

Solution of Gases in Oriented Poly(ethylene Terephthalate)

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Synopsis

The solubilities of nitrogen, oxygen, argon, methane, and carbon dioxide in thin films of crystalline oriented poly(ethylene terephthalate) in the glassy state were studied by the static sorption method. High pressure sorption isotherms were obtained for carbon dioxide. Results indicate that, above a certain film thickness, solubilities of all gases in the crystalline oriented polymer (Mylar) are virtually identical to those in the unoriented crystalline polymer. Solubility constants are correlated with gas force constants, ϵ/\bar{k} , and the heats of sorption obtained for methane and carbon dioxide are nearly the same for both the oriented and unoriented films. The sorption isotherms obtained for carbon dioxide are nonlinear but may be well described by considering dual sorption modes. One of these, ordinary dissolution, is described by Henry's law, while the other, "hole filling," is characterized by a Langmuir expression. Solubilities of carbon dioxide in the thinnest oriented films (1 mil) are markedly higher than in the unoriented film. Analysis of the sorption data indicates that both the hole saturation constant, and the hole affinity constant, are larger in the 1-mil oriented film. The amorphous phase appears to be different also, exhibiting a larger capacity for dissolved gas. Different thermal history, relating to the manufacture of the film, is advanced as a possible explanation for increased solubility.

INTRODUCTION

Several investigations dealing with the diffusion and solubility of gases in polyethylene and poly(ethylene terephthalate) (PETP) have been carried out in this laboratory¹⁻⁴ in addition to work performed by Meares⁵⁻⁷ and Stannett and Szwarc⁸ on these and other polymers, and useful information was obtained for comparing the glassy and rubbery states of several polymers. In the case of polyethylene in the rubbery state, it was found that dissolution of noncondensable gases occurs primarily in the amorphous phase and that Henry's law is obeyed.

$$C = kp \quad (1)$$

In contrast, when comparing sorption data for carbon dioxide in glassy amorphous and crystalline PETP, Michaels, Vieth, and Barrie⁴ found that, generally, the decrease in solubility accompanying crystallization was smaller than the corresponding reduction in amorphous volume fraction. They utilized the concept of microvoids in the glassy polymer⁵ and sug-

gested that the crystallization process tends to leave in the residual amorphous phase a higher volume concentration of microvoids than that present in the completely amorphous polymer. They proposed the following equation to fit their data:

$$C = C_H + C_D = [C_H'bp/(1 + bp)] + k_D^*p\alpha \quad (2)$$

where b is the "hole affinity constant" (in atm.⁻¹), C is the solubility (in cc. STP/cc. total polymer), C_H' is the hole saturation constant (in cc. STP/cc. total polymer), k_D^* is Henry's law dissolution constant (in cc. STP/cc. atm.), p is pressure (in atm.), and α is the amorphous volume fraction. The first term, C_H , represents "hole-filling," or Langmuir-type sorption and the second term, C_D , represents ordinary dissolution.

To test the validity of this equation, the solubilities of a series of gases was obtained. Low pressure sorption data for helium, nitrogen, oxygen, carbon dioxide, methane, and ethane at 25°C. demonstrated that, at pressures of the order of 1 atm., sorption isotherms for all the gases except carbon dioxide and ethane are linear. However, since solubilities of all the gases were abnormally high, consideration of these data continued to indicate the existence of an additional mode of sorption.

By using high pressures (up to about 10 atm.) carbon dioxide sorption data in glassy amorphous and crystalline films of PETP were obtained, and assuming that k_D^* was independent of the degree of crystallinity, Michaels et al.⁴ were able to calculate the constants in eq. (2), i.e.,

$$C = 1.89p/(1 + 0.45p) + 0.38p\alpha \quad (3)$$

A useful result of this work was the establishment of a simple correlation for the prediction of gas solubility in terms of easily measurable parameters. More important, the indication of the existence of microvoids in the polymer demonstrated the merit of the sorption technique as an analytical tool in the study of polymer microstructure.

With this background, it was decided to study the gas-sorption properties of an oriented glassy film in order to determine how the process of orientation affects the microstructure of a glassy polymer and to evaluate the gas transmission properties of oriented films for possible use as separation barriers. Once again, it seemed natural to choose poly(ethylene terephthalate) for this work.

Although relatively little sorption data on oriented films is available, data on permeability of gases in oriented polymer films is reported by Reitlinger and Yarkho⁹ and Barrie and Platt¹⁰ studying natural rubber, as well as Lasoski and Cobbs,¹¹ considering poly(ethylene terephthalate). Their combined findings indicate that orientation does not seem to effect permeability until crystallization occurs. Michaels, Vieth, and Bixler¹² observed only a small decrease in permeability after uniaxial cold drawing of dibutyl maleate-ethylene copolymers into the stable "necking" region (elongation of 490%); however, stretching to near the breaking point (about 600% elongation) did significantly reduce permeability.

In this paper, results of extending the solution study to glassy oriented crystalline PETP are reported. The validity of the previously postulated solution model is discussed, and information is presented relating to the effects of film treatment on the properties of the amorphous phase.

EXPERIMENTAL

Materials

The polymer film used in the sorption experiments was commercial grade biaxially oriented Mylar supplied by the Mylar Laboratory of E. I. du Pont de Nemours & Co. The number-average molecular weight was in the range of 15,000–20,000. Stretch ratios for these films are in the range of $3.0\times$ – $3.5\times$ for both the longitudinal and transverse directions. Films of 3 and 1 mil nominal thickness were used. The densities of the films, as determined in density gradient columns at the Mylar Laboratory, were reported as 1.394 and 1.388 g./cc., respectively. Assuming a value of 1.455 g./cc. for the density of crystalline phase, as calculated by Bunn et al.,¹³ and 1.331 g./cc. for the amorphous polymer, the amorphous volume fraction (α) of the 3-mil film was calculated to be 0.49, while that of the 1-mil film was 0.54.

The gases employed in this study, carbon dioxide, argon, methane, nitrogen, and oxygen had a minimum purity of 99.5% except for methane, which had a purity of 99%.

Apparatus

The data were obtained by the static sorption method. The apparatus for the low pressure runs (about 2 atm., absolute) is described by Michaels et al.⁴

High pressure data were obtained in apparatus consisting of a 186-cc. stainless steel pressure bomb equipped with a 0–350 psig pressure gage. Approximately 3 in. wide strips of Mylar were tightly wound in a cylindrical shape (with $\frac{1}{2}$ -in. wide Mylar strips used as spacers) and introduced into the bomb. Auxiliary tubing was of $\frac{3}{32}$ -in. I.D., stainless steel. High pressure $\frac{1}{4}$ -in. Aminco valves were used. A high vacuum system was connected to the bomb outlet.

The bomb was immersed in a water bath and held at constant temperature by means of either a mercury switch or a Sargent Thermonitor.

Procedure

Prior to introduction of the test gas, the system was evacuated to about 0.01 mm. Hg in about 12 hr. The system was then quickly pressurized, and care was taken to obtain several pressure readings within the first few seconds of the run, in order to obtain an accurate determination of initial pressure. Pressures were recorded until the system reached equilibrium, and gas solubilities were derived from the initial and equilibrium pressure

readings. In the interest of saving time, sequential runs were made in some cases, by incrementally raising the pressure of the equilibrated system and following the pressure drop until pressure leveling occurred once again.

RESULTS AND DISCUSSION

Low Pressure Experiments

For all gases with the exception of carbon dioxide, the sorption isotherm is linear to 1 atm., and Henry's law is obeyed for the overall sorption process in the 3-mil oriented film.

Overall solubility constants k for nitrogen, oxygen, methane, and argon in oriented glassy crystalline poly(ethylene terephthalate) are presented in Table I. The estimated precision of the experimental method at the 95% confidence level, as determined for nitrogen sorption, is $\pm 8\%$. This uncertainty is due mainly to fluctuations in the final, or equilibrium, sorption pressure caused by fluctuations in the ambient temperature. The precision should be greater for gases with higher solubility constants than nitrogen. The solubilities are compared to those obtained by Michaels et al.⁴ for the unoriented film. In comparing the data the fact that the oriented film contained a slightly lower amorphous fraction ($\alpha = 0.49$) than the unoriented film ($\alpha = 0.58$) should be noted. Notwithstanding this restriction, the data of Table I clearly indicates that gas solubility in the oriented film is very nearly the same as that in unoriented film, perhaps slightly higher, per unit volume of amorphous phase. This result is quite significant when considering the differences in the films being compared, the oriented film having been stretched about 200–250% in two directions.

TABLE I
Solubility Constants for Oriented and Unoriented Poly(ethylene Terephthalate)

Gas	ϵ/\bar{k} , °K.	Temp., °C.	k , cc. STP/cc. \times atm.	
			Oriented film ($\alpha = 0.49$)	Unoriented film ($\alpha = 0.58$) ^a
N ₂	95	25	0.044	0.048
O ₂	118	25	0.076	0.073
CH ₄	150	25	0.200	0.220
A	106	25	0.0077	—
CH ₄	150	40	0.130	0.140
CH ₄	150	55	0.087	0.092

^a Data of Michaels et al.⁴

Further indication of the similarity in the solution behavior of gases in both the oriented and unoriented films is presented in Figures 1 and 2. There it is seen that the carbon dioxide sorption isotherm in the oriented film exhibits curvature in the same pressure range as does the isotherm for the unoriented film. Again solubility in the oriented polymer appears to be only slightly higher than in the crystalline film. However, the solubility

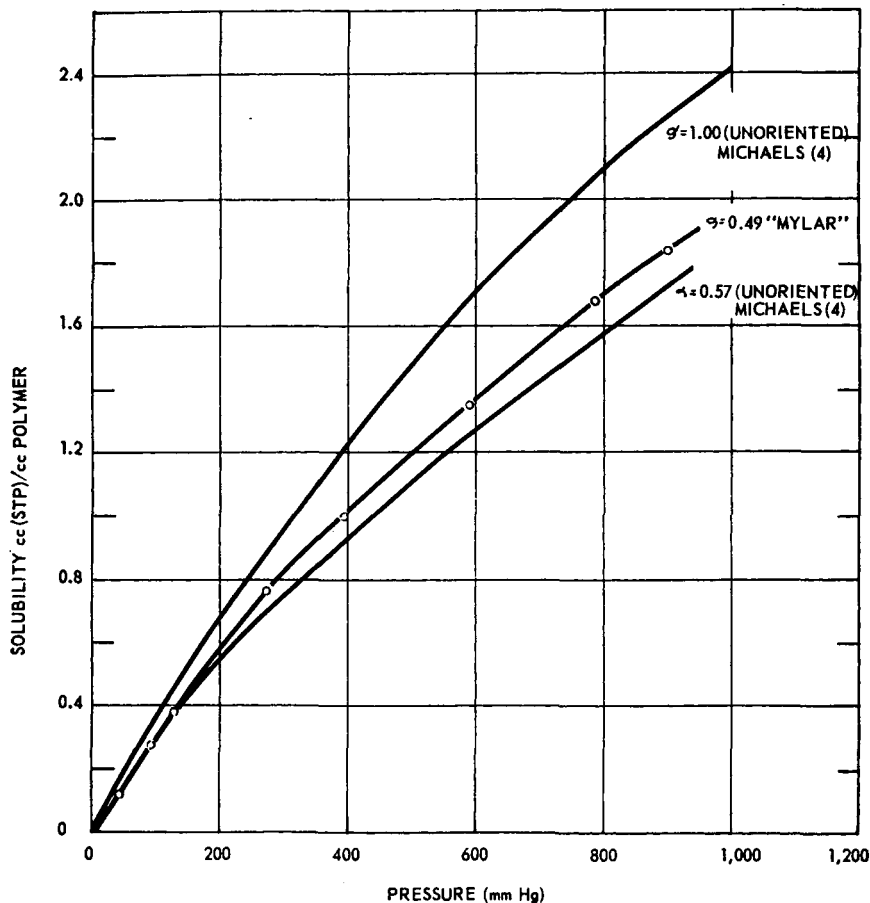


Fig. 1. Comparison of sorption isotherms for CO_2 in oriented and unoriented poly(ethylene terephthalate) at 25°C .

in the unoriented amorphous polymer ($\alpha = 1.0$) exceeds the solubility in both these crystalline samples.

The solubility constants obtained for the oriented polymer could be correlated by plotting $\ln k$ versus the gas force constant, ϵ/\bar{k} . These data are plotted in Figure 3 and show that a correlation of the Jolley-Hildebrand type¹⁴ is applicable. The parameter ϵ/\bar{k} from the Lennard-Jones potential is a measure of the tendency of the gas to condense. Furthermore, it is characteristic of solute-solvent interactions; thus, the fact that the correlation holds similarly for the oriented and unoriented polymer is in agreement with the observed solubility behavior of these polymers.

The type of sorption process taking place is also reflected in the overall heats of sorption. Heats of sorption calculated for carbon dioxide and methane in the oriented polymer are obtained from Figure 4 and shown in Table II. The data indicate very little difference between the oriented and

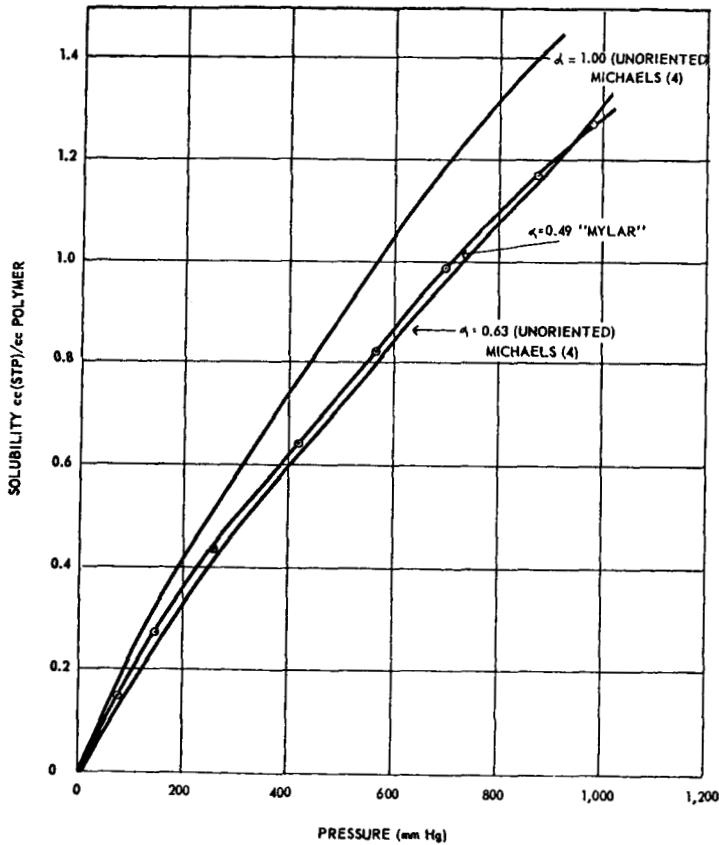


Fig. 2. Comparison of sorption isotherms for CO₂ in oriented and unoriented poly(ethylene terephthalate) at 40°C.

unoriented film, lending more support to the previous findings, indicating a surprisingly low response to a significant degree of stretching of the polymer.

TABLE II
Heats of Sorption

Gas	ΔH_{s3} , kcal./g.-mole	
	Oriented film ($\alpha = 0.49$)	Unoriented film ($\alpha = 0.57$) ^a
CO ₂	-7.4	-7.5
CH ₄	-5.4	-5.3

^a Data of Michaels et al.

At this point it should be reiterated that all the data discussed so far was obtained by means of low pressure sorption experiments in the 3-mil oriented poly(ethylene terephthalate) film.

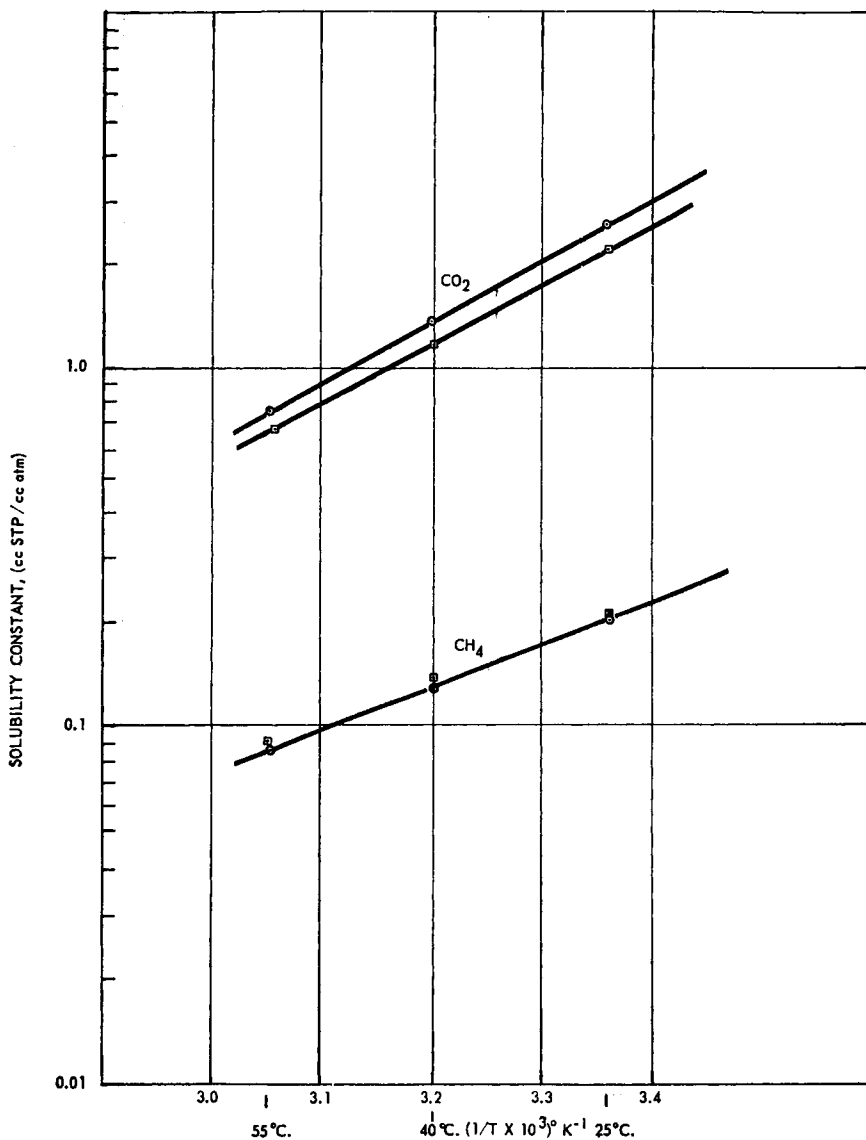


Fig. 4. Solubility constants vs reciprocal temperature: (○) present study, Myla ($\alpha = 0.49$); (□) Michaels,⁴ crystalline film ($\alpha = 0.58$).

This simple expression does not provide any insight into the structure of the polymer. On the other hand, nonlinear sorption as exhibited by carbon dioxide, even at low pressure, requires use of eq. (2) for description. This type of expression yields some insight into the structure of a sample through the constants that are incorporated into it; i.e., the hole affinity constant b and the hole saturation constant C_H' . In order to obtain a direct estimate of these parameters the several sorption processes must be separated.

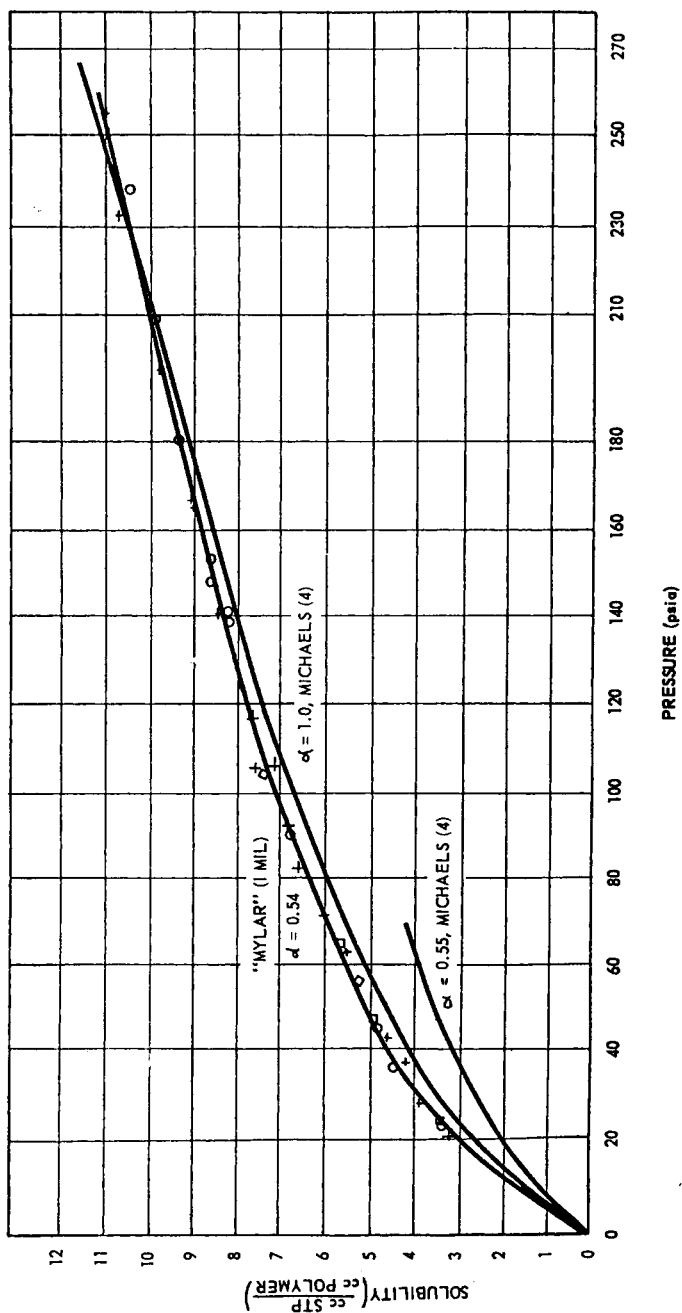


Fig. 5. CO₂ sorption in Mylar at 25°C.

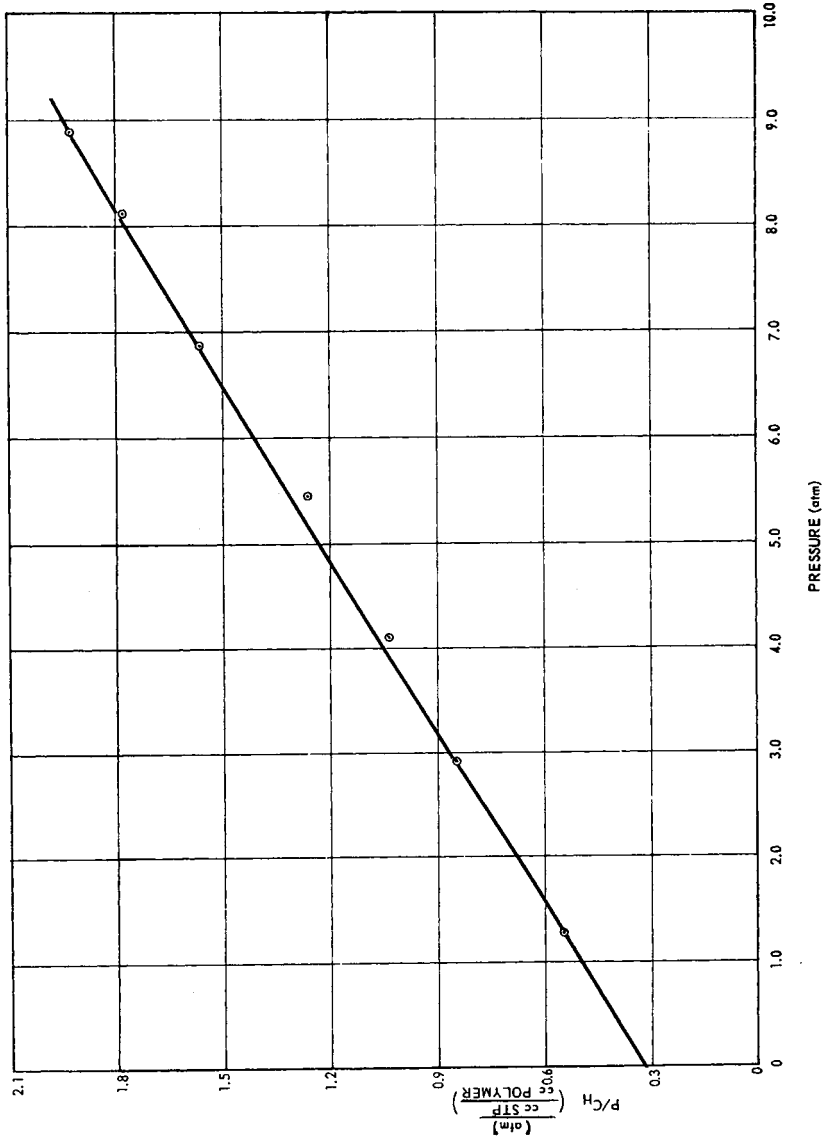


Fig. 6. Langmuir plot for CO_2 sorption by "hole-filling" in Mylar at $25^\circ C$.

This requires knowledge of k_D^* , the Henry's law constant for dissolution, which can only be obtained from the straight-line portion of the sorption isotherm at high pressures after the "holes" have been saturated. To obtain these parameters, a carbon dioxide isotherm extending to about 15 atm. was determined for the 1-mil film. Since many experiments had to be performed, the thinner film was used to reduce the time of an individual experiment to reasonable proportions (12 hr.).

Figure 5 compares the sorption isotherms for the 1-mil oriented polymer ($\alpha = 0.54$) with the unoriented amorphous and crystalline ($\alpha = 0.57$) polymer films. The greater sorptive capacity of the 1-mil oriented film represents the most striking and unexpected result of this study. In previous work with unoriented films, varying in thickness from 3 to 65 mils, no effect of thickness on sorption had ever been detected.

The first step in analyzing these results requires the determination of the constants for eq. (2). The slope of the straight line portion of the isotherm in Figure 5 yields a value of k_D^* of 0.69. By subtracting $k_D^*p\alpha$ from the total solubility C , the hole-filling contribution, C_H , is determined at each pressure. The expression for C_H is:

$$C_H = C_H'bp/(1 + bp) \quad (4)$$

or

$$p/C_H = (1/bC_H') + (p/C_H') \quad (5)$$

Thus a plot of p/C_H versus p should yield a test of the model. Such a plot is shown in Figure 6, where the reciprocal of the slope gives the hole saturation constant C_H' , while the intercept on the ordinate yields the value of the hole affinity constant, b . The resulting equation is:

$$C = [2.94p/(1 + 0.52p)] + 0.69p\alpha \quad (6)$$

The significance of these results is evident from Table III, which compares constants of this equation for different types of PETP film. The data suggest several effects of film treatment on sorption for the oriented crystalline 1-mil film. First, the saturation constant at 25°C. is higher, 5.7 cc. STP/cc. total polymer versus 5.3 for the amorphous polymer and 4.2 for the crystalline polymer, indicating that the void volume available for carbon dioxide sorption is larger. A more revealing quantity C_H'/α which may be viewed as the "hole" saturation limit per unit volume of amorphous phase, also indicates a much larger sorption capacity in the oriented film than in the amorphous film. It further suggests that the processing of the 1-mil Mylar tends to concentrate microvoids in the residual amorphous phase. This phenomenon was observed previously,⁴ a larger value of C_H'/α being noted for the crystalline polymer (7.4) than for the amorphous polymer (5.3).

From eq. (5) it is observed that the hole affinity constant b for the oriented film is slightly higher, 0.52 versus about 0.45 for both amorphous and crystalline unoriented polymers. This seems reasonable because stretching

TABLE III
 Constants for CO₂ Sorption in Poly(ethylene Terephthalate)

Description of poly(ethylene terephthalate) film	Temp., °C.	α	k_D^*	b	C_H'	C_H'/α
Glassy amorphous (5 mil) ^a	25	1.0	0.38	0.44	5.3	5.3
Glassy crystalline (5 mil) ^a	25	0.57	0.38	0.45	4.2	7.4
Glassy oriented (1 mil)	25	0.54	0.69	0.52	5.7	10.6

^a Data of Michaels et al.⁴

should cause strain to be stored in the amorphous regions. The strained amorphous regions bounding holes would be expected to exhibit a higher affinity for the gas.

Another marked difference between the oriented 1-mil film and the un-oriented film appears in the value of the Henry's law dissolution constant. The higher value of k_D^* for the oriented film is in line with the observed increase in the solubility. More significantly, it indicates a further difference in the properties of the amorphous phase of this polymer. It would appear that the gross amorphous phase in the oriented polymer may contain some relatively "loose" regions, of lower cohesive energy density than the unoriented amorphous film, as well as the strained amorphous regions.

In this investigation, orientation as a result of stretching cannot by itself be regarded as a cause for a markedly increased solubility for the 1-mil film. Thompson and Woods¹⁵ do suggest a possible propagation of holes upon stretching PETP. However, no large increase in solubility was noted in the case of low pressure sorption of carbon dioxide and other gases in the 3-mil oriented polymer, and an explanation based along these lines is probably not warranted. The remaining difference between the films studied was thickness itself, and the question arises as to whether consideration of the method of preparation of the films yields an explanation for the increased solubility in the 1-mil film.

Films of poly(ethylene terephthalate) are prepared by melt extrusion of the polymer, cooling, and biaxial drawing of the film at a temperature above the glass transition, followed by quenching of the product. It is entirely conceivable that the thermal history of the 1-mil film would be different than that for the 3-mil or 5-mil films. Since transient conduction is involved, the cooling rate would be proportional to the square of the film thickness and quenching after stretching would occur much more rapidly in the 1-mil film. It is likely that these heat transfer conditions contribute to differences in structure between the 1-mil film and thicker films. In this light, it should be recalled that the postulated sorption mechanism involves occupancy of holes as well as ordinary dissolution. The holes may be thought of as larger-than-average separations between polymer chains that are "frozen" in the glassy state. The chance of freezing-in a hole is greater

with more rapid cooling, which results in a rapid decrease of chain mobility within the polymer. This appears to be the case with the 1-mil film. Furthermore, stretching with rapid cooling induces crystallization in the more dense regions, leaving behind a large fraction of looser regions in which chain separations are smaller than for holes, approaching in size the diameter of a penetrant molecule. These latter regions would account for the higher dissolution constant for carbon dioxide.

In summation, it was determined that the solubilities of nitrogen, oxygen, methane, carbon dioxide, and argon in 3-mil oriented crystalline poly(ethylene terephthalate) are virtually the same as in the unoriented crystalline film. The solubility constants are correlated with the Lennard-Jones force constants, ϵ/k , in a similar fashion to previous data on unoriented films. Heats of sorption for methane and carbon dioxide in the oriented polymer are nearly the same as in the unoriented crystalline polymer.

Carbon dioxide sorption isotherms are nonlinear. These isotherms may be described by postulating dual sorption modes; i.e., dissolution and hole-filling. The former obeys Henry's law and the latter, a Langmuir expression.

Solubility of carbon dioxide in 1-mil oriented film is markedly greater than in thicker oriented films. Analysis of the data indicates a greater hole saturation constant and a different amorphous character for the 1-mil film. Heat transfer considerations in the manufacture of the film are advanced to explain the observed behavior.

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References

1. Michaels, A. S., and R. B. Parker, Jr., *J. Polymer Sci.*, **41**, 53 (1959).
2. Michaels, A. S., and H. J. Bixler, *J. Polymer Sci.*, **50**, 413 (1961).
3. Michaels, A. S., W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 13 (1963).
4. Michaels, A. S., W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
5. Meares, P., *J. Am. Chem. Soc.*, **76**, 3415 (1954).
6. Meares, P., *Trans. Faraday Soc.*, **53**, 101 (1957).
7. Meares, P., *Trans. Faraday Soc.*, **54**, 40 (1958).
8. Myers, A. W., C. E. Rogers, V. Stannett, and M. Szwarc, *Mod. Plastics*, **34**, 157 (1957).
9. Reitlinger, S. A., and I. S. Yarkho, *Kolloid. Zh.*, **17**, 367 (1955).
10. Barrie, J. A., and B. Platt, *J. Polymer Sci.*, **54**, 261 (1961).
11. Lasoski, S. W., Jr., and W. H. Cobbs, Jr., *J. Polymer Sci.*, **36**, 21 (1959).
12. Michaels, A. S., W. R. Vieth, and H. J. Bixler, to be published.
13. de P. Daubeny, R., C. W. Bunn, and C. J. Brown, *Proc. Roy. Soc. (London)*, **A226**, 531 (1954).
14. Jolley, J. E., and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958).
15. Thompson, A. B., and D. W. Woods, *Nature*, **176**, 78 (1955).

Résumé

Les solubilités de l'azote, de l'oxygène, de l'argon, du méthane, et de l'anhydride carbonique dans des films minces de téréphtalate de polyéthylène cristallisé orienté à l'état vitreux ont été étudiées par la méthode statique d'absorption. On a obtenu des isothermes d'absorption à pression élevée pour l'anhydride carbonique. Les résultats montrent que, au dessus d'une certaine épaisseur de film, les solubilités de tous les gaz dans le polymère cristallin orienté (Mylar) sont virtuellement identiques à celles obtenues pour le polymère cristallin non orienté. Les constantes de solubilité sont reliées aux constantes de force de gaz, ϵ/\bar{k} , et les chaleurs d'absorption obtenues pour le méthane et l'anhydride carbonique sont pratiquement les mêmes pour les films orientés et non orientés. Les isothermes d'absorption obtenues pour l'anhydride carbonique ne sont pas linéaires mais peuvent être bien décrit en considérant deux modes d'absorption.

L'un; ordinairement la dissolution, est décrit par la loi de Henry, tandis que l'autre, \llcorner le remplissage des trous \gg est caractérisé par une expression de Langmuir. Les solubilités de l'anhydride carbonique dans le film orienté le plus mince (un millième de pouce) sont nettement plus élevées que dans le film non orienté. L'analyse des résultats d'absorption montrent que \llcorner la constante de saturation des trous \gg et \llcorner la constante d'affinité des trous \gg sont beaucoup plus grandes dans le film orienté épais d'un millième de pouce. La phase amorphe semble également être différente, et présente une plus grande capacité pour le gaz dissous. L'historique des différents traitements thermiques en rapport avec la fabrication du film est présenté comme une explication possible de l'augmentation de solubilité.

Zusammenfassung

Die Löslichkeit von Stickstoff, Sauerstoff, Argon, Methan und Kohlendioxyd in dünnen Filmen kristallinen, orientierten Polyäthylenterephthalats im Glaszustand wurde nach der statischen Sorptionsmethode untersucht. Hochdruck-Sorptionsisothermen wurden für Kohlendioxyd aufgenommen. Die Ergebnisse zeigen, dass oberhalb einer gewissen Filmdicke die Löslichkeit aller Gase im kristallinen, orientierten Polymeren (Mylar) praktisch mit derjenigen im nichtorientierten kristallinen Polymeren identisch ist. Die Löslichkeitskonstanten werden zu Gas-Kraftkonstanten, ϵ/k , in Beziehung gebracht; die Sorptionswärme ist bei Methan und Kohlendioxyd für orientierte und nichtorientierte Filme fast die gleiche. Die für Kohlendioxyd erhaltenen Sorptionsisothermen sind nicht linear, können aber durch einen dualen Sorptionsmechanismus gut erfasst werden. Der eine Mechanismus, die normale Lösung, gehorcht dem Henry'schen Gesetz, während der andere "die Lochauffüllung" durch einen Langmuir-Ausdruck charakterisiert wird. Die Löslichkeit von Kohlendioxyd im dünnsten, orientierten Film (ein Mil) ist merklich höher als im nichtorientierten Film. Eine Analyse der Sorptionsdaten zeigt, dass sowohl die "Loch-Sättigungskonstante" als auch die "Loch-Affinitätskonstante" in den orientierten 1-mil-Filmen grösser ist. Auch die amorphe Phase scheint verschieden zu sein und eine grössere Kapazität für gelöstes Gas zu besitzen. Als mögliche Erklärung für die erhöhte Löslichkeit wird die verschiedene, in der Filmerzeugung begründete, thermische Vorgeschichte herangezogen.

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