

Non-Fickian Vapor Sorption Kinetics in Rubbery Poly(dimethyl silamethylene) and the Effect of Radiation-Induced Crosslinking

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ABSTRACT: Successive sorption runs of *n*-hexane vapor in supported amorphous poly(dimethyl silamethylene) films at 25°C are presented and discussed. Deviations from Fickian sorption kinetics were observed, and they were more distinct in the as-prepared films and in the lower *n*-hexane vapor pressure runs. Polymer films, γ -irradiated to produce various degrees of crosslinking, exhibited closer conformity to Fickian sorption kinetics and enhanced diffu-

sivity of *n*-hexane vapor. These results were consistent with the presence in the as-prepared polymer of some labile structural order (undetectable by differential scanning calorimetry or X-ray diffraction), which tended to be eliminated by radiation-induced crosslinking or strong swelling. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 226–230, 2005

Key words: crosslinking; diffusion; irradiation

INTRODUCTION

In general, the sorption kinetic behavior of polymer/organic-vapor systems below or near the glass-transition temperature (T_g) often exhibits a variety of non-Fickian features. This behavior is most commonly attributed to slow viscous molecular relaxation of the glassy polymer structure (in response to penetrant-induced swelling stresses), which occurs on a time-scale comparable to that of the diffusion process.^{1–3} In rubbery polymers, Fickian diffusion is usually observed because the macromolecular rearrangements, which are necessary for the accommodation of sorbed penetrant molecules, are normally fast on the diffusion timescale.

Poly(dimethyl silamethylene) {PDMSM; i.e., $[\text{Si}(\text{CH}_3)_2\text{CH}_2]_n$ } belongs to a class of organosilicon polymers, the synthesis and study of which are motivated by their potential use as ceramic precursors or as gas-separation polymeric membrane materials.^{4,5} PDMSM is a rubbery polymer ($T_g = -92^\circ\text{C}$). Accordingly, it is remarkable that, in the course of an investigation of the sorption kinetics of *n*-hexane vapor in PDMSM, significant non-Fickian features were observed. Here

we report these data as well as the effect of γ -ray irradiation on the kinetic behavior. Radiation-induced changes in a polymer's structure, including chain scission, crosslinking, and the formation of small defects in the polymer matrix through degradation processes, are known to affect the transport properties of polymers in complex ways^{6,7} and are thus interesting in many technological applications, such as the use of polymeric materials as coatings in the lithographic step of integrated circuit fabrication and as gas-separation membranes. In the latter case, crosslinking has been proposed as a strategy for overcoming one of the main problems in gas-separation technology: the loss of membrane selectivity in the presence of plasticizing components (e.g., CO_2) in the feed mixture.^{8,9}

EXPERIMENTAL

Two samples of PDMSM with molecular weights of 1,100,000 and 366,000 (density = 0.906 g/cm^3 , $T_g = -92^\circ\text{C}$) were used in this study, being prepared as described in ref. 10. The as-prepared (uncrosslinked) polymer was a gluelike substance, from which free-standing films could not be produced. Accordingly, supported films of uniform thickness were prepared with the following procedure. A chloroform solution of the polymer (4–5 wt %) was placed in a shallow cup (5 cm in diameter) made from aluminum foil, and the solvent was allowed to evaporate slowly. Because of

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the strong adhesion of the polymer to the wall of the cup, the central flat portion of the cup (a disc 1.5 cm in diameter) was cut off with a sharp cork borer to ensure that the supported film sample used in subsequent measurements had uniform thickness L . To prevent adhesion of the sticky film to the cork borer, the cup was first cooled in liquid N_2 . Four supported films, prepared as described, were used for sorption measurements. They were designated M-491, M-376, and M-184 (all derived from the polymer with a molecular weight of 1,100,000) and M-142 (derived from the polymer with a molecular weight of 366,000); the numbers indicate L (μm) of the relevant film.

Polymer samples with a molecular weight of 366,000, prepared as described, were crosslinked to various extents by being subjected to γ irradiation *in vacuo* from a Co^{60} source. Under the irradiation conditions used, an exposure of 205 h was found to be necessary to produce a rubbery, nonsticky, self-supporting film, which came off the supporting aluminum disc. Supported irradiated films exposed to γ irradiation for exposure times of $\tau = 68$ –139 h were used for sorption measurements. These films were designated MA-237 ($\tau = 68$ h, $L = 237$ μm), MB-244 ($\tau = 104$ h, $L = 244$ μm), and MC-349 ($\tau = 139$ h, $L = 349$ μm). The last film still adhered reasonably well to its support.

The *n*-hexane was analytical-reagent-grade.

The sorption apparatus included a liquid–vapor generator continuously stirred and thermostated to $\pm 0.05^\circ\text{C}$, a mercury manometer for vapor pressure measurements, and a jacketed glass vessel (thermostated to $25 \pm 0.05^\circ\text{C}$) containing the polymer film. The last was suspended from a quartz spring (with a sensitivity of ca. 27 cm/g), the elongation of which was monitored with a cathetometer (reading to 0.01 mm). The vacuum, provided by a two-stage rotary pump, was approximately 10^{-3} Torr.

The sorption kinetic behavior of the films was studied in series of interval absorption experiments. According to the experimental protocol, an initially dry film was subjected to a series of successive absorption runs covering relatively narrow vapor pressure intervals ($\Delta p = p_F - p_I$, where p_F for one run serves as p_I for the next one). For Fickian sorption kinetics, the effective diffusion coefficient (D) could be deduced from the slope of the initial linear part of each absorption curve, plotted on a $t^{1/2}$ basis, with the following expression:

$$M_t/M_\infty = 2(Dt/\pi L^2)^{1/2} \quad (1)$$

where M_t and M_∞ are the penetrant uptakes at time t and at the final equilibrium ($t \rightarrow \infty$), respectively.

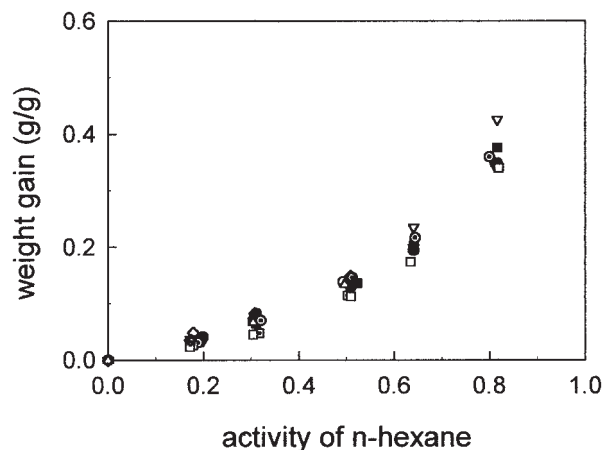


Figure 1 Absorption isotherm for the *n*-hexane-vapor/PDMSM system at 25°C , including data from as-prepared films (open symbols) and irradiated films (filled symbols): (\circ , \odot , \diamond , \triangle , \square , \bullet , \blacktriangledown , \blacksquare) first and (∇ , \square) second series. The nonirradiated films were (\circ , ∇) M-491, (\odot) M-225, (\triangle) M-184, (\square , \square) M-142, and (\diamond) M-376. The irradiated films were (\bullet) MA-237 ($\tau = 68$ h), (\blacktriangledown) MB-244 ($\tau = 104$ h), and (\blacksquare) MC-349 ($\tau = 139$ h).

RESULTS AND DISCUSSION

As-prepared polymer films

As-prepared (nonirradiated) dry films were subjected to a series of three or five successive absorption runs, up to a final pressure of 97 or 124 Torr, respectively. After complete desorption, effected either by a series of the same number of desorption runs or by a one-run evacuation, a second series of five absorption runs was performed.

The sorption isotherm, obtained from equilibrium uptake data, is shown in Figure 1. The data from different polymer films and from different series of absorption runs on the same film agreed satisfactorily.

The absorption kinetic curves obtained from the first series of runs exhibited distinct deviations from those of subsequent absorptions or desorption series, as illustrated by the example of film M-491 in Figure 2. More specifically, the first run of the first absorption series on M-491 (open circles) differed appreciably from the corresponding desorption run (filled circles), which agreed with the first run of two subsequent absorption series (open squares and inverted triangles). That this was not a peculiarity of the particular film was shown by the fact that the first run of the first absorption series on film M-376, which is also included in Figure 2 (open upright triangles), agreed with that on M-491. Both kinetic curves exhibited distinct non-Fickian behavior attributable to an irreversible relaxation process, which was annealed out during the first series of absorption runs and was therefore, not characteristic of the fundamental kinetic sorption behavior of the system.

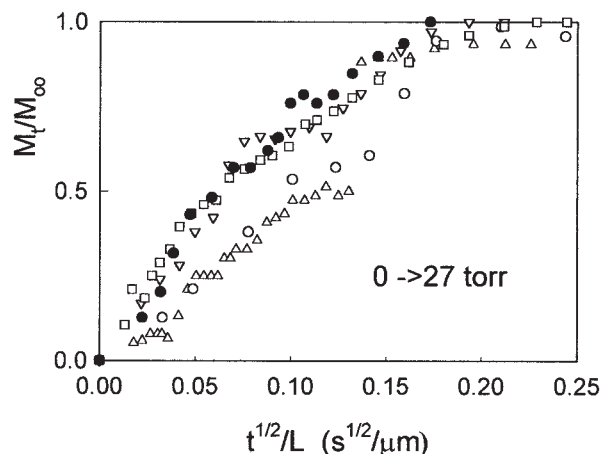


Figure 2 First kinetic run of a series of *n*-hexane absorption runs (open symbols) and desorption runs (full symbols) in as-prepared PDMSM films (○, □, ▽) M-491 and (△) M-376: (○, △, ●) first, (□) second, and (▽) third series.

Accordingly, attention was focused exclusively on data from subsequent series. An example is shown in Figure 3, in which the second series of five absorption runs in M-491 is presented. Here, there are significant deviations from Fickian kinetics, which progressively diminish with increasing *n*-hexane vapor pressure. This behavior is best illustrated in Figure 4, in which the data of Figure 3 have been replotted on a $(Dt/L^2)^{1/2}$ scale, where D is the apparent diffusion coefficient deduced from the slope of the initial linear part of each curve on the basis of eq. (1). A comparison of the experimental curves of Figure 4 with the corresponding calculated Fickian curve, also shown in Figure 4, shows that although the said deviations became less prominent as the *n*-hexane vapor pressure increased, they were still discernible even at the highest pressure studied, in the form of a slower than normal approach to the final equilibrium. As already discussed, such non-Fickian behavior, indicating macromolecular relaxations that are relatively slow in comparison with the diffusion timescale, is rather unexpected for a polymer at temperatures far above its glass transition, as is the case here. Previous, less extreme examples of such behavior have been reported, such as the case of successive absorptions of ethyl benzene vapor in amorphous poly(ethyl methacrylate) films approximately 50°C above the pure polymer's T_g .¹¹ In the case studied here, we assumed the presence of some structural order in the polymer, which tended to be destroyed at an increasing rate with increasing swelling. No clear evidence for any structural order was forthcoming from X-ray diffraction (XRD)¹² or modulated differential scanning calorimetry (DSC) performed in this study. On the other hand, it is noteworthy that what "may possibly be classified as a conformationally disordered me-

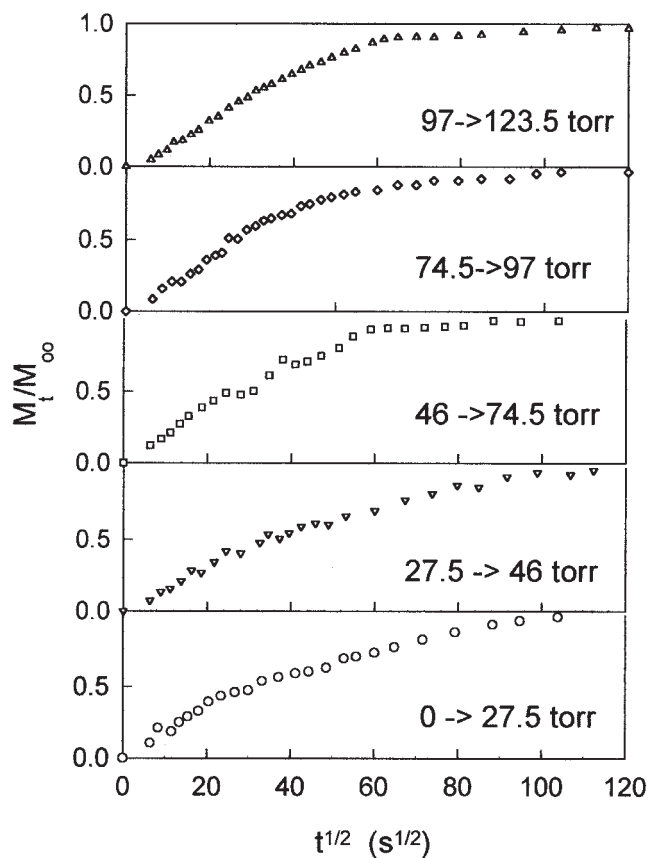


Figure 3 Second series of five successive absorption kinetic runs of *n*-hexane vapor in as-prepared PDMSM (M-491). The pressure interval p_i-p_F was (○) 0–27.5, (▽) 27.5–46, (□) 46–74.5, (◇) 74.5–97, or (△) 97–123.5 Torr.

sophase"¹³ was evidenced below isotropization in the di-*n*-propyl analogue.

Irradiated polymer films

To gain further insight into the reported behavior, we studied the sorption kinetic behavior of *n*-hexane va-

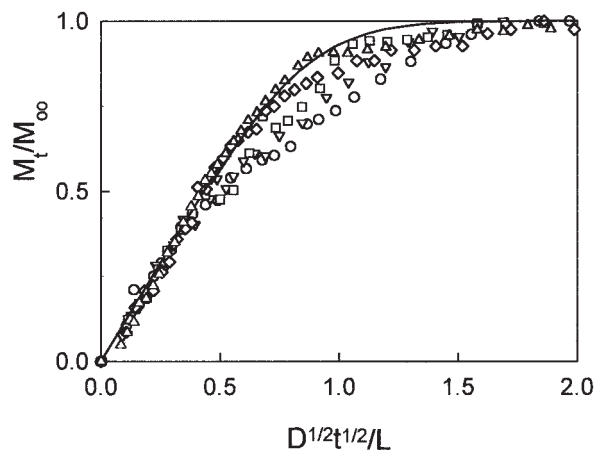


Figure 4 Kinetic data from Figure 3 plotted on a $D^{1/2}t^{1/2}/L$ scale (see Fig. 3 for the notation). The solid curve represents the calculated Fickian curve.

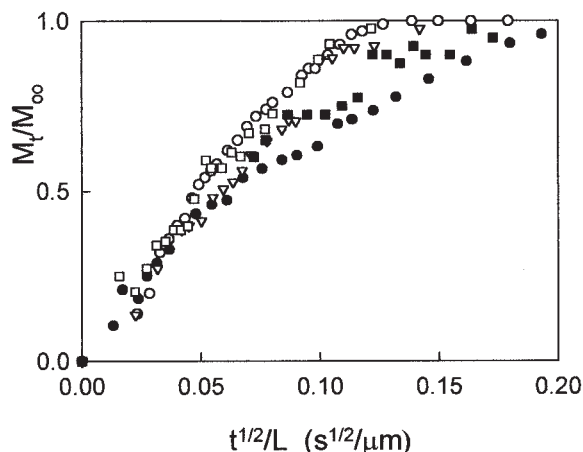


Figure 5 Comparison of the first *n*-hexane absorption run in irradiated films (open symbols) with the first run of the second series of absorption runs in as-prepared films (filled symbols). The as-prepared films were (●) M-491 and (▼) M-376. The irradiated films were (○) MA-237 ($\tau = 68$ h), (▽) MB-244 ($\tau = 104$ h), and (□) MC-349 ($\tau = 139$ h).

por in films γ -irradiated for various periods of time (see the Experimental section) to series of five successive absorption runs up to a final pressure of 123 Torr.

The equilibrium sorption values remained quite close to those found for as-prepared (nonirradiated) films at all investigated vapor activities, as shown in Figure 1.

In Figure 5, the kinetic curves, obtained from the 0–27 Torr absorption run on irradiated films, are compared with the corresponding results obtained from the second series of runs on nonirradiated films. Even for this low degree of swelling, the former curves clearly approach Fickian behavior more closely than the latter, mainly because of increased absorption rates during the later stages of the sorption process. The kinetic behavior of the irradiated films, as a function of increasing swelling, can be best seen in Figures 6 and 7, in which the kinetic curves obtained from successive absorption runs on films MA-237 and MB-244, respectively, are plotted on a $(Dt/L^2)^{1/2}$ scale. A comparison of these plots with the corresponding one for the as-prepared film M-491 shown in Figure 4 indicates that a marked shift toward Fickian kinetics is caused by radiation-induced crosslinking.

In Figure 8, the D values deduced from all the studied films are plotted as a function of the *n*-hexane vapor activity. No clear systematic tendency of the D values of both nonirradiated and irradiated films to vary with the concentration is noticeable. On the other hand, although the D values for nonirradiated samples are less reliable because of the non-Fickian character of the corresponding kinetic curves, a discernible tendency of D to increase upon irradiation is revealed. This is also evident from the data of Table I, which presents a mean value of D for each sample studied. D

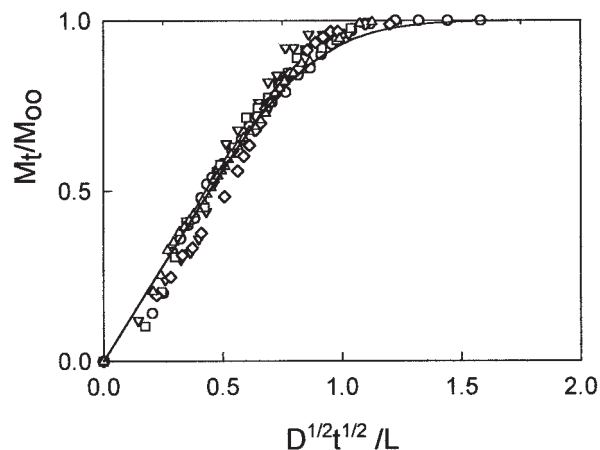


Figure 6 Series of five successive absorption kinetic runs, plotted on a $D^{1/2}t^{1/2}/L$ scale, of *n*-hexane vapor in film MA-237 irradiated for 68 h. The pressure interval p_i-p_F was (○) 0–27, (▽) 27–47, (□) 47–77, (◇) 77–97, or (△) 97–123 Torr. The solid curve represents the calculated Fickian curve.

for the highest degree of crosslinking studied clearly exceeds those of the two lower degrees of crosslinking.

Both the observed shift of the penetrant transport toward pure Fickian kinetics and the increased diffusivity upon irradiation find an interpretation in terms of our previous hypothesis regarding the presence of some structural order in the as-prepared films. In particular, this behavior indicates that the structural order is destroyed by radiation-induced crosslinking. The resulting more highly amorphous structure, which is stabilized by crosslinking, enhances the mobility of sorbed penetrant molecules. The latter effect is observable because, as shown by the corresponding equilib-

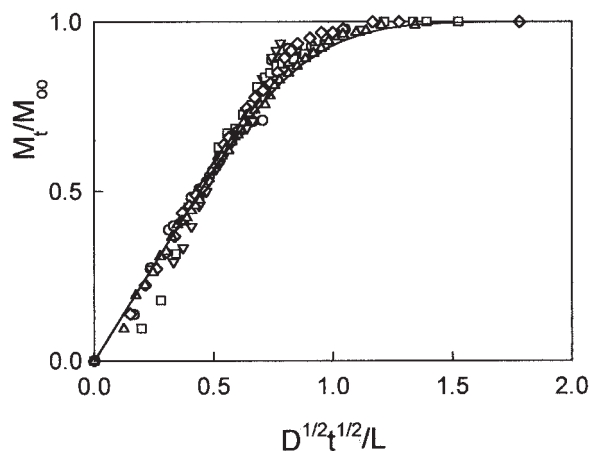


Figure 7 Series of five successive absorption kinetic runs, plotted on a $D^{1/2}t^{1/2}/L$ scale, of *n*-hexane vapor in sample MB-244 irradiated for 104 h. The pressure interval p_i-p_F was (○) 0–27, (▽) 27–47, (□) 47–77, (◇) 77–97, or (△) 97–123 Torr. The solid curve represents the calculated Fickian curve.

rium data of Figure 1, the degree of crosslinking obtained here is not sufficient to restrict appreciably the degree of swelling and thus hamper the movement of penetrant molecules in the irradiated polymeric medium.

CONCLUSIONS

The data presented here on *n*-hexane vapor sorption kinetic behavior in supported PDMSM amorphous polymer films revealed unexpected, but significant, deviations from Fickian kinetics in films of the as-prepared polymer at low swelling. This behavior may plausibly be interpreted in terms of the presence of some labile structural order (undetectable by DSC or XRD) in the as-prepared polymer, which tended to be destroyed by strong swelling or radiation-induced crosslinking. There is an analogy between the phenomena in rubbery PDMSM and the mechanical conditioning that unvulcanized rubber undergoes when first subjected to a tensile stress. In particular, the first loading–unloading cycle shows improved mechanical properties in comparison with subsequent cycles, which soon assume a constant reproducible manner. This behavior is usually attributed to the presence of a quasistable superstructure, induced by the molding process, which can be subsequently destroyed by mechanical deformation, thermal annealing, radiation-induced crosslinking, or swelling.¹⁴

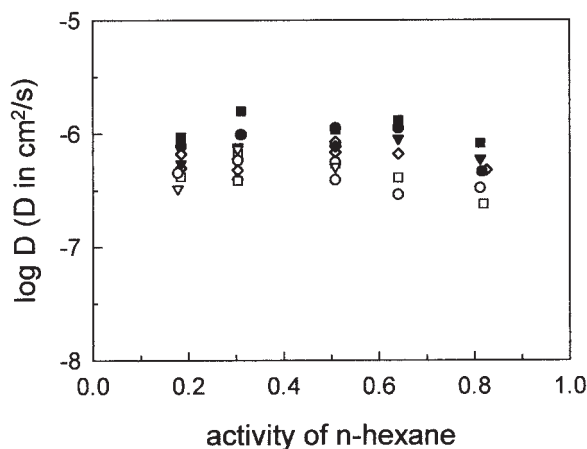


Figure 8 Effective *D* values of *n*-hexane vapor in as-prepared PDMSM films (open symbols) and irradiated PDMSM films (filled symbols) at 25°C versus the *n*-hexane vapor activity. The as-prepared films were (◇) M-491, (□) M-142, (○) M-184, and (▽) M-376. The irradiated films were (●) MA-237 ($\tau = 68$ h), (▼) MB-244 ($\tau = 104$ h), and (■) MC-349 ($\tau = 139$ h).

TABLE I
Mean *D* Values of *n*-Hexane Vapor in PDMSM Films at 25°C

As-prepared (nonirradiated) films				
Film	MW	<i>L</i> (μm)	<i>D</i> × 10 ⁷ (cm ² /s)	
M-491	1,100,000	491	5.7 ± 1.8	
M-184	1,100,000	184	3.8 ± 1.4	
M-376	1,100,000	376	5.2 ± 2.0	
M-142	366,000	142	4.4 ± 1.3	
Irradiated films				
Film	MW	<i>L</i> (μm)	τ (h)	<i>D</i> × 10 ⁷ (cm ² /s)
MA-237	366,000	237	68	8.9 ± 2.7
MB-244	366,000	244	104	7.2 ± 1.4
MC-349	366,000	349	139	11.7 ± 3.0

MW = molecular:weight.

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