

Measurements of Vapor Sorption/Desorption Properties of Ultrathin Polymeric Films*

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Synopsis

After a brief review of various standard methods of diffusion measurements of vapors into and out of polymeric solids, a direct gravimetric method for studying the sorption/desorption process in thin polymer films is discussed. The apparatus used consisted of a sensitive electrical balance housed in a vacuum pump. The sorption and desorption characteristics of thick polystyrene films were studied for comparison with literature values. The system polystyrene/methylene chloride was chosen to calibrate the system because of its known data. Experiments were carried out using the polystyrenes PS-5 and Dow Trycite 1000 at 35 and 50 mm Hg. Results agreed well with those reported in the literature. The apparatus was also suitable for measuring the very initial uptake of vapor. This information is important in the study of very thin films where the amount of vapor absorbed is minimum and the initial rate of uptake is almost instantaneous.

INTRODUCTION

The phenomenon of vapor sorption on polymeric substrates has technical importance in the dyeing of fibers and is theoretically important in biochemical and thermodynamic studies. Our direct interest is in the vapor fixing of xerographic images¹ and the vapor development of migration images.²

Diffusion measurements of vapors into polymeric solids have been obtained by many methods. The most common methods include absorption and steady-state flow through a membrane.³ In the absorption method, the amount of vapor sorbed and/or desorbed is measured either directly or indirectly. In the direct method, the change in weight of the sample due to sorbed penetrant into and out of the polymer is measured gravimetrically. Sensitive helical quartz springs,⁴ tungsten helical springs,⁵ and electrical balances⁶ have been used. Most of the work reported in the literature on sorption and desorption of vapors in polymers was carried out using a quartz or tungsten spring balance on which the polymer film is suspended in an evacuated chamber. The vapor is introduced at the desired pressure and the vapor sorption is measured as a function of time by observing the extension of the spring with a microscope. After reaching equilibrium, the chamber is evacuated and desorption is measured. Measurements of sorption kinetics may extend to several days and yet require exact information concerning the rapid, initial rate of vapor sorption and desorption⁷ so that anomalous changes in rate during the initial interval can be determined.

The quartz spiral balance technique requires periodic readings of the exten-

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sions with a traveling microscope.⁸ This data-collection procedure has the limitations of inconveniences inherent in the time required for a single reading, arbitrary selection of data intervals, sensitivities of the spiral, and prolonged attention required.

Using the indirect method of absorption, the volume and/or pressure change of the vapor is measured.⁹ Measurement is made by recording either the vapor pressure change or the vapor volume consumed by, or evolved from, the sample under constant vapor pressure and temperature.

Pressure and/or volume change is attributed to sorption and desorption into and out of the polymer. Accurate calibration, clean apparatus, and excellent temperature stability are required. However, the method does not lend itself to the study of sorption and desorption when very small pressure/volume changes occur.

In the other common method of steady-state flow through a membrane,⁵ the rate is measured at which the vapor (from the constant high-pressure side) diffuses through the "polymer membrane" into the constant lower-pressure side. Diffusion coefficients determined by this method agree well with values obtained from nonsteady-state measurements well above the glass transition of the polymer.¹⁰ Less common methods used for specific applications include measurement by interferometry,¹¹ tritium-labeled water technique,¹² and dielectric loss measurement.¹³ After a study of the above-mentioned techniques of sorption measurements, a direct gravimetric method was chosen as being the most suitable for studying the sorption/desorption process in thin polymer films.

EXPERIMENTAL

Description of Apparatus

The apparatus used in this investigation consisted of a sensitive electrical balance housed in a vacuum bottle, a glass vacuum line, pressure gauges, a millivolt recorder, and a vacuum pump. A schematic diagram is given in Figure 1.

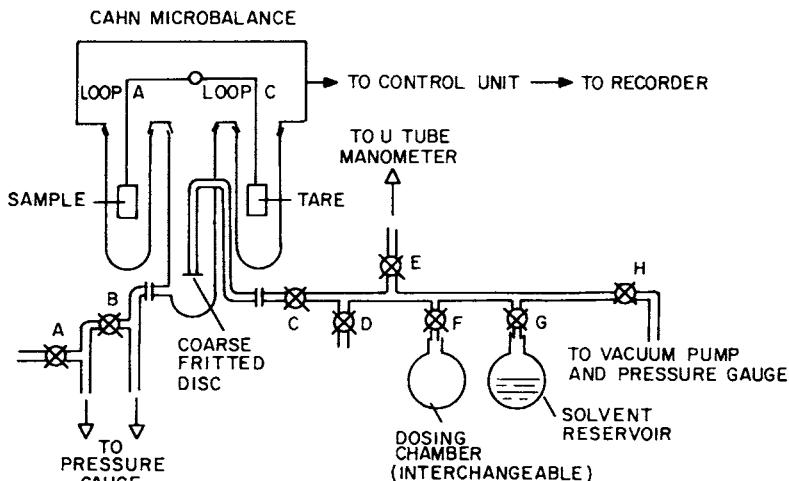


Fig. 1. Schematic diagram of apparatus used in sorption/desorption experiments.

A very sensitive balance equipped for continuous detection of weight change was required because of the small amounts of vapor sorbed and desorbed in thin polymer films and because of the anticipated fast initial rate of sorption and desorption.

The Cahn automatic recording electromicrobalance Model RG was chosen because of the following desirable properties: direct method, high sensitivity, and continuous reading. The microbalance is based on the null-balance principle, has a maximum capacity of 1 g from loop A, and is not damaged by common organic vapors. It also offers the advantage of continuous, automatic, and unattended recording of sample weight change. With its high sensitivity (approx. 3×10^{-4} g vapor/g polymer), aerodynamic "noise" is an important factor. The evacuation of the system from atmospheric to low ($\sim 10^{-3}$ mm Hg range) pressure and the introduction of vapor (or gas) into the system will cause aerodynamic "noise" which introduces uncertainty into the balance reading.

System pressure, hang-down tube diameter, and horizontal area of the sample are all important factors in the magnitude of aerodynamic noise. It was found, as reported elsewhere,¹⁴ that noise increased with horizontal area of the sample. Hence, the sample and tared counterbalance were placed vertically (minimizing the horizontal area) and attached to loop A and loop C using Nichrome hangdown wires of small diameter. The use of hangdown wires with small diameter and relatively short length, equal sample geometry on both loops, minimum area exposure, and a fritted disk placed at the end of the glass line inside the vacuum bottle resulted in a reproducible apparent weight loss during introduction of the vapor that could be corrected using a blank run. Also, a reproducible apparent sample weight loss recurred when going from atmosphere to low pressure.

The middle hangdown tube of the glass bottle was modified to allow introduction and evacuation of vapors into and from the system. The vacuum line (see Fig. 1) consisted of:

(1) Middle hangdown tube fitted with (a) a glass tube, connecting on one side to the vacuum line through an O-ring joint (#7), isolated from it by stopcock C, and terminating on the other side with a coarse-fritted disk to evenly spread the incoming vapor and to reduce the shock to the balance beam resulting from the admittance of the vapor from a high to a low pressure; and (b) a glass tube, provided with stopcocks A and B, for connecting to a pressure gauge (MKS Baratron Type 77) for measuring the system pressure.

(2) The glass line itself, connected to (a) vacuum pump (Duo-seal Welch Model #1402B) and pressure gauge (Type GTC-100 dual channel) by stopcock H; (b) interchangeable solvent reservoir by stopcock G; (c) interchangeable dosing chamber by stopcock F; (d) U-tube manometer, to measure the vapor pressure in the dosing chamber by stopcock E; (e) opening to the surrounding atmosphere through stopcock D; and (f) middle hangdown tube by stopcock C.

The total volume of the system, i.e., vacuum bottle and vacuum line, was about 4.4 liters. The above apparatus was suitable for directly measuring sorption and desorption of vapors into and out of polymeric films and was built utilizing readily available components.

Calibration Procedure

Materials

Polystyrene PS-5. PS-5 is a polystyrene made by the Dow Chemical Co.¹⁵ Molecular weights and molecular weight distribution were obtained by gel permeation chromatography (GPC) with the following results: $\bar{M}_w = 3.3 \times 10^5$, $\bar{M}_n = 1.3 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.54$.

Polystyrene Dow Trycite 1000. Trycite 1000 is a polystyrene film¹⁶ about 2 mils thick, prepared by extrusion. Molecular weights and distribution were obtained by GPC with the following results: $\bar{M}_w = 2.15 \times 10^5$, $\bar{M}_n = 5.65 \times 10^4$, $\bar{M}_w/\bar{M}_n = 3.80$. The organic vapor used was methylene chloride (Eastman Kodak #342).

Sample Preparation

Sorption and desorption measurements were made on polymers, either as 1–5 mil self-supporting films or as thin 1–20 μ films. The thin films were fabricated by solution coating onto a substrate, generally mill-washed aluminum sheets 5 mils thick. Generally, thin coatings were made from toluene solution by gravure techniques and oven dried for 1 hr at 70°C. The samples were cut to dimensions of 2.0 cm \times 5.0 cm.

The film thickness was determined by both interferometric (Leitz and/or Zeiss interference microscope) and gravimetric methods. Agreement between the two measurements was within 10%.

The sample area in cm² was known to better than 0.1 cm², or a relative error less than 1%. Solvents were degassed prior to used.

Sorption and Desorption Determination

The polymer sample and the counterbalance weight (tare) were attached to the hangdown wires of loop A and loop C, respectively, of the calibrated microbalance. The difference between the weights on loop A and loop C was maintained within 2–3 mg for maximum sensitivity. The sample hangdown tube was then connected to the vacuum bottle. With the recorder range in Z position (zero output from the balance), the balance was turned on. After waiting for the beam to snap into position, the recorder range was returned counterclockwise to a more sensitive position and the pen brought to the desired position (usually zero point) by using the mass dial (MD), the mass dial range (MDR) having already been chosen.

The sample–tare weight difference, temperature, and recorder chart speed were recorded, and the evacuation of vacuum bottle, glass vacuum line, and dosing chamber was begun. The MD reading under vacuum was then recorded. Next, vapor was introduced from the solvent reservoir into the dosing chamber by opening stopcock G (after closing stopcocks C and H), and the vapor pressure of the dosing chamber was measured. The amount of vapor introduced was dependent on the desired final vapor pressure of the system. This was known from a calibration curve of system versus dosing chamber vapor pressures, obtained by plotting vapor pressure of the dosing chamber versus system pressure. Stopcock F was then closed, the vacuum line evacuated, and stopcock C opened,

and finally the vapor was introduced from the dosing chamber into the system. The gain in weight of the sample was recorded as a function of time. When sorption was completed, stopcock H was opened to evacuate the system, and the weight loss was recorded as a function of time. At the end of desorption, the system was brought to atmospheric pressure by introduction of air by opening stopcock D. The sample was removed from the balance, and its weight and area were determined. If more than one sorption was made using the same sample, subsequent sorption and desorption were done as above prior to introducing air into the system. Because of buoyancy effects as described previously, blank runs using an uncoated sample were made for each vapor and each vapor pressure used.

Calibration of the Apparatus

The sorption and desorption characteristics of thick polystyrene films were studied using the previously described apparatus for comparison with literature values. Thick films were needed because available literature dealt exclusively with this type of film. The system polystyrene/methylene chloride was chosen to check out the apparatus because of previous studies by Park.¹⁷ The polystyrenes used were PS-5 and Dow Trycrite 1000, which have molecular weights comparable to those of polystyrene films used by Park. Experiments with these polystyrenes were carried out at 35 and 50 mm Hg and compared with Park's data.

EXPERIMENTAL RESULTS

The reduced sorption and desorption curves of polystyrene-methylene chloride at 50 mm Hg are given in Figure 2 for PS-5 (126 microns), in Figure 3 for Dow Trycrite 1000 (51 microns), and in Figure 4 for Dow Trycrite 1000 (51 microns) at 35 mm Hg.

Comparison with Literature Data

The reduced sorption curve of Figure 2 is replotted in Figure 5 with Park's data for comparison. From the above reduced curves the diffusion coefficients were calculated and are given in Table I. From the reduced curves of Figures 2-5 and

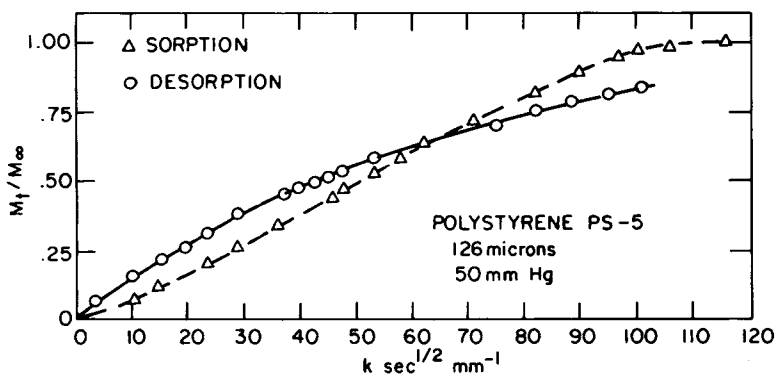


Fig. 2. Reduced sorption and desorption curves for polystyrene-methylene chloride system.

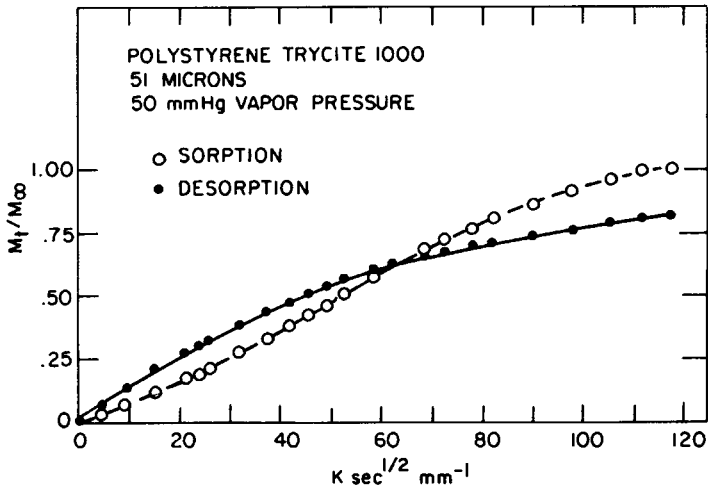


Fig. 3. Reduced sorption and desorption curves for polystyrene-methylene chloride system.

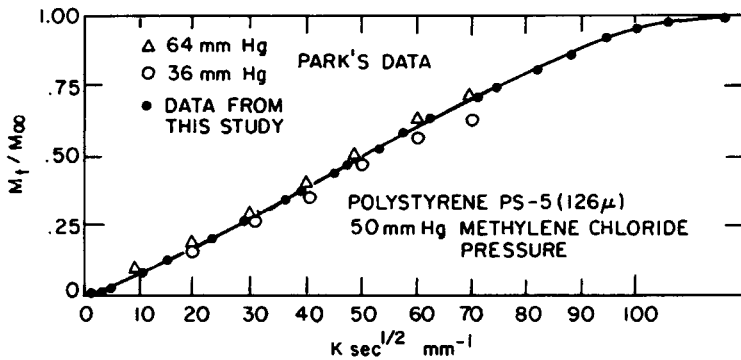


Fig. 4. Reduced sorption curve for polystyrene-methylene chloride system.

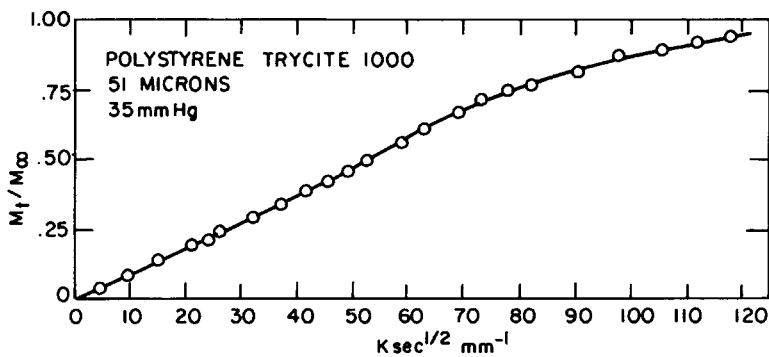


Fig. 5. Sorption of polystyrene-methylene chloride system; comparison with Park.²⁶

the results reported in Table I, it was clear that the apparatus was working properly. More important, it was suitable for measuring the very initial uptake of vapor as shown in Figure 6. Such data have not been reported in the literature because of the difficulties involved. This information is particularly important in the study of very thin films, where the amount of vapor absorbed is minimum while the initial rate of uptake is almost instantaneous.

TABLE I
Mean Diffusion Coefficients of Polystyrene

Sample	Thickness, Microns	Vapor Pressure, mm Hg	D(S), cm ² /sec
PS-5	126	50	1.9×10^{-10}
Trycite 1000	51	50	1.8×10^{-10}
Trycite 1000	51	35	1.7×10^{-10}
Park's	73	36	$\sim 1.7 \times 10^{-10}$
Park's	78	64	$\sim 2.0 \times 10^{-10}$

Thin-Film Measurements

This apparatus could be used to measure the sorption and desorption properties of thin polymer films. Figure 7 shows the sorption/desorption characteristics of a 1.4- μ film of a styrene/*n*-hexyl methacrylate (70/30) copolymer using

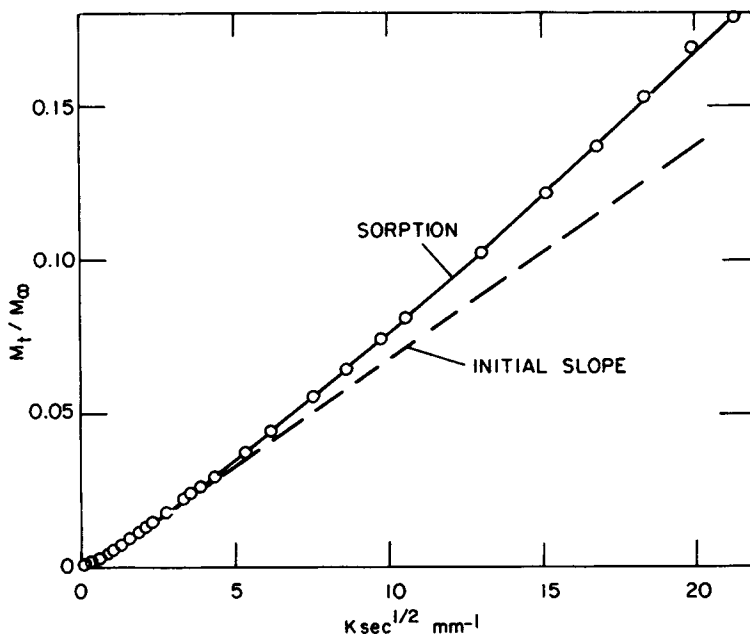


Fig. 6. Initial sorption curve (from Fig. 2).

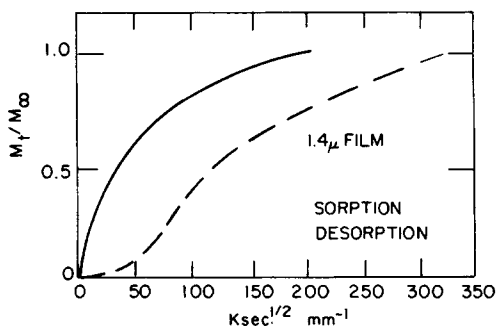


Fig. 7. Sorption and desorption of styrene/*n*-hexyl methacrylate copolymer-methylene chloride system.

methylene chloride vapor at 28 mm Hg. The sorption/desorption characteristics of such thin films are quite different from conventional thicker films. Thickness studies are in progress and will be reported in the future.¹⁸

In conclusion, the agreement of our results with reported literature data was excellent.

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