

Diffusion of Vapors in Poly(2-vinylpyridine)

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The diffusion kinetics of benzene, dichloromethane, methanol, and water vapors in poly(2-vinylpyridine) was studied by the weighing method using a quartz spring at 25°C. Benzene, dichloromethane, and methanol are good solvents for the polymer, and water is a nonsolvent. In agreement with other works on penetrants with small molecular sizes such as simple gases, absorption and desorption curves for water in the region of lower and medium vapor pressures were found to be of Fickian type. At higher pressures, however, definitely non-Fickian features were observed in the kinetics of absorption and desorption. The integral absorption and desorption curves for methanol were of Fickian type in the entire range of vapor pressure studied. However, the reduced plots of uptake, or loss, for films of different thickness did not give a single curve when plotted against the Fickian variable $t^{1/2}/X$, where t is time and X is film thickness: that is, the thickness anomaly was observed. The absorption curves for benzene and dichloromethane vapors were of sigmoidal shape, corresponding to the typical non-Fickian process.

KEY WORDS: Absorption/ Desorption/ Water/ Methanol/ Benzene/ Dichloromethane/ Sorption isotherm/ Non-Fickian behavior/

INTRODUCTION

Poly(vinylpyridines) have the unique property to be transformed easily into polyelectrolytes by quaternization of nitrogen atoms of the pyridine units. Thus efforts to prepare block or graft copolymers of vinyl pyridine with a hydrophobic component have been made, and reverse osmosis properties¹⁻³⁾ or association behavior in solution^{4,5)} of the copolymers have been studied. In contrast with rather extensive studies in these fields, there have been few studies of sorption and diffusion of low-molecular-weight compounds in copolymers of vinyl pyridines.^{6,7)} Especially, to the authors' knowledge, no investigations have been made into sorption and diffusion behavior of vapors in homopolymer of vinyl pyridines.

This paper describes sorption and diffusion behavior of vapors in poly(2-vinylpyridine) (P2VP) studied by the weighing method at 25°C. The vapors studied were benzene, dichloromethane, methanol, and water. Benzene, dichloromethane, and methanol are good solvents for P2VP, and water is a nonsolvent. The glass transition temperature of P2VP has been determined as 104.5°C by the differential thermal analysis.⁸⁾ Since the non-Fickian behavior is usually observed for diffusion of vapor in glassy polymers, the diffusion process of the vapors in P2VP at 25°C is expected to be also of non-Fickian. However, if the size of a penetrant is very small and also if the penetrant is less soluble in a given polymer, the Fickian behavior has been observed even when the polymer concerned is in the glassy state.^{9,10)} Therefore

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the absorption and desorption processes for water and methanol were here investigated in somewhat more detail compared with those for other larger organic penetrants.

EXPERIMENTAL

Materials

Poly(2-vinylpyridine) (P2VP) used in the present study was polymerized anionically in tetrahydrofuran at -78°C with *n*-butyllithium as initiator. The sample was generously provided by Dr. M. Fukuda of the Central Research Laboratory, Toyo Soda Manufacturing Company.

The polymer sample was purified twice by precipitation from an 8% benzene solution by adding *n*-hexane. The precipitated polymer was washed several times with *n*-hexane, and dried and stored in vacuum at room temperature. Molecular weight of P2VP, determined by osmometry in methanol solution at 25°C , was 1.0×10^5 .

Films used for measurements were prepared by solvent casting. Methanol of G.R. grade was employed for casting. A polymer solution of about 3% was poured in a glass open-ended cylinder placed on the surface of freshly distilled mercury. The solvent was allowed to evaporate slowly in a desiccator at room temperature. Final traces of solvent were removed from the cast film by heating in vacuum to 40°C for more than 10 days. Since the thermal instability of P2VP was indicated by Noël,¹¹⁾ special care was taken to control the temperature during the drying procedure.

The film thickness was determined by taking the arithmetic average of numerous readings of a micrometer screw gauge over the area of the film. Films used for measurements were from 7.0×10^{-3} to 1.48×10^{-2} cm thick.

Benzene, dichloromethane, and methanol used as penetrant were of G.R. grade. No attempt was made to effect further purification. Also, distilled water was used as penetrant.

Method

The rate of absorption or desorption of the vapors was measured by weighing in the absence of air. A quartz spring balance with a maximum capacity of 2 g was hung from the top of a sorption chamber with a volume of 790 cm^3 . Using calibration weights, a spring constant of $100.00 \pm 0.01 \text{ mg/cm}$ was obtained. The rectangular P2VP film was suspended from the quartz spring. Sample films were between 60 and 140 mg in mass. A travelling microscope, capable of detecting displacements as small as 0.001 cm, was used to observe the length of the spring. Thus, displacements as small as 0.1 mg in terms of mass were detectable.

The sorption chamber was immersed in a water bath regulated to $\pm 0.05^{\circ}\text{C}$. A large vapor reservoir, a ten-liter flask, was used to eliminate measurable fluctuations in pressure within the sorption system. The flask was immersed in another water bath which was regulated also to $\pm 0.05^{\circ}\text{C}$ of the set point. About 100 cm^3 of the liquid were degassed in a liquid reservoir by successive freezing, pumping, and thawings, and then vapor of a test liquid was introduced in the vapor reservoir. A wide-bore mercury manometer was connected to the vapor system, and the vapor pressures

were measured by the manometer to within ± 0.2 mm of the height of the mercury column. In experiments with water vapor, a dioctyl phthalate manometer was employed, and the vapor pressures of water were measured also to within ± 0.2 mm of the height of dioctyl phthalate. The external vapor-containing volume was wrapped with heating tape and insulation to prevent condensation of test vapor in the lines.

Integral absorption from, and desorption to, zero vapor pressure were investigated at 25°C using films of various thickness. The error in determining the amount of the vapor absorbed by the P2VP film at absorption equilibrium was less than 1.5%.

RESULTS AND DISCUSSION

Sorption isotherms

Figure 1 shows the sorption isotherms of the vapors in P2VP at 25°C. Here the ordinate, C , represents the amount of penetrant in grams sorbed per gram of the polymer in the dry state, and the quantities p and p_0 are respectively the pressure and saturation pressure of the respective vapors.

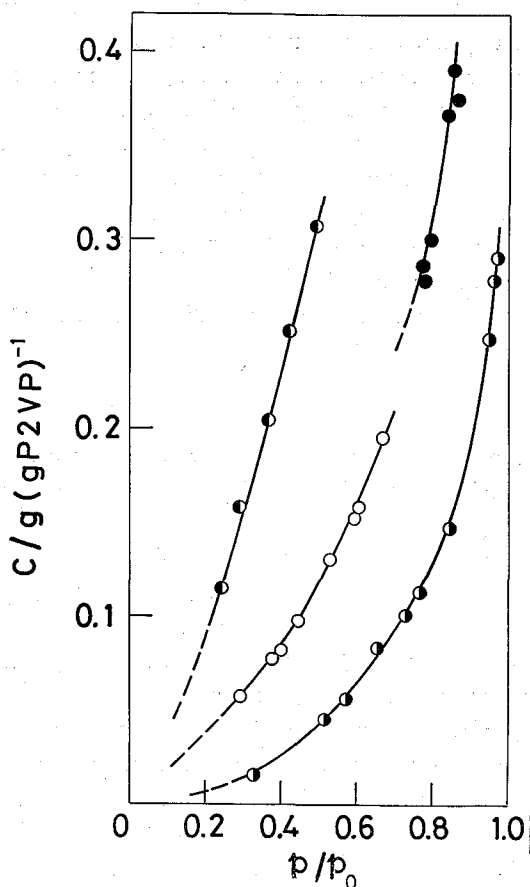
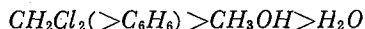


Fig. 1 Sorption isotherms of the vapors in P2VP at 25°C. ●: dichloromethane ; ●: benzene ; ○: methanol ; ●: water.

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Within four penetrants tested, the value of C seems to decrease in the order



at a given relative vapor pressure, in the region of medium pressure. The values of the solubility parameter for these penetrants in the above order are reported respectively as 20.1, 18.8, 29.7, and 47.9 in $10^3(J\ m^{-3})^{1/2}$.¹²⁾ As described previously, three organic liquids are good solvents and water is a nonsolvent of P2VP. Thus it may be suggested that the value of the solubility parameter of P2VP is close to that for dichloromethane (or benzene). According to the literature,¹³⁾ the solubility parameter of pyridine is $21.9 \times 10^3 (J\ m^{-3})^{1/2}$.

Barrie and Machin have reported that the sorption isotherms for water in silicone rubbers¹³⁾ and poly(alkyl methacrylate)¹⁴⁾ are practically linear in the region of lower relative pressure, 0~0.6 for silicone rubbers and 0~about 0.4 for poly(alkyl methacrylate), and that all isotherms are of type III in the B. E. T. classification.¹⁵⁾ Unlike the isotherms studied by them, no linear portion is observed in the type III isotherm for water in P2VP, though our measurements are not extended to the region of fairly low pressure (0~0.3). Relatively low water solubility and the shape of the observed isotherm may suggest that the thermodynamic interaction between the absorbed water molecules and the polar groups in P2VP is relatively weak. Barrie and Machin have interpreted the sorption isotherms in terms of the clustering tendency of the penetrant molecules in the polymer matrix.^{13,14)}

Sorption isotherm of methanol seems to be a part of type III isotherm. This is also the case for isotherms of dichloromethane and benzene, though measurements with these organic vapors were limited to narrow pressure region.

Absorption and Desorption Kinetics

Water

The paired absorption and desorption curves for water vapor at 25°C in the medium

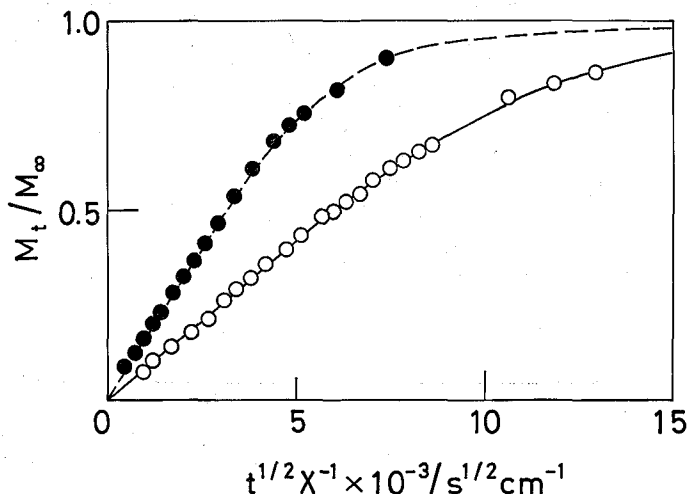


Fig. 2 Reduced absorption and desorption curves for water in P2VP at 25°C. Initial concentration : 0 ; final concentration : 0.0488 g/g ; solid line : absorption ; dashed line : desorption ; film thickness : 103 μ m.

pressure region are shown in Fig. 2. M_t and M_∞ are the mass of water absorbed by the polymer film, or desorbed from the film, at time t and at equilibrium, respectively, and X the thickness of the film. The final (or initial) relative vapor pressure in absorption (or desorption) of this run is 0.51. Each of the absorption and desorption curves consists of an initial linear part followed by an upward convex tail. Thus, these curves seem to meet the criteria for Fickian-type diffusion.^{16,17} The linear part for absorption and desorption extends over about 50% of M_∞ . The features of absorption and desorption curves obtained at p/p_0 of 0.33 were quite similar to those shown in Fig. 2.

Figures 3 and 4 show paired absorption and desorption curves at relative pressures of 0.73 and 0.96, respectively. With increasing the concentration of water in P2VP, the non-Fickian character becomes apparent for the absorption curves. Namely, the linear part of the absorption curve shown in Fig. 3 is limited to only in the initial stage and the curve has a point of inflection. The sigmoid character of the absorption curve is more noticeable in absorption shown in Fig. 4. In contrast to the absorption curves, the shape of the desorption curves is not affected much by the water concentration at equilibrium.

From the above observations, together with data of other systems of small penetrant and glassy polymer,^{9,10} the following conclusion may be drawn. However the size of a penetrant is very small like water molecule, the diffusion process of the penetrant in a glassy polymer exhibits the non-Fickian features if the penetrant concentration at absorption equilibrium is fairly high. The absorbed penetrant molecules would swell the polymer solid leading to slow relaxation motions of the polymer chain which occur within a time scale comparable to that of the concurrent diffusion process. On the other hand, if the penetrant amount in the polymer is sufficiently small that the

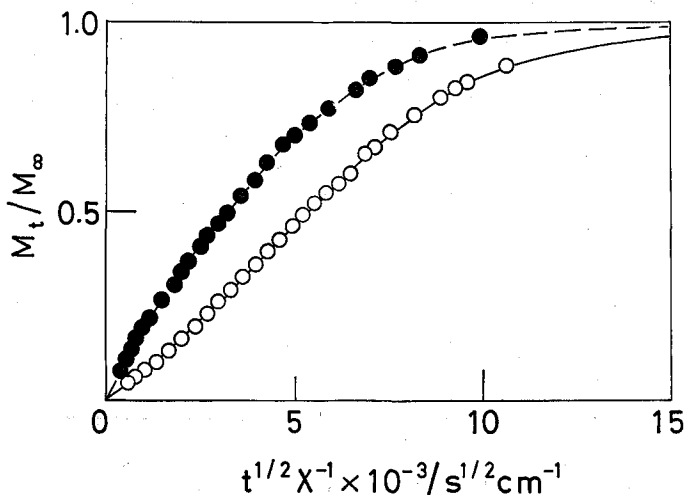


Fig. 3 Reduced absorption and desorption curves for water in P2VP at 25°C. Initial concentration : 0 ; final concentration : 0.1007 g/g ; solid line : absorption ; dashed line : desorption ; film thickness : 111 μ m.

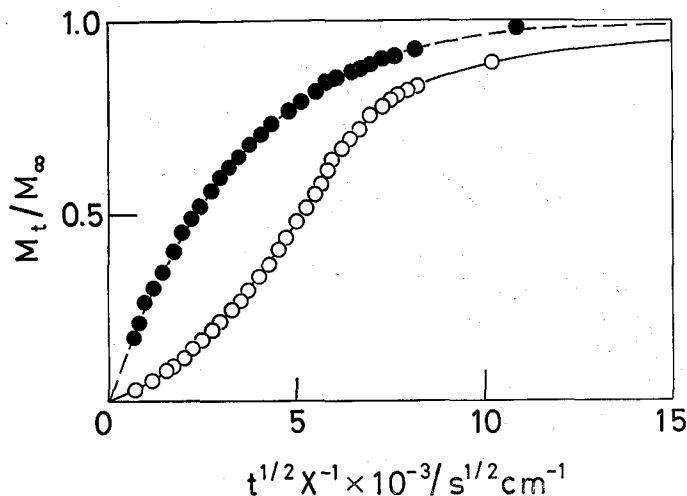


Fig. 4 Reduced absorption and desorption curves for water in P2VP at 25°C. Initial concentration : 0, final concentration : 0.2784 g/g ; solid line : absorption ; dashed line : desorption ; film thickness : 96 μm .

structure of the polymer solid does not undergo any swelling or other rearrangement, the integral absorption and desorption curve of Fickian type are observed frequently.

In all pairs of the reduced absorption and desorption plots shown in these figures, the desorption rate is faster than the absorption rate for conjugate curves. This behavior has been observed for the diffusion of water vapor in silicone rubbers¹³⁾ or in poly(*n*-propyl acrylate) and poly(*n*-butyl methacrylate).¹⁴⁾ In these systems, pairs of conjugate integral absorption and desorption curves show the Fickian character, and the diffusion coefficient D , determined from the initial rates of absorption and desorption, decreases with increasing concentration of absorbed penetrant. The concentration dependence of D has been interpreted in terms of the clustering of water molecules in the polymer matrix. In the system of water and poly(vinylacetate) or poly(methyl acrylate), on the other hand, concentration independent diffusion coefficient has been obtained.⁹⁾

Contrary to the diffusion behavior of these water and rubbery polymer systems, the absorption and desorption processes of the present system exhibits definitely the non-Fickian character as mentioned above. Since all the procedures available for evaluating diffusion coefficient from the absorption and/or desorption experiments resort to the Fickian-type absorption and desorption curves, we did not attempt to evaluate diffusion coefficients of the present system even in an empirical way. However, the observed absorption and desorption curves seem to suggest that D will decrease with increasing concentration, at least in the concentration region where the experiments were made.

Methanol

Figures 5 and 6 summarize a part of data of absorption and desorption of methanol vapor, at several concentrations, in P2VP films of various thickness. The absorption

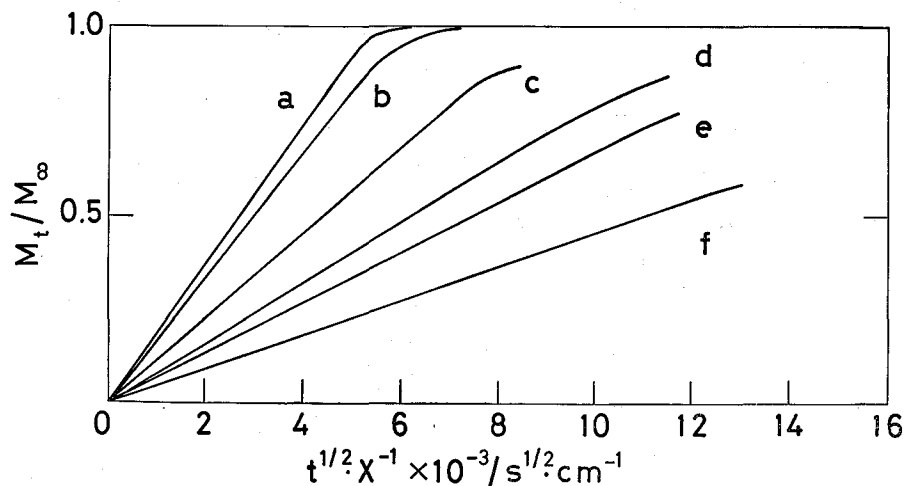


Fig. 5 Reduced absorption curves from zero concentration to various final concentrations C_f for methanol in P2VP film of various thicknesses X at 25°C.

	a	b	c	d	e	f
C_f/gg^{-1}	0.1581	0.1523	0.1309	0.0981	0.0766	0.0577
$X/\mu m$	143	132	117	142	148	139

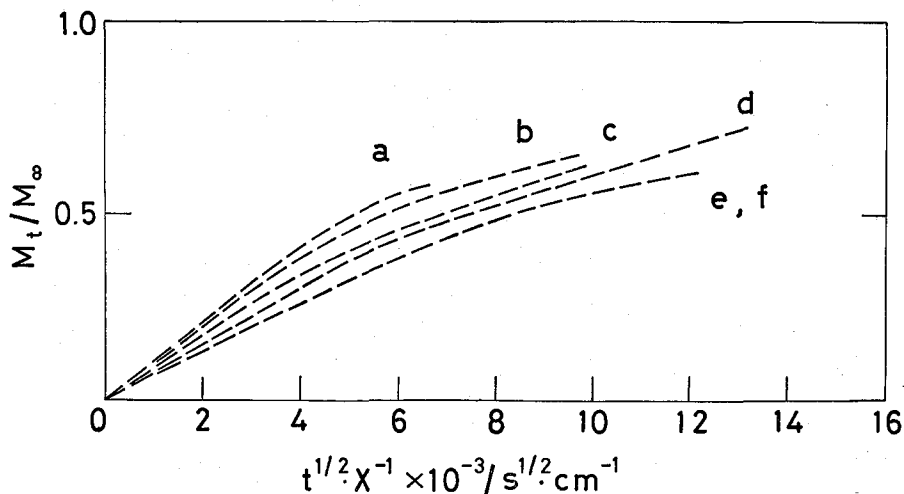


Fig. 6 Reduced desorption curves from various initial concentrations C_i to zero concentration for methanol from P2VP films of various thicknesses X at 25°C.

	a	b	c	d	e	f
C_i/gg^{-1}	0.1581	0.1523	0.1309	0.0981	0.0766	0.0577
$X/\mu m$	143	132	117	142	148	139

curves are shown in the former figure by solid lines and the desorption curves in the latter one by dashed lines. It is seen that all absorption and desorption processes are of Fickian type and that a linear part of each absorption curve extends over more than 70% of M_∞ . In all cases studied, absorption and desorption curves of Fickian type were observed.

Two points should be noticed in these reduced plots. First, if we compare the absorption curve a with b (Fig. 5), the thickness anomaly is apparent. That is, the initial slope of the absorption curve for thicker film is greater than that for thinner one, though the final solvent concentrations of these runs are practically the same. This is also the case with desorption curves a and b shown in Fig. 6. According to the criteria for Fickian-type diffusion,^{16,17)} these curves should fall on a single curve.

This non-Fickian feature has been observed in the absorption and desorption processes of organic vapors in amorphous polymers at temperatures slightly above their glass transition temperatures.^{18,19)} Also, the thickness anomaly was observed for the diffusion of organic vapors in block copolymers.^{7,20,21)} In view of the results of diffusion kinetics of water in P2VP, it seems natural to expect that the diffusion process of a large molecule, *i.e.* methanol, in P2VP is typical non-Fickian. However, in this system, the magnitude of the deviations from purely Fickian behavior is small as described above. Though the reason for the behavior has not been known to us yet, the smaller size of methanol molecule compared with that of the segment of P2VP and relatively strong thermodynamic interaction between methanol and P2VP might be responsible for the observed facts.

The second point that we want to notice is concerned with the concentration dependence of the rates of absorption and desorption. If comparison of the initial slopes of the curves a, d, e, and f in Fig. 5 is made, the slopes of the plots increase with increasing penetrant concentration. Thicknesses of sample films used in these runs are not different much from each other. The same trend is observed for desorption shown in Fig. 6. The results suggest that the diffusion coefficient increases with penetrant concentration. Since the thickness anomaly for the diffusion of methanol is not very apparent in the concentration region studied, we have evaluated the integral diffusion coefficient employing an empirical procedure which utilizes the initial slopes of the reduced absorption and desorption plots.⁷⁾ The integral diffusion coefficient thus evaluated increases with increasing concentration. The concentration dependence of the integral diffusion coefficient has been reported already in our previous paper (Fig. 8 of Ref. 7), and is not reproduced here.

Benzene and Dichloromethane

Typical absorption curve for the system of benzene and P2VP at 25°C is shown in Fig. 7. The shape of the curve is sigmoid. This is also the case with all absorption curves for this system. Also, quite the same behavior was observed in absorption of dichloromethane in the polymer.

As indicated in Fig. 7, the sample film becomes opaque during the course of absorption. The whitening starts at edges of the sample film in the end of the initial stage of the absorption process, and the film becomes more opaque with increase of the amount absorbed by the film. By further increase of penetrant concentration, however, the film becomes almost clear again, and soon after the deformation of the film starts.

The whitening of the sample film, mostly in the middle stage of absorption, would be attributable to the formation of crazes or microcracks in the vicinity of a rather

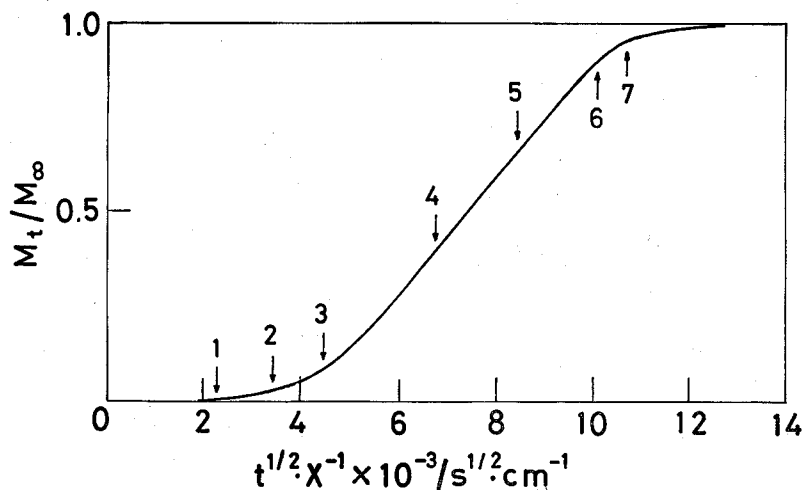


Fig. 7 Reduced absorption curve for benzene in P2VP at 25°C. Initial concentration : 0 ; final concentration : 0.3740 g/g ; film thickness : 74 μ m. Appearance of the film changes as : 1, opaque, edges ; 2, opaque + ; 3, opaque + + + ; 4, opaque + + ; 5, opaque + ; 6, almost clear ; 7, deform.

sharp boundary which separates an inner glassy core of essentially zero penetrant concentration from an outer swollen, rubbery shell of uniform concentration. In the later stage of absorption, fading of the whitening was observed. This phenomenon may be considered as due to the healing of the crazes or the microcracks by enhanced segmental motions in the polymer matrix containing fairly large amount of the penetrant. Though the whitening phenomenon appears to resemble the behavior of the Case II transport and related crazing of glassy polymers by vapors,²²⁾ the absorption curve of Fig. 7 still showed a sigmoid shape when re-plotted against time. The Case II transport behavior is characterized by a linear relationship between initial uptake of penetrant by polymer and time.

As indicated in Fig. 7, it was observed that the deformation of sample films started at almost the end of absorption process. After the absorption equilibrium was attained, the deformation became much greater. Therefore, the desorption experiments were not made for the benzene- and dichloromethane-P2VP systems.

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