

Characterization of Penetrant Interactions in Kapton* Polyimide Using a Gravimetric Sorption Technique

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Synopsis

Sorption of pure anhydrous ammonia and pure sulfur dioxide in Kapton polyimide has been measured at 30 and 35°C at subatmospheric pressures using a McBain quartz spring balance. The sulfur dioxide sorption and desorption was well described by the Fickian transport model; however, the ammonia sorption exhibited significant deviations from Fickian behavior. A substantial fraction of the initially sorbed ammonia remained in the film after extended periods under vacuum at 35°C. Infrared analysis of the treated film revealed the presence of new carbonyl and nitrogen-hydrogen stretching peaks characteristic of primary and secondary amides. These observations suggest that the ammonia reacts chemically with some of the imide linkages. Based on infrared analysis of the ammonia-exposed Kapton, heating the sample under vacuum at 120°C caused re-formation of most of the originally disturbed imide structures, with attendant evolution of ammonia as a condensation product.

INTRODUCTION

Gas separators based on permselective glassy polymer membranes offer an economical means for recovering valuable components from mixed gas streams. Choice of the correct polymer permits almost total blockage of the transfer of undesirable gaseous molecules while allowing the desired species to diffuse rapidly through the membrane.¹ In the synthesis of ammonia, the process stream from the reactor contains high concentrations of nitrogen and hydrogen along with other gases such as argon and ammonia in small, but significant, concentrations.¹ Gas permeators can be used to salvage hydrogen from the reactor purge gas stream, while preventing the accumulation of inerts in the system. Inside the separator, the hydrogen molecules sorb into polymeric hollow fibers, diffuse from a high-pressure region surrounding the fiber to a low-pressure region within the bore of the fiber, and are then recycled to the reactor.² After exposure to the process stream for a long period of time, the ability of the membrane to separate hydrogen from the mixed gas stream may decrease if the polymer is attacked by the components of the stream.

The present study focuses on a possible new polymer for gas separation service in demanding process environments such as the ammonia example cited above. Kapton, an aromatic poly(ether-imide) developed by du Pont, has been found to be resistant to both chemical and thermal attack. Furthermore, Kapton is a matrix polymer for use in novel graphite-reinforced composites which offer outstanding properties for important aerospace applications.³ The sorption, transport and possible chemical attack of ammonia in this polymer is therefore

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of interest in several areas and motivated the choice of this polymer/penetrant pair as the focus of the present study.

Koros et al.⁴ and Patton⁵ have studied sorption of SO₂ in Kapton at 35°C, and Sacher and Susko⁶ have studied H₂O in Kapton between 20 and 55°C. Similar data for SO₂ were measured in the present study to substantiate the experimental techniques employed here. Whereas data existed for comparison with the SO₂/Kapton work, no previous studies of ammonia sorption in this polymer have been reported. Pulsed NMR data for ammonia interactions with polystyrene have, however, been reported by Assink, who observed normal sorption/desorption behavior in that system.⁷

SORPTION KINETICS OF GASES IN POLYMERS

Sorption kinetics of gases and vapors at low activities in polymers generally obey Fick's law given by

$$N = -D \frac{\partial C}{\partial x} \quad (1)$$

where N is the diffusive flux, C is the local concentration, D is the diffusion coefficient of the penetrant in the polymer, and x is the coordinate direction in which transport is occurring.⁸ Although the diffusion coefficient may be concentration dependent, it is known that as long as eq. (1) applies in each local region of the polymer, an effective average diffusion coefficient can be used in the standard infinite series solution for an approximate description of the sorption and desorption process. In such cases, the effective diffusion coefficient D_{AV} appropriate for describing transport processes over a range of concentrations from C_1 to C_2 can be conveniently defined according to

$$D_{AV} = \frac{\int_{C_1}^{C_2} D(c) dC}{\int_{C_1}^{C_2} dC} \quad (2)$$

and evaluated from the "short time" solution of the infinite series expression given in eq. (3) for uptake into (or desorption from) a slab of thickness l :

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{l^2} \right)^{1/2} \left[\frac{1}{\pi^{1/2}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \left(\frac{nl}{2(Dt)^{1/2}} \right) \right] \quad (3)$$

where M_t and M_∞ are the mass sorbed (or desorbed) at time t and at "infinite" time, respectively. For values of $M_t/M_\infty \leq 0.5$, this equation can be approximated well by neglecting the infinite series contribution.⁸ Alternatively, one can evaluate M_t/M_∞ at the half-point of either sorption or desorption and thereby calculate a separate effective diffusion coefficient from the sorption run (D_s) and the desorption run (D_d)⁸:

$$D_s = \frac{0.0492l^2}{(t_{1/2})_s} \quad (4a)$$

$$D_d = \frac{0.0492l^2}{(t_{1/2})_d} \quad (4b)$$

where $(t_{1/2})_s$ and $(t_{1/2})_d$ correspond to respectively the time for sorbing and desorbing one half of the penetrant which eventually is sorbed (or desorbed) in the run under consideration. Conventionally, in cases where the diffusion coefficient is dependent on concentration, one generally equates the average of the diffusion coefficients determined in the sorption and desorption runs to D_{AV} :

$$D_{AV} = \frac{D_d + D_s}{2} \quad (5)$$

This technique was applied by Koros et al.⁴ for SO₂ sorption in Kapton at 35°C. To verify our experimental techniques and equipment operation, we performed a similar characterization of our Kapton sample.

It is known that, in a given polymer, diffusion coefficients are strongly dependent on the molecular size of the penetrant molecule considered. A correlation between the Lennard-Jones collision diameter and the diffusion coefficients of various penetrants in a given polymer is well established.⁸ Therefore, the diffusion coefficient of ammonia in Kapton can be estimated using reported diffusion coefficients in Kapton of water and sulfur dioxide which bracket ammonia in terms of molecular size. The semilogarithmic plot of D vs. the Lennard-Jones collision diameter shown in Figure 1 using the SO₂ data from Patton⁵ and the water data from Sacher and Susko⁶ at 30°C suggests that an average diffusion coefficient, corresponding to eq. (5), should have a value of approximately 1.24×10^{-9} cm²/s. Therefore, it was anticipated that an easily measurable response for ammonia sorption would be observed with a half-time for sorption calculated from eq. (4a) of approximately 4.19 min (or 2.05 min^{1/2}) in a 1-mil film and 1.05 min (or 1.02 min^{1/2}) in a 1/2-mil film.

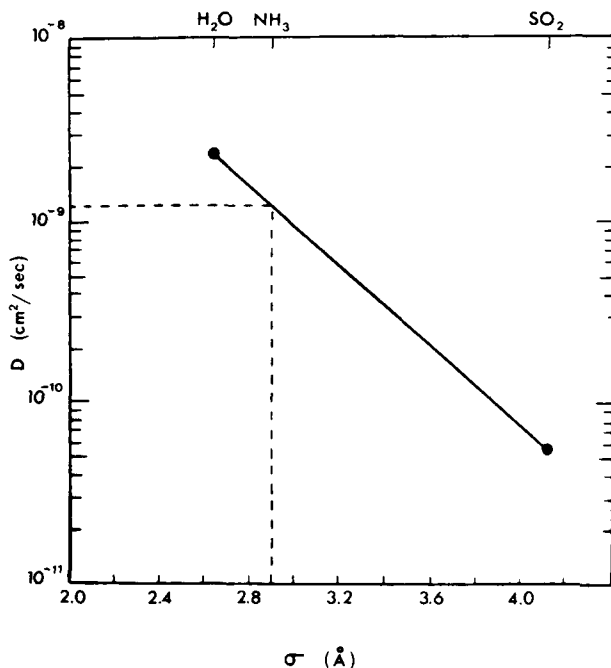
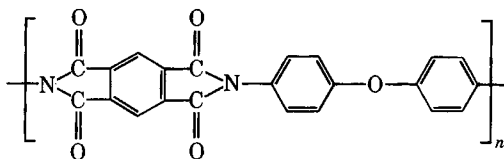


Fig. 1. Estimation of the diffusivity of NH₃ in Kapton polyimide at 30°C using the Lennard-Jones collision diameter as a characteristic size correlation parameter.

EXPERIMENTAL

Materials

The Kapton poly(ether-imide) used in the present study was kindly supplied by the E. I. du Pont Company, Circleville, Ohio.



Kapton poly(ether-imide)

Measurements by precision micrometry indicated film thicknesses of 1 ± 0.01 and 0.5 ± 0.01 mil, respectively, for the two different samples studied. Both the SO_2 and anhydrous ammonia used as penetrants in sorption experiments were obtained from Air Products and Chemicals, Inc., Raleigh, NC, at a purity of 99.9%. The gases were used as received without further treatment.

Apparatus

A McBain quartz spring balance was constructed following the design described by Hopfenberg et al.⁹ With this system, a direct gravimetric measure of penetrant uptake within the polymer as a function of time can be determined by observing changes in spring extension. To collect data, a polymer sample is suspended from a calibrated quartz spring within a constant temperature and pressure sorption cell. The mass of the penetrant sorbed by the polymer film is then determined by measuring spring extension with a cathetometer.

The sorption cell and supporting apparatus are shown in Figure 2. A quartz spring with a maximum capacity of 100 mg, corresponding to a maximum extension of approximately 200 mm, was hung from the cell cap. Using calibration weights, a spring constant of 0.500 ± 0.006 mg/mm extension was obtained. The polymer sample was then hung at the base of the spring. A glass reference fiber was hung parallel to the spring to compensate for small shifts in the spring support position which might occur during the experiment. A precision microscope, capable of detecting spring deflections as small as 0.005 mm, was used to observe spring extension. Thus, deflections represented by masses as small as 2.5 μg were detectable.

The sorption cell was maintained at a constant temperature by circulating an ethylene glycol mixture from a bath through a fluid jacket enclosing the cell. Aluminum foil was wrapped around portions of the cell and grounded to reduce static attraction between the cell wall and the polymer film. A large vapor reservoir was used to increase the total volume of the sorption system, thereby eliminating measurable fluctuations in pressure within the sorption cell.

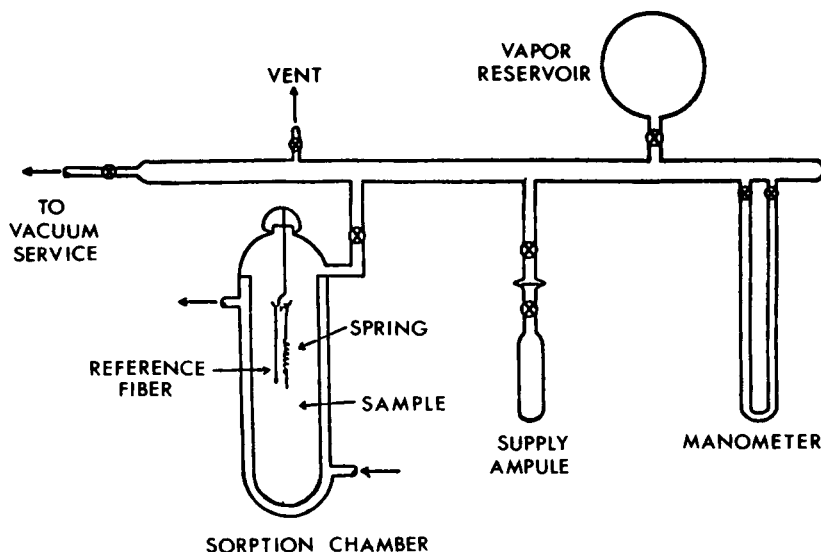


Fig. 2. McBain balance apparatus used for gravimetric determination of vapor sorption data.

Procedures

A Kapton sample of known weight was hung from the quartz spring and degassed for 24 h. An apparently, constant weight of the degassed sample was obtained within 10h. The system, excluding the sorption cell, was pressurized with penetrant to an empirically determined value that would give the desired sorption pressure when the stopcock to the sorption cell was opened. At time zero, penetrant was admitted into the sorption cell, and the spring extension was measured as a function of time. The system pressure was monitored during the experiment and was permitted to vary no more than ± 5 mm Hg. System pressure was adjusted by either introducing more penetrant or by raising or lowering the heating tape temperature in the exterior lines. To begin a desorption experiment, the valve connecting the sorption cell to the vacuum line was opened, and the contraction of the spring was observed as a function of time.

RESULTS AND DISCUSSION

SO₂ Sorption Kinetics

A typical normalized sorption/desorption cycle for sulfur dioxide in $1/2$ -mil Kapton is shown in Figure 3 as a plot of M_t/M_∞ . For the sorption cycle, M_t is the mass of penetrant sorbed at any time t , and M_∞ is the mass of penetrant sorbed at equilibrium. For the desorption cycle, M_t and M_∞ refer to the mass of penetrant desorbed at time t and at equilibrium, respectively. As shown in the figure, penetrant uptake initially varies linearly with $t^{1/2}$, consistent with Eq. (3) for values of $M_t/M_\infty < 0.5$, and eventually becomes concave to the time axis. Molecules initially sorb into the polymer at a rapid rate due to the large concentration gradient at the film surface; and as the concentration gradient diminishes, the rate of penetrant uptake slows and eventually reaches a saturation point at equilibrium. The sorption and desorption processes are well

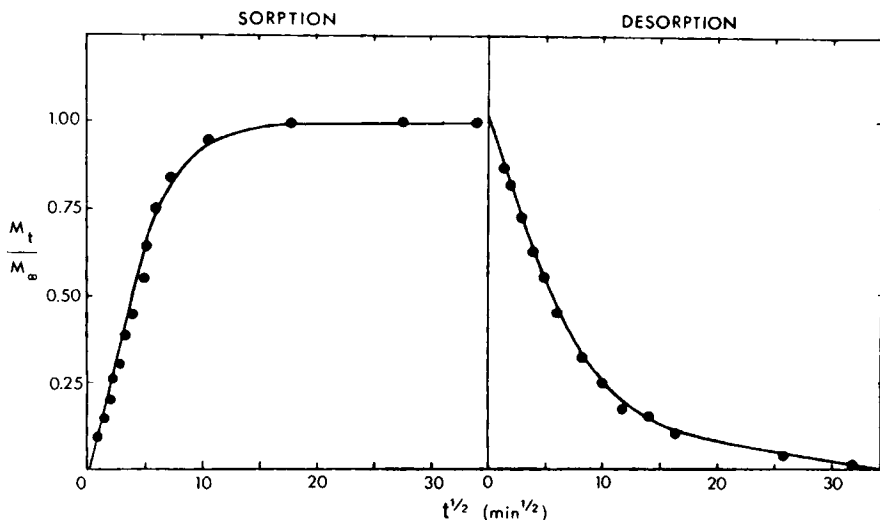


Fig. 3. Sorption/desorption kinetic runs for a $\frac{1}{2}$ -mil Kapton polyimide film at 35°C and at a SO_2 pressure of 0.33 atm.

described by Fick's law; the lines drawn through the sorption and desorption curves were calculated using eq. (3) with the respective value of $D_s = 6.75 \times 10^{-11}$ cm^2/s and $D_d = 4.37 \times 10^{-11}$ cm^2/s , determined using Eqs. (4a) and (4b). It was expected that sorption/desorption curves for ammonia in Kapton would be similar in shape to those for SO_2 but, as discussed earlier, would show that ammonia sorbs and desorbs roughly 20 times faster on a normalized basis (M_t/M_∞) because of its smaller relative molecular size.

Ammonia Sorption/Desorption Kinetics

Using the system described previously, with 1-mil-thick Kapton as the polymer and ammonia as the penetrant, the sorption experiment shown in Figure 4 was made at 35°C . The resulting sorption curve was significantly more protracted than was expected for a small penetrant like ammonia, which is not much larger than water in terms of collision cross section (Fig. 1). Another Kapton film ($\frac{1}{2}$ -mil-thick) was loaded into the cell, and a similar response at 30°C was discovered for this film also. Figure 5 shows that the approach to equilibrium was not complete even after two weeks, although the sorption half-time at 30°C was calculated from eq. (4a) using the ammonia D estimated in Figure 1 to be only 1.05 min for ammonia in a $\frac{1}{2}$ -mil film of Kapton.

Such a protracted process in the case of a small penetrant such as ammonia suggests that simple Fickian sorption as described by eq. (3) was not adequate to explain the observed data.¹⁰ It was originally suspected that a physical relaxation of the polymer chains was occurring and causing the extremely slow uptake and was responsible for the observed deviations from Fickian uptake kinetics. If the deviations arose due to strictly physical interactions, one would expect that during a corresponding desorption run, the amount of gas desorbed should nevertheless equal the amount sorbed when the surrounding desorption bath pressure was essentially zero (i.e., $< 10^{-3}$ torr). As shown in Figure 5, only about one-half of the ammonia which was sorbed into the polymer was removed

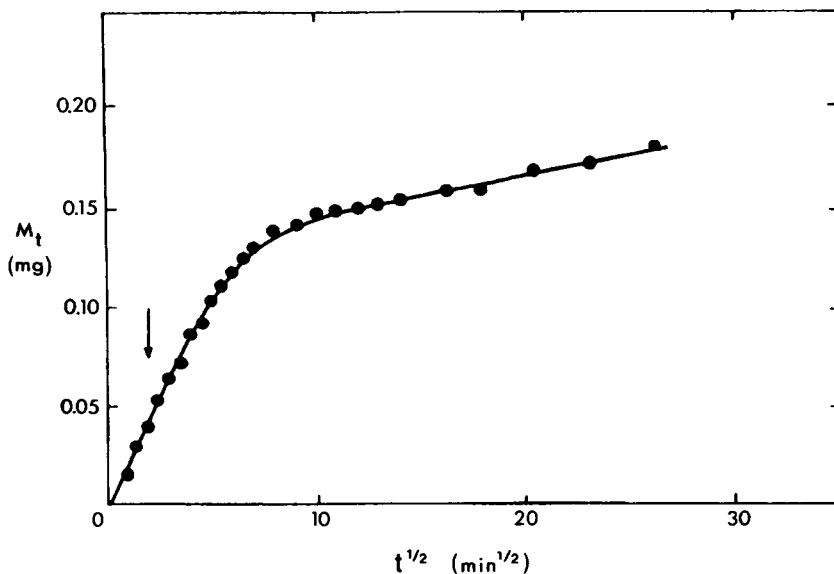
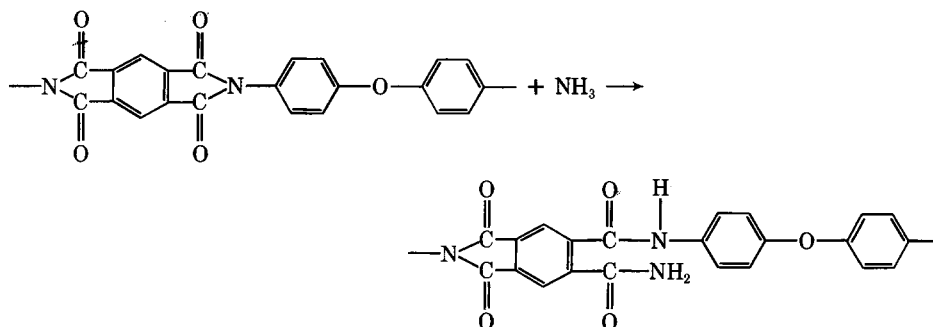


Fig. 4. NH_3 sorption kinetics in a 1-mil Kapton film at 35°C and at an NH_3 pressure of 0.29 atm. Arrow marks the expected sorption half-time for ammonia in 1-mil Kapton at 30°C on the basis of simple size dependent diffusion calculated from eq. (4a) using the value for D estimated from Fig. 1. One would expect the diffusion coefficient of ammonia to be even larger under the 35°C test conditions than at 30°C , so the half-time might be expected to be even shorter than indicated by the arrow. The kinetics are therefore being protracted by some complex factors.

even after prolonged pumping (>12 days, not shown in Fig. 5). Using the information from the sorption cycle, it is reasonable to assume that the ammonia might be chemically attacking the polymer and thereby becoming a nondesorbable component of the sample.

The most likely point of ammonia attack on the polymer is at the imide linkage, with resultant formation of primary and secondary amides:



One method of determining whether such an attack takes place is through the use of infrared spectroscopy. Amide groups will become apparent as new carbonyl peaks in the range $1630\text{--}1700\text{ cm}^{-1}$, and nitrogen-hydrogen stretching will appear in the region $3200\text{--}3500\text{ cm}^{-1}$.¹¹ Infrared spectra for both the as-received sample and the exposed sample corresponding to the sorption run in Figure 5 are presented in Figures 6 and 7. Clearly, the presence of the new carbonyl and nitrogen-hydrogen stretching peaks supports the postulated attack of ammonia at the imide linkage.

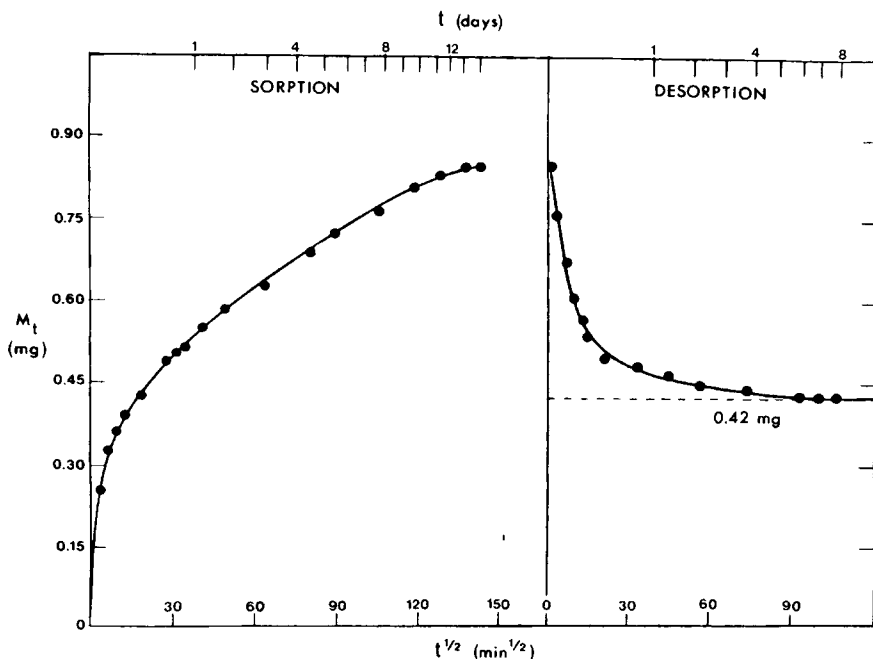


Fig. 5. Sorption/desorption kinetic runs for a $\frac{1}{2}$ -mil Kapton polyimide film at 30°C and at an NH_3 pressure of 0.36 atm. Note that at equilibrium 0.42 mg of the penetrant remained in the polymer sample after protracted desorption under vacuum.

During the desorption cycle, the sorbed ammonia in the Kapton sample is quickly removed, as shown in Figure 5; hence the rate of reaction of ammonia falls rapidly. If one neglects the small extent of reaction which occurs during the desorption process and replots the data in the form (M_t/M_∞) consistent with eq. (3), the plot shown in Figure 8 results. Application of eq. (4b) to the data in Figure 8 yields a value of the diffusion coefficient for ammonia equal to $2.35 \times 10^{-11} \text{ cm}^2/\text{s}$. The dashed line through the data points in Figure 8, calculated from eq. (3) using the above value of D , describes the process quite well up to a value of $M_t/M_\infty = 0.6$. The tendency of the model equation to deviate from the data at long times is characteristic of systems in which the diffusion coefficient increases with increasing local penetrant concentration. In the final phases of desorption, the lower diffusion coefficient associated with the low level of penetrant remaining in the film causes the protracted desorption process. If one compares the effective diffusion coefficient estimated from Figure 1 strictly on the basis of size-dependent factors, it is obvious that the diffusion coefficient lies approximately 50 times lower than the expected mobility determined from strictly size-dependent factors.

The activation energy E_d for diffusion in polymeric media is generally associated with the energy required to produce a sufficiently large gap between chains to permit the passage of a penetrant.¹² Diffusion coefficients decrease sharply with increasing penetrant size due to the fact that more energy must be available to cause formation of a large gap to permit passage of a large penetrant than to cause formation of a small gap to permit passage of a small penetrant. This fact can be seen from consideration of Eq. (6):

$$D = D_0 \exp\left(\frac{-E_d}{RT}\right) \quad (6)$$

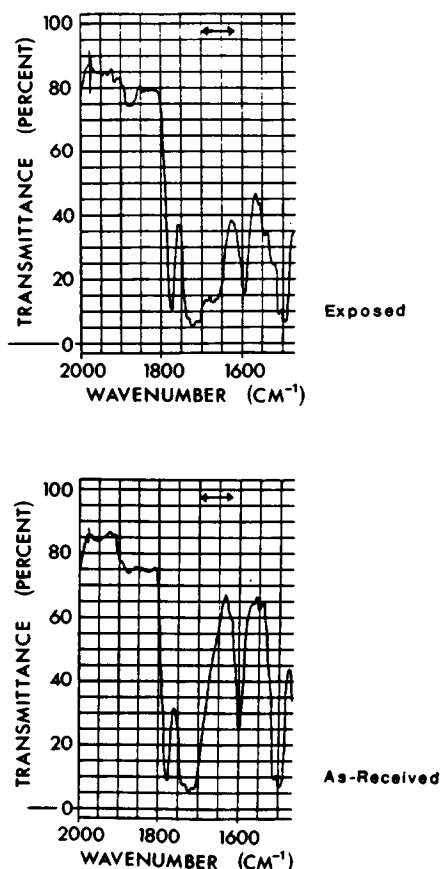


Fig. 6. Infrared spectra of the as-received and the NH_3 -exposed Kapton polyimide samples. Note the increased absorbance in the $1630\text{--}1700\text{ cm}^{-1}$ range consistent with the reaction shown between NH_3 and the imide structure.

Although additional factors enter into determination of D_0 and hence D , the above discussion regarding E_d still deals with the major issues in simple size-dependent diffusion.¹² The above discussion, which assumes that E_d is associated simply with generation of a hole into which the penetrant can move, implies that if a hole opens next to a penetrant, no additional activation energy is required to permit the penetrant to execute the diffusional jump into the hole. In cases of strongly interacting penetrant/polymer systems, such an assumption is not necessarily correct, and one may expect that the effective activation energy is the sum of the polymer-related activation contribution E_1 and the penetrant-related activation contribution E_2 , i.e., $E_d = E_1 + E_2$.

If one neglects, as a first approximation, differences in D_0 between a weakly interacting penetrant (whose D should be given by the correlation line in Fig. 1) and a strongly interacting penetrant such as ammonia, an estimate of the $\Delta E_d = (E_1 + E_2) - E_1$ between the two cases can be evaluated:

$$\ln \left[\frac{D_{\text{NH}_3}}{D_{\text{Fig. 1}}} \right] = \frac{-(E_1 + E_2 - E_1)}{RT} \quad (7a)$$

$$\Delta E_d = 2.4 \text{ kcal/mol} \quad (7b)$$

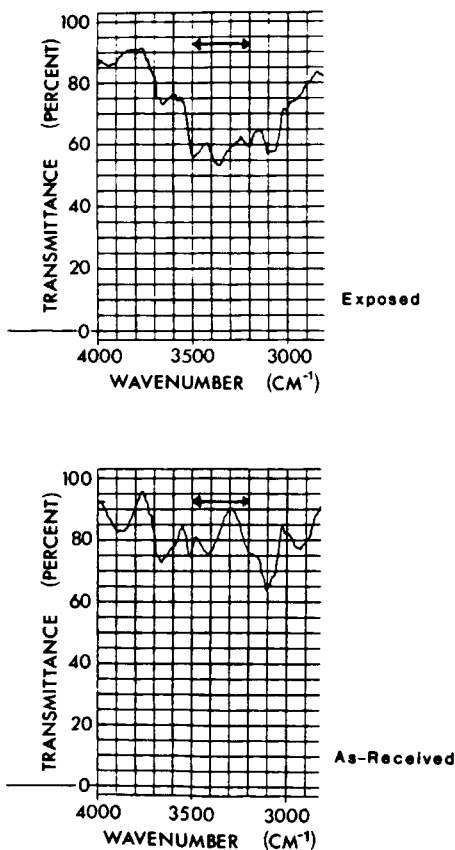


Fig. 7. Infrared spectra of the as-received and the NH_3 -exposed Kapton polyimide samples. Note the increased absorbance in the $3200\text{--}3500\text{ cm}^{-1}$ range consistent with the reaction shown between NH_3 and the imide structure.

One can therefore explain the observed lower value of the NH_3 diffusion coefficient compared to the prediction from Figure 1 on the basis of an additional activation contribution of slightly over 2 kcal/mol. This additional contribution arises from the need to overcome strong specific NH_3 -Kapton interactions prior to executing a diffusional jump and is of a reasonable order of magnitude for hydrogen bonding interactions. To demonstrate this effect completely, one should compare the diffusion coefficient and activation energy of NH_3 in Kapton to another less strongly interacting penetrant of the same approximate size (e.g., neon, $\sigma = 2.82\text{ \AA}$).

Sample Heat Treatment

The sample corresponding to the sorption/desorption runs in Figure 5 was removed from the sorption cell and heated under vacuum at 120°C for 72 h. It was found that the IR spectrum of the heat-treated sample again approached that of the as-received Kapton, suggesting that the disrupted imide linkages reform at elevated temperatures with the elimination of NH_3 . This observation is consistent with the fact that the standard technique for producing such imide

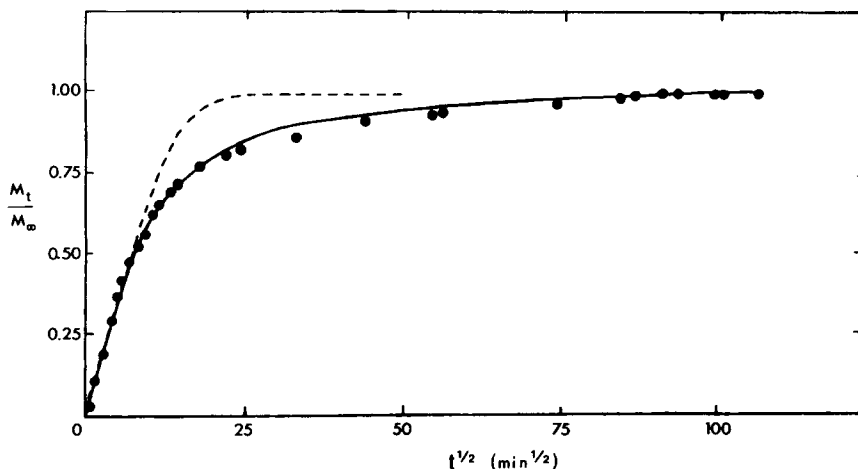
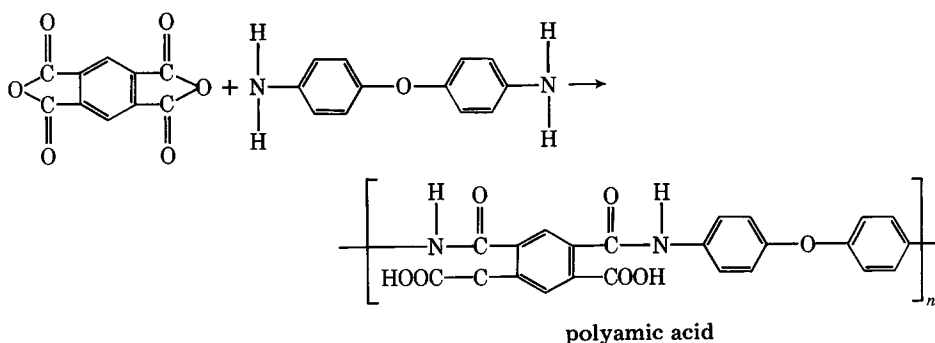
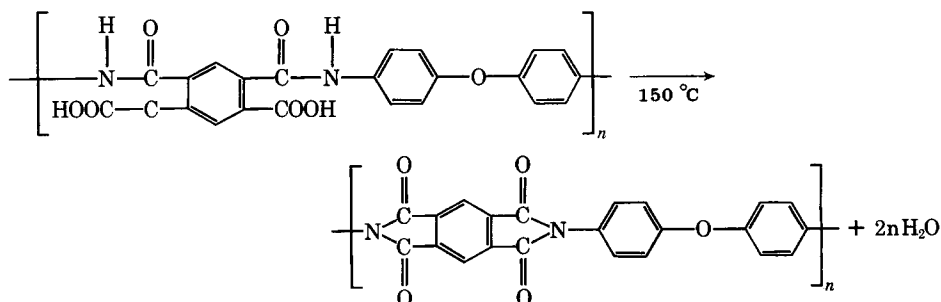


Fig. 8. Desorption kinetic run for 0.5-mil Kapton polyimide film at 30°C and at a NH_3 pressure of 0.36 atm. Using the diffusion coefficient calculated from eq. (4b), the dashed line represents Fickian desorption.

linkages involves condensing pyromellitic dianhydride with bis(4-aminophenyl) ether. The first step, to the polyamic acid intermediate, occurs readily at room temperature:

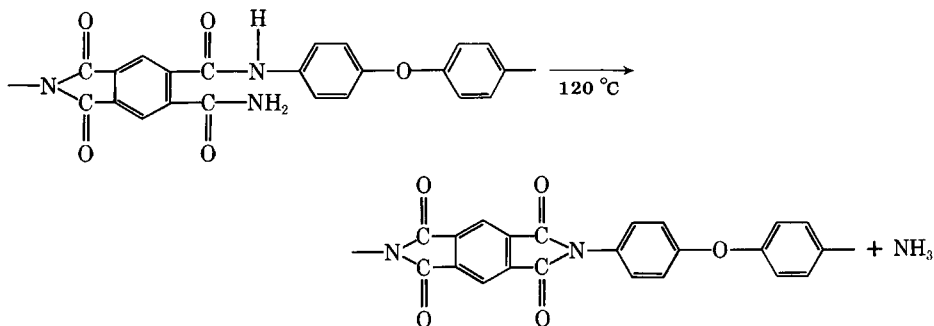


Upon heating above 150°C, the amic acid dehydrates by cyclization to form the insoluble polyimide¹³:



Presumably, in the present case, the recyclization process at 120°C simply gives

rise to ammonia as the condensation product rather than water as in the amic acid case:



CONCLUSIONS

Ammonia has been shown to interact chemically with Kapton at 35°C. The point of attack appears to be the imide group present in the chain backbone. Over a two-week period, approximately 17% of the imide structures were reacted under the conditions studied.

It is likely that many polymers formed by the reaction of amine-ended monomers and carbonyls have a similar propensity to undergo ammonia attack. This fact could be of considerable importance, since many of the exotic, high-temperature polymers use amine-ended monomers as starting materials. The susceptibility of these polymers to ammonia attack may be considered an "Achilles' heel" for such otherwise robust material. It is also possible that other basic and, to a lesser degree, acidic compounds may react with the imide structure of Kapton. Imide structures tend to be quite stable in neutral aqueous environments but are known to be susceptible to attack by either basic or strongly acidic compounds. This fact might be of considerable importance in graphite-reinforced applications where the bonding between matrix and filler is critical.

Further research, involving the use of pulsed NMR and Raman spectroscopy, could be useful to investigate the molecular environment experienced by the sorbed ammonia and further aid in distinguishing the fraction of sorbed molecules that are physically dissolved from those that have undergone a specific chemical reaction with Kapton. The diffusion coefficient estimated for ammonia in Kapton suggests the existence of strong physical as well as weak chemical interactions between this penetrant/polymer pair. To completely model the coupled processes of diffusion and reaction over the range of practical importance, the concentration dependence of this diffusion coefficient and the temperature dependence of both the diffusion and reaction rate coefficients needs to be evaluated. This work is currently under way.

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