

The Transport of Methyl Methacrylate Monomer in Poly(methyl Methacrylate)

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Synopsis

The absorption kinetics and equilibria of methyl methacrylate monomer into poly(methyl methacrylate) were studied over a range of penetrant activities. The interval sorption kinetics at elevated activities were determined, compared, and contrasted with the integral sorption experiments in previously unpenetrated film samples. The sorption kinetics in previously unpenetrated films were predominantly case II or relaxation controlled at high activities. A Fickian contribution to the overall kinetics was apparent at lower activities. In contrast, interval sorption, at elevated activities in previously equilibrated and plasticized samples, followed Fickian kinetics rather closely, whereas resorption, over an activity range which involved a traversal of the effective T_g , was characterized by more complicated kinetics involving a super case II mechanism at long times. These composite results reinforce the notion that the kinetics describing penetration of a single penetrant into a single polymer are extremely sensitive to the boundary conditions imposed upon the polymeric sorbent.

INTRODUCTION

Frequently, sorption data which appear sigmoidal or "anomalous" when penetrant weight gain is plotted as a function of the square root of time will be nearly linear when weight gain is plotted versus linear time. Kwei¹ has shown that the "anomalous" diffusion data of Kishimoto et al.² for methyl acetate in poly(methyl methacrylate) over pressure intervals of 0 to 25 mm Hg and 25 to 50 mm Hg were represented by a straight line when weight gain was replotted as a function of time. At higher pressure intervals, the transport was termed "pseudo-Fickian," which is best described as an intermediate combination of Fickian diffusion and case II transport. Holley et al.³ and Hopfenberg and Frisch⁴ have shown that, although case II transport predominates at high activities, anomalous transport is apparent at intermediate activities and Fickian diffusion controls transport at low activities for *n*-alkane sorption in polystyrene.

Fickian diffusion and case II transport have been presented by Alfrey et al.⁵ as the two limiting cases describing the transport kinetics of a penetrant in a consolidated glassy polymer. Fickian, or case I transport, refers to the classical diffusion of penetrant in polymer described by Fick's equations⁶ where the initial sorption of penetrant proceeds linearly with the square root

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of time. Case II transport occurs when sorption is entirely controlled by stress-induced relaxations taking place at a sharp boundary separating the swollen and unswollen regions of the polymer.³ During an unsteady-state experiment, this boundary moves through the polymer at a constant velocity, and the penetrant weight gain is directly proportional to time for case II (relaxation-controlled) transport rather than proportional to the square root of time as in Fickian transport.⁵

It is convenient, therefore, to correlate sorption data with the relationship

$$M_t = k t^n \quad (1)$$

where M_t is the mass of penetrant sorbed at time t , and k and n are system parameters. For a Fickian system, $n = 0.5$ and k is related to the diffusion coefficient over the initial half-time of the experiment.⁶ For case II transport, $n = 1.0$ and k is proportional to the velocity of the discontinuous sorption boundary moving through the polymer.⁵

The primary objective of this investigation was to characterize in detail the transport of methyl methacrylate monomer in poly(methyl methacrylate). The data were required to incorporate the role of monomer transport into the overall kinetic scheme of methyl methacrylate polymerization. This aspect of the work will be considered in detail in a separate paper coauthored with Professor R. M. Fitch of the University of Connecticut. Moreover, development of techniques for eliminating monomer residuals from formed polymers depends upon detailed characterization of the kinetics of monomer transport in the parent homopolymer.

The kinetics of monomer sorption by PMMA films were determined over significantly different pressure ranges to determine whether the form of the transport kinetics varies significantly with activity range.

EXPERIMENTAL

Poly(methyl methacrylate) with a number-average molecular weight of about 100,000 was prepared by irradiating methyl methacrylate monomer with a cobalt-60 source for 70 min at 0.85 Mrad/min to about 20% conversion. Polymer preparation has been described in more detail in a previous publication.⁷ The viscous methacrylate polymer-monomer solution was cast on a glass plate and allowed to dry overnight at room temperature. The dried film was removed from the glass plate by washing in distilled water and annealed in a vacuum of 10^{-5} mm Hg for 24 hr at 60°C to remove the residual monomer. The final PMMA film was approximately 1 mil thick.

Film samples 4 cm² in size weighed to the nearest 0.0001 g were used in the vapor sorption experiments. In order to prevent the highly plasticized films from collapsing during monomer sorption at high activities, each film sample was reinforced by a quartz fiber weighing less than 1 mg, which was passed several times through the top of the film sample.

The kinetics and equilibria of methyl methacrylate vapor sorption were monitored gravimetrically using quartz helical springs supplied by Worden Quartz Products, Inc., Houston, Texas. Spring extension was calibrated as a function of weight gain to a precision of $\pm 2 \mu\text{g}$. A fixed amount of monomer, sufficient to maintain a specified partial pressure throughout the experiment,

was bled into a sorption chamber maintained at $30^\circ \pm 0.1^\circ\text{C}$. The saturation pressure of methyl methacrylate monomer at 30°C is 49 mm Hg. The consequent spring extension was measured as a function of time to determine the sorption kinetics. Sorption equilibria were determined from the final weight of monomer sorbed by the PMMA films.

RESULTS AND DISCUSSION

Sorption Kinetics

The sorption kinetics of methyl methacrylate monomer in previously unpenetrated PMMA contacting monomer vapor at activities of 0.458, 0.600, and 0.796, respectively, are presented in Figure 1 as linear plots of penetrant weight gain versus time. The time required to establish sorption equilibria varied from about 6 hr at a methyl methacrylate activity of 0.796 to over 900 hr at an activity of 0.458.

The values of n from eq. (1) are presented in Table I for the data in Figure 1. The sorption of methyl methacrylate monomer by unpenetrated PMMA films in general seems to be largely controlled by polymer relaxations, especially at the higher activities, although perfect case II kinetics were not observed.

The kinetics of methyl methacrylate sorption in films previously saturated at 0.600 and 0.808 are presented in Figure 2 as penetrant weight gain versus the square root of time over the activity ranges 0.6 to 0.808 and 0.808 to 0.89, respectively. The sorption of methyl methacrylate at an activity of 0.808 by a PMMA film, previously saturated with monomer at an activity of 0.600, is apparently two-stage. The first stage is typically Fickian and is characterized by an n value of 0.54. The second stage is characterized by an $n \gg 1.0$. This accelerated sorption, during the approach to equilibrium, has been described previously by Jacques, Hopfenberg, and Stannett as super case II transport.⁸

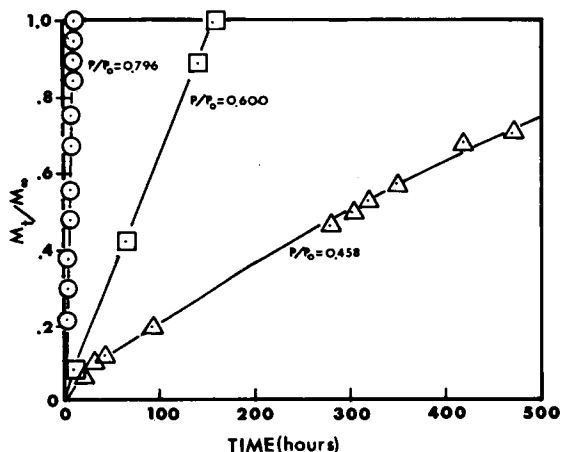


Fig. 1. Sorption kinetics for the transport of methyl methacrylate at activities of 0.458, 0.600, and 0.796 into unpenetrated PMMA films at 30°C .

TABLE I
Summary of Kinetic Parameters Describing Transport of Methyl Methacrylate in Poly(methyl Methacrylate) at 30°C

P/P_0	$t_{1/2}$, min Slope of $\log M_t$ vs. $\log t$ (n)	D , cm ² /sec	Comments	
0.0 → 0.796	0.84 ± .05	150	N/A	predominately case II kinetics
0.0 → 0.600	0.80 ± .10	4000	N/A	predominately Case II kinetics
0.0 → 0.458	0.74 ± .10	18,000	0.8×10^{-13}	D calculated from initial slope of M_t/M_∞ versus $t^{1/2}$ plot
0.600 → 0.808	0.54 ± .05 (1st stage)	7.5 (1st stage)	3×10^{-11}	2-stage sorption D calculated from 1st stage
0.808 → 0.890	0.55 ± .05	1.2	4.4×10^{-9}	Fickian kinetics

The rapid increase in the rate of sorption midway through this experiment was accompanied by a change in the physical properties of the film from a rigid glass to a limp rubber. Sufficient penetrant is absorbed by a Fickian mechanism to reduce the T_g of the plasticized film to 30°C or below. When the T_g of the polymer at the film midplane is reduced to the temperature of the experiment, the film changes from a glass to a rubber. The accelerated, terminal sorption is most likely a consequence of the overlap of advancing waves of penetrant which increases the rate of polymer relaxations which control the terminal sorption kinetics.

The amount of monomer absorbed by a PMMA film (previously equilibrated at an activity of 0.808) at an activity of 0.890 is directly proportional to the

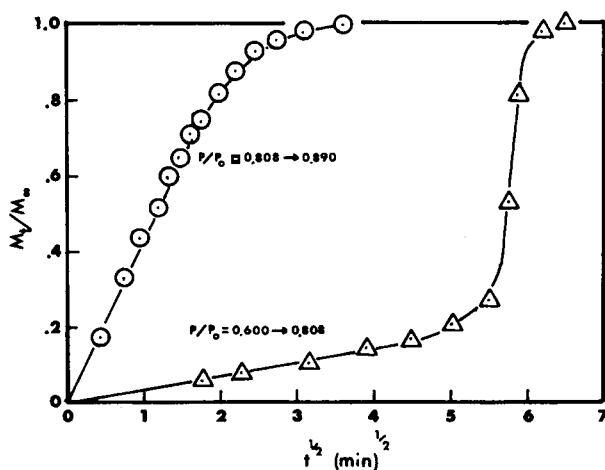


Fig. 2. Sorption kinetics for the interval transport of methyl methacrylate from activities of 0.600 to 0.808 and 0.808 to 0.890 into PMMA at 30°C.

square root of time over the first half of the interval sorption experiment as shown in Figure 2. The value of n for this experiment is 0.55, suggesting that nearly perfect Fickian kinetics are obeyed for the diffusion of methyl methacrylate monomer into a plasticized, rubbery PMMA film.

Diffusion Coefficients

Diffusion coefficients for the sorption of methyl methacrylate monomer into unpenetrated PMMA films and into PMMA films previously saturated with monomer at a given activity are presented in Table I. Diffusion coefficients were calculated⁶ from the equation

$$D = \left[\frac{\pi^{1/2} l (M_t)}{4 (M_\infty)} \right]^2 / t \quad (2)$$

where D is the mean diffusion coefficient, cm^2/sec ; l is the film thickness, cm ; M_t is the weight of penetrant sorbed at time t , sec ; and M_∞ is the final equilibrium weight of methyl methacrylate absorbed by the PMMA film at a given monomer activity.

A diffusion coefficient for the diffusion of monomer into the unpenetrated PMMA films was calculated from the initial slope of the sorption curves in Figure 1 at a penetrant activity of 0.458. Sorption at this activity was predominately Fickian over the first 20 hr of the experiment. Presumably, Fickian diffusion is observed in the first 20 hr of these experiments because of the initial steep concentration gradient. However, once swelling of the outer regions of the film occurs, polymer relaxation becomes rate controlling and predominately case II sorption kinetics are observed. The diffusion coefficients calculated from the initial slopes of these two curves are equal (within the experimental error associated with this type of an estimation) and are on the order of $10^{-13} \text{ cm}^2/\text{sec}$.

A diffusion coefficient of $3 \times 10^{-11} \text{ cm}^2/\text{sec}$ was calculated from the first stage of the sorption of methyl methacrylate at an activity of 0.808 into a PMMA film previously equilibrated at an activity of 0.600. A PMMA film equilibrated with monomer at an activity of 0.600, though partially plasticized, is still rigid and glassy. Fickian diffusion of methyl methacrylate at an activity of 0.890 into a rubbery PMMA film previously saturated by monomer equilibrated with an activity of 0.808 is characterized by a diffusion coefficient of $1.2 \times 10^{-9} \text{ cm}^2/\text{sec}$.

Sorption Equilibrium

The equilibrium solubility of methyl methacrylate monomer in PMMA films at 30°C is presented as a function of penetrant activity in Figure 3. The equilibrium solubility rises from less than 10 g of monomer per 100 g of dry polymer at an activity of 0.458 to more than 80 g of monomer per 100 g of dry polymer at an activity of 0.890. PMMA dissolves in liquid monomer (unit activity). The PMMA film equilibrated with methyl methacrylate at an activity of 0.890 was so extensively plasticized at the end of the sorption experiment that it dropped off the supporting quartz hook into the sorption chamber.

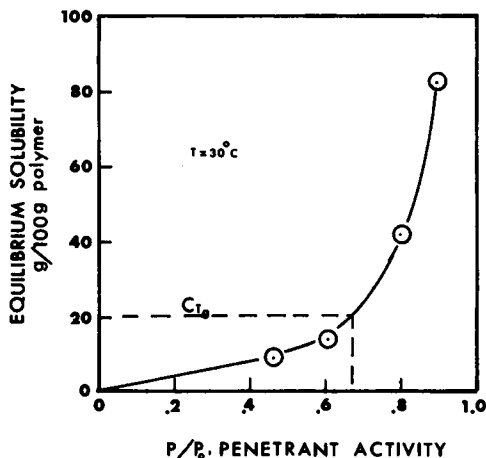


Fig. 3. Equilibrium solubility of methyl methacrylate in PMMA at 30°C as a function of penetrant activity.

The equilibrium concentration of methyl methacrylate necessary to reduce the T_g of PMMA to 30°C may be estimated⁹ from the equation

$$T_{g12} = \phi_1 T_{g1} = (1 - \phi_2) T_{g1} \quad (3)$$

where T_{g12} is the glass transition temperature of the plasticized film, °K; T_{g1} is the glass transition temperature of the dry polymer; and ϕ_1 and ϕ_2 are the volume fractions of polymer and monomer. The concentration of methyl methacrylate necessary to reduce the T_g of PMMA to 30°C, C_{T_g} , shown in Figure 3 was calculated from eq. (3) assuming a glass transition temperature of 90°C for dry PMMA. The calculated C_{T_g} is in agreement with the change in the physical properties of PMMA from a glass to a rubber observed during the sorption of methyl methacrylate monomer in films previously equilibrated with vapor at an activity of 0.600 and sorbing monomer subsequently from a vapor at an activity of 0.808.

The shape of the sorption isotherm shown in Figure 3 appears to change at a concentration sufficient to reduce the effective T_g of the plasticized film to the temperature of the experiment. Below T_g , equilibrium solubility is nearly linear with penetrant activity; however, above T_g , equilibrium solubility rises sharply with increasing penetrant activity. Similar changes in the shape of the sorption isotherm at the T_g of the plasticized polymer have been reported for acetone in polycarbonate¹⁰ and for *n*-hexane in polystyrene, poly(phenylene oxide), and blended films of these two polymers.¹¹

CONCLUSIONS

The sorption of methyl methacrylate monomer from the vapor phase into unpenetrated PMMA films, at activities of 0.600 and 0.796, is largely controlled by polymer relaxations. The zero-order sorption kinetics are adequately described by a single parameter, the velocity of the sorption boundary moving through the film. At lower activities (e.g., $p/p^0 = 0.458$) the slower sorption of methyl methacrylate monomer, into previously unpenetrated

PMMA, is controlled by a combination of Fickian diffusion and polymer relaxations.

In contrast, the transport of methyl methacrylate into previously penetrated PMMA films is apparently controlled by Fickian kinetics if the plasticized PMMA films are initially rubbery before "resorption." However, "anomalous" or two-stage sorption kinetics may be observed if the partially plasticized PMMA films are initially glassy and the T_g is traversed during the secondary sorption experiment.

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