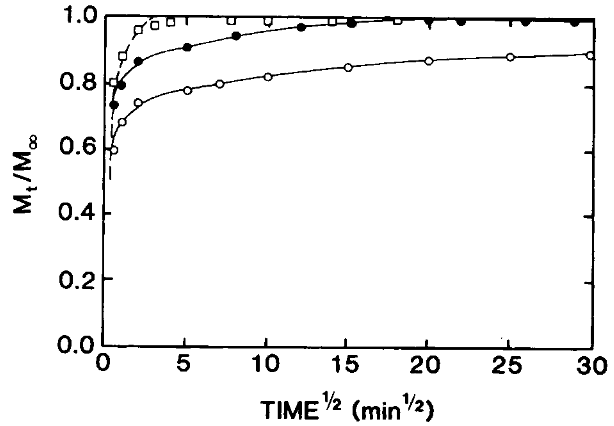

Fig. 6. Comparison of the normalized kinetics of propane sorption at 350 mm Hg in as-received and propane-preswollen polystyrene. $T = 30°C$, $d = 0.534$ μm. (○) as-received; (●) resorption; (□) preswollen with propane at 700 mm Hg; (---) Fickian model, $D = 10^{-12}$ cm^2/s.

sorption kinetics become more protracted as the prior vacuum time is increased. These data are completely consistent with the observations of Enscore et al. for the *n*-hexane/polystyrene system,[6] where the sorption kinetics in preswollen samples also became more protracted as vacuum aging time increased. Presumably, the excess volume created in the polymer by the preswelling treatment relaxes during vacuum aging, and the sorption kinetics become more prolonged as the polymer densifies.

The time dependence of propane sorption at a much lower propane pressure (350 mm Hg) in polystyrene microspheres, which have been previously dilated by exposure to propane 700 mm Hg and 30°C, is shown in Figure 6. Also shown in the figure, for comparison, are data for propane sorption and resorption in an as-received sample at the same temperature and pressure. As was the case for sorption in *n*-hexane-preswollen samples, the rate of sorption is increased by the preswelling treatment. The sorption kinetics for the propane-preswollen samples, however, are quite different than those for either the *n*-hexane-preswollen or as-received samples. The contribution of relaxation controlled sorption in the samples, dilated by propane, was negligible over the time scale of the experiment. The sorption levels achieved in the samples in the first few minutes of a sorption experiment remained essentially constant for at least 2–5 days.

The difference between the sorption kinetics for samples exposed to the *n*-hexane and propane preswelling treatments, respectively, may be due to the creation of specifically sized voids within the polymer during the preswelling treatment. If the size and arrangement of the molecular scale gaps are determined by the specific templating associated with the dimensions of the preswelling penetrant, the resulting polymer "structure" would not have to rearrange to accommodate propane molecules optimally in the case of propane-preswollen samples, while in the case of *n*-hexane-preswollen samples additional chain motion might be required to accommodate propane. Presumably, this would result in a decrease in the contribution of relaxation controlled sorption for the propane-preswollen sample as compared to the as-received and *n*-hexane-preswollen samples, as is observed.

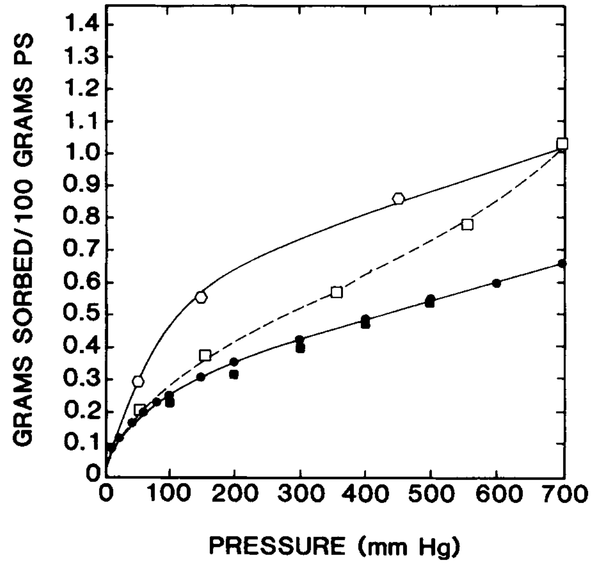

Fig. 7. Comparison of the apparent equilibrium sorption isotherm for propane in propane-preswollen polystyrene with the short term and apparent equilibrium sorption isotherms for propane sorption in as-received polystrene: (●) short term measurements; (■) Barrie et al.[25] short term measurements; (□) long term measurements; (○) preswollen with propane, 700 torr, 30 min prior vacuum, short term measurements.

Apparent Equilibrium Sorption in As-Received and Preswollen Polystyrene

A comparison of propane sorption isotherms in as-received and propane preswollen polystyrene is presented in Figure 7. Four different sets of data are plotted in the figure. The closed circles in Figure 7 represent short term, pseudo-equilibrium sorption levels, i.e., the mass of propane sorbed in the first (essentially Fickian) stage of sorption, in as-received polystyrene. The apparent equilibrium sorption levels for these conditions are represented by the open squares. The independently performed sorption measurements of Barrie et al.[25] for this system are also presented in the figure as the closed squares, and agree quite well with the short term data of the present study. Each hexagon in Figure 7 represents the apparent equilibrium sorption of propane in a sample individually preswollen with propane. These data are identical to the short term values for propane sorption in the preswollen samples, since, as noted above, the sorption levels achieved in the samples in the first few minutes of a sorption experiment remained constant over the relatively brief time period of the experiment.

The sorption isotherm for the propane-preswollen sample is quite different than either the short term or apparent equilibrium sorption isotherm in as-received polystyrene. In general, the sorption levels in the propane-preswollen samples are significantly higher than those of the as-received samples. Presumably these higher sorption levels result from an increase in excess volume of the polymer caused by the preswelling treatment. This phenomenon has often been observed before, and it is common procedure in high pressure gas sorption experiments to "condition" the polymer sample by exposing it to the highest penetrant pressure to be studied, before beginning the sorption experiments.[9] Conditioning results in a stable isotherm, but with higher sorption levels than the unconditioned sample. The propane preswelling treatment described here could, therefore, be referred to as propane conditioning.

The apparent equilibrium isotherm for propane in as-received polystyrene exhibits dual mode behavior at low pressures and an upturn characteristic of a Flory–Huggins isotherm at higher penetrant pressures. This S-shaped isotherm, which has been proposed as the general isotherm for penetrant/glassy polymer sorption, is encountered if a sufficiently wide range of penetrant concentrations is studied.[18] At low concentrations, classical dual mode behavior is observed. At higher penetrant concentrations, the effective glass transition temperature of the penetrant/polymer phase decreases, approaching the temperature of the experiment, and, if the concentration of penetrant is high enough, Flory–Huggins type swelling results. As discussed by Connelly et al.,[8] the classic dual mode sorption isotherm appears to be the low pressure limit of a more general isotherm for penetrant sorption in glassy polymers, which consists of the sum of a Langmuir isotherm and Flory–Huggins isotherm. At low activities, the Flory–Huggins isotherm reduces to a linear form, and the general isotherm reduces, therefore, to the conventionally observed dual mode model. When the concentration range studied is large enough to encompass both types of behavior, the general S-shaped isotherm combining Flory–Huggins with Langmuir sorption is observed.

Another subclass of the general isotherm has recently been reported by Chiou et al.[26,27] and Kamiya et al.[28] They have published high pressure CO_2 sorption data for systems in which the stable isotherm exhibits dual mode nature at low pressures and a linear Henry's law portion at higher pressures. In these systems, the extrapolation of the linear region to zero pressure passes through the origin, rather than intersecting the concentration axis at a concentration equal to the Langmuir capacity of the glass. At sufficiently high concentrations, the gas appears to plasticize the polymer sufficiently to lower the effective T_g below the temperature of the experiment, thereby eliminating the Langmuir contribution to the total sorption, without significant Flory–Huggins type swelling of the polymer (and a resulting upturn in the sorption isotherm) occurring.

The propane preswelling treatment also affects the shape of the subsequent propane sorption isotherm. Interestingly, only dual mode behavior is observed in the isotherm for propane-preswollen samples, even though the concentration range studied is identical to that for as-received samples which exhibited the S-shaped isotherm. No swelling, which produces the upturn in the sorption isotherm, occurs during the sorption experiment because the samples were preswollen before determination of the propane isotherm. Similar effects have been reported for high pressure gas sorption measurements. An upturn at high pressure is often observed in the sorption isotherm for the initial exposure of a gas to a glassy polymer. The upturn is eliminated, however, by the conditioning treatment described above.[9] The isotherms measured in the conditioned glass obey the dual mode sorption model, but possess a Langmuir capacity parameter which is larger than the initial capacity of the unswollen glass.

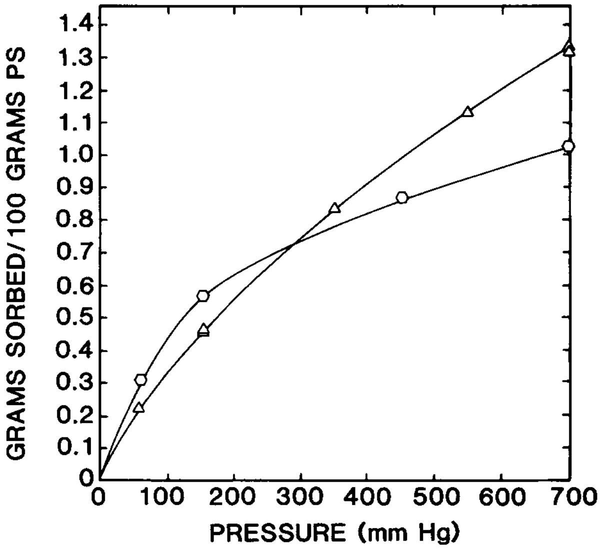

Fig. 8. Comparison of the apparent equilibrium sorption isotherm for propane in propane-preswollen and *n*-hexane-preswollen polystyrene: (○) preswollen with propane; (△) preswollen with hexane; $T = 30°$ C.

It is apparent that, due to the extremely protracted response of a glassy polymer to a perturbation, the type of isotherm observed for the sorption of a gas or vapor in a glassy polymer depends not only upon the temperature and concentration range of the experiment, but also upon the prior history of the polymer sample and the duration of the sorption measurements.

Another example of a history effect is shown in Figure 8 where a comparison of propane sorption isotherms in propane and *n*-hexane-preswollen polystyrene is presented. The open triangles represent the apparent sorptive equilibrium of propane in polystyrene, preswollen with *n*-hexane, and the open hexagons represent the apparent equilibrium of propane in propane-preswollen samples. As was the case with the propane-preswollen samples, the propane sorptive capacity of polystyrene is greatly increased by preswelling the sample with *n*-hexane, and no upturn was observed in the propane sorption isotherm for the *n*-hexane-preswollen samples.

The propane sorption levels in *n*-hexane-preswollen samples are greater than those in propane-preswollen samples above 300 mm Hg. At pressures below approximately 300 mm Hg, however, the propane-preswollen samples sorb more. Apparently, the *n*-hexane preswelling treatment creates more excess volume in the polymer than the less severe propane preswelling treatment, but this excess volume is not optimally configured to accommodate propane molecules. The greater excess volume of the *n*-hexane-preswollen samples results in higher propane sorption levels, at pressures where propane initiates significant relaxations in polystyrene. The two isotherms for the preswollen samples intersect at about 300 mm Hg propane pressure, which is also the approximate pressure of the upturn in the as-received, equilibrium sorption isotherm presented in Figure 7. It appears, therefore, that a "critical" propane concentration must be reached before large-scale relaxations and rearrangement of the excess volume are initiated by propane sorption in

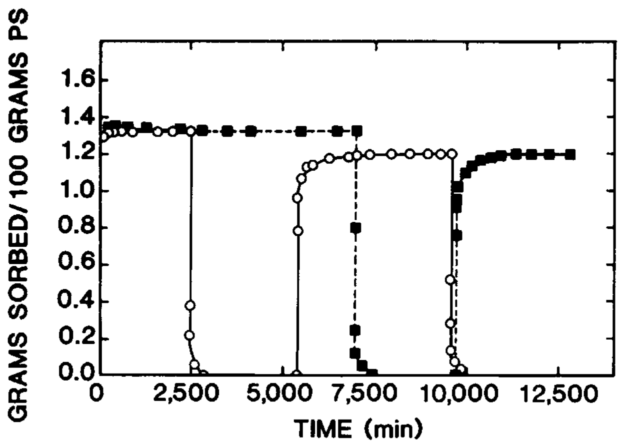

Fig. 9. Comparison of propane sorption in *n*-hexane-preswollen polystyrene samples with different prior vapor times but equal prior vacuum times: (○) sample 1; (■) sample 2; $T = 30°C$.

polystyrene. Thus, below approximately 300 mm Hg, these rearrangements do not occur to a significant extent, and the *n*-hexane-preswollen samples, therefore, sorb less than the propane-preswollen samples, which do not have to undergo rearrangements to accommodate propane molecules optimally. These same rearrangements would also explain the protracted sorption kinetics in the *n*-hexane-preswollen samples compared to the propane-preswollen samples.

Consolidation of Preswollen Polystyrene

Both the rate and apparent equilibrium of propane sorption in polystyrene are increased by preswelling the polymer with *n*-hexane. Moreover, the rate of sorption in subsequent cycling experiments decreases dramatically when the preswollen sample is exposed to vacuum for long periods prior to resorption (Fig. 5). These results are consistent with those of Enscore et al.[7] for *n*-hexane sorption in polystyrene. Enscore et al.[7] also demonstrated that the increased apparent equilibrium sorption observed in preswollen samples decays when the sample is exposed to vacuum prior to resorption. Similar results were obtained in this study.

A comparison of the resorption of propane at 700 mm Hg and 30°C, for two preswollen samples with different first cycle contact times, is presented in Figure 9. The first cycle sorptions are included to emphasize the difference in prior contact times. The results presented in Figure 9 demonstrate that the apparent equilibrium propane uptake in the preswollen sample is virtually independent for the prior contact with 700 mm Hg propane. Specifically, both samples sorbed to 1.20 g propane/100 g polystyrene after differing contact times with vapor 2500 and 7000 min, but the same total prior vacuum aging time 2650 min. This indicates that the presence of propane at a low activity arrests the consolidation of the preswollen polymer over the protracted time scale of these experiments. Presumably, penetrant molecules sorbed in the hole-filling mode of sorption restrict chain motions, which would otherwise lead to consolidation of these expanded regions in the absence of the penetrant.[8] This process might be termed "antiplasticization." Presumably,

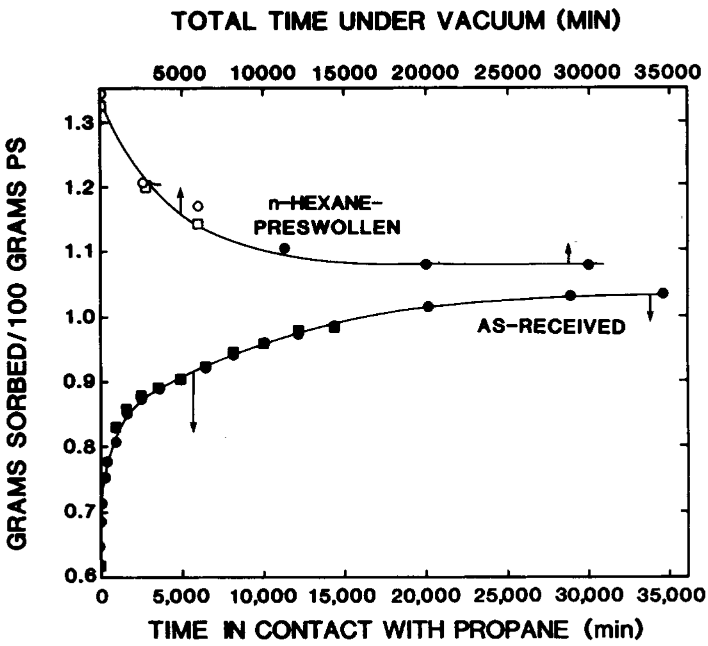

Fig. 10. Comparison of the increase in sorption capacity of an as-received polystyrene sample during exposure to propane with the decrease in sorption capacity of an *n*-hexane-preswollen sample during vacuum aging. Resorption equilibria for multiple cycles decreases with total prior vacuum time. $T = 30°C$, $P = 700$ mm Hg, $d = 0.534$ μm. $M_\infty = 1.075$, $M_\infty^0 = 1.340$, $k_c = 2.46 \times 10^{-4}$ min^{-1}.

the more expanded regions of the glass preferentially absorb gas molecules at relatively low pressures resulting in densification and stiffening of the composite polymer–gas mixture.

The apparent equilibrium concentration for each cycle was also found to correlate with the total prior vacuum desorption time of the sample, independent of the cycle number of the total time of exposure to propane at 700 mm Hg. This also indicates that the presence of propane during aging arrests the relaxation of the preswollen polymer. These results are shown in Figure 10. The latter stages of propane sorption in as-received polystyrene are shown for comparison in the lower portion of Figure 10. The changes in sorptive capacity of the polymer, with time, shown in Figure 10 trace the swelling relaxation of the as-received sample (which occures in the continuing presence of propane) and consolidative relaxation of the preswollen samples (which occurs only in the absence of propane). The same apparent equilibrium sorptive capacity is approached asymptotically from both directions, suggesting the approach to a true equilibrium concentration for propane in polystyrene at these conditions. These results are very similar to those reported by Enscore et al.[7] for probing polystyrene with *n*-hexane and Connelly et al.[8] for *n*-propanol sorption in PMMA.

The solid line through the consolidation data in Figure 10 was calculated using an arbitrary first order relaxation model:

$$\frac{M'_\infty - M_\infty}{M_\infty^0 - M_\infty} = \exp(-k_c t) \tag{1}$$

where M'_∞ is the apparent equilibrium concentration after a given cumulative vacuum time t, k_c is the first order relaxation constant, and M_∞ equals the asymptotic concentration of propane in the glassy polymer at long times or true equilibrium. The apparent equilibrium concentration of propane in the preswollen sample when $t = 0$ or immediately after dilation by preswelling, M^0_∞, can be obtained by extrapolation, but was approximately equal to M'_∞ of the first cycle in Figure 10 which was performed after only 62 min of prior vacuum. The model fits the data quite will, implying that a simple first-order relaxation process describes the consolidation of the preswollen sample during protracted storage under vacuum.

The relaxation constant k_c was found to be approximately 2.5×10^{-4} min^{-1} in fair agreement with the relaxation constant found by Enscore et al. of 6.7×10^{-4} min^{-1} for *n*-hexane in polystyrene.[7] The agreement of the first-order consolidation constants between the two studies confirms that the mechanism of consolidation of polystrene *in vacuo* is independent of the penetrant used to monitor the consolidative relaxations.

SUMMARY

The sorption of propane in the as-received samples was initially rapid and Fickian, followed by a relaxation-controlled sorption stage, whose contribution to the total sorption increased as the penetrant activity increased. The apparent equilibrium sorption isotherm for these samples was concave towards the pressure axis at low propane pressures and convex at high pressures where swelling becomes more important. This behavior appears to reflect rather general behavior characterizing the absorption of penetrants in polymeric glasses if a sufficient range of activities, and, in turn, concentration is encompassed by the experimental protocol.

Preswelling with 0.90 activity *n*-hexane at 15°C or 700 mm Hg propane at 30°C increased both the rate and apparent equilibrium of subsequent propane sorption, and decreased the contribution of long-term relaxation controlled sorption. At pressures above approximately 300 mm Hg of propane, *n*-hexane preswelling resulted in a greater increase in sorption, but, below this pressure, propane preswelling resulted in greater increases. At all pressures, the kinetics of sorption were more rapid for the propane-preswollen samples in which the contribution of relaxation controlled sorption was negligible. It seems likely that *n*-hexane preswelling creates more excess volume in the polymer than does propane preswelling, but the excess volume of the *n*-hexane-preswollen samples must rearrange to accommodate propane molecules optimally. It appears that this rearrangement, which also produces the long term drift in the sorption kinetics, occurs to a significant extent only when the concentration of propane sorbed in the polymer is above a certain level.

Finally, cyclic sorption experiments revealed that the increased levels and rates of sorption observed in the preswollen samples decayed during vacuum aging, although the presence of low levels of propane in the polymer during aging arrested these relaxations. The results reported here regarding the effect of sorbed penetrants on consolidative aging are entirely consistent with those reported earlier for *n*-hexane in polystyrene and for *n*-propanol in PMMA.

Penetrant molecules sorbed in the hole-filling mode of sorption presumably restrict the chain motions which would otherwise lead to consolidation of these expanded regions in the absence of the penetrant. The presence of propane in polystrene arrested the consolidation of the polymer. These findings confirm earlier results which suggest that low concentrations of penetrants arrest consolidative aging of preswollen glassy polymers, however, much more study is called for to incorporate these limited findings into the more complex tapestry woven from the data for the aging of preswollen PMMA in the presence of ethanol, methanol, and water.

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