

Transport Properties and Their Correlation with the Morphology of Thermally Conditioned Polypropylene

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Synopsis

Time-lag and static sorption experiments were employed to measure permeability, diffusivity and solubility constants of He, A, and CF₄ in polypropylene films cooled at various rates from the melt and subsequently annealed at varying temperatures near the melting point. While solubility constants in films annealed above 90°C showed the normal variation with the amorphous content of the polymer, solubility constants for all unannealed, quenched films were remarkably constant and independent of the rate of cooling. In fact, all quenched films appeared to have the same amorphous content (ca. 41%). The remaining material is believed to be a mixture of monoclinic and hexagonal crystallinity, the volume ratio of the two being a function of the rate of quenching, and changing on annealing, in favor of the more stable, monoclinic form; the transition occurring rather sharply at 90°C. X-ray diffraction provided supporting evidence for the presence of the hexagonal crystals. The diffusion behavior in crystalline polypropylene is normal and Fickian but instead of the usual decline with increasing crystallinity, diffusivities showed definite enhancement in the case of the annealed films, i.e., the expected monotonic decline of D with increasing crystallinity is not observed. This behavior is attributed to a reduction in diffusional impedance through formation of defects in existing crystallites, as the lamellae thicken, in a manner similar to that observed on annealing of polyethylene single crystals. The apparent activation energies of diffusion were essentially constant and independent of thermal history. This suggests that in a highly crystalline polymer diffusion is not so much impeded by the restricted mobility of chain segments but rather by the extremely small dimensions of the available diffusive pathways. In support of the argument that the transport properties of polypropylene are controlled at a level of microstructure well below the characteristic dimensions of spherulites, it was observed that bulk-crystallized polypropylene has a spherulitic structure whose size and texture do not change significantly on annealing.

INTRODUCTION

For semicrystalline polymers, it is well established that the crystalline microstructure plays a dominant role in influencing the macroscopic properties exhibited by the polymer. For example, tensile and tear strength, optical properties, selectivity, and fluid-transport properties of a polymer are all directly related to the film's crystalline substructure.

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Knowing in detail what this microstructure is and how it can be altered during and after film fabrication, by controlling such variables as the rate of cooling from the melt and the extent of annealing, would make it possible to optimize such desirable film properties as high gloss, low haze, high tensile strength, and low permeability.

Although electron microscopy and x-ray diffraction provide means for observation of microcrystallinity, the extremely complex microstructure of bulk polymers has made detailed morphological studies difficult by these means alone. On the other hand, analysis of data on the solution and diffusion of small inert gas molecule has in the past¹⁻⁷ proven very successful in elucidating aspects of polymer microstructure which are relatively insensitive to other analytical techniques.

The semicrystalline polymer most extensively studied by this gas permeation technique is polyethylene.^{4-6,8} From such studies it was postulated that a semicrystalline polymer behaves like a two-phase system; namely, a well-ordered crystalline phase dispersed in a less rigid, amorphous matrix. The crystalline regions are imagined to dissolve no gas and to be quite impermeable, so that all gas transport takes place in the amorphous phase, which is thought to have the same specific permeability, irrespective of the extent of crystallinity. This model further suggests that increasing crystallinity decreases permeability by the combined effects of reducing the volume of amorphous material available to carry the flux and impeding the flow by forcing the diffusing molecule to by-pass impenetrable crystallites. The relationships that evolved from the experimental observations for semicrystalline polyethylene are

$$k = \alpha k^* \quad (1)$$

which states that the solubility in a partially crystalline polymer k is directly proportional to the amorphous volume fraction α , with the proportionality constant k^* being the solubility in completely amorphous polymer, and

$$D = D^*/\tau\beta \quad (2)$$

which expresses the effect of crystallinity on diffusivity in that D , the diffusivity in the partially crystalline polymer is considered to be reduced from what it would be in completely amorphous polymer D^* by the "geometric impedance factor" τ , reflecting the more circuitous diffusion path due to the presence of the impermeable crystallites, and by β , the "chain immobilization factor," initially attributed to the "crosslinking" action of the crystallites on sequential mobility.

However, Jeschke and Stuart² and others^{1,5,8} have observed inconsistencies in this two-phase model, especially in the case of diffusion. For example, they found that, while β depends strongly on the molecular diameter of the diffusing gas, it is essentially constant for each gas and independent of α and the thermal history of the polymer. Another observation that is difficult to explain on the basis of a two-phase model is the

small decrease—rather than anticipated increase—in diffusional activation energies with increasing α . Nevertheless, the concept of impermeable crystallites suspended in an amorphous matrix has successfully explained most of the permeation data for polyethylene and poly(ethylene terephthalate).

The present study was undertaken to elucidate the morphology of another semicrystalline polymer and close relative of polyethylene, namely, the isotactic stereoisomer of polypropylene. Specifically, the study was designed for three principal purposes: (1) to use sorption and diffusion studies to ascertain the nature of the crystalline phase and to determine the extent of its interaction with the amorphous phase; (2) to analyze the effect of changes in thermal history on the polymer's microstructure by observing changes in permeation properties; and (3) to interpret gas permeation data in conjunction with evidence from other polymer characterization methods.

THEORETICAL ASPECTS

Monoclinic and Quenched Crystal Forms

Isotactic polypropylene is known to exist in at least two crystal modifications. Natta⁹ and others^{3,10,11} have established that slow cooling from the melt or annealing results in stable crystals with a monoclinic unit cell. Low-angle x-ray diffraction shows that the chains in this crystal phase are in a helical conformation with left and right-handed helices alternating regularly.

However, when isotactic polypropylene is quenched or rapidly cooled from the melt, a second, less stable, crystalline phase appears. Although quenched samples have been repeatedly studied by x-ray scattering, infrared absorption, and NMR,¹²⁻¹⁵ the exact structure of the "quenched" crystal has to this date been rather elusive. Nevertheless, more and more evidence^{16,17} points to the hypothesis that the quenched crystalline phase is made up of small crystals of hexagonal unit cell.

Since commercial film fabrication always involves some degree of quenching of the melt and a substantial fraction of the film's total crystallinity will consequently be in this quenched state, consideration must be given to this form when discussing the morphology of polypropylene.

Lamellar Structure

The earliest model proposed to explain the crystallinity-dependent properties observed in many polymers was the "fringed-micelle" concept. The solid polymer was pictured as a tangled mass of molecular chains each of which passes randomly through a number of small crystallites and intervening amorphous areas. This concept successfully accounted for a large number of the early experimental observations but became increasingly less plausible as new experimental evidence accumulated. For

example, in 1947, Bunn and co-workers studied polyethylene¹⁸ and nylon¹⁹ spherulites and showed that they contained molecular chains arranged in a regular manner tangential to the radial growth elements of the spherulite. Then, in 1957, Keller²⁰ and others^{21,22} reported the growth, from dilute solutions, of single crystals of linear polyethylene. Subsequent electron diffraction showed that in these single crystal platelets the molecular chains were oriented in a direction normal to the flat surface of the crystal. This fact, together with the observation that these platelets were only about 100 Å thick, while the extended length of an average molecular chain is many thousands of angstroms, led Keller²³ to the conclusion that the chains must be folded, with the fold period corresponding to the thickness of the platelet. Since then, solution growth of single crystals has been reported for many other polymers.²⁴

Although the most conclusive evidence for a chain-folded, lamellar structure has initially come from the study of single crystals grown from solution, it is now widely believed²⁵ that bulk samples of bulk crystalline polymers also consist largely of lamellar structures. Electron microscopic examination of surfaces of spherulitic films,²⁶ fracture surfaces,²⁷⁻³⁰ and samples of bulk polymer dispersed by means of a nitric acid digestive treatment³¹ provides strong evidence that lamellae exist throughout melt-crystallized specimens of most crystalline polymers, including polypropylene.^{26,32}

While solution-grown single crystals are generally thin platelets or lamellae about 100 Å thick and many microns in lateral dimensions, the crystallites in bulk samples are believed to be generally less perfect and more anisometric in their lateral dimensions.

On annealing, the chain-folded lamellae tend to thicken or increase their step height. From experiments with single crystals of polyethylene³³ and polychlorotrifluoroethylene³⁴ it was seen that thickening of the lamella was accompanied by the formation of microholes and, strangely enough, no change in the lateral dimension of the lamella. For the latter to be the case, chain ends must be continuously introduced into the crystal interior to allow the thickening process to proceed.³⁵ Eventually, chain ends must be pulled through the crystal, leaving vacant rows or microholes in the lamella. This is shown schematically in Figure 1.

The experimental observations of the present study strongly support this concept of "row-vacancy" defect formation. It was found that the diffusion of small gas molecules in films crystallized from the melt and subsequently annealed is markedly enhanced and this is attributed to the appearance of just such defects.

When cooling from the melt is slow enough or when films are subjected to extensive annealing, crystallites are given the opportunity to aggregate into larger structural units called spherulites. When viewed in the polarizing microscope, polypropylene films, too, show the typical Maltese cross patterns associated with the presence of spherulites. Although spherulites may give a qualitative indication of a film's thermal history, it

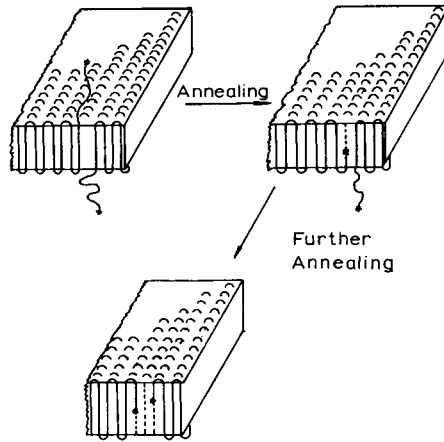


Fig. 1. Thickening of lamella with row-vacancy defect formation.

is generally felt that these structures are too large to be “seen” by the diffusing gas molecule. Instead, the gas molecule interacts with the intra- and interlamellar material on its passage through the film.

To shed more light on such morphological features as the “quenched” crystalline phase and the row-vacancy defects, the solution and diffusion of small gas molecules in films of varied thermal history were studied.

Permeation

The steady-state, uni-directional flow of gas across a polymer can be described by Fick’s first law of diffusion

$$J = -D(\partial c/\partial x) \quad (3)$$

where J is the permeation flux, D is the diffusion constant, and $\partial c/\partial x$ is the concentration gradient.

For the gases studied in the present work,

$$D \neq f(c) \quad (4)$$

and Henry’s law describes the solubility

$$C = kP \quad (5)$$

Thus,

$$J = DK[(P_1 - P_2)/l] \quad (6)$$

where k is the Henry’s law solubility constant, and P_1 and P_2 refer to the pressures at the upstream and downstream film surfaces, respectively.

By definition, the product of D and k is \bar{P} , the permeability constant,

$$\bar{P} \equiv kD \quad (7)$$

The dependence of the three constants on temperature is of the Arrhenius type for rubbery materials. Strictly speaking, the activation energies

should be slightly temperature-dependent; however, over the temperature ranges considered here the following equations are very good approximations:

$$\bar{P} = P_0 e^{-E_p/RT} \quad (8)$$

$$D = D_0 e^{-E_D/RT} \quad (9)$$

$$k = k_0 e^{-\Delta H_s/RT} \quad (10)$$

where E_p and E_D are the activation energies for permeation and diffusion, respectively, and ΔH_s is the enthalpy of sorption.

EXPERIMENTAL

Materials

The film samples were molded in a laboratory platen press from 651A Profax supplied by Hercules Inc., Wilmington, Delaware. The polymer had an average molecular weight of 320000 and an isotactic content of 95%, based on customary viscosity and solubility measurements. Furthermore, the polymer contained about 1% oxidation inhibitors.

The atactic polypropylene used as analog for completely amorphous isotactic polypropylene was supplied by the Avisun Corporation under the trade name Oletac 100. It had a molecular weight of 16000 and was 100% soluble in boiling hexane.

The gases studied were helium, argon, and carbon tetrafluoride. The minimum purity of the gases was 99.8%. The gases were passed through a bed of CaSO_4 to remove any last traces of water-vapor, but were otherwise used as received. The properties of the gases are summarized in Table I.

TABLE I
Physical Properties of the Gas Molecules Used

Gas	Mol. wt.	d , Å	d^2 , Å ²	ϵ/\bar{k} , °K	\bar{V} , cc/g-mole ^a	T_c , °K
He	4	2.2	4.8	10	39	5.3
A	40	3.6	12.9	122	42	151
CO ₂	44	3.7	16.4	189	40	304
CH ₄	16	4.2	17.6	148	52	191
CF ₄	88	4.6	21.1	152	75	228

^a Estimated by Bixler.⁴²

The films were given their various thermal histories by cooling them at different rates from the melt and by annealing them at various elevated temperatures. The films were quenched in hot water (90°C), ice water, or ethyl orthosilicate at -72°C and were annealed for 60 min at 80, 100, 110, 130, 140, or 150°C. The samples were sealed between thin metal plates to avoid contact with the silicone oil of the annealing bath.

The properties of the films used in the permeation and sorption studies

appear in Table II. The thickness recorded is the arithmetic average of numerous measurements over the area of the sheet. Values of the per cent amorphous volume α were calculated from polymer densities determined in isopropanol-water density-gradient columns. The density of completely amorphous, isotactic polypropylene was taken as 0.858 g/cc^{36,37} and that of completely crystalline polypropylene as 0.936 g/cc.³⁶

X-ray diffraction was used to verify the per cent crystallinity calculated

TABLE II
Properties of Films Studied

Film	Description ^a	<i>l</i> , cm	$\rho_{23^\circ\text{C}}$, g/cc	α^* , % ^b
1	RA	0.0388	0.8920	56.5
2	RA	—	0.8923	56.0
3	RA	0.0370	0.8940	53.0
3a	RA-150	0.0364	0.9145	27.5
4	RA-150	0.0388	0.9132	29.0
5	RA-150	—	0.9135	28.7
6	MA	0.0427	0.9012	44.5
7	MA-80	0.0427	0.9020	43.5
8	MA-100	0.0442	0.9065	37.8
9	MA-110	0.0405	0.9069	37.3
10	MA-130	0.0410	0.9106	32.6
11	MA-140	0.0436	0.9105	32.7
12	MA-150	0.0431	0.9136	28.8
13	MA-150	0.0388	0.9132	29.0
14	MA	0.0372	0.8963	51.0
14a	MA-150	0.0369	0.9136	28.8
15	SA	0.0383	0.9055	39.0
16	SA-150	0.0396	0.9123	30.5
17	RH	0.1161	0.8971	50.0
18	RH	0.1039	0.8963	51.0
19	RH-150	0.1105	0.9119	31.0
20	MH	0.0901	0.8970	50.0
21	MH-150	0.0899	0.9127	29.5
22	SH	0.1129	0.9055	39.0
23	SH-150	0.1130	0.9117	31.0
24	RF	0.0148	0.8953	52.2
24a ^c	RF-150	0.0148	0.9150	27.0
25	MF	0.0169	0.8952	52.4
25a ^c	MF-150	0.0169	0.9144	27.5
26	SF	0.0154	0.9063	38.2
26a ^c	SF-150	0.0154	0.9148	27.4
27	cast	0.0178	0.8907	58.0
Atactic	cubes	0.60	0.8580	100.0

^a Key: RA-150 ← annealing temperature (°C)
 ↑ gas studied (Argon, Helium, Freon 14)
 — rate of cooling from melt

^b Calculated from $\alpha = [(\rho_c - \rho)/\rho_c - \rho_a] \times 100$, where: $\rho_c = 0.9360$ g/cc, $\rho_a = 0.8580$ g/cc.

^c In each case the "a" film is the immediately preceding film, after annealing.

from density measurements as well as to establish the presence of the less stable crystalline form in the quenched samples.

Calorimetric measurements were made to establish glass transition temperatures and to check the crystallinities as determined from density measurements.

Procedure

Time-Lag Method. Most of the values of diffusion and solubility constants for helium, argon and carbon tetrafluoride were obtained via the classic time-lag technique developed by Barrer³⁸. The experiment consists of evacuating the membrane, applying a constant pressure to one side, and recording the pressure rise in the previously evacuated downstream reservoir as a function of time. From the transient portion of the experiment, the diffusion constant D can be calculated by the relationship

$$D = l^2/360\theta \quad (11)$$

where θ is the time lag expressed in minutes and l the film thickness in centimeters.

The permeability \bar{P} is calculated from the rate of pressure increase in the downstream volume during the steady-state period. The solubility constant is determined indirectly from eq. (7), namely,

$$\bar{P} = kD$$

The temperature dependence of the transport coefficients was determined by making runs over a 30–40°C range.

One of the major innovations in the classical time-lag system was the use of a capacitance-type pressure transducer to measure the downstream pressure.

For the time-lag experiments, the precision of \bar{P} , D , and k at the 95% confidence limits was $\pm 5.2\%$, $\pm 9.5\%$ and $\pm 11\%$, respectively. The major contribution to error came from the inevitable variations in sample thickness.

Sorption Methods. To obtain diffusion and sorption data for the tacky and structurally unsound atactic polypropylene as well as to confirm some of the solubility values obtained indirectly from the time-lag technique, low-pressure sorption and desorption experiments were performed. This technique was developed in this laboratory and first described in a paper by Michaels and Parker.³⁹ Briefly, the method consists of equilibrating an initially evacuated sample of polymer, in strip or pellet form, with the desired gas at pressures up to one atmosphere. A simple material balance yields the solubility constant while diffusion constants are calculated from an analysis of the transient sorption curve using appropriate solutions of Fick's second law. Again, the use of a pressure transducer made it possible to monitor pressure changes very accurately.

The estimated precision at the 95% confidence limits was $\pm 1.5\%$ for k and $\pm 8.3\%$ for D .

High-Pressure Sorption

To extend the investigation into the glassy region of poly(propylene) and to check the applicability of Henry's law, solubility constants of A and CO₂ were measured in unoriented, cast film (supplied by Hercules and from the same batch of resin as the laboratory-molded films) over a pressure range of 30 atmospheres and temperatures ranging from -40°C to +40°C. The apparatus was similar to the low pressure sorption system except that it was designed for high pressure work. The error analysis placed the precision limits of this method at $k \pm 8.2\%$.

RESULTS AND DISCUSSION OF RESULTS

Permeability Constants

Permeability data, *per se*, offer little insight into the permeation process, because of the two-step nature of the permeation process—sorption and diffusion. For this reason, any attempts at understanding this process must logically be directed toward separate analyses of the sorption and diffusion processes. Nevertheless, from an engineering viewpoint, permeability data are of prime interest and probably constitute the greatest single incentive for continued attempts to understand the morphology of crystalline polymers. Consequently, these data merit some discussion in their own light.

The temperature dependence of the permeability constants is presented in Figure 2. As in the case of polyethylene and poly(ethylene terephthalate),

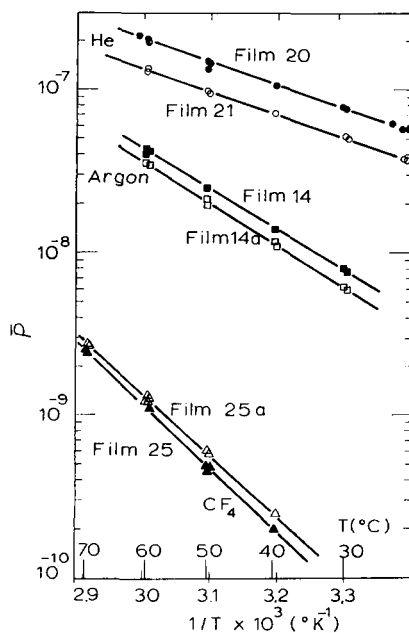


Fig. 2. Permeability constants for moderately cooled films.

the data were well correlated by the Arrhenius expression $\bar{P} = P_0 e^{-E_p/RT}$ over the 30–70°C temperature range. The fact that this relationship, originally derived for completely rubbery materials, should describe permeation in highly crystalline films is somewhat surprising and points to the rubbery nature of the chain ends and tie-chains between the crystallites, through which, presumably, most of the diffusion takes place. The activation energies for permeation, E_p , were on the average 6.4, 10.9, and 17.8 \pm 0.2 kcal/g-mole for helium, argon, and CF₄, respectively. The values of E_p showed no significant variation with the level of crystallinity or thermal history of the film.

The most interesting and somewhat unexpected result, however, was the observation that extensive annealing resulted in a net increase in permeability for CF₄ in spite of a significant reduction (ca. 20% in the case of films quenched in ice water) in the amorphous content of the polymer.

Thus, one is led to the conclusion that the gas permeability of isotactic polypropylene is not only a function of the level of crystallinity but may depend significantly on the perfection and thermal history of the crystallinity. To explain this phenomenon, one must examine separately the sorption and diffusion processes occurring in the polymer.

Solubility in Crystalline Polypropylene

The solubility data were collected by two different techniques: time-lag and static sorption experiments. The equivalence of the solubility constants determined by either method has been satisfactorily established by using the same film both in the time-lag and low-pressure sorption systems and finding that the solubility constants were identical.

The temperature dependence of the solubility constants for all gases was expressed by the van't Hoff expression $k = k_0 e^{-\Delta H_s/RT}$ and found to apply within the experimental error for all films studied over the temperature range 30–70°C. The enthalpies of sorption for argon were negative and usually of the order of 0.5 to 1.0 kcal/g-mole, while the enthalpies of sorption for helium and CF₄ were positive and 1.7 and 2.2 kcal/g-mole, respectively. The values of ΔH_s fluctuated randomly from film to film with apparently no consistent variation of ΔH_s with crystalline content or thermal history. Nevertheless, on the average, the values of ΔH_s were of the same order of magnitude as the values previously determined for polyethylene.

Effect of Crystallinity on Solubility. From gas permeation studies with polyethylene and poly(ethylene terephthalate), both in the rubbery crystalline form, it was postulated that these semicrystalline polymers behave like two-phase systems, one phase being completely amorphous and permeable to gases and the other being crystalline and completely impermeable to gases. In polyethylene the data for all gases, with the possible exception of helium, were well correlated by the relation $k = \alpha k^*$, where k^* is the solubility constant in the completely amorphous polymer and α is the amorphous volume fraction. Surprisingly enough, in the case of polyethylene

this relationship was found to be applicable even at high crystalline levels. This observation was unexpected because at the high crystalline levels (70% and greater) one would expect the interlamellar amorphous material to be strained and to show different solution characteristics than the completely amorphous polymer.

Since isotactic polypropylene, like polyethylene, is never completely amorphous in its solid state, atactic polypropylene was used as its amorphous analog. The fact that atactic polypropylene is a simple stereoisomer of the isotactic form and has a refractive index comparable to that of the isotactic form in the molten state² justified this substitution.

Figures 3 and 4 summarize the solubility data for all the films studied in relation to their amorphous content, as determined from density measurements and the assumption of a two-phase system: monoclinic crystallinity and completely amorphous material. If semicrystalline polypropylene were indeed a simple two-phase system, then one would expect the data to fall on a straight line connecting the origin and the point for 100% amorphous polymer. However, it appears that all the quenched films have a solubility significantly lower and independent of amorphous content.

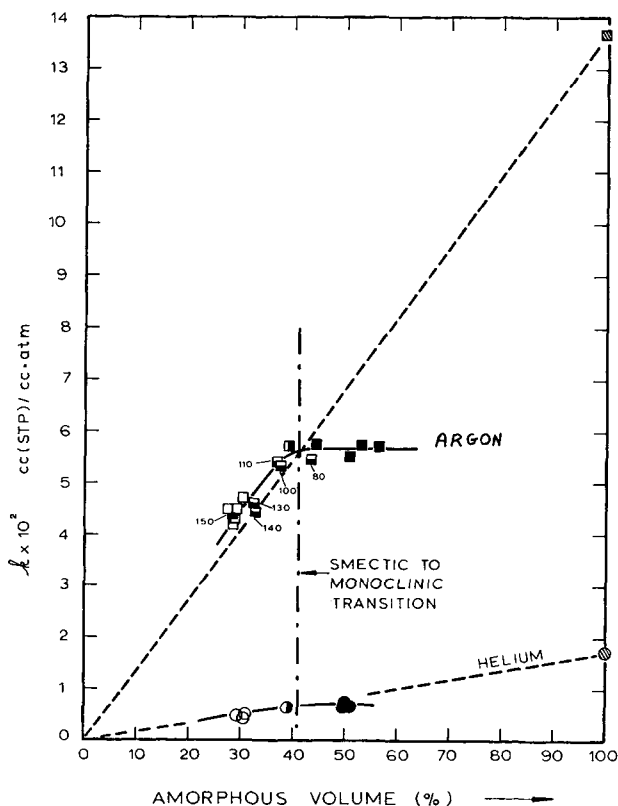


Fig. 3. Solubility constants at 40°C related to amorphous volume.

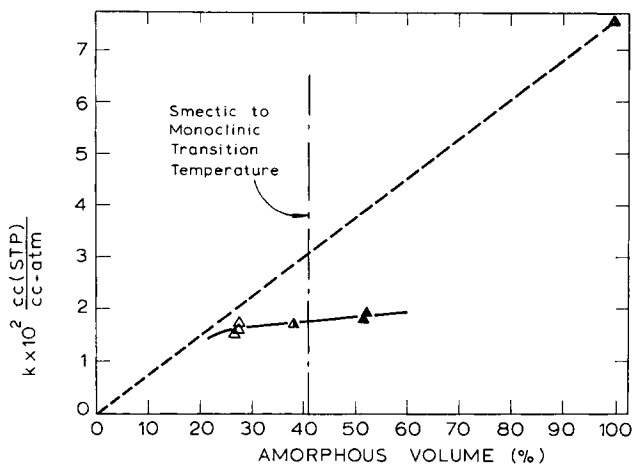


Fig. 4. Solubility constants at 40°C related to amorphous volume for CF_4 .

This difference is greatest for the largest gas molecule, CF_4 , and tends to disappear for the annealed films. In fact, in the case of argon solubility drops off rather suddenly, reminiscent of a phase change, as the polymer is annealed at temperatures at or above 90°C.

The solubility data seem to reflect the observations made by many authors^{12,13,40,41} who, using x-ray diffraction, infrared absorption, NMR, and dynamic mechanical measurements, have found evidence for a second crystalline phase in the quenched polypropylene samples. The most recent DTA and infrared study by Gailey and Ralston¹⁶ of this second crystalline phase has convinced these authors that this crystalline phase consists most probably of hexagonal crystals of an intermediate density (0.907 g/cc) which on annealing, at temperatures greater than 90°C, are converted to the more stable, monoclinic crystal modification.

Thus "rapid" or "moderate" cooling of polypropylene from the melt produces a mixture of monoclinic and hexagonal crystallites, with the ratio of the two being a function of the rate of quenching from the melt. For some as yet unknown reason, the total amount of crystallinity appears to be fixed at approximately 59% by volume; i.e., the level at the breakpoints in Figures 3 and 4. Since both morphological forms are crystalline, it is not unreasonable to suggest that both forms are impermeable to gas, thus accounting for the constant solubility up to the point where films were either slowly cooled from the melt or annealed at temperatures greater than 90°C and only the monoclinic crystal mode is known to exist.

The concept of a distinct "quenched" phase of most probably very small hexagonal crystallites is further supported by the fact that the x-ray diffractions (see Figs. 5 and 6) of film 2, a rapidly cooled sample, showed the typical two, broad scattering maxima which many authors^{12,16,17} have attributed to hexagonal crystals of very small size.

The observation that the argon solubility of the annealed samples is

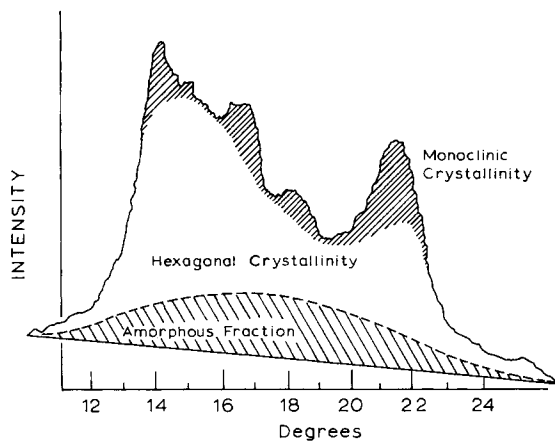


Fig. 5. X-ray diffraction curve of film 2, (a sample of rapidly cooled, isotactic polypropylene).

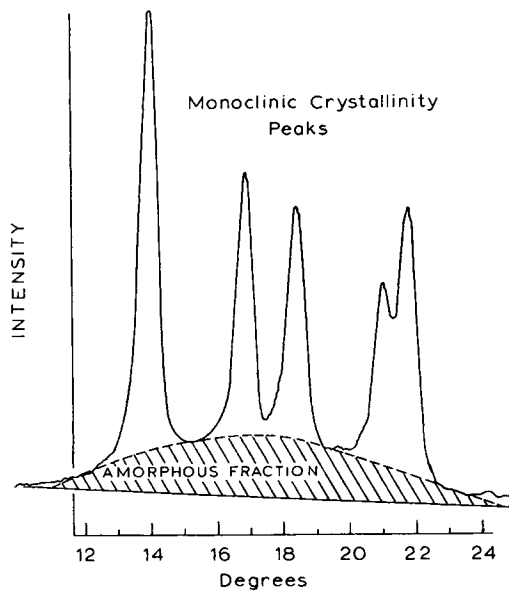


Fig. 6. X-ray diffraction curve of film 5, (a sample of rapidly cooled isotactic polypropylene subsequently annealed).

slightly higher than what one would predict on the basis of two, well-segregated phases is most probably due to local variations in the cohesive energy density (CED) of the intercrystalline, amorphous material.

The solubility of helium is intrinsically quite low and only slightly lower in the quenched material. Nevertheless, the data for helium do show the same break at the 41% amorphous contents and the approach to normal two-phase solution behavior at levels of α less than that.

The observation that, in the case of CF_4 which was the largest molecule studied, the solubility of the annealed samples only approaches the two-phase solubility curve is probably the result of inaccessibility; namely, the large CF_4 molecule is excluded from some regions of the intercrystalline amorphous material, and the solubility never reaches the level commensurate with the volume fraction of amorphous material actually present.

Relation of Solubility to Gas Molecular Parameters. Ideally, one would like to be able to predict the permeability of a given membrane to a given gas from well-known parameters of the membrane and the gas, such as the cohesive energy density of the polymer and the force constant of the gas. In the case of polyethylene, successful steps have been made in this direction by developing a technique⁴² to predict the solubility of the completely amorphous film, k^* , thence estimating the solubility of the partially crystalline film from the relationship $k = \alpha k^*$.

As was seen above, the solubility behavior in polypropylene is complicated by the presence of the second crystal mode. However, at least for the annealed and slowly cooled samples, the solubility is approximated by the relationship $k = \alpha k^*$.

The idea that the solubility of a gas in the polymer can be related to the force constant of the gas was initially proposed by Jolley and Hildebrand,⁴³ who found that the solubility constants of various nonpolar gases in nonpolar solvents correlated well with their gas force constants as defined by the Lennard-Jones potential functions.

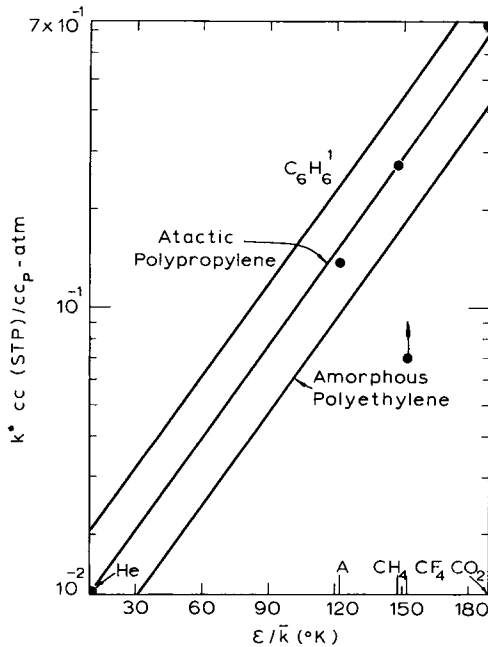


Fig. 7. Correlation of solubility constants at 25°C.

Such a correlation was attempted for the solubility of the various gases in atactic polypropylene and it was found (Fig. 7) that the data for atactic polypropylene fall on a straight line lying parallel to—and midway between—lines obtained by Jolley-Hildebrand⁴³ and Bixler⁴² for C_6H_6 and polyethylene, respectively. This strongly suggests that the process of dissolution in completely amorphous polypropylene occurs by the same mechanism as the dissolution of similar, permanent gases in either nonpolar solvents or amorphous polyethylene. However, the value of k^* for CF_4 falls considerably below this correlation. This discrepancy parallels the behavior observed by Bixler⁴² for SF_6 . Now, as then, the most plausible explanation for this phenomenon is probably the appreciably higher partial molar volume of the fluorocarbons compared to that of other molecules of a similar ϵ/\bar{k} .

Since the enthalpy of sorption is a measure of the degree of interaction between the polymer and the dissolving molecule, an attempt was made to correlate ΔH_s with ϵ/\bar{k} . In the face of the successful correlation of k^* with ϵ/\bar{k} and the inherent connection between solubility and enthalpy of sorption, it was believed that ϵ/\bar{k} should correlate ΔH_s just as well. Figure 8 is the resulting plot with the data for linear poly(ethylene) as background. The average values of ΔH_s for helium and argon fit the best line through the poly(ethylene) data very well. This observation reflects the nearly identical values of the cohesive energy density of the two polymers, i.e., 62.3 and 65.6 cal/cc for polyethylene⁴⁴ and polypropylene, respectively. For both polymers, ΔH_s becomes increasingly negative, or exothermic, with increasing ϵ/\bar{k} . However, as before, the value for CF_4 is anomalous, in that ΔH_s is endothermic. Initially, it was considered that the high positive value of ΔH_s for CF_4 was due to a steric effect, in that the large CF_4 molecule may be

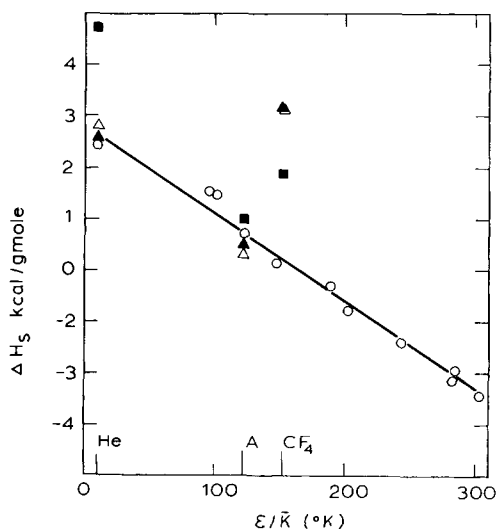


Fig. 8. Heat of sorption related to force constant of gas.

physically barred from some of the intercrystalline amorphous sites due to its size. If so, then at higher temperatures, these sites should become accessible due to thermal expansion, giving rise to the larger positive heats. However, this possibility was eliminated by the observation that the ΔH_s for the completely amorphous material, i.e., the atactic polypropylene, was similarly positive, contrary to other gases of comparable ϵ/\bar{k} values.

Solubility in Glassy Polypropylene. With the glass transition of semicrystalline polypropylene in the vicinity of 0°C ,⁴⁵⁻⁴⁸ it is conceivable that in some of its applications polypropylene will be used below its glass transition temperature. The work of Meares⁴⁹ and Vieth⁵⁰ has shown that the solubility behavior of the glassy material may be quite different from that of the rubbery material. For this reason, some of the sorption experiments with argon were extended into the glassy region. A plot of $\ln k$ versus $1/T$ for argon (Fig. 9) reveals a definite break at the glass transition point, with the solubility in the glassy polymer being considerably higher than what one would predict on the basis of an extrapolation from the rubbery region. This points to the existence of "frozen-in" microvoids or holes, much like those observed in poly(ethylene terephthalate), in which sorption takes place by ordinary dissolution plus a Langmuir-type of sorption process. The higher-than-predicted solubility below T_g is thus probably made up of two sorption processes, a contribution from ordinary solution and a contribution from a Langmuir-type of adsorption process in the microvoids. However, while for poly(ethylene terephthalate) it became possible to separate the two solution processes, this was not directly possible with polypropylene. A possible explanation for this may be the low interaction of the inert argon with the nonpolar polypropylene. Nevertheless, the sorption experiments performed over the extended pressure range; i.e. up to 30 atm, did check the applicability of Henry's law. It was found that the

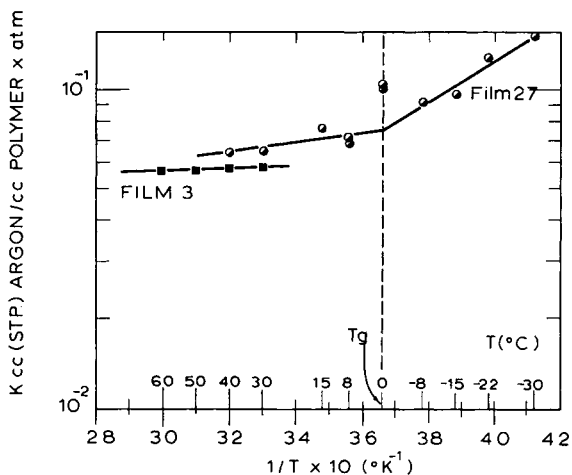


Fig. 9. Argon solubility constants from high-pressure sorption experiments.

solubility was directly proportional to pressure over the entire temperature range from -30°C to 40°C .

Entropies of Solution. An additional attempt toward better understanding of the solution of gases in a polymer consisted of an evaluation of the entropies of solution. Jolley and Hildebrand⁴³ found a remarkably good correlation between the entropy of solution ($\bar{S}_2 - S_2^g$) of various gases and their mole fraction ($R \ln x_2$) in a nonpolar solvent. Again, it was found that an equally good correlation (see Fig. 10) exists for the solution of He, A,

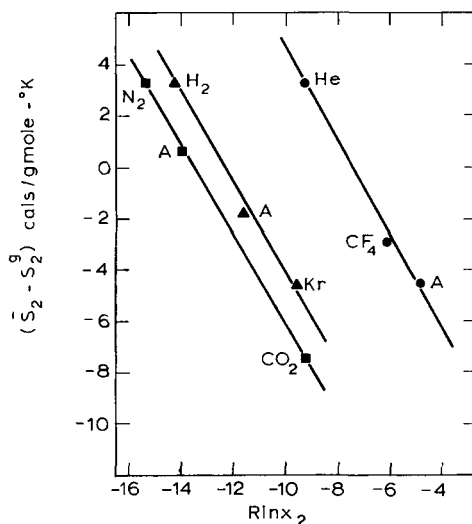


Fig. 10. Entropy of solution related to mole fraction in solution.

and CF₄ in polypropylene. In fact, the line of the data for polypropylene was parallel to the lines for various hydrocarbon solvents, as shown by Jolley-Hildebrand.⁴³ From this one can conclude that gas dissolution in polypropylene is much like that in a regular solution.

Diffusion Constants

Temperature Dependence. Without exception, the temperature dependence of the diffusion constants of He, A and CF₄ in semicrystalline polypropylene was described by the Arrhenius relationship $D = D_0 e^{-E_D/RT}$ over the temperatures 30 – 70°C . Typical data are shown in Figures 11–13. Activation energies for diffusion were essentially independent of polymer thermal history and crystalline content, and averaged 4.7 , 11.5 , and 15.7 ± 0.3 for He, A, and CF₄, respectively. These values are somewhat higher than those reported for similar gases in polyethylene but are typical in magnitude for an activated diffusion process.

In Figure 14 are plotted the activation energies as a function of the diameter of the diffusing gas molecule for both quenched and annealed isotactic polypropylene as well as atactic polypropylene. The observation that,

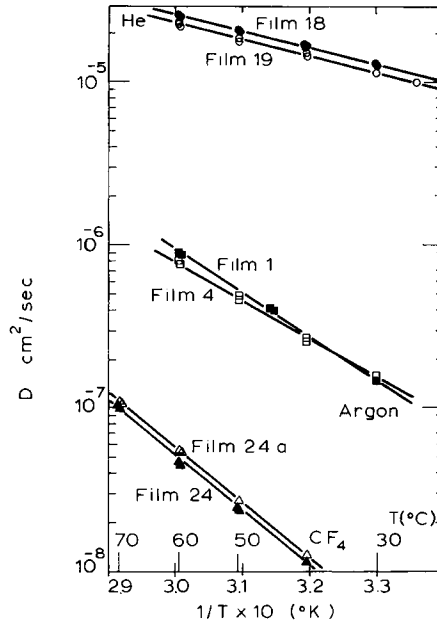


Fig. 11. Diffusion constants in rapidly cooled films.

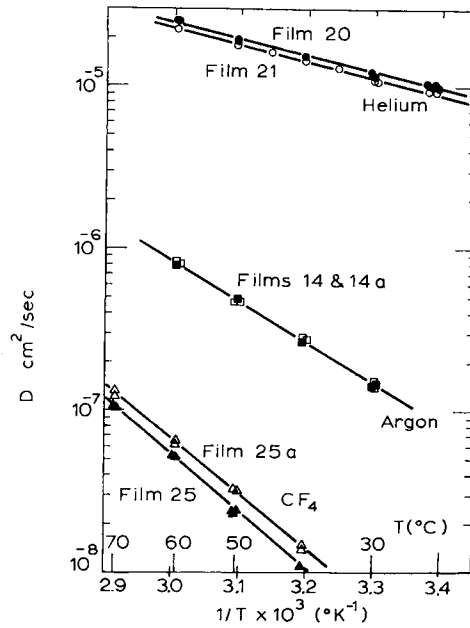


Fig. 12. Diffusion constants in moderately cooled films.

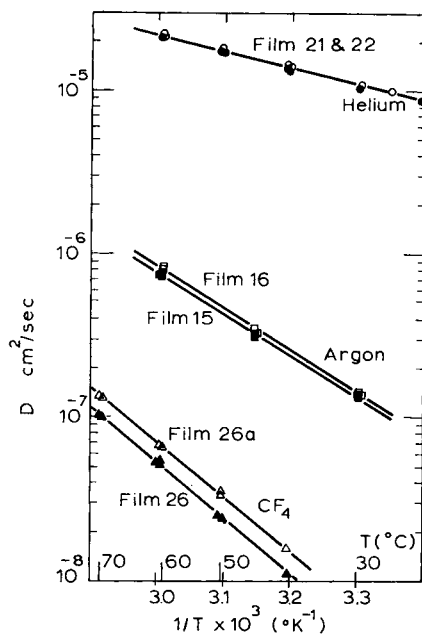


Fig. 13. Diffusion constants in slowly cooled films.

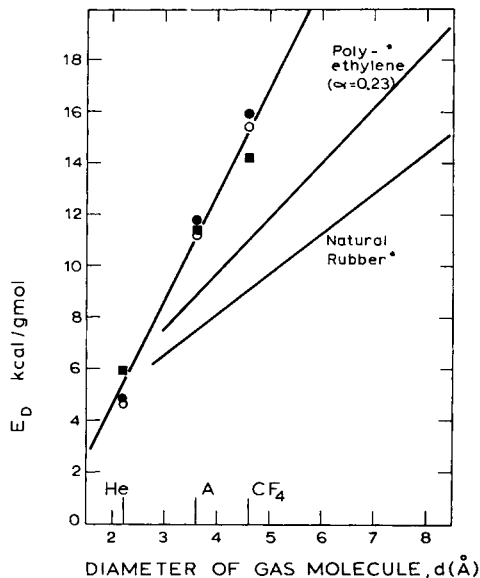


Fig. 14. Activation energy for diffusion related to the size of diffusing molecule.

within precision limits, a single straight line fits all data equally well is somewhat unexpected in the light of the high crystalline content of some samples. For if the crystallites do, indeed, have a “crosslinking” effect on the interlamellar amorphous regions, one would expect lower activation en-

ergies for the completely amorphous and less crystalline films. For this reason, as already suggested by Michaels et al.,⁵ it is probably more accurate to regard β , the chain immobilization factor, as a geometric impedance term which reflects the fact that the interlamellar distances are never much larger than the dimensions of the activated zones associated with the diffusion of gas molecules.

In comparison with natural rubber and polyethylene, the values of E_D for polypropylene are all higher and show a more marked dependence on gas molecular diameter. The higher values most probably reflect polypropylene's greater chain stiffness resulting from the chain's propensity to coil and the presence of the bulky methyl groups. In fact, this may be further support for the hypothesis that the chains are coiled in the amorphous as well as crystalline phase.

Effect of Crystallinity. In the past the effect of crystallinity on the diffusion constants has been expressed by

$$(\tau\beta) = D^*/D$$

where D^* is the diffusion constant in completely amorphous polymer at the same temperature. In the absence of completely amorphous isotactic polypropylene, atactic polypropylene was taken as its analog. The parameter τ , referred to as the geometric impedance factor, was proposed to account for the local reduction in the area available for diffusion and for the increased effective path length due to the presence of the crystallites; i.e., the impenetrable crystallites have to be by-passed. The parameter β , on the other hand, was introduced to account for the impedance to diffusion resulting from decreased chain mobility produced by the "crosslinking" effect of the crystallites. For helium, it was assumed that $\beta = 1.0$, whereupon the geometric impedance factor τ could be calculated. In the case of helium diffusion in polypropylene the values of τ determined in this way were plotted against the amorphous volume fraction, α , as shown in Figure 15. For the polymer samples cooled at varying rates from the melt, but not annealed, there is a consistent, logarithmically linear increase in τ with decreasing α , lying essentially midway between the lines reported earlier for linear and branched polyethylene.⁸ The slope of the line is -1.61 , as compared to -1.25 and -1.82 for linear and branched polyethylene, respectively. The most striking observation from this plot is that annealing of a polymer sample is accompanied by a marked reduction in τ , notwithstanding the attendant increase in crystallinity on annealing. For example, a film annealed at 150°C exhibits a measured τ of 3.75, while that predicted for a polymer at this same level of crystallinity, on the basis of the τ versus α correlation for unannealed films, is over 7.2. It is thus obvious that an attempt to predict the gas permeability of polypropylene on a basis of the level of crystallinity alone, without regard to the prior history of the film, will lead to serious error.

The same type of variation of τ with thermal history was observed by Michaels et al.⁵ in annealed films of polyethylene. They found that the

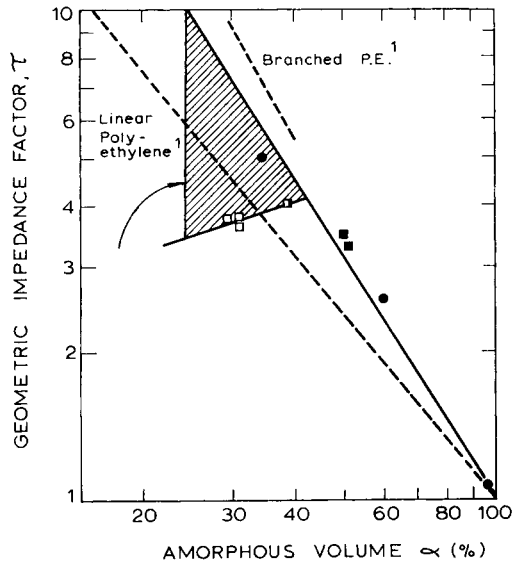


Fig. 15. Variation of τ with α for helium.

tortuosity of annealed film fell far below what one would predict from the values observed for the various quenched films.

In Figures 16-18 are plotted diffusion constants as a function of the per cent amorphous volume. If semicrystalline polypropylene were indeed a

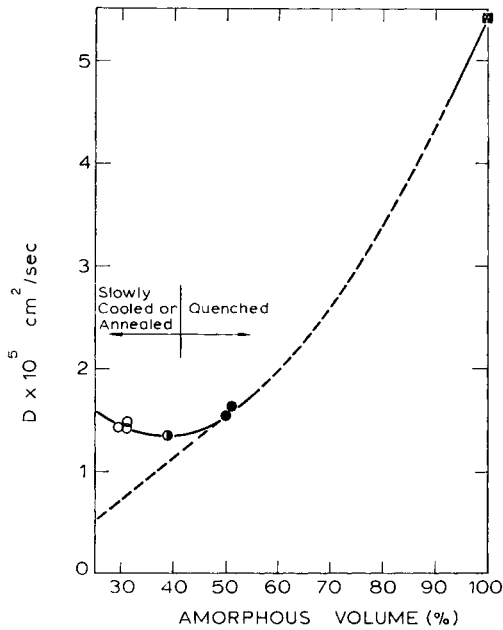


Fig. 16. Helium diffusion constants at 40°C related to amorphous volume

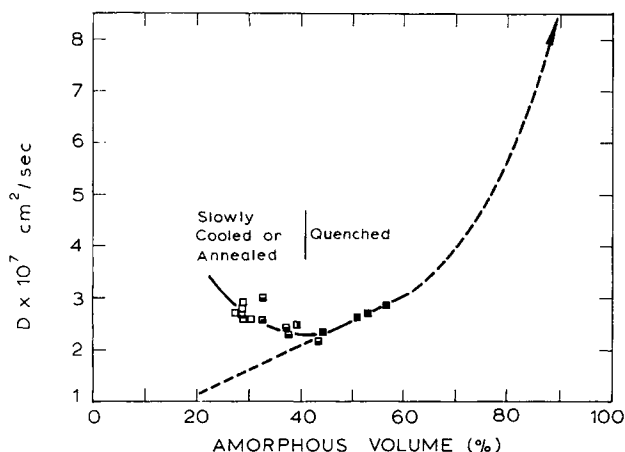


Fig. 17. Argon diffusion constants at 40°C related to amorphous volume.

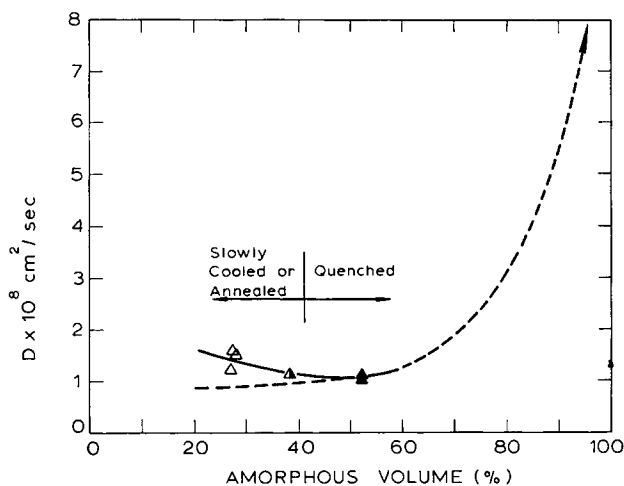


Fig. 18. CF_4 diffusion constants at 40°C related to amorphous volume.

simple two-phase system of impenetrable crystallites suspended in an amorphous matrix, one would expect a continuous decrease in diffusivity as the level of crystallinity increases; instead, one finds that the curve of diffusivity versus percent amorphous volume passes through a minimum and actually increases slightly as samples are annealed above 80°C.

In the light of the morphological changes suggested earlier by the solubility data, the following explanation evolves for the observed diffusion behavior.

Since it is now widely believed that the "quenched" crystal phase consists of very small hexagonal crystals, it is reasonable to suggest that the crystal transformation is accompanied by an association of many minute hexagonal

crystals into larger, but fewer monoclinic crystals. This would be favored thermodynamically and would become kinetically possible as the thermal motion increases during the annealing of the film. The resulting crystals offer more diffusional resistance not only because they are larger but also because they are probably more anisometric. Consequently, the diffusion constants for the unannealed films decrease as the amorphous volume decreases.

As the films are annealed, however, thickening of the lamellae as well as additional crystal growth occur. As discussed earlier, Hoffman and coworkers³⁵ picture the thickening process as one of pulling chain ends into the crystal surface and lengthening of the fold period by migration of the molecules along their own backbones and/or by partial melting and recrystallization with a larger fold-period. As the thickening process proceeds, a chain may be pulled right through a lamella, leaving behind a vacant row. A series of such row vacancies would greatly enhance diffusion, because diffusion through them would presumably no longer have to be activated but could proceed by a nonactivated diffusion mechanism. The increase in D due to such row-vacancy defects overshadows the effect of increased tortuosity completely with the net effect of causing an actual upswing of D in spite of the increasing crystallinity of the film.

The conclusion that crystalline defects rather than changes in the amorphous phase are responsible for the observed diffusional enhancement was reached on the basis of the following analysis. A change in the properties of the amorphous phase, on annealing, should be reflected by a change in the values of ΔH and E_D , a change which should be greatest for the largest molecule, CF_4 . Neither was observed—the values of E_D and ΔH_s did not change significantly on annealing, and CF_4 showed the smallest diffusional enhancement. Thus, the increase in diffusivity in spite of the increased crystallinity must be due to a decrease in the tortuosity of the diffusional path. This, in turn, could occur either by the crystals becoming more isometric or by the formation of crystalline defects large enough to allow passage of the diffusing molecule. The first possibility is unlikely because the crystals are chain-folded lamellae with additional growth at the crystal edges preferred over growth at the crystal faces. Furthermore, as mentioned earlier, observations with single-crystal lamellae of polyethylene have shown that lamellar thickening produced no decrease in the lateral dimensions of the lamella. This strongly suggests the formation of crystal defects, i.e., vacant micropores through the lamellar.

The mechanism of diffusion in the defects is probably non-activated and analogous to gas diffusing in very small pores, i.e., Knudsen-type diffusion, where the diffusion coefficient is a factor of several-fold larger than those measured in this work. However, in annealed films, activation energies equal to those in the unannealed films were observed. This militates against the possibility that there exist interconnected defect pathways through the entire film, but still allows for the existence of noninterconnected defects passing through individual lamellae. This leads to a picture

of diffusion through an amorphous phase containing a suspension of partially permeable crystallites, where the diffusing molecule spends most of its time in the amorphous phase and only occasionally passes through a lamellar defect.

Since diffusion through defects is so much easier than through the amorphous phase, the number of defects necessary to account for the observed diffusional enhancement is governed primarily by the ability of the diffusing molecule to find defects. Unfortunately, it is impossible to establish a realistic two-dimensional model for the size, shape, and orientation of the crystals in an isotropic sample of polypropylene. Therefore, it is difficult to estimate the volume fraction of defects necessary with any accuracy, so that, on the average, a diffusing molecule finds enough defects to reduce its diffusion path length through the membrane; e.g., by 97%, in the case of helium.

However, one can obtain some indication of the volume fraction of defects present from the following analysis. From entropy considerations, one finds that for the gases studied, the length of an average diffusion step in the amorphous phase is on the order of 30 Å, a value which compares well with the value of 27 Å observed by Meares⁴⁹ for similar gases in poly(vinyl acetate).

For a molecule to be never more than one diffusion step length away from a defect, it would require 0.6% defects based on total sample volume. This estimate implies defects of uniform size (4.5 Å in diameter), homogeneously distributed. This is an admittedly over-simplified picture. Nevertheless, this calculation tends to overestimate the volume fraction of defects actually present because the crystalline phase does not act like a sieve as is apparent from the observation that τ is still approximately *four* for the annealed films.

Finally, considering especially the presence of only minor differences (1.9%) between x-ray diffraction and density gradient-method estimates of crystallinity in annealed samples, one is led to the conclusion that a very small fraction of the sample (ca. a few percent) would have to be defective to account for the observed diffusional enhancement.

In addition to estimation of the volume fraction of defects, it is also possible to gain an estimate of their size. Accordingly, this discussion now turns to a consideration of the concept of row vacancy defects in relation to penetrant size. It was postulated that on thickening of the lamella, rows become vacant in the crystal lattice. The chance, however, that two or more adjacent rows are vacated concurrently becomes less and less probable, so that there must exist a size distribution of row vacancies. In other words, diffusional enhancement should depend on the penetrant size and should be smaller for the larger molecules.

Indeed, this is what one observes experimentally for the annealed films. The increase in diffusivity over what one would predict from eq. (2) at the 30% amorphous level, for example, is 97%, 66% and 44% for helium, argon and CF₄, respectively. The diffusivity of the smallest molecule, helium, is enhanced much more than that of CF₄, the largest molecule studied. If one

assumes that the mode of transport in the defects is nonactivated and that, thus, the diffusional resistance in the defects is negligible compared to that in the amorphous regions, it becomes possible to estimate a size distribution for the accessible defects; i.e., defects large enough to accommodate the helium molecule. From the diffusional enhancement for each gas one calculates the reduction in sinuosity of the diffusion path, τ_{eff}/τ , due to the defects and determines the fraction of all defects accessible to each gas. This leads to a cumulative distribution, which yields the desired size distribution by the process of differentiation.

The size of the most common defect appears to be 4.2 Å in diameter, with defects of other size distributed rather evenly around this value. From an analysis of the monoclinic crystal lattice one can conclude that the largest uniform cavity left by the removal of one chain from the lattice is approximately 4.5 Å. Thus, the size of the most common defect compares well with the size of a vacant lattice site and indeed indicates that, a large percentage of the lamellar defects are single, vacant rows in the crystal lattice.

Chain Immobilization Factor. In the light of the morphological picture evolving from the above analysis of the sorption and diffusion data, the parameters τ and β are no longer as easily calculated. Whereas previously it was assumed that the τ for helium is the same for all gases, it now appears that τ is not the same for the three different gases, at least not in the annealed films. This makes it difficult to calculate values of β , the chain immobilization factor, which is defined by the relation $\beta = D^*/\tau D$.

However, if one assumes that in the nonannealed films τ for argon and CF_4 is the same as that for helium, it becomes possible to evaluate β , at least for the nonannealed films.

Figure 19 relates β to the square of the molecular diameter. One finds that β is a strong function of the molecular diameter, with β increasing markedly with increasing molecular size. The same trend was observed for

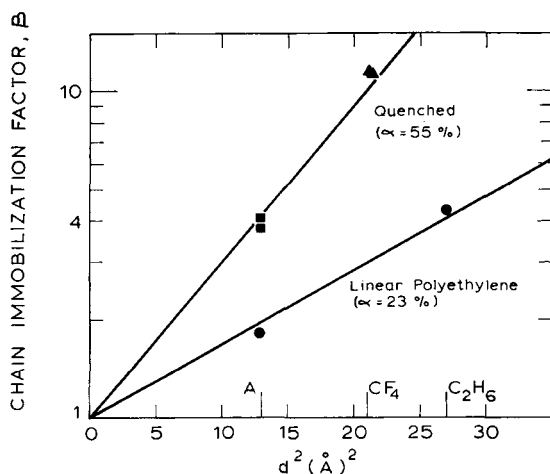


Fig. 19. Variation of β with size of diffusing molecule.

polyethylene.⁸ The marked increase of β with d would lead one to the conclusion that β must reflect the restraint on chain segment mobility arising from the "crosslinking" effect of the crystallites. However, as Michaels et al.⁵ pointed out, if this were the case then one would expect a significant increase in the value of β , as well as E_D , with increasing crystallinity. Neither was observed. The variations in β and E_D , were no greater than the probable error of the measurements, and one could confidently conclude that for polypropylene β and E_0 are essentially constant for each gas and independent of α and the thermal history. These results confirm the conclusions of Michaels et al.⁵ that it is probably more accurate to regard β as an impedance term to diffusion arising from the fact that in the highly crystalline polymer the interlamellar regions "seen" by the diffusing gas molecule are of the dimensions of the activated diffusion zones for these molecules.

Polymer Characterization

Polymer characterization of the melt-crystallized film samples has on the whole proven difficult. However, low angle x-ray diffraction provided valuable evidence for the presence of the hexagonal crystals in the unannealed samples. Similar analysis of an identical sample annealed at 150°C showed the complete absence of the hexagonal phase and provided an estimate of extent of monoclinic crystallinity which was in good agreement with that predicted by the density-gradient method.

All films showed a more or less well defined spherulitic structure readily visible in the polarizing microscope. The spherulites were characteristic in appearance and were seen as circular birefringent areas with the typical Maltese cross patterns. However, the ring structure observed for poly(ethylene) and associated with a periodic twisting of the lamellae was absent.

It was hoped that careful examination of film samples under crossed polarizers would make it possible to observe changes in spherulite size and texture which could be related to the thermal history of the films. For this purpose, film samples were ultratomed and viewed in cross section under the polarizing microscope. However, in support of the argument that the transport properties of polypropylene are controlled at a level of microstructure well below the characteristic dimensions of spherulites, it was observed that bulk-crystallized polypropylene has a spherulitic structure whose size and texture do not change on annealing.

CONCLUSIONS

The principal conclusions are as given in the abstract. Possibly the two major contributions of this study were one, the accumulation of further evidence for the existence of a less stable, hexagonal crystal form in polypropylene samples quenched from the melt, and two, the conclusion that the formation of row-vacancy defects in the crystal lamellae provides low ac-

tivation energy pathways responsible for the unexpected diffusional enhancement observed for the annealed films.

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