The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders. IV

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SYNOPSIS

Uniform, submicron-diameter polystyrene (PS) and poly(methylmethacrylate) (PMMA) microspheres were dilated by preswelling with pure organic vapors followed by rapid removal of the preswelling penetrant by protracted evacuation of the preswelling chamber to a pressure of 10^{-3} mm Hg. Aging of the preswollen polymers was carried out both in vacuum and in the presence of various penetrants at sorbed concentrations typically less than 2 wt %. Inferences about relaxations of the polymers were based upon changes in concentrations of the penetrants within the microspheres, at a given temperature and penetrant activity, which result from aging in vacuum or in the presence of penetrant. The kinetics of the relaxations were monitored by probing the expanded glasses with relatively low concentrations of penetrants. In general, the continuous presence of these low concentrations of probe molecules either arrested or retarded the ensuing relaxations as compared with the aging that occurred in vacuum. A series of lower monohydric alcohols, lower n-alkanes, and some other similar penetrants were used as probes to test explicitly and systematically the effects of size and structure of the penetrant contacting the polymer during aging on the decay of excess sorption capacity of the preswollen glassy polymers. Decay of excess sorption in the presence of penetrant was evident only when molecularly small penetrants with interactive functional groups, alcohols for example, were sorbed into preswollen PMMA. This result suggested that the relaxation occurring in the presence of penetrant involved specific interactions between the penetrants and the carbonyl groups in the PMMA.

INTRODUCTION

Berens,[1,2] investigating the sorption and transport of vinyl chloride monomer (VCM) in polyvinyl chloride (PVC), pioneered the use of uniform submicron diameter polymer microspheres for sorption experiments. Microspheres were used because similar studies in fibers and films are prohibitively long since the diffusivities of organic penetrants in glassy polymers are low. The monodispersity of the microspheres permits unequivocal interpretation of the sorption kinetics in terms of a meaningful diffusion coefficient.[3] Berens also discovered that the microspheres can be used to characterize relaxations of glassy polymers induced by low concentrations of sorbed penetrants. After a diffusive pseudoequilibrium is achieved relatively early in the experiment, a slow uptake of penetrant occurs, which is indicative of relaxation processes taking place in the polymer. The diffusion and relaxation phenomena often occur on different timescales and can, therefore, be readily separated.

Berens[1,4] observed that PVC microspheres at temperatures below T_g, preswollen by sorption, followed by rapid and complete desorption of a high concentration of VCM (3.8 g VCM/100 g PVC), sorb greater amounts of VCM in subsequent sorptions at low activities (< 1 g VCM sorbed/100 g PVC) than does untreated PVC. The apparent equilibrium sorption of VCM, for repeated sorptions in preswollen PVC, alternating with desorptions, at a constant, low activity, decreases monotonically

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with cumulative time of exposure to vacuum, approaching the level attained at equilibrium in the untreated sample. Since the sorptive capacity of a polymer, at a given temperature and vapor activity, may be taken as a direct measure of the microvoid content present in the sample at the time of the sorption experiment, the monotonic decline in sorption capacity apparently traces the course of the deswelling relaxation, consolidation from a preswollen state of high free volume.[4]

Enscore et al.[5,6] carried out similar studies of the sorption characteristics of n-hexane, at low activities, in polystyrene (PS), preswollen with n-hexane in a manner similar to that used to preswell PVC with VCM. They observed the same qualitative behavior and demonstrated that relaxations resulting in the decline in sorption capacity occur primarily in evacuated or penetrant-free samples, and relaxations occur very slowly or not at all in the presence of sorbing penetrants. The decline is, apparently, independent of the frequency and duration of sorption and is a function only of the cumulative vacuum time. This same pattern was observed by Connelly et al.[7] for sorption of low levels of n-propanol in poly(methyl methacrylate) (PMMA), preswollen with methanol, and this pattern was also observed by Stewart et al.[8] for sorption of low levels of propane in PS, preswollen with n-hexane. Figures 1–3 illustrate this pattern with data from Stewart et al.[8] on the sorption of propane in PS. The effect of preswelling on sorption is shown in Figure 1. The apparent equilibrium is higher and is achieved more rapidly in the preswollen sample than in the as-received sample. The data of Figure 2 demonstrate

that the apparent equilibrium concentration in the preswollen sample is independent of the duration of sorption. Two preswollen samples, given different sorption periods but identical vacuum treatments, reach the same apparent equilibrium. The data presented in Figure 3 show that the apparent equilibrium concentration in the preswollen sample is a monotonic function of the cumulative vacuum time and the concentration approaches the asymptotic sorption level observed in the as-received sample at long cumulative vacuum times.

Connelly et al.[7] observed a different pattern for the sorption of methanol in PMMA. They found that the methanol sorption level, at low activities, in PMMA preswollen with high activity methanol, rises rapidly to a peak and then decays monotonically during continuous sorption until the amount sorbed levels off at the concentration reached in an as-received sample at apparent equilibrium. By comparing continuous sorption with cyclic sorptions having short sorption periods, Connelly et al. concluded that the decline in methanol sorption capacity occurs at the same rate during the continuous presence of methanol as it does in vacuum. Connelly's data are shown in Figures 4 and 5. The same behavior was reported for the sorption of CO_2 in PMMA preswollen with methanol.[9]

A third pattern was observed by Connelly et al.[7] for the sorption of water and ethanol in PMMA. In these systems, the sorption capacity decays during the continuous presence of penetrant, but the concentration appears to level off higher than it does in the as-received sample. This pattern is illustrated in Figure 6.
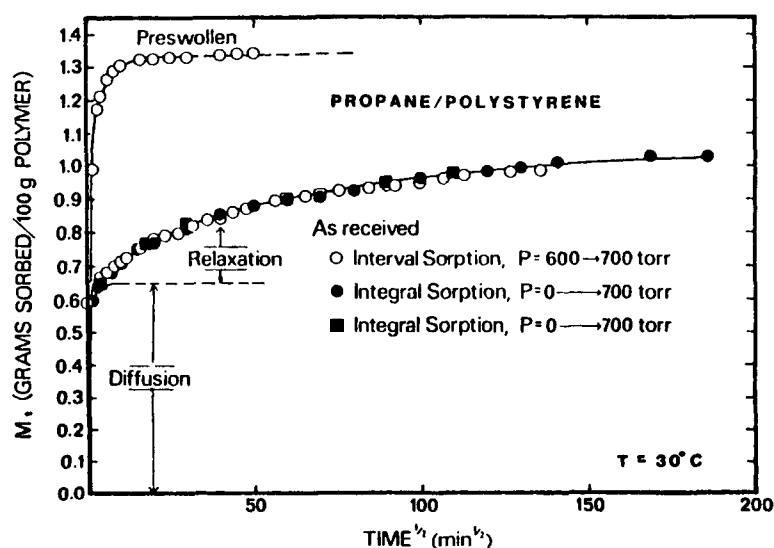

Figure 1 Propane sorption in as-received and preswollen polysterene.[8]

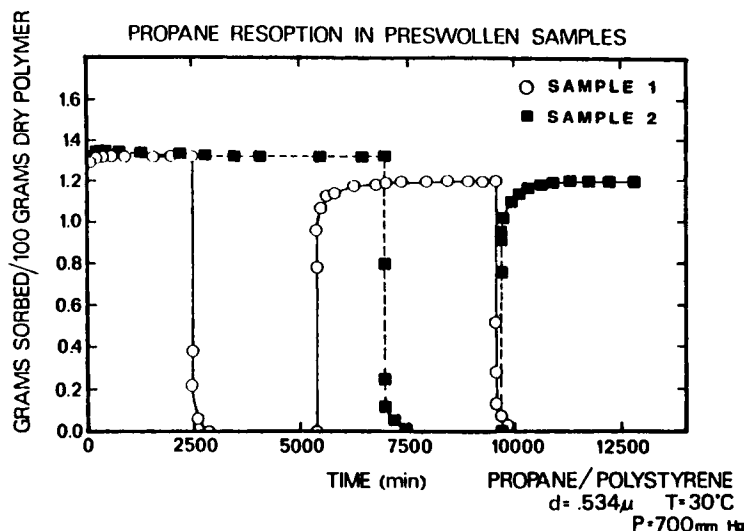PROPANE RESOPTION IN PRESWOLLEN SAMPLES

Figure 2   Comparison of propane sorption in n-hexane preswollen polystyrene samples with different prior sorption durations but equal prior vacuum treatments.[8]

Connelly et al.[7] observed that the normalized rate of sorption decay in vacuum for n-propanol in preswollen PMMA is the same as the decay rate for methanol sorption. The interpretation was that these sorption decays are indicative of identical processes taking place within the polymers; these processes are all being described as "aging" or "consolidative relaxation." The presence of n-propanol at low concentrations during aging apparently "ar-

rests" the aging of preswollen PMMA, while the aging of PMMA is unaffected by the presence of low concentrations of methanol. The pattern exhibited by aging PMMA in the presence of ethanol was intermediate to the methanol and n-propanol cases. Ethanol apparently "retards" the aging or consolidative relaxations of preswollen PMMA.

In the current study, the effects of penetrant size, polymer and penetrant polarity, temperature, and
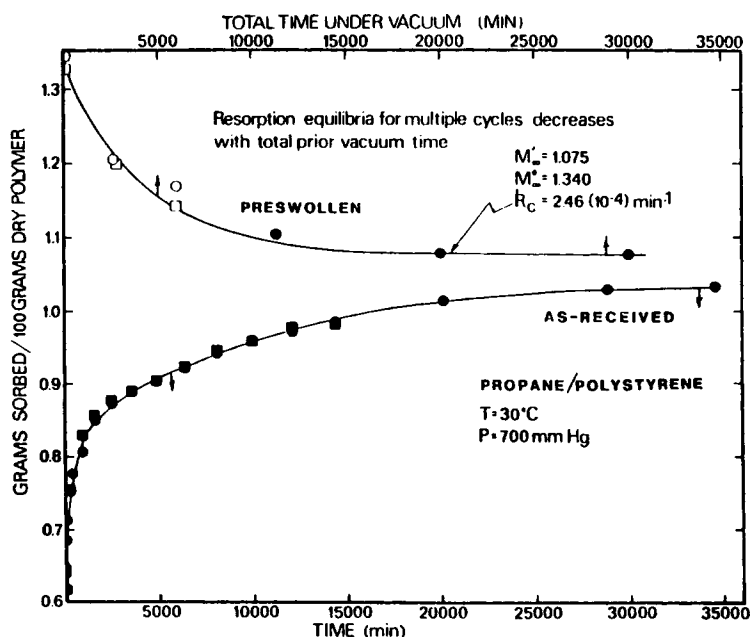

Figure 3   Monotonic decline in apparent equilibrium sorption of propane in preswollen polystyrene as a function of cumulative time under vacuum.[8]
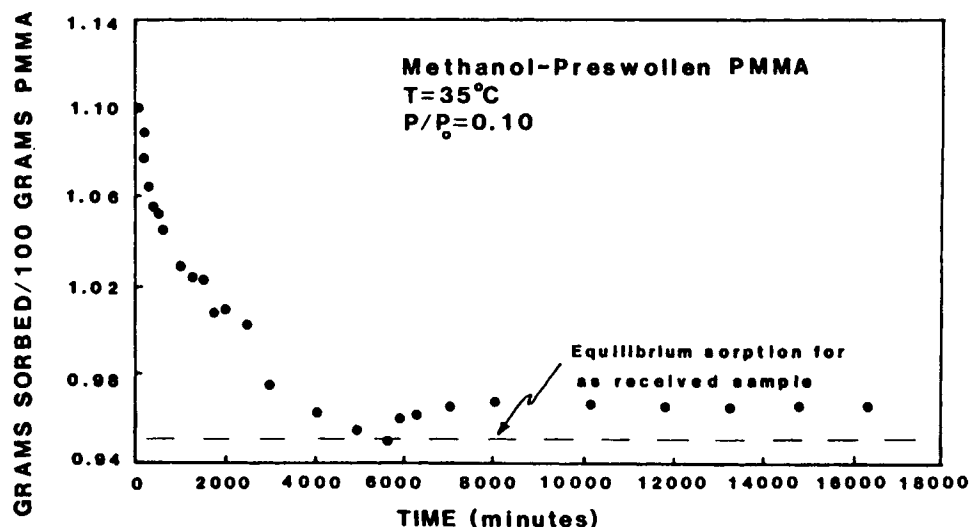
Figure 4   Sorption of methanol, 35°C, 0.1 activity, in preswollen PMMA.[7]

penetrant concentration on these aging phenomena are investigated. These parameters were chosen in an attempt to determine their effect on these sorption and aging phenomena and, ultimately, to suggest a molecular mechanism that describes the effect of sorbed penetrant on aging. These investigations may yield a basis for relating the relaxations occurring in the presence of penetrant to a free volume-based relaxation mechanism.[10] For example, larger penetrants may inhibit relaxations more than smaller penetrants by more effectively filling free volume. Also, relaxation might be more inhibited at higher penetrant concentrations because more free volume is occupied by the penetrant. Although the experimental results of the studies reported here are generally consistent with those of Connelly et al.,[7]

alternative ideas concerning the molecular interpretation of these phenomena are discussed.

EXPERIMENTAL

Materials

The emulsion polymerized PMMA and PS microspheres were provided by the B. F. Goodrich Company Research and Development Center, Brecksville, Ohio. The weight average molecular weights, determined by GPC, of the PMMA and PS are 368,000 and 270,000, respectively. The weight average diameters, measured by electron microscopy, are 0.5578 micron and 0.5479 micron. The T_gs, from DSC scans, are 126°C and 103°C.
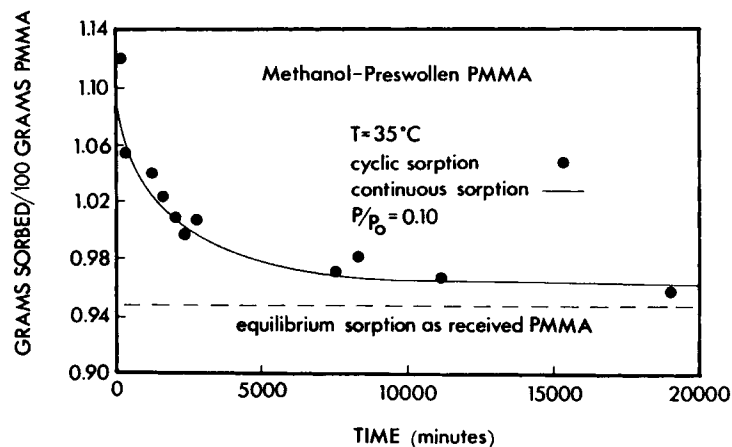

Figure 5   Comparison of continuous and cyclic sorption of methanol, 35°C, 0.1 activity, in preswollen PMMA.[7]
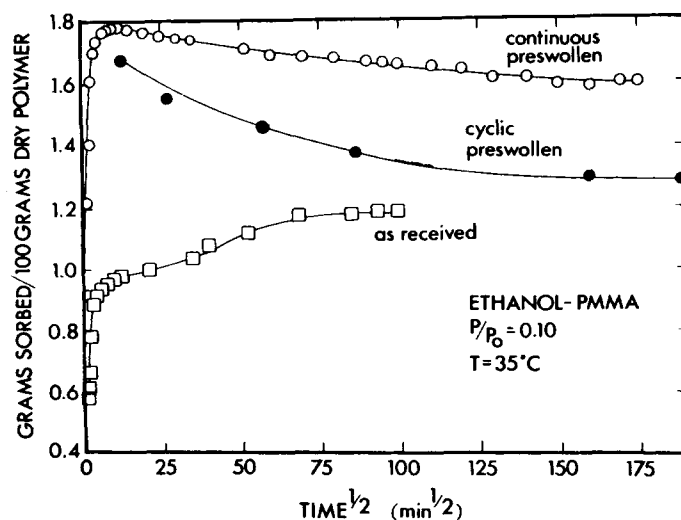
Figure 6   Sorption of ethanol, 35°C, 0.1 activity, in preswollen and as-received PMMA.

Gaseous penetrants, propane, ethane, and methyl chloride, of purity > 99 mole %, were obtained from Air Products and Chemicals, Inc. Certified methanol (99.9 mole %) and n-hexane (99 mole %) were acquired from Fisher Scientific Company. Ethyl alcohol, 200 proof, was obtained from U.S. Industrial Chemicals Company. Certified n-propanol was purchased from J. T. Baker Chemical Company. Water used in the experiments was deionized and distilled. All liquid penetrant sources, methanol, ethanol, n-propanol, n-hexane, and water, were subjected to at least two freeze–thaw cycles to remove dissolved gases.

Apparatus and Procedure

The sorption experiments, with the exception of those in which methyl chloride was used, were performed with a Cahn Electrobalance, Model RG 2000, housed in a glass vacuum system. The system included a 12 L reservoir to minimize fluctuations in penetrant pressure during the experiment. The system was enclosed within a wooden box where the temperature was controlled to ±0.2°C by a Sargent Thermonitor temperature regulator; two or three 200-watt light bulbs were used as heat sources. The glass system was connected to a pressure transducer, a penetrant source, and a vacuum service. The vacuum service, consisting of a vacuum pump in series with a high vacuum diffusion pump, could reduce the pressure in the system to about 10^{-3} mm Hg. Cylindrical sample pans, made of fused quartz, 10–15 mm in diameter and length, 90–120 mg in weight,

were suspended by thin glass fibers on both sides of the electrobalance into 12 in. glass hangdown tubes. The polymer sample was placed in one pan and tare weights in the other. The hangdown tubes and the glass surrounding the balance were wrapped with aluminum foil to shield the balance from light and to minimize static.

The experiments were begun by calibrating the balance, according to the manufacturer's instructions, over a range of 200–300 mg. Measurements could be made with a sensitivity of about ±5 μg. The polymer sample (= 205–210 mg) was placed in the sample pan and evacuated, along with the rest of the system, for 10–12 h for an untreated sample or 30–45 min for a preswollen sample. Next, the section of the system containing the Cahn balance was sealed off, and the vacuum service was closed. The remainder of the system was overfilled with penetrant, by a factor predetermined empirically, so that when the sample chamber was opened, the desired experimental pressure would be achieved. The sample chamber was then opened slowly so that none of the polymer would be blown out of the sample pan as the penetrant entered the chamber. A timer was started and the weight of the sample, as it absorbed penetrant, was recorded on a Leeds and Northrup recorder. The experiment was allowed to continue until apparent equilibrium was achieved. Generally, experiments were discontinued if negligible weight change was observed over a 24–48 h period. Desorption kinetics of the penetrant as measured similarly during evacuation of the sample after the sorption ended. For the experiments using methyl chloride, a McBain Spring System was used

in place of the Cahn Electrobalance because of anticipated chemical interactions between methyl chloride and the electrobalance. The experimental procedure for the McBain System is described by Jacques and Hopfenberg.[11,12]

Preswelling

Preswollen PS was prepared by exposure of the microspheres to n-hexane at 15°C and 0.90 activity until apparent equilibrium was reached. The high activity ensured a high level of penetrant sorption by the polymer and, therefore, a high degree of swelling. The low temperature prevented coalescence of the microspheres. The kinetics of the n-hexane sorption was followed on the Cahn Balance in the same manner as described above. After apparent sorptive equilibrium was reached in the microspheres, the swelling penetrant was rapidly desorbed, leaving the polymer dilated, since polymer consolidation lags penetrant desorption. Preswollen PMMA was prepared similarly by exposure to methanol at 10°C and 0.98 activity. The microspheres were then stored in a freezer at −10°C to quench further relaxation until the samples were used in an experiment.

RESULTS

Effects of Penetrant Size and Polymer and Penetrant Polarity on Aging

Prior results using penetrants of the homologous series, methanol, ethanol, and n-propanol in pre-

swollen PMMA, suggest that penetrant size may be a significant factor controlling aging as determined by the decay in concentration occurring during the continuous presence of penetrant. As penetrant size increases in this series, the concentration drop in the preswollen sample during the continuous presence of penetrant becomes less pronounced, with no apparent drop when the PMMA microspheres are aged in the presence of n-propanol. Since polarity decreases as penetrant size increases in this homologous series, the results also may indicate that penetrant polarity contributes to the observed behavior. Since the decline in concentration has been observed only in PMMA, which is a relatively polar polymer with carbonyl groups pendant from the chain, the polarity of the polymer may be a factor.

The effects of penetrant size and polymer and penetrant polarity on the observed decay in asymptotic sorption are elucidated by a series of experiments in which these molecular features are explored independently. Ethane and propane are penetrants of approximately the same size as methanol and ethanol, respectively, but are nonpolar. Polystyrene is less polar than PMMA and does not contain hydrogen bonding sites.

Data in Figures 7 and 8 represent sorption of ethane and methanol, respectively, at 35°C in both as-received and preswollen PMMA. The sorption decay during the continuous presence of penetrant occurs for methanol but not for ethane. The sorption decay with methanol did not exactly follow the pattern reported by Connelly et al.,[7] but instead ap-
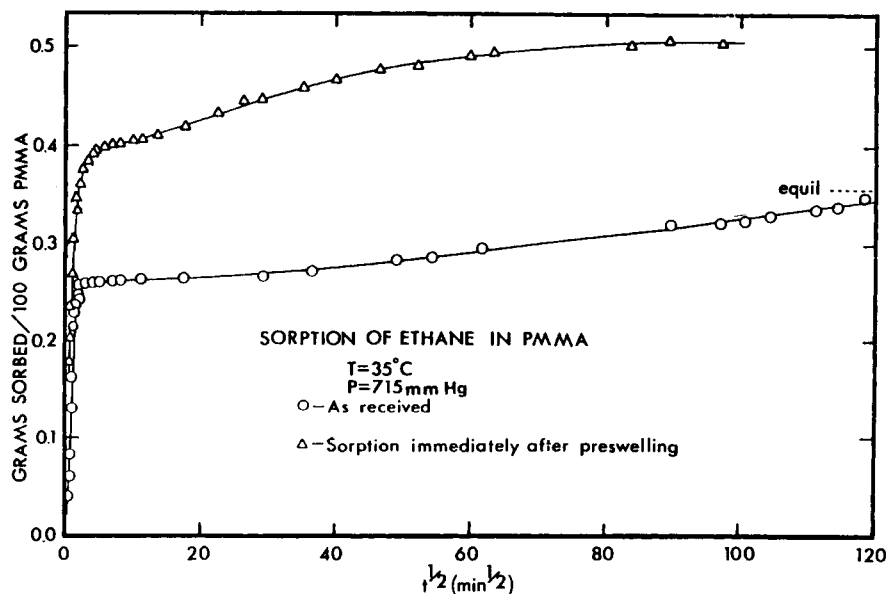

Figure 7   Sorption of ethane in preswollen and as-received PMMA (new batch).
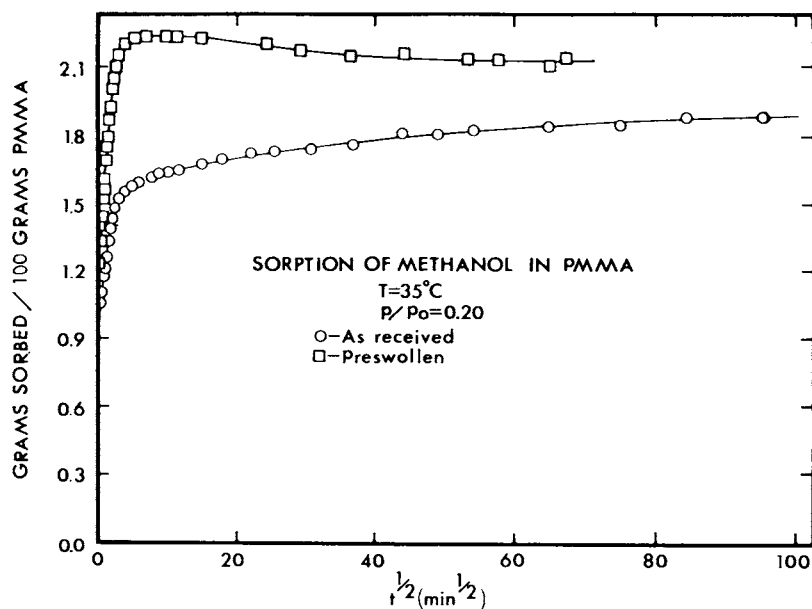
Figure 8   Sorption of methanol, 35°C, 0.2 activity, in preswollen and as-received PMMA (new batch).

peared more like ethanol/PMMA. Since the PMMA used in the experiments was from a different batch than that used by Connelly, variations between batches of polymer might contribute to the observed experimental differences. Since aging by both batches of PMMA proceeded in the presence of methanol, there would be qualitative similarities

between different polymer batches. Data presented in Figure 9 show the sorption of propane in as-received and preswollen PMMA at 35°C. No concentration drop occurs. Connelly et al.[7] reported that the concentration of ethanol does decay during the continuous presence of penetrant in the batch of PMMA used in their experiments (Fig. 6).
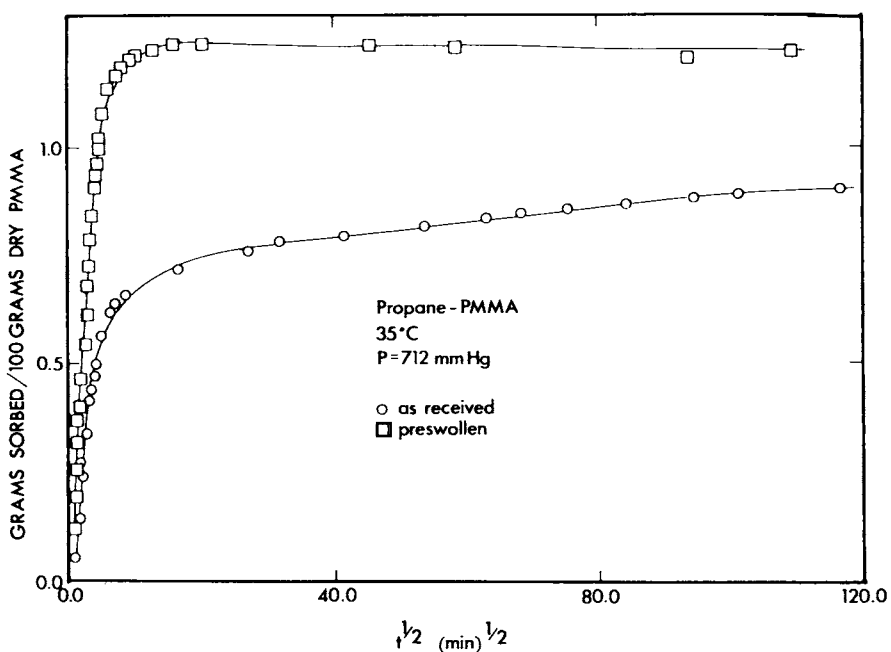

Figure 9   Sorption of propane in preswollen and as-received PMMA (new batch).
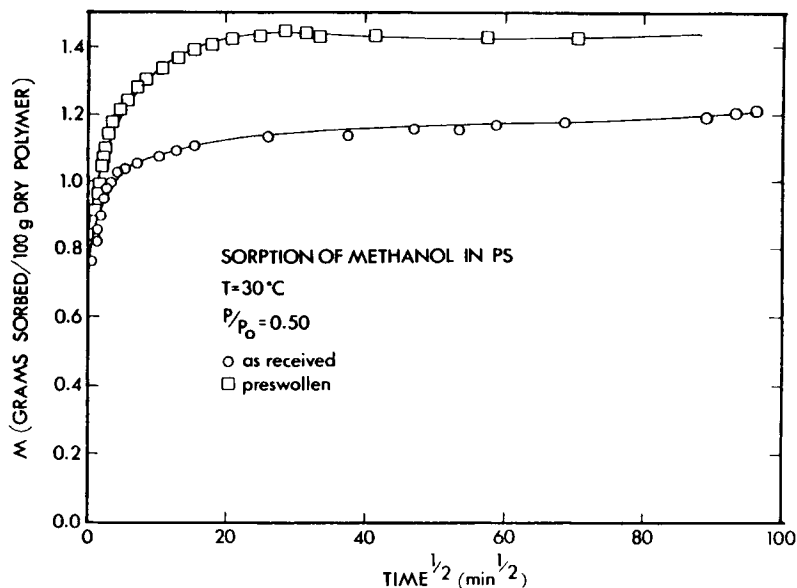
Figure 10 Sorption of methanol in preswollen and as-received polystyrene.

These composite results for polar and nonpolar penetrants demonstrate that penetrant polarity must be an important factor in these phenomena. Specifically, when penetrants of similar size, one nonpolar and the other polar (e.g., ethane and methanol), are sorbed at low concentrations into preswollen PMMA, the apparent aging in the presence of penetrant occurs only in the presence of the polar penetrant.

Data from a similar set of experiments in PS are presented in Figures 10, 11, and 1. No sorption decay occurs during the continuous presence of meth-

anol, ethane, or propane in preswollen PS. Apparently, aging in the presence of relatively small penetrants, as signified by a sorption decay, does not occur in systems in which there are no strong interactions between the polymer and penetrant; this aging may be a consequence of those strong interactions. Polar interactions between polymers and penetrants have been postulated by previous investigators.[13,14] The structures of the small alcohols, methanol and ethanol, and PMMA suggest there may be a natural attraction between the hydroxyl group in the alcohols and the carbonyl groups in
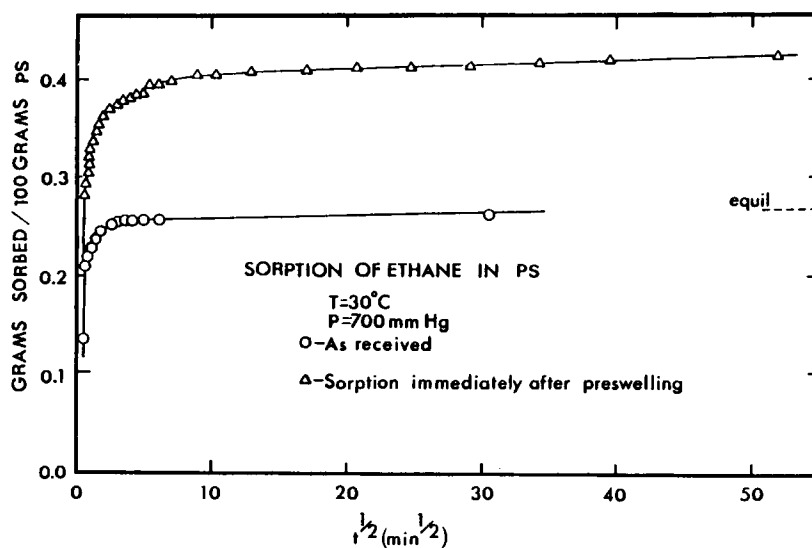

Figure 11 Sorption of Ethane in preswollen and as-received polystyrene.
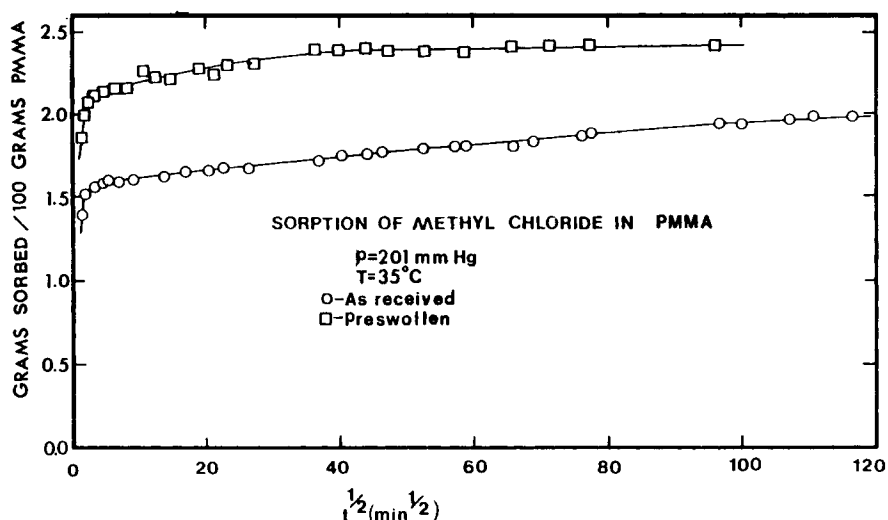
Figure 12   Sorption of methyl chloride in preswollen and as-received PMMA (new batch).

PMMA. There would not be similar interactions by the penetrants with PS.

Aging experiments for PMMA, in the presence of methyl chloride, are represented by the data in Figure 12. In this case, the decline does not occur during the continuous presence of methyl chloride in preswollen PMMA, even though methyl chloride is a polar penetrant similar in size to methanol. This case shows that polarity alone is not sufficient to yield the decline in concentration during the continuous presence of penetrant.

All results combined indicate that polarity of polymer or penetrant is neither a necessary nor a sufficient condition to yield the decline in concentration during the continuous presence of penetrant

in a preswollen polymer. With one exception $(CO_2)^9$ all of the penetrants for which the continuous concentration drop is observed are able to form hydrogen bonds and would, therefore, interact strongly with the carbonyl bonds in PMMA. Independent data on preferential sorption of CO_2 vs. a nonpolar penetrant such as CH_4 suggest that interactions between PMMA and CO_2 are strong.[15] No quantitative characterization of the strength of such interactions exists at present, as compared with hydrogen bonding penetrants. The common denominator in the systems where the decline in concentration is observed is strong interactions between the polymer and the penetrant. Although methyl chloride is polar, the halogen structure providing the polarity may
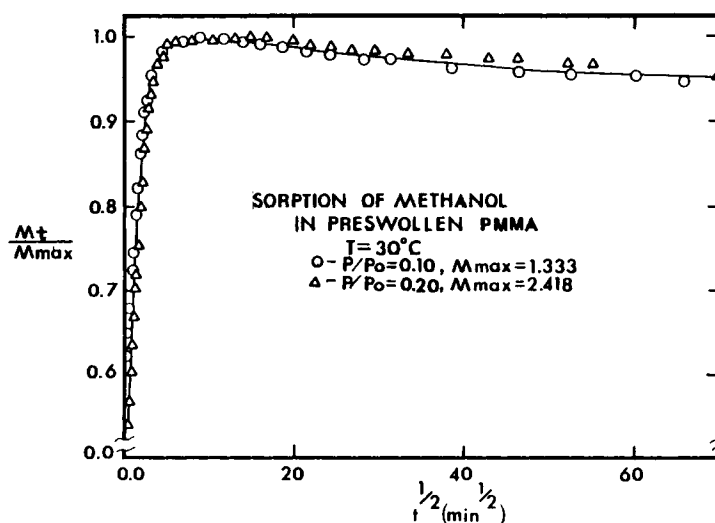

Figure 13   Comparison of normalized methanol sorption in preswollen PMMA (new batch) at 0.1 and 0.2 activities, 30°C.
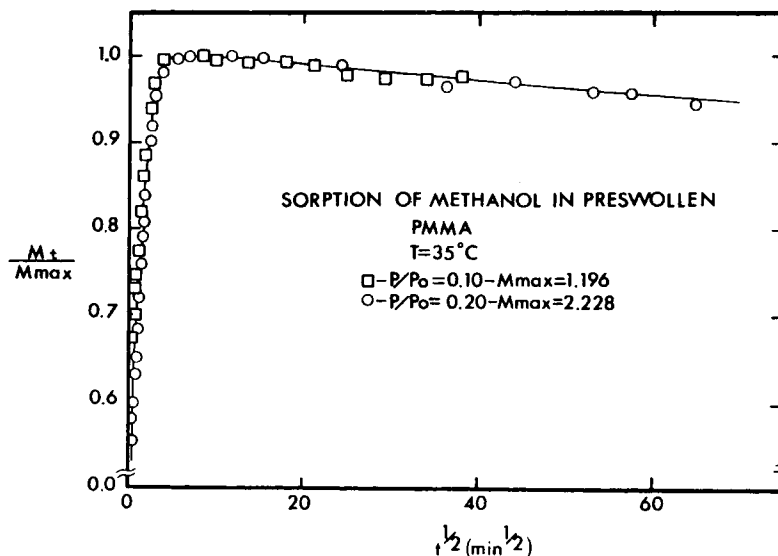
Figure 14 Comparison of normalized methanol sorption in preswollen PMMA (new batch) at 0.1 and 0.2 activities, 35°C.

not lead to the same attraction to the carbonyl group in PMMA as that expected with alcohols, water, and CO_2.

Effect of Penetrant Concentration on Aging

The data presented in Figures 13, 14, and 15 illustrate the effect of penetrant concentration on the sorption decay occurring during the continuous presence of penetrant. In these three figures, sorption data at two different activities of methanol in preswollen PMMA at 30°C and 35°C, and for ethanol in preswollen PMMA at 35°C, are normalized by the maximum concentration reached in each individual experiment, and the results for the two activities are plotted on the same coordinates. The kinetics of the decline in normalized sorption capacity, for a particular system at constant temperature, is essentially the same at the two activities examined in each case. Moreover, the magnitude of the normalized decline is the same at both activities.

Effect of Temperature on Aging

The drop in concentration resulting from annealing in vacuum, for systems uncomplicated by the drop occurring in the presence of penetrants, is modeled by the exponential relationship[6]:

$$(M'_i - M_i)/(M^0_i - M_i) = \exp(-k_r t) \quad (1)$$

where k_r is the relaxation rate constant, M'_i is the apparent equilibrium sorption capacity after vacuum

time t, M^0_i is the apparent equilibrium sorption capacity before aging of the preswollen polymer in vacuum, and M_i is the apparent equilibrium sorption capacity in the as-received polymer. Consistent with previous experimental work,[6] the temperature dependence of the rate constant, k_r, is modeled by an Arrhenius relationship. Enscore et al.,[6] using n-hexane to probe PS, found the activation energy of k_r to be about 35.3 kcal/mole. Using n-propanol to probe the PMMA in this study, the activation energy is estimated to be 22.0 kcal/mole. Thus, the relaxation effected by annealing PMMA in vacuum, and characterized by the declining apparent equilibrium concentration with increasing cumulative vacuum time, is approximately twice as fast at 35°C as at 30°C. A comparison of Figures 13 and 14, however, reveals little difference between the rate of decline in continuous sorption of methanol at 30°C and that at 35°C. This decline, occurring during the continuous presence of penetrant, is much less temperature dependent than the aging which takes place in vacuum, monitored by cyclic sorptions.

DISCUSSION

The data presented here suggest that strong interactions between polymer and penetrant contribute to the tendency of the penetrant concentration to go through a maximum and then decay during the continuous presence of penetrant. This decay (aging) has been observed primarily with small polar
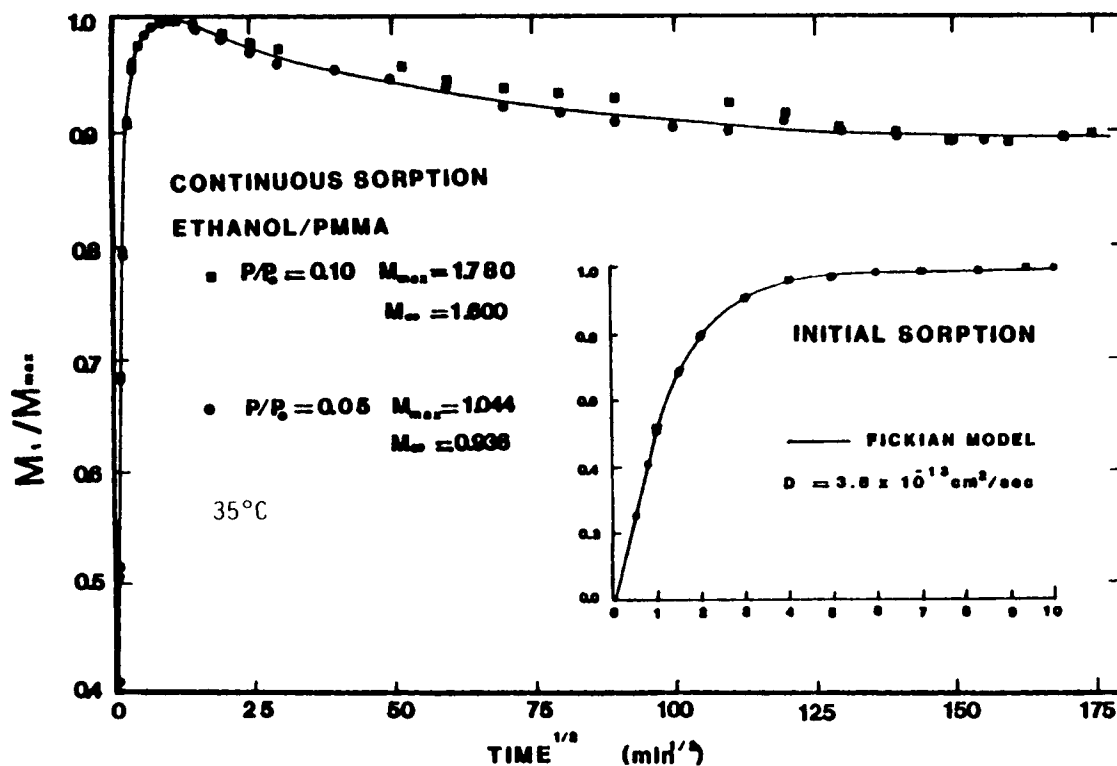
Figure 15   Comparison of normalized ethanol sorption in preswollen PMMA at 0.05 and 0.1 activities, 35°C.[17]

penetrants in preswollen PMMA, where polar interactions, and possibly even hydrogen bonding, are likely. It also has been observed with CO_2 in preswollen PMMA, a system for which there is independent evidence of strong interaction between the polymer and the penetrant.[15] The decay was not observed with any penetrant in preswollen PS. The pendant aromatic ring in PS may have less potential for attraction of penetrants than the pendant ester group on PMMA.

The interpretation of the relaxation phenomenon, exhibited by systems such as n-hexane/PS,[6] propane/PS,[8] and n-propanol/PMMA,[7] where aging apparently occurs only in vacuum, is well-supported by information in the literature. Wonders and Paul[10] directly correlated history effects, in the absence of penetrants, on the sorption of penetrants in glassy polymers to the Langmuir capacity and the specific volume of the polymer. Consistent with the work of Wonders and Paul,[10] preswelling of PMMA or PS increases the Langmuir capacity, and annealing in the absence of penetrant reverses that process. Some of the data gathered in this work, particularly those regarding the concentration and temperature effects, suggest that there are fundamental differences between the phenomena represented by the decline in

apparent equilibrium sorption capacity induced by annealing in vacuum and the decline in concentration occurring during the continuous presence of penetrant. The concentration of penetrant in the Langmuir mode approaches an asymptote as total concentration increases.[16] The data in Figures 13, 14, and 15 show that the magnitude of the decay in concentration that occurs during the continuous presence of penetrant, relative to the total concentration, is independent of penetrant concentration. Thus, this change that occurs during the continuous presence of penetrant could be modeled by a change in Langmuir capacity only at extremely low concentrations, where the Langmuir component of concentration increases linearly with concentration.

The activation energies typically reported for consolidative relaxations are high. For example, Enscore et al.[6] report an activation energy of 35.3 kcal/mole for consolidation of PS monitored by n-hexane. In the current study, consolidation of PMMA monitored by n-propanol had an activation energy of 22.0 kcal/mole, which indicates that the rate of relaxation roughly doubles for every change in temperature of five degrees. This finding is contrary to the observed insensitivity to temperature of the decline in concentration occurring during the

continuous presence of penetrant. There is little recognizable difference between the rate at 30°C and that at 35°C. This implies that the groups of atomic units involved in the relaxation occurring in the presence of penetrant are smaller than those involved in the relaxation occurring in the absence of penetrant.

CONCLUSIONS

The sorptions of ethane, propane, methanol, and n-hexane in preswollen PS increase with time to concentrations which are larger than the corresponding sorption levels observed in as-received PS. Moreover, the sorption approaches a simple asymptote without proceeding through a maximum and a subsequent decline. No decline in concentration has been observed during the continuous presence of any penetrant studied in PS even though the experiments were followed consistently over the course of several weeks. The same behavior is observed for some penetrants, ethane, propane, n-propanol, and methyl chloride, in preswollen PMMA.

When methanol, ethanol, water, or CO_2 are sorbed into preswollen PMMA, a different pattern is observed. The penetrant concentration rises to a maximum, which is higher than the apparent equilibrium reached in as-received samples, and then the concentration decays *during the continuous presence of penetrant*. The concentration in some of these cases decays to the level attained in the as-received sample. In most of these cases, it remains above the level attained in the as-received sample for the duration of the experiment. All of these penetrants for which this phenomenon occurs are penetrants which are likely to interact with the carbonyl bonds in PMMA. The sorption decay occurring during the continuous presence of penetrants is dependent upon specific interactions between the polymer and the penetrant. The mechanism by which polymer/penetrant interactions may result in the observed decay in concentration cannot be determined from existing data. Investigation of the nature of the interactions, possibly using FTIR, may provide clues concerning the mechanism.

The rate of the decay resulting from annealing in vacuum, in those systems where concentration is steady in the presence of penetrant, has a large temperature dependence. The concentration decay that occurs in the presence of penetrants is nearly independent of small (5°C) changes in temperature. Finally, the normalized decrement in sorption occurring during the continuous presence of penetrant

is independent of activity at activities up to at least 0.2 for methanol in preswollen PMMA and at least up to 0.1 for ethanol in preswollen PMMA. This concentration change cannot be modeled as a change in the Langmuir capacity within the dual-mode model.

These data suggest that the decline in concentration during the continuous presence of penetrant occurs by a mechanism that is different from the aging of preswollen glassy polymers in the absence of penetrant. These results represent a significant improvement with respect to the earlier interpretation offered by Connelly et al.[7]

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