

# The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders. I. Lower Alcohol and Water Sorption in Poly(methyl Methacrylate)

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## Synopsis

Sorption kinetics and equilibria for methanol, ethanol, and *n*-propanol in 0.544  $\mu\text{m}$  diameter poly(methyl methacrylate) microspheres were determined at 35°C over a wide range of relative pressures. Sorption isotherms were concave to the pressure axis at low relative pressures and convex to the pressure axis at higher relative pressures. These results, considered in the context of recently reported data for high pressure sorption of gases in polymeric glasses, suggest that the S-shaped isotherms reported here are examples of a generalized isotherm which describes sorption behavior of all penetrants in glassy polymers if an appropriate range of concentration is traversed by the experimental protocol. The effects of dilating the microspheres by preswelling with methanol were studied by subsequent low pressure sorption of water, methanol, ethanol, and *n*-propanol at 35°C. The preswollen microspheres exhibited initially higher sorption capacities than the as-received samples, but tended to consolidate with time following the preswelling treatment. The aging process, monitored by periodic short-term sorption with the various penetrant probes, was arrested by contacting the microspheres with an activity of *n*-propanol sufficient to maintain a sorbed concentration of approximately 1 wt %. The aging was significantly retarded by the presence of low concentrations of water and ethanol. Conversely, the aging process appeared to be essentially unaffected by the presence of correspondingly low concentrations of methanol. The complex kinetics describing the sorption of the various penetrants ranged from Fickian diffusion to polymer relaxation-controlled absorption, depending upon penetrant, relative pressure, and prior exposure history. The low temperature preswelling of the microspheres markedly increased the rate of sorption as well as the respective apparent equilibrium sorption.

## INTRODUCTION

Studies of transport in polymers have, typically, used films or fibers with characteristic dimensions of 10  $\mu\text{m}$  or more. The extremely low diffusion coefficient, characteristic of organic penetrants in glassy polymers, makes the experimental determination of transport parameters a prohibitively long process in conventional, macroscopic, films and fibers.<sup>1</sup> Berens<sup>2,3</sup> pioneered the use of monodisperse submicron glassy microspheres to shorten the duration of sorption and diffusion experiments for vinyl chloride in PVC from several

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days to a few minutes. Since these uniform, submicron diameter microspheres permit significantly more rapid experimentation, the time and history dependence of the nonequilibrium nature of glassy polymers can be studied easily through systematic cyclic sorption and aging protocols.<sup>4</sup>

Berens<sup>4</sup> observed that the sorption isotherm of vinyl chloride monomer in PVC was concave to the pressure axis at low relative pressures and convex at high relative pressures characteristic of a dual mode sorption isotherm, which combines molecular dissolution described by a Flory-Huggins isotherm with a Langmuir-type "hole" filling sorption mechanism. The Langmuir capacity decreased with increasing temperature and disappeared at the glass transition temperature ( $T_g$ ). Berens<sup>5</sup> also observed systematic variations in sorption capacity with time and polymer history which closely paralleled well-known variations in volume,<sup>6</sup> enthalpy,<sup>7</sup> and diffusivity,<sup>8</sup> which had been rationally explained by changes in the available excess volume resulting from specific thermal and/or penetrant history of the glassy polymer.

Berens<sup>9</sup> also found that the microspheres allowed rapid sorption to a pseudo-equilibrium, often followed by a much slower relaxation-controlled approach to a final sorption level. Berens and Hopfenberg<sup>10</sup> speculated that the relaxation-controlled stage of sorption was due to a rearrangement and increase in the excess volume of the polymer caused by the swelling stress and involving large scale and, therefore, slow, segmental motion of the glassy polymer chain. A model to describe this transport, formulated by combining the solution to Fick's law in spherical coordinates with a first order exponential relaxation term, has been found to be in good agreement with experimental data for several polymer-penetrant systems.<sup>10</sup>

The early success of Berens<sup>2-5</sup> in describing the time and history dependence of the vinyl chloride monomer-PVC system prompted Ensore et al.<sup>11-13</sup> to undertake a detailed study of *n*-hexane sorption and transport in polystyrene (PS) in this laboratory. The PS microspheres provided a conceptually simpler system since the atactic polymer is completely amorphous whereas a small but significant fraction of PVC is crystalline.

Ensore et al.<sup>12,13</sup> determined that annealing polystyrene for 24 h at 79°C lowered both the sorption capacity and the rate of transport of *n*-hexane in PS microspheres. Conversely, both the rate of transport and the sorption capacity of *n*-hexane in PS were increased by preswelling at low temperature and high penetrant concentration. The effects of preswelling and annealing decayed slowly upon repeated cycling between low *n*-hexane pressure ( $P_r = 0.10$ ) and vacuum. In contrast, at high *n*-hexane pressure ( $P_r = 0.75$ ), these effects were essentially erased by the first sorption cycle. The observed monotonic decrease in sorption capacity at low pressure in the preswollen (and therefore dilated) PS microspheres was presumably due to densification of the sample caused by decreases in excess volume during the penetrant-free stage between sorption cycles. This monotonic decrease followed a first-order exponential decay.<sup>13</sup> The convergence of preswollen and as-received samples to the same sorption capacity suggests the attainment of a true thermodynamic equilibrium for the two-component, two-phase system of PS contacting *n*-hexane vapor.

The present study was undertaken to extend the observations obtained with the nonpolar polystyrene/*n*-hexane system to another totally amorphous,

albeit polar polymer, poly(methyl methacrylate) PMMA. The lower monohydric alcohols (methanol, ethanol, and *n*-propanol) represent a homologous series with a systematic variation in structure and properties, providing a more comprehensive test of the tentative conclusions offered in the earlier, related studies.

## EXPERIMENTAL

### Materials

The 0.544  $\mu\text{m}$  diameter PMMA microspheres used in this study were provided by the Research and Development Center of the B. F. Goodrich Co., Brecksville, OH. The microspheres were prepared by potassium persulfate-initiated emulsion polymerization with a low surfactant concentration. The number average molecular weight of the sample was reported to be 137,000. The glass transition temperature of the microspheres was determined by DSC runs to be 120°C.

Methanol, ethanol, and *n*-propanol of 99 mol % purity, were obtained from Aldrich Chemical Co., Milwaukee, WI and used after removal of dissolved permanent gases by repeated freeze-thaw cycles under vacuum. Distilled, deionized water was also subjected to repeated freeze-thaw cycles to remove dissolved gases.

### Sample Preswelling

Dilated PMMA microspheres were prepared by exposing as-received microspheres to a high activity ( $p/p^0 = 0.98$ ) of methanol at  $-10^\circ\text{C}$ , resulting in 17.5 g methanol sorbed/100 g PMMA at apparent equilibrium. The samples were held at these conditions for 2 weeks, after which the methanol was quickly removed by contacting the powder samples with a vacuum of  $10^{-6}$  mm Hg. The microspheres were stored in a sealed container in a freezer at  $-15^\circ\text{C}$ .

### Apparatus and Procedures

Sorption measurements were made on a Cahn RG Electrobalance with recorder readout. The balance was enclosed in a glass vacuum system with service lines to a vapor source, reservoir bulb, a mercury manometer, and a high vacuum pumping system. Sample holders were made of fused quartz and were 10–15 mm in diameter. Sample holders were suspended from the balance beam into 12 in. long hangdown tubes by either steel wire or thinly drawn glass fibers.

To minimize static charge buildup, the outsides of the glass vacuum bottle and hangdown tubes were wrapped in aluminum foil and grounded. Also, a 500  $\mu\text{Ci}$  polonium source, a Static Ionizing unit, made by Nuclear Products Co., El Monte, CA, was attached to the inside of the hangdown tube near the sample pan.

The microbalance, manifold, and gas reservoir were housed in an air bath maintained at a constant temperature ( $\pm 0.1^\circ\text{C}$ ) by a Sargent-Welch temperature controller.

The same general experimental procedures were followed in all sorption runs. To start a run, the glass vacuum bottle containing the Cahn microbalance was isolated from the rest of the system. The stopcock to the vacuum service was closed and the reservoir bulb and service lines were overpressurized to an empirically determined value that would give the desired sorption pressure when the stopcock to the microbalance was opened. When it was certain that the pressure was correct and the temperature was constant, the stopcock to the microbalance was opened, the timer was started, and sorption was monitored with the recorder. After completion of a run, the system was either vented to atmospheric pressure and the sample removed, or the system was evacuated and kept under vacuum until a resorption was performed.

## RESULTS AND DISCUSSION

### Sorption Isotherms

Equilibrium isotherms for methanol, ethanol, and *n*-propanol sorption at 35°C in as-received microspheres are presented in Figures 1, 2, and 3, respectively. All three isotherms are similar in form. The sorption (at a given relative pressure) increases with the molecular weight of the penetrant. The slopes of the three isotherms increase sharply at high relative pressure typical of Flory-Huggins solution behavior. Similar behavior has been reported for sorption of methyl methacrylate in PMMA,<sup>14</sup> acetone in polycarbonate,<sup>15</sup> and *n*-hexane in polystyrene.<sup>16</sup>

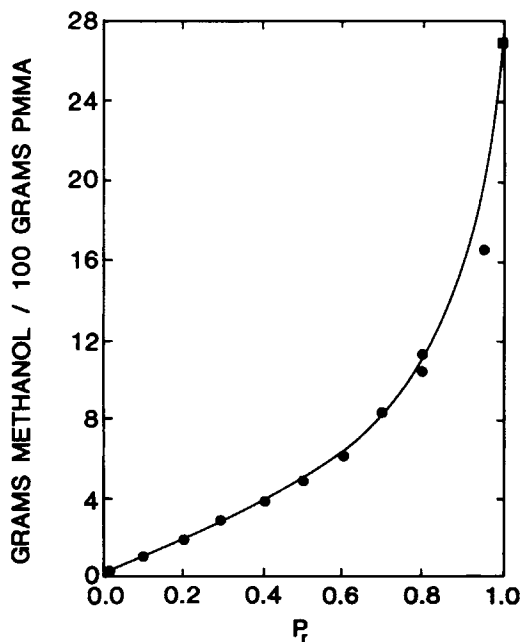


Fig. 1. Equilibrium sorption of methanol in 0.544  $\mu$ m diameter PMMA spheres at 35°C.

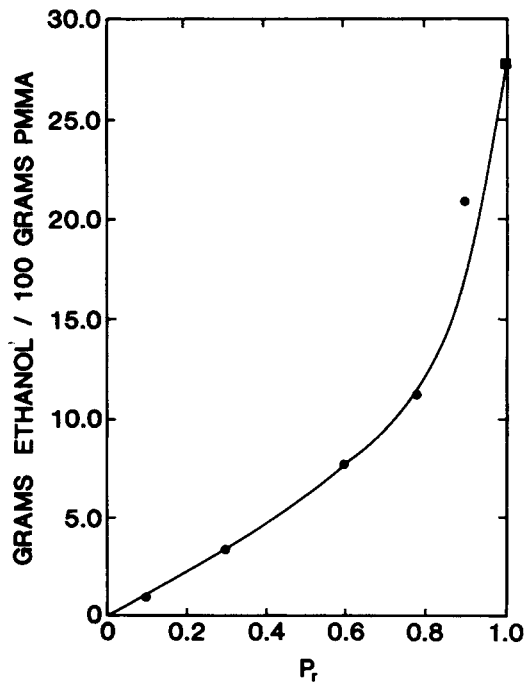


Fig. 2. Equilibrium sorption of ethanol in 0.544 μm diameter PMMA spheres at 35°C.

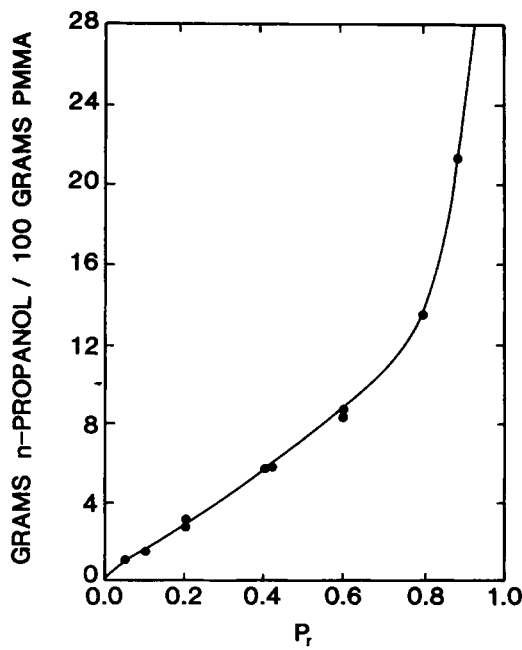


Fig. 3. Equilibrium sorption of *n*-propanol in 0.544 μm diameter PMMA spheres at 35°C.

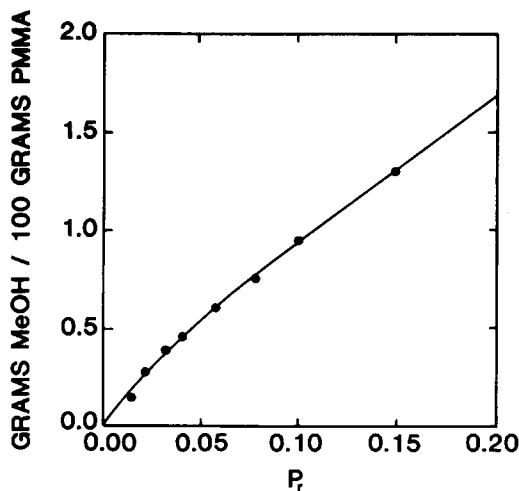


Fig. 4. Equilibrium sorption of methanol in 0.544  $\mu\text{m}$  diameter PMMA spheres at 35°C. Low relative pressure region.

The *n*-propanol isotherm appears to be concave to the pressure axis at very low relative pressures characteristic of dual mode sorption. Casual inspection of the methanol and ethanol isotherms does not suggest dual mode behavior. A more careful examination, however, of the low  $P_r$  data of methanol presented in Figure 4 does, in fact, reveal an isotherm which is concave to the pressure axis characteristic of dual mode sorption.

In experiments which encompass high degrees of swelling, the dual model nature of sorption of these swelling penetrants in glassy polymers may be obscured due to the relatively small amount of Langmuir type sorption compared with the large amount of Flory-Huggins swelling observed in the overall experiment. Conversely, experiments at low sorption levels (e.g., gas sorption in polymeric glasses at moderate pressures) display marked Langmuir type behavior but typically do not exhibit an isotherm which is convex to the activity or pressure axis. The apparent absence of Flory-Huggins behavior in these systems is due to the low sorption level, in which limit Henry's law serves as a limiting case of the Flory-Huggins isotherm.

At low concentrations, the Flory-Huggins isotherms can be rearranged and simplified to yield

$$v_1/a_1 = \exp[-(1 + \chi_{12})] \quad (1)$$

where  $v_1$  is the volume fraction of penetrant in the polymer in equilibrium with an activity  $a_1$  and  $\chi_{12}$  is the Flory-Huggins solvent-polymer interaction parameter. The Henry's law constant  $k_D$  is directly proportional to  $v_1/a_1$  with the proportionality constant determined by the desired units of  $k_D$ .

Dual mode behavior has also been observed for systems which would normally exhibit the more general S-shaped isotherm, when the sorption measurements are halted before significant, long-term, swelling relaxations occur. Berens<sup>9</sup> reported that the pressure dependence of VCM sorption levels achieved in PVC during the initial, Fickian stage of sorption were well

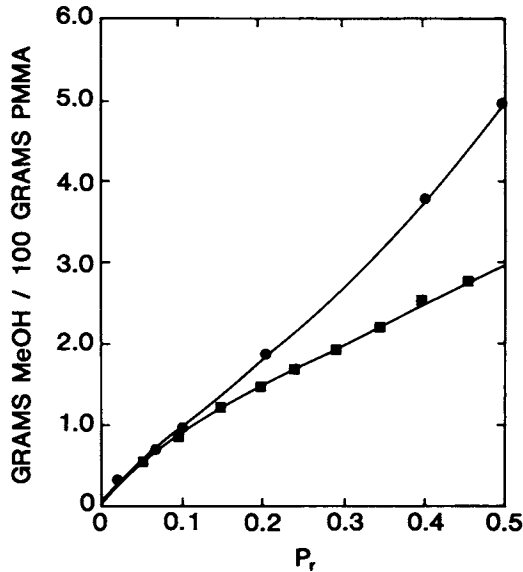


Fig. 5. Comparison of equilibrium sorption (●) and 30 s sorption (■) of methanol in 0.544  $\mu\text{m}$  PMMA spheres at 35°C.

described by the classical dual mode sorption model given by

$$C = k_D p + C'_H b p / (1 + b p) \quad (2)$$

where  $C$  is the total concentration,  $k_D$  is the Henry's law constant,  $b$  is the Langmuir affinity parameter,  $C'_H$  is the Langmuir capacity parameter, and  $p$  is the penetrant pressure.

A low-activity, pseudo-equilibrium isotherm for methanol sorption in PMMA, obtained for a series of interval sorptions of 30 s duration, is presented as the lower set of data in Figure 5. These short-term measurements allow for more than 99% (as calculated using a diffusivity determined in an experiment with larger polymer samples) of the Fickian diffusive equilibrium to be reached. The contribution of relaxation-controlled sorption over the course of the experiment, however, is negligible resulting in lower sorption levels than the long-term equilibrium measurements which are presented as the upper curve of Figure 5. As expected, the short term sorption behavior for methanol in PMMA is well described by the dual mode sorption model. The solid line through the short-term data was calculated using the model and parameter values of  $k_D = 0.21$  (g MeOH)/(100 g PMMA atm),  $b = 0.051$  mm Hg<sup>-1</sup>, and  $C'_H = 0.84$  (g MeOH)/(100 g PMMA), which were determined using a Fletcher-Powell optimization of the model to the data.

### Transport

The kinetics of *n*-propanol sorption at 35°C and three relative pressures are presented in Figure 6. Sorption of *n*-propanol at relative pressures of 0.20 and 0.61 exhibits combined elements of Fickian diffusion and relaxation-moderated sorption kinetics. The data for sorption at a relative pressure of 0.05

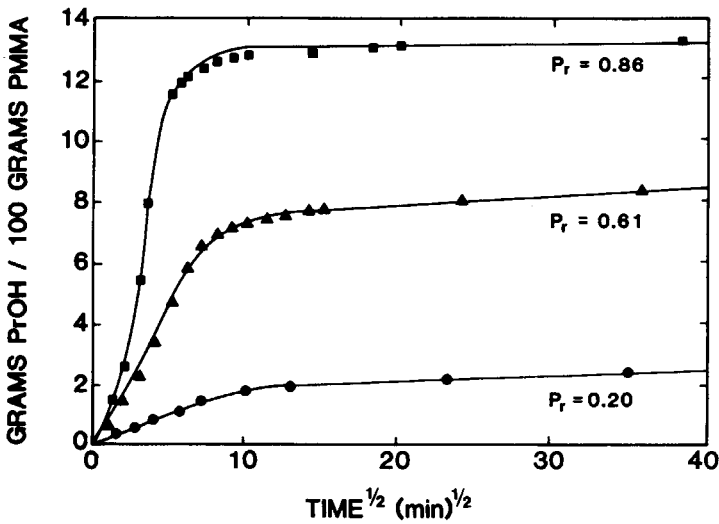


Fig. 6. Comparison of *n*-propanol sorption kinetics in 0.544  $\mu\text{m}$  PMMA spheres at 35°C and three relative pressures.

are not shown but no relaxation component to the sorption process was observed. The sorption kinetics at this pressure were Fickian. Sorption vs. the square root of time at high relative pressure ( $P_r = 0.86$ ) is strongly sigmoidal and is well described by the Case II model which assumes sorption is totally relaxation-controlled.<sup>11</sup>

In summary, over the concentration range covered, an entire spectrum of behavioral features are observed. At low concentration, Fickian diffusion predominates. At high concentration, relaxation-controlled Case II transport is observed, while anomalous transport is observed at the intermediate concentration. These results are quite consistent with the transport of other

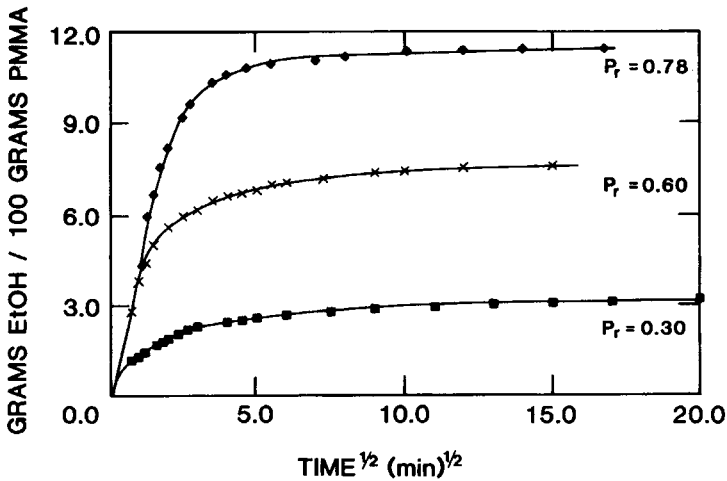


Fig. 7. Comparison of ethanol sorption kinetics in 0.544  $\mu\text{m}$  PMMA spheres at 35°C and three relative pressures.



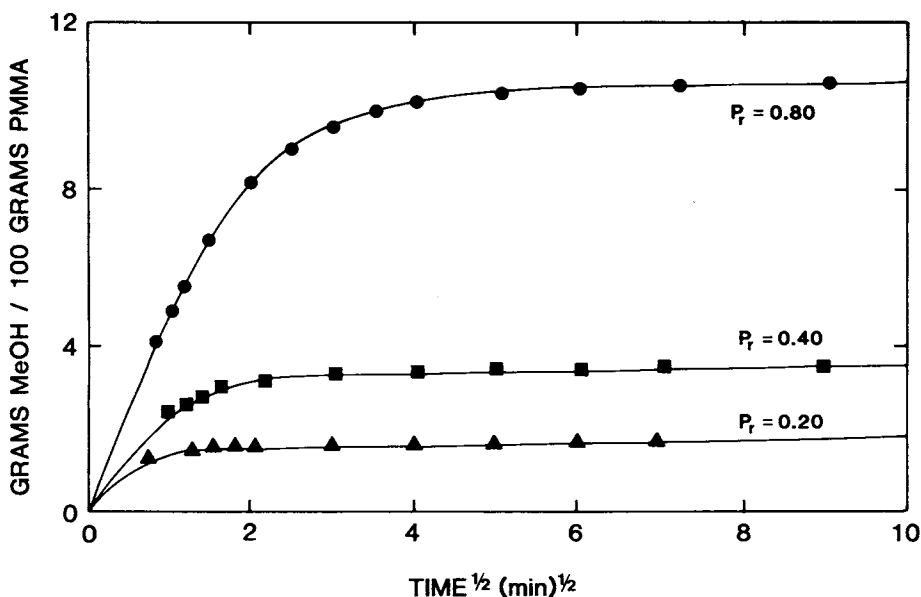


Fig. 8. Comparison of methanol sorption kinetics in  $0.544 \mu\text{m}$  PMMA spheres at  $35^\circ\text{C}$  and three relative pressures.

organic penetrants in glassy polymers such as *n*-hexane in polystyrene.<sup>11</sup> These results, however, show for the first time Case II transport in submicron spheres.

The time dependence of ethanol sorption at  $35^\circ\text{C}$  and three relative pressures ( $P_r = 0.30, 0.60,$  and  $0.78$ ) is shown in Figure 7. At low and intermediate relative pressures ( $P_r = 0.30$  and  $0.60$ ), the latter stages of ethanol transport in PMMA microspheres are controlled by long-term relaxations. At high relative pressure, where Case II transport is observed for *n*-propanol transport, Fickian diffusion is observed for ethanol sorption.

The kinetics of methanol sorption at  $35^\circ\text{C}$  and three relative pressures are presented in Figure 8. Transport of methanol at intermediate relative pressures ( $P_r = 0.20$  and  $0.40$ ), like *n*-propanol, and ethanol exhibits diffusion and relaxation contributions, and can also be described using the Berens-Hopfenberg model.<sup>10</sup> At high relative pressure ( $P_r = 0.80$ ) methanol sorption, like ethanol, is well described by the simple Fickian model.

#### THE EFFECT OF ENVIRONMENTAL CONDITIONS ON THE AGING OF PRESWOLLEN PMMA MICROSPHERES

As-received microspheres were preswollen with methanol as described in the Experimental section. The methanol was subsequently removed and the ensuing aging was monitored with methanol or *n*-propanol as molecular probes at  $35^\circ\text{C}$  and lower vapor activities. Sorption kinetics and equilibria for *n*-propanol in as-received and preswollen PMMA microspheres at  $35^\circ\text{C}$  and  $P_r = 0.10$  are presented in Figure 9. Clearly, the preswollen sample has a significantly higher sorption capacity than the as-received sample ( $2.08 \text{ g}/100$

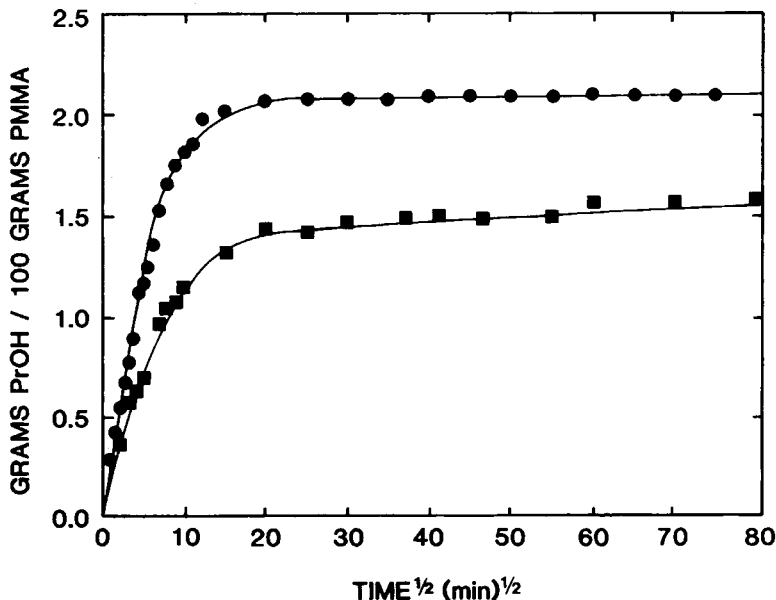


Fig. 9. Comparison of *n*-propanol sorption in preswollen (●) (30 min vacuum time) and as received (■) 0.544  $\mu\text{m}$  PMMA spheres at  $P_r = 0.10$  and 35°C.

g PMMA vs. 1.55 g/100 g PMMA). The approach to apparent equilibrium in the two samples is also quite different: the as-received sample reached 1.55 g *n*-propanol/100 g of PMMA after 10,000 min and remained constant from 10,000 to 19,000 min while only 400 min were required for the preswollen samples to equilibrate. Whereas the kinetics of sorption in the as-received sample are anomalous, the sorption kinetics in the preswollen sample are well described by the simple Fickian diffusion model. Sorption in the preswollen sample is characterized by a diffusion coefficient of  $2.36 \times 10^{-14} \text{ cm}^2/\text{s}$ , which is almost 50% larger than the as-received sample diffusion coefficient of  $1.61 \times 10^{-14} \text{ cm}^2/\text{s}$  determined using the Berens-Hopfenberg model.<sup>10</sup> Presumably, preswelling increases the free volume of the glassy PMMA allowing more rapid diffusion to a higher sorption capacity.

The time-dependent sorption capacities  $M_t'$  of *n*-propanol in preswollen PMMA are presented vs. total prior vacuum time in Figure 10. The abscissa corresponds to the sum of all of the time after preswelling during which the sample was under vacuum. The total run time in Figure 10 was approximately 65,000 mins, of which 29,000 occurred in the absence of penetrant. Clearly, the sorption capacity decreases monotonically with each cycle and apparently approaches the sorption capacity of the as-received sample as an asymptotic limit over the time scale of the experiment. Since the data of Figure 9 indicate that sorption of *n*-propanol at a relative pressure of 0.1 arrests the aging of the preswollen PMMA over the experimental time scales studied here, consolidative aging must occur only during the intermittent penetrant-free vacuum time.

The observed behavior of *n*-propanol in preswollen PMMA is consistent with the reported behavior of *n*-hexane in preswollen polystyrene.<sup>13</sup> The

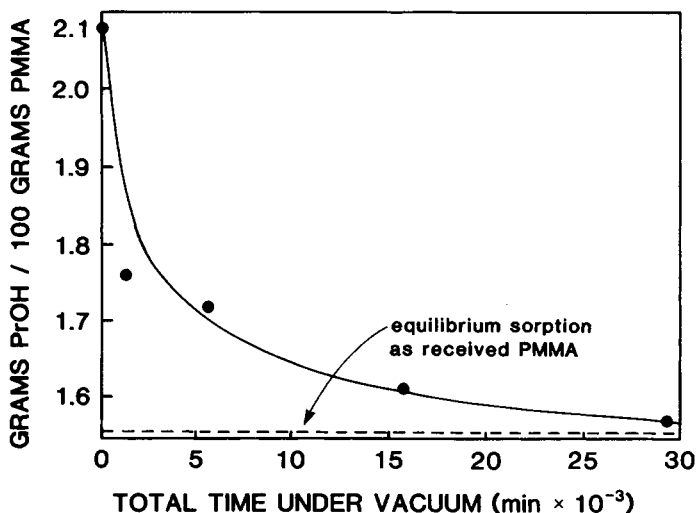


Fig. 10. Aging of preswollen 0.544  $\mu\text{m}$  PMMA spheres at 35°C monitored by cyclic sorption of *n*-propanol at  $P_r = 0.10$ .

reported effects are:

- (1) An increased sorption capacity due to preswelling which subsequently decays under vacuum.
- (2) The consolidative aging is quenched or arrested by the presence of low concentrations of penetrant.
- (3) Sorption occurs more rapidly in preswollen samples than in as-received samples.

The similarity between the *n*-propanol/PMMA results and the earlier *n*-hexane/polystyrene data suggests that these combined behavioral features may be typical of the complex sorption behavior to be expected for all penetrants sorbing into and affecting the consolidative aging of dilated glassy polymers. The following data for methanol in PMMA limit the generality of this tentative conclusion.

Methanol-preswollen samples were also contacted continuously with methanol vapor at  $P_r = 0.10$  and 35°C and the decrease in the sorption capacity in the presence of methanol is presented as the solid circles in Figure 11. The sorption of methanol in preswollen PMMA rapidly reaches a maximum and then slowly decreases (even in the presence of methanol) to a value close to the sorption capacity of the as-received PMMA. The very rapid initial sorption to a maximum is not shown since it occurred too rapidly to follow with the Cahn system. The decrease in methanol sorption level even in the presence of a low activity of methanol vapor is in marked contrast to the behavior of *n*-propanol in preswollen PMMA and *n*-hexane in preswollen polystyrene where the presence of penetrant quenches aging.

The time dependence of the methanol sorption capacities determined by cyclic probing of preswollen PMMA is also presented in Figure 11 ( $\square$ ). The agreement between the cyclic and continuous sorption experiments is very

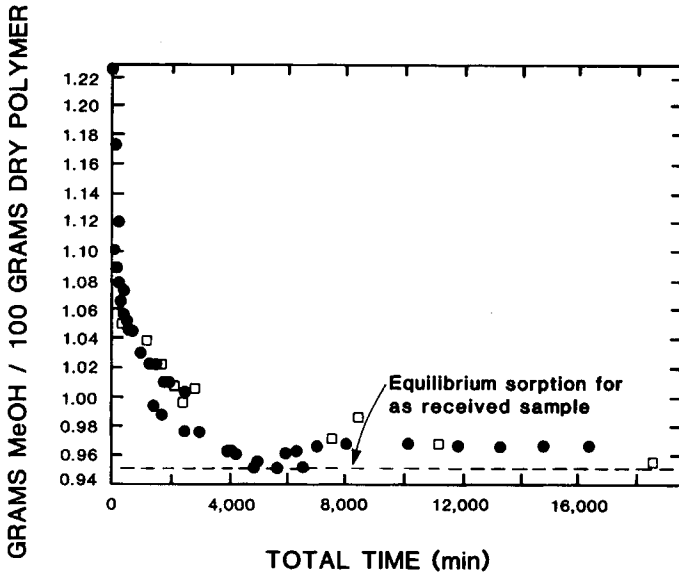


Fig. 11. Comparison of cyclic ( $\square$ ) and continuous ( $\bullet$ ) sorption of methanol ( $P_r = 0.10$ ) in preswollen  $0.544 \mu\text{m}$  PMMA spheres at  $35^\circ\text{C}$ .

close, indicating that the presence of methanol at this concentration in PMMA has little or no effect on the aging of preswollen PMMA.

Enscore et al.<sup>13</sup> reported that the decrease in sorption capacity of *n*-hexane in preswollen polystyrene could be described by a first-order exponential decay, e.g.,

$$\frac{[M'_\infty - M_\infty]}{[M_\infty^0 - M_\infty]} = \exp(-k_c t) \quad (3)$$

where  $M'_\infty$  is the apparent equilibrium sorption capacity of penetrant at time  $t$ ,  $M_\infty$  is the asymptotic sorption capacity at long time,  $M_\infty^0$  is the initial sorption capacity at zero time, and  $k_c$  is the first order aging constant.

In Figure 12 the logarithm of the change in normalized sorption capacity,  $\ln([M'_\infty - M_\infty]/[M_\infty^0 - M_\infty])$ , is plotted vs. time for cyclic *n*-propanol and methanol sorption in preswollen PMMA from the present study along with data of Fechter<sup>17</sup> for cyclic carbon dioxide sorption at 700 mm Hg in identical preswollen PMMA microspheres. Since *n*-propanol essentially arrested aging, the time scale used for this penetrant was taken to be the time under vacuum. Since methanol did not arrest aging, and since the  $\text{CO}_2$  contact time was short compared with the total aging time in the  $\text{CO}_2$  experiments, total time is used to correlate aging data in the presence of methanol or  $\text{CO}_2$ . This behavior is similar to the direct determination of consolidative aging by measuring the time dependence of the specific volume following stepwise changes in temperature or pressure,<sup>18</sup> and analyzed in terms of the normalized volume change,  $[V - V_\infty]/[V_0 - V_\infty]$ , where  $V$  is the specific volume at any time,  $V_\infty$  is the equilibrium specific volume, and  $V_0$  is the volume at zero time. Such an approach appears to be analogous to monitoring  $[M'_\infty - M_\infty]/[M_\infty^0 - M_\infty]$ , consistent with Ensore et al.'s choice of the form of the normalized reduction in sorption capacity given in eq. (2). The apparent absence of the rapid early

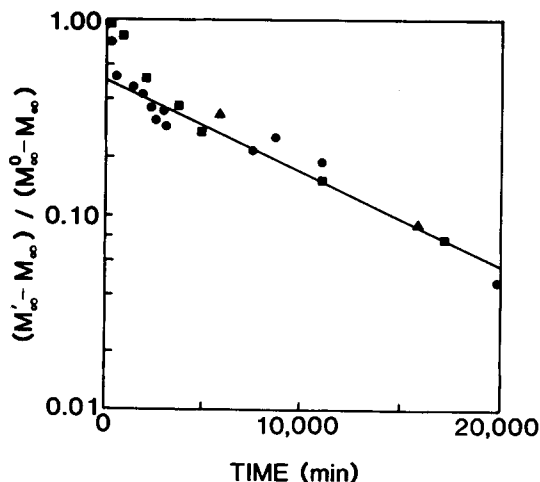


Fig. 12. Comparison of aging kinetics of preswollen  $0.544 \mu\text{m}$  PMMA spheres monitored by methanol ( $\bullet$ ) ( $P_r = 0.10$ ),  $n$ -propanol ( $\blacktriangle$ ) ( $P_r = 0.10$ ), and carbon dioxide ( $\blacksquare$ ) ( $P_r = 700 \text{ mm Hg}$ ) at  $35^\circ\text{C}$ .

sorption capacity loss in the data of Ensore et al.<sup>13</sup> could be due to aging occurring too quickly to allow the large  $n$ -hexane molecule to reach diffusive equilibrium, thereby masking the short-time relaxation process.

The long time region of Figures 10 and 11 can be fitted by the model of Ensore et al.<sup>13</sup> Aging constants for preswollen PMMA are, for methanol,  $k_c = 1.04 \times 10^{-4} \text{ min}^{-1}$ , propanol,  $k_c = 1.09 \times 10^{-4} \text{ min}^{-1}$ , and carbon dioxide,  $k_c = 1.07 \times 10^{-4} \text{ min}^{-1}$ . The agreement of the rate constant justifies the conclusion that the presence of methanol has no effect on aging while the presence of  $n$ -propanol completely arrests the related physical aging.

The results obtained with methanol were clearly unexpected based upon the wealth of data obtained by Ensore et al. for the  $n$ -hexane/polystyrene system and the results obtained here with  $n$ -propanol and PMMA. It had been tacitly assumed, based upon the completely consistent earlier findings, that the absorption of approximately 1 wt % of a penetrant effectively antiplasticizes the polymer and, thereby, arrests the consolidative relaxations or aging which would otherwise ensue in the absence of these penetrants. The seeming contradiction between the earlier results and the effects of aging PMMA in the presence of methanol vapor suggested that a systematic investigation of the effects of the properties of the penetrant contacting the polymer during aging was required. PMMA was, therefore, aged in ethanol vapor or water vapor to develop a more comprehensive set of observations to interpret the effect of penetrant structure on aging. These aging penetrants were selected since ethanol completes the homologous series of lower monohydric alcohols and water is even smaller than methanol, which is the lowest molecular weight compound in the alcohol series.

The long term sorption kinetics of ethanol in "as-received" PMMA are compared in Figure 13 with the sorption kinetics of ethanol, placed in continuous contact with preswollen PMMA. The drift in the apparent sorption equilibrium of preswollen PMMA, which was aged *in vacuo* and probed

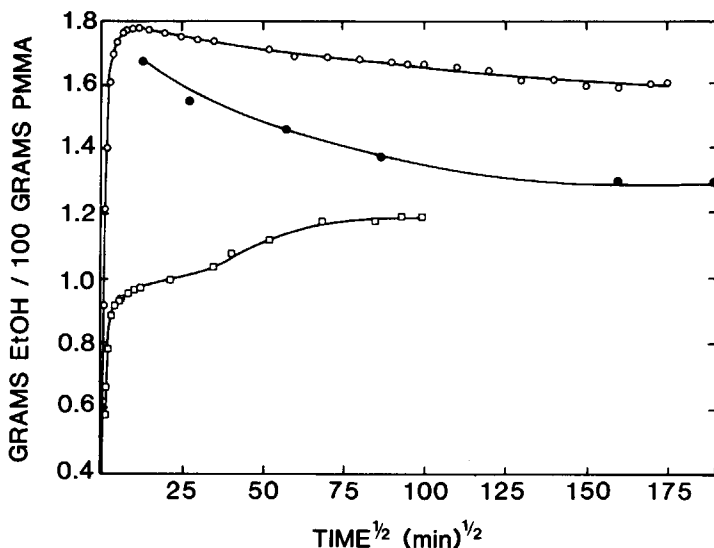


Fig. 13. Aging of preswollen  $0.544 \mu\text{m}$  PMMA spheres at  $35^\circ\text{C}$  monitored by continuous and cyclic sorption of ethanol at  $P_r = 0.10$ : (○) continuous preswollen; (●) cyclic preswollen; (□) as received.

with ethanol periodically rather than continuously, is also presented on the same set of coordinates. In the latter case, the time scale refers to the time *in vacuo* only since it was presumed that relatively little aging would take place in the presence of sorbed ethanol vapor.

The data of Figure 13 clearly reveal behavior which is intermediate between the propanol results and the methanol observations. Specifically, whereas propanol arrests consolidative aging and methanol does not appear to have any effect on the rate of aging, the continuous presence of ethanol merely retards, rather than arrests, aging, and the consolidative relaxations are decidedly more rapid when the PMMA powder sample is aged *in vacuo* and probed periodically with ethanol. Specifically, the aging constant determined from the cyclic ethanol experiments is  $1.7 \times 10^{-4} \text{ min}^{-1}$ , which is only 70% larger than the aging constant for cyclic *n*-propanol probing. Presumably, the small difference between the consolidation constant determined with *n*-propanol probing and ethanol probing relates to the aging which proceeds in the presence of the ethanol during probing.

Consistent with the earlier findings, preswelling markedly increases the apparent or transient sorption capacity of the polymer and the true equilibrium of sorption appears to be independent of prior history. The rate of approach to true equilibrium is exceedingly slow, although discernably and reasonably path dependent. Clearly, the *n*-propanol sorption values reported here are higher than the values anticipated at a true equilibrium which would only be established by waiting prohibitively long times in the presence of *n*-propanol.

These composite results qualify significantly the earlier simplistic conclusion which held that the presence of small quantities of dissolved penetrants generally antiplasticize polymeric glasses. There appears to be a systematic

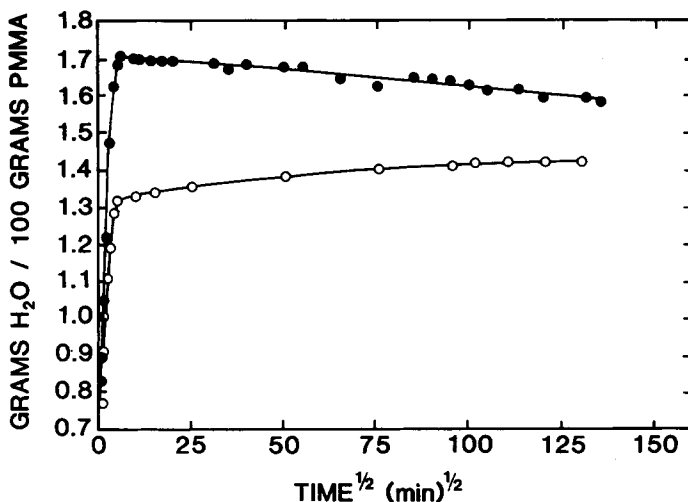


Fig. 14. Aging of preswollen 0.544  $\mu\text{m}$  PMMA spheres at 35°C monitored by continuous sorption of water at  $P_r = 0.72$ : (●) preswollen; (○) as received.

variation in effects, depending, at least, upon the molecular size of the penetrant since the variation in apparent aging kinetics uncovered here is monotonically related to the molecular size of the compounds comprising the monohydric series of alcohols studied here.

The effect of physicochemical characteristics of the penetrant comprising the aging environment is further revealed by the absorption kinetics of water at a relative pressure of 0.72 in PMMA, which are presented in Figure 14. Quite surprisingly, the data are more similar to the observations obtained with ethanol than to those obtained with molecularly smaller methanol. These results suggest that the water at a relative pressure of 0.72 is associated or clustered in PMMA and that the associated aggregates are the principal species cooperating in the antiplasticization process. A consistent mechanism for explaining all of the seemingly disparate findings regarding the role of penetrant structure on aging may be based simply on molecular size, given that water may associate in PMMA. As penetrant size decreases, the relative mobility of the penetrant clearly increases and, in the limit, the penetrant is sufficiently mobile to move rapidly from the locus of polymeric motions responsible for consolidative aging of dilated samples. In this limit, represented by the methanol data, the presence of penetrant does not contribute to the overall observed aging behavior. This speculation, although internally consistent with the data obtained to date, stimulates the pursuit of an even more comprehensive study of the effect of physicochemical characteristics of environmental penetrants on the observed aging kinetics. The anticipated comprehensive study, involving a wide variation in molecular size and polar characteristics, will provide a more unified overview of the effect of dissolved penetrants on the detailed kinetics of aging. The results of the study, when completed, will be published in this series, dealing with the overall problem of the effect of aging environment on physical aging of polymeric glasses.

Clearly, the effects are, and should be, dependent upon the concentration of penetrant. Presumably, the Langmuir or hole filling molecules are essentially

space filling and, therefore, retard consolidation whereas the Flory-Huggins or dissolved species are dilating and facilitate consolidation. However, even as the overall concentration of penetrant approaches zero, the ratio of hole filling ( $C_H$ ) to dilating ( $C_D$ ) molecules is not very large and, according to simple, limiting dual mode theory, is given by

$$C_H/C_D = C'_H b / [k_D(1 + bp)] \quad (4)$$

and at very low partial pressures, e.g., as  $p \rightarrow 0$ , eq. (4) reduces to

$$C_H/C_D = C'_H b / k_D \quad (5)$$

In general, therefore, penetrant molecules will tend to be predominantly antiplasticizing at relatively low concentrations when the ratio  $C_H/C_D$  is typically larger than unity, although the same compounds will predominately plasticize at relatively high total concentrations (or pressures) as  $C_H$  becomes small compared with  $C_D$  according to the predictions of eq. (4). The dependency of  $C_H/C_D$  with environmental partial pressure is simply monotonic according to eq. (4) and, therefore, no *a priori* or distinct transition in behavior between plasticization and antiplasticization would be expected.

### SUMMARY

Results have been presented which demonstrate that alcohol sorption in PMMA involves the superposition of Langmuir-type sorption and Flory-Huggins solution behavior. This combined behavior is thought to be general for all penetrants in glassy polymers if a sufficient activity range is studied. Through the use of a homologous series of penetrants, a spectrum of transport behavior is observed ranging from pure Fickian diffusion to relaxation controlled Case II uptake.

Glassy state aging, following the dilation of the polymer with high levels of penetrant, was shown to be easily monitored using low sorption levels of various probe molecules. Penetrants may either arrest aging or behave as totally noninteracting probes which are expelled as the polymer chains relax. Specifically, methanol has no effect on the aging of preswollen PMMA, while low levels of *n*-propanol markedly retard aging. Ethanol, intermediate in molecular size and polarity compared with methanol and *n*-propanol, retards relaxation and, therefore, exhibits an intermediate effect compared with methanol and *n*-propanol. Water also exhibits an intermediate effect, suggesting that water associates or clusters in PMMA.

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