

## VINYL CHLORIDE MONOMER IN PVC: FROM PROBLEM TO PROBE

A. R. Berens

BFGoodrich R&D Center, Brecksville, Ohio 44141

**Abstract** - Study of the transport of vinyl chloride monomer (VCM) in PVC was initially undertaken to help design processes for removing residual monomer from the polymer. Vapor sorption experiments on PVC powder samples obey simple Fickian kinetics at low VCM concentrations and provide a convenient method of determining the diffusivity of VCM in PVC. From a simple model of diffusion in uniform spherical particles, it was predicted that essentially complete monomer removal from particles of diameter under 5  $\mu\text{m}$  could be achieved in a few minutes at temperatures near 100°C. The design of continuous steam stripping systems which exploit this rapid desorption rate, combined with a progressive reduction in non-porous particle content, has resulted in a remarkable reduction in residual VCM concentration of commercial suspension PVC over the past five years.

In addition to their practical value in helping overcome "the VCM problem", vapor sorption experiments have proven to be highly useful in characterizing the structure and properties of PVC powders. Analysis of sorption kinetics through a Fickian diffusion model for heterodisperse spheres has been employed to determine particle size distributions for all common types of PVC resins. Variations of sorption isotherms have been found to reflect history-dependent changes in the free volume of PVC, and study of non-Fickian sorption kinetics has led to new methods of observing glassy-state relaxation processes. Vapor sorption techniques have now been applied to a variety of polymer powder/vapor combinations and have shown that effects observed in the VCM/PVC system are quite characteristic of the general interactions between organic vapors and glassy polymers. The use of small organic molecules as probes in vapor sorption experiments represents a broadly applicable technique for the characterization and study of polymer structure and properties.

### INTRODUCTION

The recognition, in 1974, that vinyl chloride monomer (VCM) is a probable carcinogen presented the PVC industry with a grave and unprecedented problem. Public concern and regulatory actions seemed to threaten the survival of one of the most widely used and versatile of plastic materials. Yet, in 1980, the PVC industry is not only alive, but vigorously expanding. Clearly, the "VCM problem" has been effectively solved.

An important factor in overcoming this problem has been the determination of the transport properties of VCM in PVC, which provided the basis for practical and effective methods of removing residual monomer from PVC resins. In the course of studies on the diffusion and solubility of VCM in PVC, it became apparent that vapor sorption experiments could also provide useful new methods for characterizing PVC resins and gaining new information about the structure and properties of the polymer. In other words, VCM could be used as a "molecular probe" for the study of PVC.

This paper briefly reviews the studies which defined the basic transport properties of VCM in PVC, and describes the application of these results to the reduction of residual monomer content in PVC resins. The paper then discusses some of the characteristics of PVC which have been investigated through vapor sorption studies with VCM and other probe molecules.

## DIFFUSION OF VCM IN PVC

To assure the continued application of PVC without risk to employees, customers, or the public, a major task of the PVC industry was to reduce the residual monomer content of the polymer to such a low level that no significant further escape of VCM would occur during storage, shipping, fabrication, or service. A rational approach to this problem required a knowledge of the diffusivity of VCM at low concentrations in PVC.

At the time, studies of diffusion in rigid polymers had been largely limited to simple gases or to organic solvents at rather high concentrations. The diffusivities of several gases in unplasticized PVC had been determined by Tikhomirov, et.al. (1) For organic liquids or vapors at high activity, sorption behavior in glassy polymers involves a complex superposition of diffusion and relaxation-controlled swelling and cannot be described by simple Fickian diffusion equations (2). Hopfenberg and Frisch (3) had suggested that simple Fickian diffusion might be expected at very low penetrant concentrations in glassy polymers, but experimental confirmation was not available because of the low diffusivities and the resultant prohibitively long sorption times encountered for organic vapors in conventional thin polymer film specimens. Thus there was a notable lack of data relevant to the problem of removing traces of monomer from PVC.

A fortunate resolution of this difficulty was provided by the availability of PVC in the form of uniform, spherical, submicron particles prepared by emulsion polymerization. Such PVC samples present a simple, well-defined geometry, favorable for analysis of sorption kinetics, with diffusion dimensions much smaller than in the thinnest feasible polymer films. Since the time scale of a diffusion process is proportional to the square of the diffusion distance, use of submicron particles allows vapor sorption experiments to be carried to equilibrium in convenient time periods. Gravimetric sorption experiments on emulsion PVC powders, using a recording vacuum microbalance, provided the essential data for the determination of VCM diffusivity in PVC (4,5).

The kinetics of VCM sorption by monodisperse emulsion PVC powders are illustrated by Fig. 1, showing the amount sorbed,  $M_t$ , plotted against the square root of sorption time,  $t^{1/2}$ . For experiments producing a total uptake less

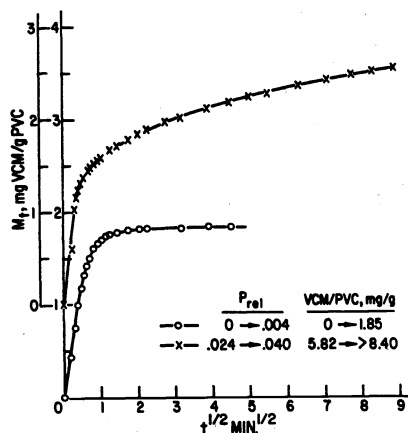


Fig. 1. VCM sorption kinetics in 0.44  $\mu$ m emulsion PVC, 23°C.

than about 2 mg VCM/g PVC, the sorption kinetics closely obey the solution of Fick's Law given by Crank (6) for diffusion in a sphere:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4n^2 \pi^2 Dt/d^2) \quad (1)$$

Here,  $M_\infty$  is the limiting value of  $M_t$  at long time,  $D$  the diffusion coefficient, and  $d$  the diameter of the spherical particles. Under experimental conditions yielding greater amounts of sorption, the rapid, apparently Fickian initial sorption is followed by a slower, long-continued further uptake of VCM attributable to a non-Fickian, relaxation-controlled sorption

process (7); this second-stage sorption is considered further in a later section of this paper.

From experiments using PVC samples of known  $d$  and obeying Fickian sorption kinetics, the diffusion coefficient is readily determined through the solution of Equation (1) at  $M_t/M_\infty = 0.5$ ,

$$D = 7.66 \times 10^{-3} d^2/t_{.5} \quad (2)$$

where  $t_{.5}$  is the half-sorption time. Using data for PVC resins of varied particle size, VCM diffusivities in PVC were determined by this method at temperatures from 23 to 110°C (5). The results are presented as an Arrhenius plot in Fig. 2; the slope of the line shown yields an activation energy for diffusion of 71 kJ/mol (17 kcal/mol).

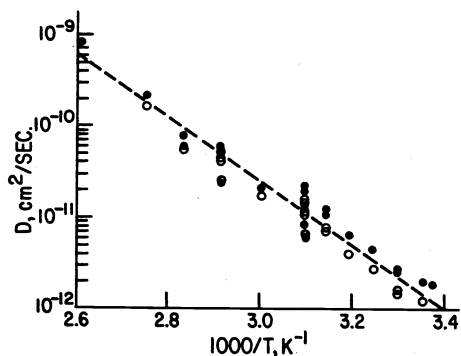


Fig. 2. Diffusivity of VCM in PVC vs.  $1/T$ .

Parallel experiments involving desorption to a vacuum atmosphere demonstrated that Equation (1), with  $M_t$  and  $M_\infty$  the time-dependent and ultimate weight loss, also accurately describes the kinetics of VCM desorption from PVC powders (4). Desorption data yield values of  $D$  somewhat lower than do sorption data, as is characteristic of systems in which  $D$  increases with increasing penetrant concentration (6). The concentration dependence of  $D$  has been investigated by interval sorption and desorption experiments involving incremental changes in VCM pressure (5). Over the concentration range from 0 to 2 mg VCM/g PVC, the variation of  $D$  is less than the experimental uncertainty in determinations of  $D$  from data on varied PVC samples (cf. Fig. 2). Moreover, sorption and desorption appear completely reversible to within the precision of the gravimetric procedures used (approximately  $\pm 0.005$  mg VCM/g PVC). Thus the sorption and desorption of up to 2 mg VCM/g PVC are adequately described by Fickian diffusion equations with a single, temperature-dependent diffusion coefficient.

#### APPLICATION TO RESIDUAL MONOMER REMOVAL

With  $D$  known, Equation (1) can be used to predict the rate of VCM removal from PVC particles of various uniform particle diameters. For desorption,  $1 - M_t/M_\infty = C/C_0$ , where  $C$  is the VCM concentration remaining in a PVC sample originally containing VCM at concentration  $C_0$ . Figure 3 presents plots of  $\log(C/C_0)$  vs.  $t$  for several particle diameters, calculated from Equation (1) with the 90°C value of  $D$  for VCM in PVC,  $2 \times 10^{-10}$  cm<sup>2</sup>/sec. In this coordinate system, the asymptotic approach to equilibrium, predicted by Equation (1), becomes a straight line extending indefinitely in time. The calculations show that any desired degree of monomer removal should be achievable in a few minutes at  $T \geq 90^\circ\text{C}$  for PVC particles of diameter less than about 5  $\mu\text{m}$ . Implicit in the calculations are the assumptions that the rate-determining process is the diffusion of VCM through PVC, and that the vapor-phase VCM concentration is zero throughout the desorption.

Experimental data for comparison with these "Fickian uniform-sphere" predictions have been obtained for a wide variety of PVC resin samples both by the gravimetric, vacuum-microbalance technique and by a more rapid procedure using a gas chromatograph (GC) (8). In the GC method, a thermal conductivity or ionization detector is used to monitor the VCM content of a carrier gas stream passed through a PVC sample initially equilibrated with a low concentration of VCM vapor.

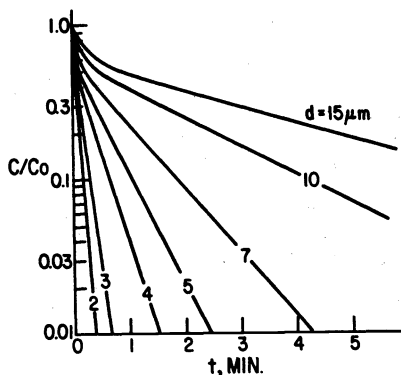


Fig. 3. Calculated VCM desorption curves for uniform PVC spheres of varied diameter, 90°C.

By both gravimetric and GC methods, it has been found that emulsion PVC powders of submicron size desorb VCM down to the low ppm detection limits of the instruments in less than one minute at 90°C (8), in agreement with the prediction of Fig. 3. For PVC's produced by suspension or mass-polymerization processes, however, VCM desorption curves deviate markedly from the Fickian, uniform sphere predictions, and vary greatly among resin samples, as illustrated in Fig. 4. In many cases, the initial desorption occurs at the rates

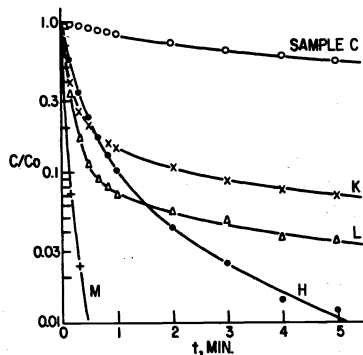


Fig. 4. Experimental VCM desorption curves, suspension PVC's, 90°C.

predicted for 2-3  $\mu\text{m}$  particles, indicating that it is the size of the primary particles, within the 100-200  $\mu\text{m}$  porous agglomerates (9), which governs initial desorption kinetics. The reduced rate in later stages of desorption suggested the presence of varying proportions of particles having larger diffusion-controlling dimensions (4). This interpretation of the desorption curves is qualitatively consistent with microscopic observations of "glassy particles" (optically transparent, non-porous grains) in many suspension PVC's, and was supported by the desorption behavior observed for deliberate mixtures of porous and non-porous PVC resins (4).

It followed from these laboratory desorption results that practical, rapid "stripping" of PVC resins to very low monomer levels might be achieved if two significant requirements were met: First, the stripping operation should ensure that VCM is carried away from the resin particles as fast as it diffuses to their surfaces, so that VCM-in-PVC diffusion is effectively the only rate-limiting process; and, second, PVC resins should be produced with the minimum possible content of non-porous or "glassy" particles. Practical developments since 1974 have been directed toward both these requirements.

Commercial monomer removal from suspension-type PVC is now commonly performed in a continuous, countercurrent steam-stripping operation (10-12). The PVC slurry from the polymerization vessels is passed down a stripping column against an upward flow of steam. The continuous process limits the PVC exposure at steam temperatures to a few minutes, thus minimizing thermal damage

to the polymer while exploiting the rapid VCM desorption rates demonstrated in laboratory experiments. Countercurrent operation ensures that the PVC particles are continuously exposed to a maximum VCM concentration gradient (from particle to surrounding vapor) and thus approximates the conditions of zero VCM vapor concentration assumed in the diffusion calculations. Actual performance of the stripping columns closely follows rates predicted from GC VCM desorption kinetic data on small resin samples.

To take full advantage of the continuous stripping technology, evolutionary developments have been made over the past five years in the control of particle structure of suspension PVC. Figure 5 compares the GC VCM desorption curves for three suspension resins of the same molecular weight, identified by year of manufacture (13). The major difference in desorption kinetics is

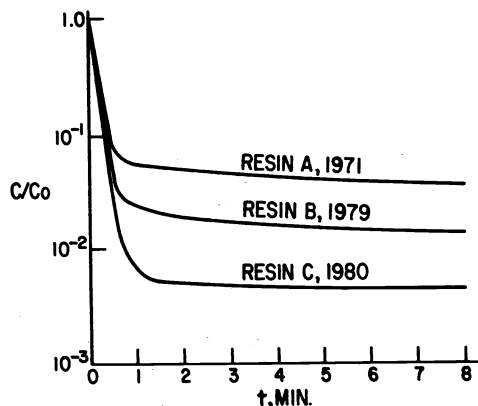


Fig. 5. VCM desorption curves, commercial suspension PVC's, 90°C.

in the fraction of residual VCM removed before the desorption rate slows down. According to the concept that the desorption rate "tail" is due to "glassy particles", these data indicate a progressive reduction in the glassy particle content of these otherwise similar resins.

The introduction of more effective stripping procedures and the development of resins showing more favorable VCM desorption kinetics have resulted in a remarkable reduction in the residual monomer content of commercial suspension PVC resins over the past five years, as shown in Fig. 6 (14). The consistent, large-scale production of PVC with residual monomer content of 1 ppm or less has now been achieved.

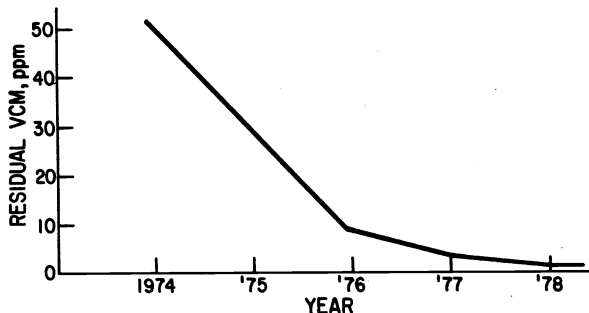


Fig. 6. Reduction of average residual VCM content of commercial suspension PVC since 1974.

#### VAPOR SORPTION STUDIES OF PVC

##### Particle size and distribution

Vapor sorption data for VCM in suspension PVC resins clearly suggested at least a qualitative relation between sorption/desorption kinetics and the size distribution of particles in a PVC powder sample. As a possible basis for quantifying this relation, it was suggested (5) that the sorption kinetics of

heterodisperse powders might be modeled by modification of Equation (1) to

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_i x_i \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4n^2 \pi^2 D t / d_i^2) \quad (3)$$

where  $x_i$  is the weight fraction of particles having diameter  $d_i$ . This model implies that an experimental determination of  $M_t$  as a function of  $t$ , under Fickian diffusion conditions, may provide sufficient data for derivation of a complete weight-fraction particle size distribution for a polymer powder, given prior knowledge of  $D$ . Recovery of the size distribution requires resolution of the experimental sorption kinetic data into contributions of the individual elements of the size population.

Several methods based on Equation (3) have been used to derive particle size distributions for PVC powders from VCM sorption or desorption kinetic data. Daniels and Longeway (15) assumed a specific form of bimodal distribution and developed a method for computing parameters of this distribution (diameters and weight fractions) from experimental GC VCM desorption data on PVC suspension resins. A simpler graphical method, using the initial and longer-time slopes of  $\log(C/C_0)$  vs.  $t$  curves obtained from GC data, has also proven useful for comparing PVC suspension resins in terms of a bimodal approximation of their size distribution (13).

Very recently, a method has been developed for deriving particle size distributions from sorption kinetic data without assuming a specific functional form of distribution (16). The basis of this approach is a "histographic" distribution consisting of varied weight fractions of spheres having an assigned, finite set of discrete diameters. The analysis computes the weight fractions which best match Equation (3) to the experimental sorption data.

This histographic procedure has been applied to gravimetric vapor sorption data on PVC powders polymerized by emulsion, mass, suspension, and microsuspension processes and ranging in effective particle diameter from 0.2 to 100  $\mu\text{m}$ . Vapors having diffusivities both higher and lower than VCM were needed as probes in order to keep sorption experiments within an accessible time scale over this wide diameter range, since sorption times are governed by the ratio  $d^2/D$ .

For samples whose particle structure approaches the heterodisperse, homogeneous spheres assumed in the diffusion model, this analysis yields histographic distributions closely approximating the particle size distributions determined by conventional microscopic and sedimentation methods. Figures 7 and 8 illustrate results obtained on emulsion and microsuspension types of PVC, respectively.

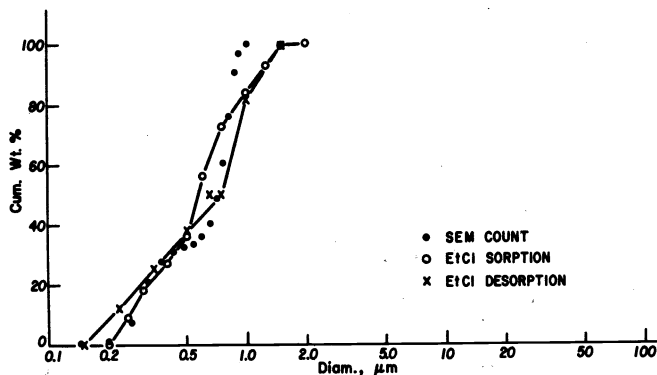


Fig. 7. Particle size distributions determined by scanning electron microscopy (SEM) and by sorption kinetics analysis, emulsion PVC sample.

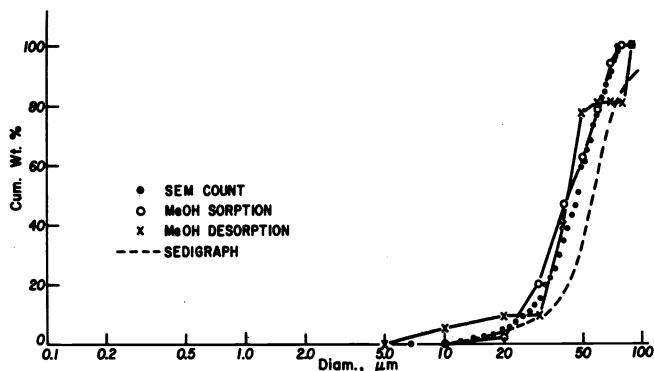


Fig. 8. Particle size distributions determined by SEM, sedimentation and sorption kinetics analysis, microsuspension PVC sample.

Application of this analysis to commercial suspension PVC resins yields results illustrated by Fig. 9. For such agglomerated or porous particles, the derived size distribution does not reflect the gross dimensions of the grains

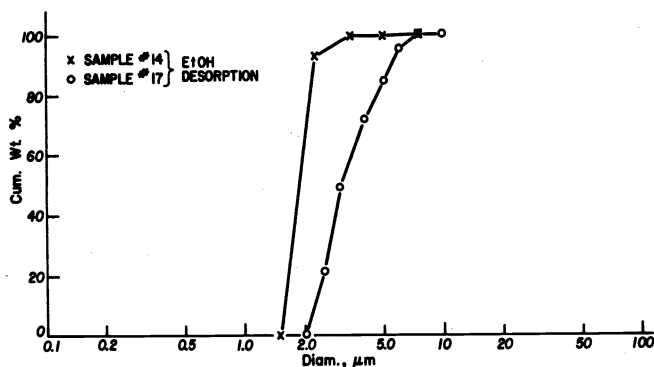


Fig. 9. "Equivalent sphere size distributions" from sorption kinetics analysis, suspension PVC resins.

(100-200  $\mu\text{m}$ ), but may be interpreted as an "equivalent sphere distribution", i.e., a distribution of sphere sizes which would reproduce the observed sorption kinetics. The examples in Fig. 9 show that the sorption behavior of suspension PVC can be described by rather narrow equivalent sphere distributions in the 2-10  $\mu\text{m}$  range. Although these distributions are approximate, they seem quite useful as a means of assessing and quantitatively describing the effects of varied polymerization recipes and conditions upon the particle morphology of suspension PVC resins.

#### Free volume and history effects

In addition to kinetic data, gravimetric measurements of VCM sorption by PVC powders also provide data on the apparent equilibrium solubility of VCM in PVC. Sorption isotherms have been determined by measurements at varied temperatures and VCM pressures (17-19). At temperatures and VCM concentrations above the glass transition conditions, sorption isotherms have the form of the Flory-Huggins equation, and are apparently temperature-independent when plotted as a function of  $P_{rel}$ , the VCM relative pressure. ( $P_{rel} = P/P_0$ , where  $P$  is the actual VCM pressure and  $P_0$  the saturated vapor pressure at the experimental temperature.) The rubbery-state isotherms also appear independent of PVC type, molecular weight, and prior sample history. Below the glass transition, however, the sorption isotherms show a reversal of curvature, VCM solubility at a given  $P_{rel}$  increases markedly with decreasing temperature, and the solubility varies significantly with the prior history of the sample. The forms of isotherms over the pressure and temperature ranges studied are shown in Fig. 10. The glassy-state isotherms have been interpreted in terms of the dual-mode sorption hypothesis (20); the additional sorption, above the Flory-Huggins curve, is ascribed to a Langmuirian sorption process involving the filling of microvoids or holes frozen into the polymer.

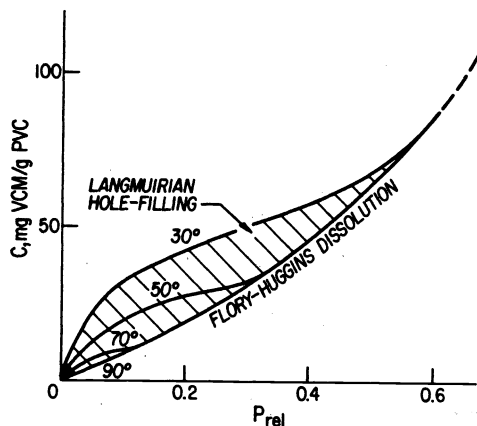


Fig. 10. Sorption isotherms, VCM/PVC.

The dependence of glassy-state VCM/PVC sorption isotherms upon prior history of the PVC is illustrated by the data shown in Fig. 11 (18). The "original" sample was recovered from the polymerization without heating above 50°C; the

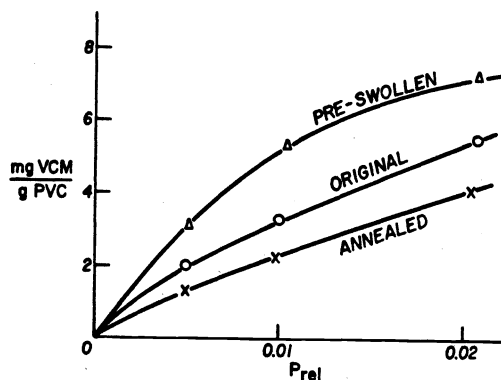


Fig. 11. Effect of sample history on VCM/PVC sorption isotherms, 30°C.

"annealed" sample was heated to 100°C and slowly cooled; and the "preswollen" sample was exposed to VCM vapor for 4 days at  $P_{rel} = 0.2$  and 30°C, then evacuated to remove the sorbed VCM. The observed changes in sorptive capacity parallel well-known volume-relaxation processes in glassy polymers (21), and appear to involve only the hole-filling mode of sorption (22). It therefore may be inferred that the "holes" involved in the Langmuirian mode of sorption are, in effect, elements of excess free volume in the glassy polymer. The sorptive capacity of PVC for VCM thus seems to be a direct measure of the frozen-in free volume. Since sufficiently precise density measurements on powder samples are difficult or impossible, vapor sorption measurements now seem to be the most feasible method available for characterizing changes of free volume in glassy polymer powders.

#### Relaxation effects

Under experimental conditions producing a significant non-Fickian, second stage sorption of VCM vapor (e.g., the upper curve in Fig. 1) the rapid attainment of diffusion equilibrium in fine PVC powders permits a clear separation of the individual contributions of diffusion and relaxation-controlled swelling to the overall sorption process (7,23). Long-time experiments can therefore be used to determine the kinetics of vapor-induced, glassy state relaxations. It is also possible to follow consolidation or deswelling relaxations, induced by removal of a swelling penetrant, through cyclic resorption experiments; a slow decrease in sorptive capacity is observed upon periodic reexposure of a preswollen sample to VCM at low  $P_{rel}$  (18,23). The rates of swelling and consolidation relaxations are dependent upon the prior sample history, decreasing after thermal treatments which reduce free volume, and increasing after preswelling. As an example, Fig. 12 compares the VCM sorption kinetics at 30°C and  $P_{rel} = 0 \rightarrow 0.10$  for "never-heated" and annealed



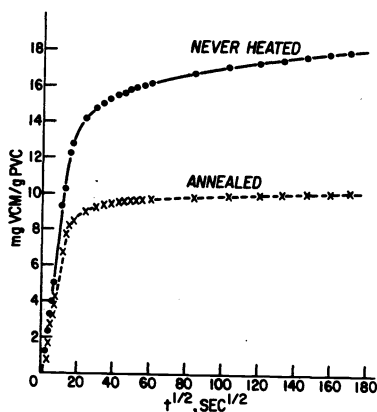


Fig. 12. Effect of sample history on VCM sorption kinetics, emulsion PVC, 30°C,  $P_{rel} = 0 \rightarrow 0.10$ .

samples of an emulsion PVC powder; both the extent of sorption and the rate of swelling relaxation were markedly reduced by annealing. Vapor sorption here offers a convenient means of assessing both the amount and the effect of free volume in a polymer powder sample. Effects observed in vapor sorption experiments seem quite consistent with studies of glassy state relaxations by more conventional methods such as dilatometry (24,25), calorimetry (26) and creep or stress relaxation (27).

Further vapor sorption experiments have indicated that swelling and deswelling relaxations may be retarded by the presence of low concentrations of vapor in the polymer (23). A tentative explanation of this effect is that penetrant molecules, particularly those sorbed in the "hole-filling" mode, may pre-empt some of the free volume required for relaxation. The possible relevance of this effect to the mechanism of solvent-crazing and to the poorly-understood phenomenon of antiplasticization seems to warrant continued study.

#### Effects of probe molecule size

Sorption studies on PVC powders parallel to studies first carried out with VCM have now been extended to a wide range of other gases and vapors (28). For all probe molecules so far studied, it has been possible, at sufficiently low concentrations, to distinguish a contribution of Fickian diffusion to the total sorption process, and thus to determine diffusion coefficients from data on PVC samples of known particle size. In Fig. 13, diffusivities determined

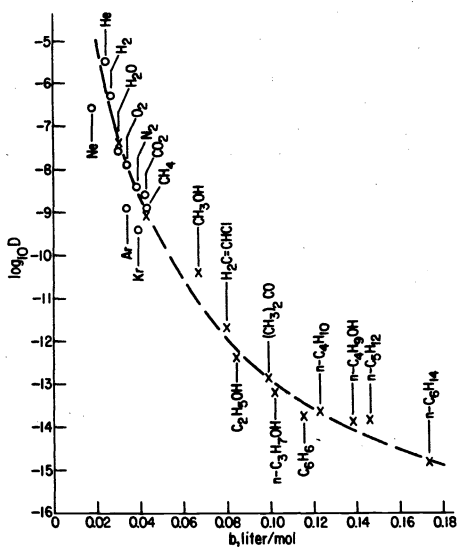


Fig. 13. Diffusivities of gases and vapors in PVC at 30°C, plotted vs. van der Waals molecular volume constant,  $b$ .

from PVC powder sorption experiments at 30°C, together with values for gases reported by Tikhomirov, et.al. (1), are plotted against the probe molecular volume constant,  $b$ , of the van der Waals equation of state (29). Together, the two sets of data define a single smooth curve extending over more than nine orders of magnitude of  $D$ , from helium ( $2.8 \times 10^{-6}$  cm<sup>2</sup>/sec) to n-hexane ( $1.5 \times 10^{-15}$  cm<sup>2</sup>/sec). For n-pentane and n-hexane, unlike the smaller probe molecules, gravimetric sorption data show a nearly instantaneous initial weight gain, followed by sorption of the diffusion-plus-relaxation form observed with other swelling vapors. The rapid initial weight gain may reasonably be attributed to surface adsorption of the n-alkanes, and the absence of this effect implies negligible surface adsorption for smaller penetrants. As indicated in Fig. 14, showing data for n-hexane, the separate contributions of surface adsorption, Fickian diffusion, and relaxation-controlled swelling may

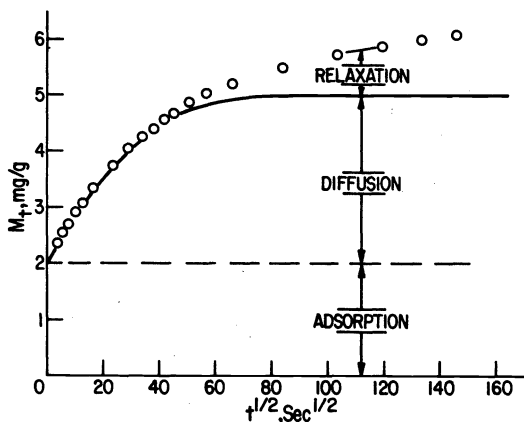


Fig. 14. Sorption kinetics for n-hexane in 0.11  $\mu$ m emulsion PVC, 30°C,  $P_{rel} = 0 \rightarrow 0.109$ .

be estimated from a single sorption experiment by fitting Equation (1) to the early portion of the  $M_t$  vs.  $t$  curve. An extension of the trend toward slower diffusion and greater surface adsorption with increasing molecular weight of n-alkanes has led to the successful use of n-octane as a probe molecule in a new method for determining surface areas of PVC powders (30).

The sorption isotherms of all other probe molecules studied with PVC powders also show the dual-mode form and history dependence first noted for the VCM/PVC system (22). Quite analogous effects have also recently been found in studies of gas and vapor sorption in other glassy polymers such as polystyrene (31,32), PMMA (33), and polycarbonate (34). Thus it now appears that the behavior of the VCM/PVC system is quite typical of the general interactions of gases or small organic probe molecules with polymers in the glassy state. Studies originally undertaken to help overcome the problem of residual VCM in PVC therefore also have contributed significantly to the general understanding of polymer-vapor interactions and to the use of molecular probes in fundamental studies of polymer structure and properties.

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