Diffusion in Glassy Polymers. II. Effects of Polymer-penetrant Interaction; Diffusion of Ethyl Methyl Ketone in Atactic Polystyrene

By Hisashi ODANI, Jun HAYASHI and Mikio TAMURA

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Sorption processes of organic vapors in glassy polymers exhibit a variety of anomalous or "non-Fickian" features[1]. In the hope of obtaining information about how the polymer-penetrant interaction affects these feature, we have measured in the present work the rates of absorption of ethyl methyl ketone by atactic polystyrene, using both the integral and differential absorption techniques and have compared the data obtained with those reported previously for the system benzene-atactic polystyrene[1,2]. Ethyl methyl ketone and benzene have about the same molecular volumes, but their solvent powers for polystyrene are different; ethyl methyl ketone is less soluble in polystyrene than benzene is. Thus it is expected that the comparison of the present data with the previous ones for benzene will provide us with some useful information pertaining to the purpose mentioned above.

Experimental

The atactic polystyrene (A-PS) used was the same as that described previously[1]. Its viscosity-average molecular weight was 2.2×10^5. Films 2.40×10^{-3} cm. thick were used. Ethyl methyl ketone was purified by fractional distillation after drying over anhydrous potassium carbonate. Both integral and differential sorptions were studied under a variety of conditions at 25°C. This temperature is well below the glass transition temperature of the polymer[3].

Results and Discussion

Absorption Isotherms.—Absorption isotherm data for this system at 25°C are given in Fig. 1. Here the ordinate represents the mass of absorbed penetrant in grams per gram of dry polymer and the abscissa the relative pressure of ambient vapor. The data from integral absorption experiments and those from differential ones fall satisfactorily on a single curve. The corresponding data for the system A-PS-benzene at the same temperature are included in the figure for comparison. We see that the solubility of ethyl methyl ketone in A-PS is lower than that of benzene over the entire range of vapor pressure investigated.

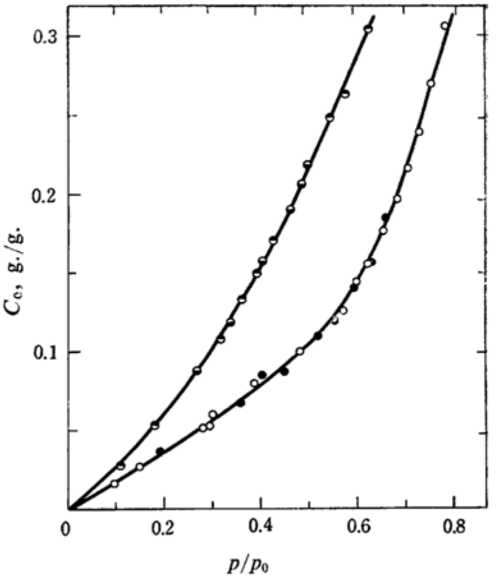

Fig. 1. Absorption isotherms of A-PS-ethyl methyl ketone and A-PS-benzene at 25°C.

	Integral absorption	Differential absorption
A-PS-ethyl methyl ketone	○	●
A-PS-benzene	◓	◒

Successive Differential Absorptions.—The data of successive differential absorptions for the A-PS-ethyl methyl ketone system at 25°C are given in Fig. 2. The increments of ethyl methyl ketone concentration in successive steps were kept approximately constant, about 0.01 g. of penetrant per gram of dry polymer, which is almost the same as those used in the previous experiments for benzene at the same temperature. The successive differential absorption curves shown in Fig. 2 change their type with the initial concentration according to the following scheme;

sigmoid type → pseudo-Fickian type
→ two-stage type → pseudo-Fickian type
→ Fickian type.

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[1] A. Kishimoto, H. Fujita, H. Odani, M. Kurata and M. Tamura, *J. Phys. Chem.*, **64**, 594 (1960).

[2] H. Odani, S. Kida, M. Kurata and M. Tamura, This Bulletin, **34**, 571 (1961).

[3] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems", Interscience Pub. Inc., New York (1950), p. 347.

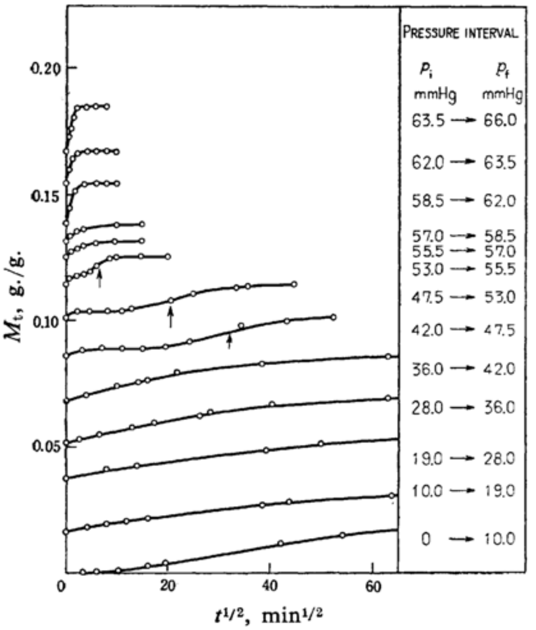

Fig. 2. Successive differential absorptions. Initial and final pressures, p_i and p_f, of each step are given in the right columns.

Though the general character of the family of curves for the present system is similar to that obtained for the benzene system[1], we may point out some significant and interesting differences between the two systems.

First, in the region of fairly low initial concentrations, only the first step is sigmoid and the second step already exhibits the pseudo-Fickian character. On the other hand, for benzene the shift from the sigmoid type to the pseudo-Fickian type began at a much higher concentration than for the present system. This relation is also the case with the initial concentration at which the transition from the pseudo-Fickian type to the two-stage type occurs. Secondly, the ninth and the tenth steps in Fig. 2 exhibit the typical pseudo-Fickian character, differing from the data for benzene where the transition from two-stage to the normal Fickian process occurred without the intervention of any pseudo-Fickian process.

It was demonstrated in the previous paper[1] that the successive differential absorption curves changed their type from pseudo-Fickian to Fickian when the penetrant concentration passed the point at which the polymer-penetrant mixture underwent glass transition at the temperature of the experiment. From the data shown in Fig. 2 and also from other differential absorption data obtained with concentration intervals of nearly the same magnitude, we may estimate such a critical concentration for the present system to be 0.139 g. ethyl methyl ketone per gram of dry A–PS. This value is lower than that for benzene at the same temperature. In that case the critical concentration of benzene was 0.191 g./g. As noted above, the solubility of ethyl methyl ketone in A–PS is lower than that of benzene, and the molar volumes of the two penetrants do not differ appreciably from each other. It appears, therefore, that for a given polymer at a given temperature a penetrant of poorer solubility gives a lower critical concentration if comparison is made for penetrants of about the same molar volumes. This implies that a penetrant molecule of less solvent-ability for the polymer will cause a greater decrease in the activation energy required for the segmental motion of polymer chains. In this connection it is of interest to note that Jenckel and Heusch[4] demonstrated that with solvents of about the same molar volumes the weaker the thermodynamic interaction with the polymer molecule the lower was the solvent concentration at which the mixture underwent the glass transition at a given temperature.

Concentration Dependence of the Second-stage Mechanism. — As mentioned in the previous paper[1], it is generally accepted that the second stage portion of a two-stage absorption is governed by the rate at which the network of polymer chains changes configuration under swelling pressure, while the first stage involves the ordinary diffusion mechanism. In accordance with the treatment presented in the previous investigation[1], we have chosen the quantity t_* to characterize the position of the second stage portion on the time axis, where t_* is the time corresponding to the inflection point on the second stage of the two-stage curve. In general, the value of t_* for the given initial concentration, C_1, increases with the decrease of the pressure interval Δp of each experiment and converges to the limit characteristic of the given C_1. This is also true in the case of the present system.

The values of t_* determined from the data of Fig. 2 and from other differential absorption data with about the same magnitude of Δp are plotted semi-logarithmically against C_1 in Fig. 3*. For the sake of comparison, the corresponding data for other systems reported in the previous paper[1] are included in the figure. It is seen that the data for the present system are approximately linear and that the slope of this line is as steep as those for the other amorphous polymer-organic vapor systems indicated. It is of special interest that the plot for the A–PS-ethyl methyl ketone system is nearly

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4) E. Jenckel and R. Heusch, *Kolloid-Z.*, **130**, 89 (1953).

* The magnitudes of Δp used in these differential absorption experiments are sufficiently small to give the values of t_* characteristic of a given C_1. This will be seen later in Fig. 6.

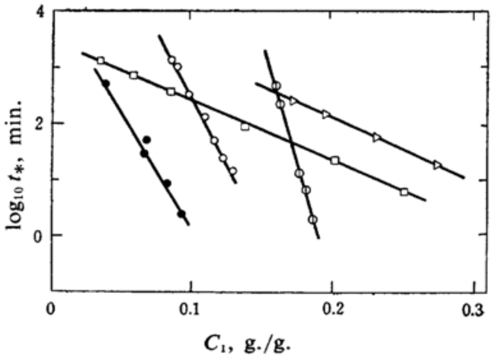

Fig. 3. Logarithmic correlation plots of t_* and initial concentration C_1 for some polymer-vapor systems. t_* is the time corresponding to the inflection point of the second stage of the two-stage process;

- ○ A-PS-ethyl methyl ketone at 25°C;
- ⌽ A-PS-benzene at 25°C;
- ● Polymethyl methacrylate-methyl acetate at 30°C;
- □ Cellulose acetate-methyl acetate at 20°C;
- △ Cellulose nitrate-acetone at 25°C.

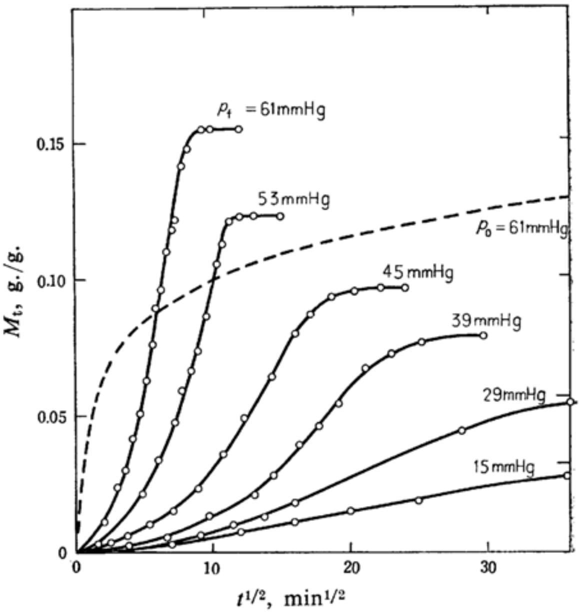

Fig. 4. Integral absorption and desorption curves from and to zero concentration. p_f is the final pressure of a particular run. Solid line, absorption; Dashed line, desorption.

parallel with that for the A-PS-benzene system at the same temperature. This suggests that for a given polymer the slope of $\log t_*$ vs. C_1 plot is approximately independent of penetrant species. As noted above, it is generally conceived that the rate-determining factor for the second stage absorption process is the rate of relaxation of the polymer chains. Thus it appears reasonable that the second stage absorption process primarily reflects the characteristic relaxation-motion of the network chains of a given polymer, irrespective of any difference in penetrant species. This may explain the independence of the slope of $\log t_*$ vs. C_1 plot upon penetrant species. The position of the $\log t_*$ vs. C_1 plot for methyl ethyl ketone is in the region of values of C_1 lower than that for benzene. This is the reflection of the fact that the value of C_1 at which absorption curves change their shape from pseudo-Fickian to two-stage type is lower for the former system than for the latter.

Integral Absorptions. — We have studied integral absorptions by choosing the initial concentrations in the regions corresponding to the four types of differential absorption, i. e., sigmoid type, pseudo-Fickian type, two-stage type and Fickian type.

Fig. 4 gives data of integral absorptions from zero concentration, and this initial concentration corresponds to a differential absorption of sigmoid type. The integral absorption processes are sigmoid for all pressure intervals studied and the initial rate of desorption is greater than that of the corresponding absorption. The absorption curves show a pronounced dependence on the final concentration, C_f.

In accordance with the treatment of the A-PS-benzene system[2], we chose the value of $1/(t/l^2)_{1/2}$ as a measure of the absorption rate of each curve, where l is the thickness of the film, t is time and $(t/l^2)_{1/2}$ is the value of t/l^2

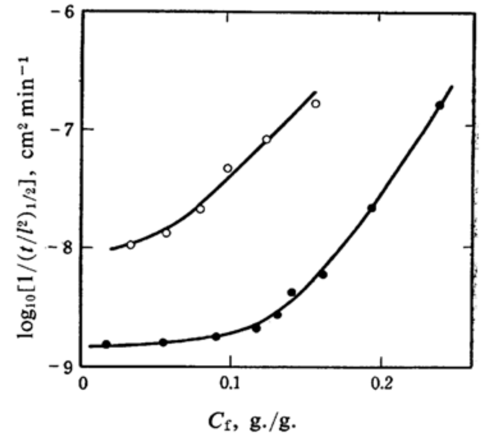

Fig. 5. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and final equilibrium concentration C_f for A-PS-ethyl methyl ketone and for A-PS-benzene at 25°C. $(t/l^2)_{1/2}$ is the value of t/l^2 when the amount of vapor in polymer reaches one half of the final equilibrium value; l is the thickness of film and t is time. ○, A-PS-ethyl methyl ketone. ●, A-PS-benzene.

when the amount of vapor in the film reaches one half of the final equilibrium value. The values of $1/(t/l^2)_{1/2}$ determined from Fig. 4 are plotted semi-logarithmically against C_f in Fig. 5, where the corresponding data for benzene system are also included for the sake of comparison. We see that the values of $1/(t/l^2)_{1/2}$ for ethyl methyl ketone increase with increasing C_f and, though the slope of the curve is quite similar to that for benzene they are always higher than those for benzene when compared at fixed values of C_f. This fact implies that the rate of diffusion of ethyl methyl ketone into A-PS is faster than that for benzene in the region of C_f studied.

Integral absorptions from an initial concentration corresponding to a differential absorption of pseudo-Fickian type were investigated at $C_i=0.055$ g./g. Although the results are not given here, the shape of absorption curves for small values of Δp was of pseudo-Fickian type, and with further increase in Δp the absorption curves changed to the sigmoid type and this feature persisted up to the largest of the Δp investigated. The values of $1/(t/l^2)_{1/2}$ increased with the difference between the initial and final concentrations, $\Delta C(=C_f-C_i)$, and the dependence of $1/(t/l^2)_{1/2}$ upon ΔC was about the same as that obtained for the series of absorption curves from $C_i=0$.

Fig. 6 shows integral absorption curves from $C_i=0.100$ g./g. This C_i was in the region where differential absorption curves exhibited two-stage behavior. It is seen that for small Δp the curves are similar in shape and the values of t_* are practically the same. With further increase in Δp the inflection point on the second stage portion shifts markedly to the short time region. The two-stage behavior is still apparent at $p_f=62$ mmHg, but the absorption curve for $p_f=80$ mmHg exhibits a sigmoid character. For this C_i the absorption rates changed more mildly with ΔC than in the regions of C_i corresponding to differential absorptions of sigmoid and pseudo-Fickian types.

Integral absorptions and desorptions from an initial concentration corresponding to a differential absorption of Fickian type were studied at the critical concentration at which the A-PS-ethyl methyl ketone mixture undergoes the glass transition at the temperature of the experiment. The features of the curves obtained were those of the true Fickian diffussion in which the diffusion coefficient increases with increasing concentration. However, the results from experiments with films of various thicknesses revealed a thickness anomaly as in the case of the corresponding experiments with the A-PS-benzene system[2]. A detailed study of the sorption behavior in this region of C_i is now in progress in this laboratory and will be reported in near future. The dependence of $1/(t/l^2)_{1/2}$ on ΔC in this region of C_i was much milder than those in the regions of lower C_i corresponding to non-Fickian differential absorptions.

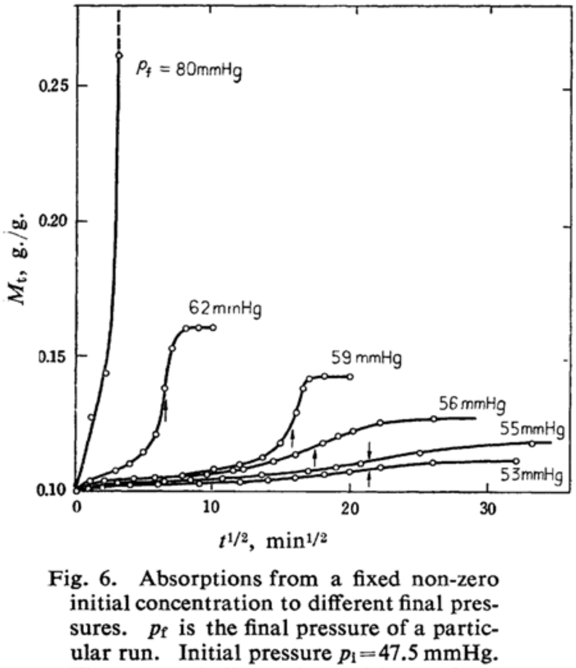

Fig. 6. Absorptions from a fixed non-zero initial concentration to different final pressures. p_f is the final pressure of a particular run. Initial pressure $p_i=47.5$ mmHg. The arrows indicate the positions of the inflection points of the second stage curves.

Summary

The successive differential absorptions for the A-PS-ethyl methyl ketone system change with the initial concentration according to the same scheme as that presented previously as typical systems of amorphous polymer-organic vapor; that is,

sigmoid type → pseudo-Fickian type
→ two-stage type → pseudo-Fickian type
→ Fickian type

The last transition, from pseudo-Fickian to Fickian types, for ethyl methyl ketone occurs at lower concentration than that for benzene. The second stage portion of the two-stage process shifts rapidly to the short time regions as the initial concentration of each step increases. The rate of this shift depends upon initial concentration in nearly the same manner as in the A-PS-benzene system. The general features of integral absorptions for the present system are very similar to those for benzene system, irrespective of the difference in the penetrant-polymer interaction between the two systems. The dependence of absorption rate

upon ΔC is also similar in general character to that for benzene system.

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Department of Industrial Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto