# Anionic Copolymers of Octanelactam with Laurolactam (Nylon 8/12 Copolymers). VII. Study of Diffusion and Permeation of Gases in Undrawn and Uniaxially Drawn (Conditioned at Different Relative Humidities) Polyamide Films

IOANNIS ARVANITOYANNIS[1,*] and JOHN M. V. BLANSHARD[2]

[1]Institute of Polymer Technology & Materials Engineering (I.P.T.M.E.), University of Technology, Loughborough, Leicestershire, LE11 3TU United Kingdom; and [2]Department of Food Science, School of Agriculture, University of Nottingham, Sutton Bonington, Loughborough, Leicestershire, LE 12 5RD, United Kingdom

## SYNOPSIS

The permeability coefficient of a wide range (0/100–100/0 octanelactam/laurolactam [OL/LL] mol/mol) of novel copolyamides (nylon 8/nylon 12) was determined and related to the diffusion rate over a range of temperatures: $T_g - 30$ to $T_g + 40°C$. An inflection in the plot of permeability vs. $1/T$ (K) provided an indirect indication of glass transition value and agreed satisfactory with DSC and DMTA measurements. Both uniaxially drawn and undrawn membranes were evaluated and the permeability values were correlated with the % crystallinity. The reduction in solubility, diffusivity, and permeability with increasing draw ratio was attributed to a substantial increase in % crystallinity. Finally, the effect of absorbed water on gas permeability of polyamide films was examined. In most homopolyamides and copolyamides, the higher the water absorption of films the higher the permeability values. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The synthesis and characterization of a new series of statistical copolyamides obtained by anionic polymerization of octanelactam (OL) with laurolactam (LL) (nylon-8/nylon-12) and some of their general properties have already been reported (Part I) and discussed.[1] In Parts II, III, IV, V, and VI of this series, the kinetics of isothermal crystallization, thermal, mechanical, and thermomechanical properties and the annealing effect upon the crystallinity and the decomposition kinetics with thermogravimetry were studied.[2–6]

The commercial applications of the selective permeability of natural and synthetic polymeric films to certain gases have led to several workers investigating the permeability–diffusivity for a wide range of film–gas combinations.[7–18] Particular interest was recently expressed in the effect of cross-linked polymeric films on the diffusivity and permeability of gases.[19–25]

It is generally accepted that Fick's law of diffusion applies to the transmission of gases through a film from one side to the other side. Consequently, the solubility and the rate of diffusion of a gas through a polymer are of major importance to the process of permeation. The following definition is given for permeability ($q$) or permeation coefficient:

$$q = \frac{P \cdot (p_1 - p_2) \cdot A \cdot t}{d} \tag{1}$$

where $q$ is the quantity of permeating gas, $A$, the area of the film; $P$, the permeability coefficient; $P_1$ and $P_2$, the pressures on either sides of the membrane; $d$, the thickness of the membrane; and $t$, the time.

The diffusivity ($D$) or diffusion coefficient may be extracted from the following equation:

$$D = \frac{1}{6}\frac{\delta^2}{\theta} \qquad (2)$$

where $\theta$ is the time lag in the permeation process, and $\delta$, the solubility parameter (the square root of the cohesive energy density). The lag is related to the time required by the gas to establish an equilibrium in an originally gas-free film. The extrapolation of the pressure increase–time curve to the zero-axis will produce the time lag. However, this extrapolation should be made only when equilibrium has actually been attained.[7,8] The definition of solubility ($S$) is as follows:

$$P = D \cdot S \qquad (3)$$

The effect of crystallinity, and its increase by drawing, on the permeation coefficient of gases in polymers has been extensively investigated. In general, an increase in crystallinity—for both natural and synthetic polymers—induces a decrease in permeation.[17,26–28] Enhanced molecular order and a further perfection of crystal size were considered to be the main reasons for the above-mentioned decrease of permeability due to drawing or annealing.[27,28]

However, the actual moisture content of polymeric films was found to be of an importance comparable to crystallinity for the permeability of gas. Conditioning films at different relative humidities substantially affected permeability values. The latter either increased or decreased depending on the mechanism governing the processes of diffusivity, solubility, and permeability.[9–11,13,14]

The aim of the work reported in this paper was

(a) to study the results of diffusion and permeation of a variety of gases ($N_2$, $O_2$, $CO_2$, $H_2$, and He) in copolyamides (OL/LL) both for undrawn and uniaxially drawn films;

(b) to correlate these results with the copolyamide % crystallinity of the copolyamide and the diameter of gas-molecules;

(c) to study the effect of moisture content of the film on the permeability of the films by gases; and

(d) to show the dependence of the activation energy of permeation and diffusion on the molar composition of OL/LL copolyamides.

## EXPERIMENTAL

### Materials

The copolyamide samples used for permeability measurements were similar to those synthesized in a previous publication.[1]

### Techniques

#### Preparation of Samples

Coherent, void-free circular membrane specimens were prepared by compressing a central metal plate with an opening of a circle shape ($d = 4$ cm) into which the polymer sample (approx. 2 g) was placed. Compression was attained by juxtaposing a Teflon sheet on each side of the sample and the metal plates. The whole system was then placed in a hydraulic press (Edwards, U.K.), the plates of which had been heated at $T = T_m + 20°C$. While the sample was melting, a pressure of 560 N m$^{-2}$ was applied for 20 min. The heating was stopped after 20 min and the plates were cooled down to room temperature by passing tap water through the interior tubes. The resistant-molded samples of the polyamides were a white–yellow color. Five to six samples were tested over a range of molar compositions of copolyamides. The thickness of all the samples was measured at different points with the aid of a micrometer and their average value was used to calculate the cross-sectional area.

#### Uniaxial Drawing of the Films

The drawing was carried out by a solid-state extruder.[29–31] Each polyamide film was inserted into split high-density polyethylene (HDPE) billets that were press-fitted into the barrel of an Instron rheometer. The billet assemblies were then pushed through conical brass dies of 20° including the entrance angles at 180° and 90 for the copolyamides and polyethylene, respectively. The draw ratio was determined from the ratio of the displacements of ink markers in the films before extrusion ($R_1$) and after extrusion ($R_2$), i.e., $\lambda = R_1/R_2$.[17,18]

#### Conditioning of Samples at Different Relative Humidities

Saturated solutions of various salts in water were used to obtain known relative humidities of air circulated in sealed enclosures that were maintained at a room temperature of $23.0 \pm 1.0°C$ with the aid of an incubator and circulating fan (size 2, Gallencamp). Table I shows the relative humidity of air

**Table I  Relative Humidity (RH) of Air over Saturated Salt Solutions at 23 ± 1°C**

| Saturated Salt Solution | RH (%) |
|---|---|
| Potassium nitrate | 97 |
| Magnesium nitrate | 60 |
| Potassium acetate | 25 |

over saturated salt solutions.[32] The relative humidity was measured with a hygrometer (J 3309-60 LCD Thermohygrometer, Cole-Parmer) according to ASTM (D 4230).[33]

The moisture content of the polyamide samples was determined according to the following two methods:

(a) The polyamide samples were initially dried in a vacuum oven (60°C) to constant weight and then equilibrated over an appropriate saturated salt solution. Usually after 10 days, no further increase in weight was observed.

(b) By using an automatic Moisturemeter (Mitsubishi, CA-05). Samples (10 mg) of every specimen were placed overnight in 2.5 mL of anhydrous formamide. The formamide used to suspend the sample was subsequently titrated; a blank titration of the formamide was also performed. The results showed that the polyamide samples tended to absorb greater quantities of water if they remained in a closed container having solutions of high relative humidity.

### X-Ray Measurements

X-ray diffraction measurements were performed using a Philips PW 10.20 diffractometer from 5–40° (2θ). The crystallinity was determined according to a method previously described.[18,34]

### Measurements of Permeability

The measurements of permeability were carried out using a Davenport apparatus for permeability coefficient measurements, which had been connected to a PC/2 IBM according to ASTM D1434-66.[35]

## RESULTS

Figures 1–10 show the effect of temperature, in conjunction with molar composition (OL/LL), on the permeability and diffusivity of $N_2$, $O_2$, $CO_2$, $H_2$, and He gases in copolyamides OL/LL. Figures 11 and 12 and Table II give the values of the glass transition temperature $(T_g)$ determined from permeability measurements and those determined by DSC and DMTA for comparison. $T_g$ is defined as the intersection of the extrapolation of lines 1 and 2 (Fig. 11, see He).

Figures 13 and 14 and Table III show the effect of draw ratio, in conjunction with molar composition (OL/LL), on the permeability and diffusivity of $N_2$, $O_2$, $CO_2$, $H_2$, and He gases in copolyamides OL/LL. Figures 15 and 16 and Table IV show the effect of absorbed water on gas permeability after having conditioned the polyamide films at environments of different relative humidities. Finally, the values of the permeability, diffusivity, and activation energies $W$ and $E$ (permeation and diffusion, respectively) vs. the composition of OL/LL copolyamide samples are given in Tables V and VI and Figures 17 and 18.

## DISCUSSION

### Effect of Molar Composition of Copolyamides (OL/LL) on Gas Permeability in Polyamide Films

It is known that a polymeric film can be plasticized either internally or externally by either having a low degree of copolymerization or by the addition of substances of low molecular weight (plasticizer), respectively. The plasticizer may either reduce the cohesive forces, giving rise to easier penetration by the diffusing species, or may block the filling holes and be adsorbed on active polymer groups (i.e., —OH in cellulose).[9] The validity of the former assumption in the case of copolyamides is evident from both the larger diffusion/permeability coefficient and the lower diffusion/permeation activation energies for the copolyamides of intermediate composition (20/80–20/80 OL/LL mol/mol) (Tables V and VI).

It follows that the occurrence of internal plasticization should be the main reason for allowing a faster diffusion of the penetrant gases (Figs. 1–10). Although according to Arrhenius plots permeability values can be predicted at lower or higher temperatures from the data at any one temperature, any such extrapolation is invalidated within the range of the glass transition temperature $(T_g)$. The observed inflection in the Arrhenius plots (perme-
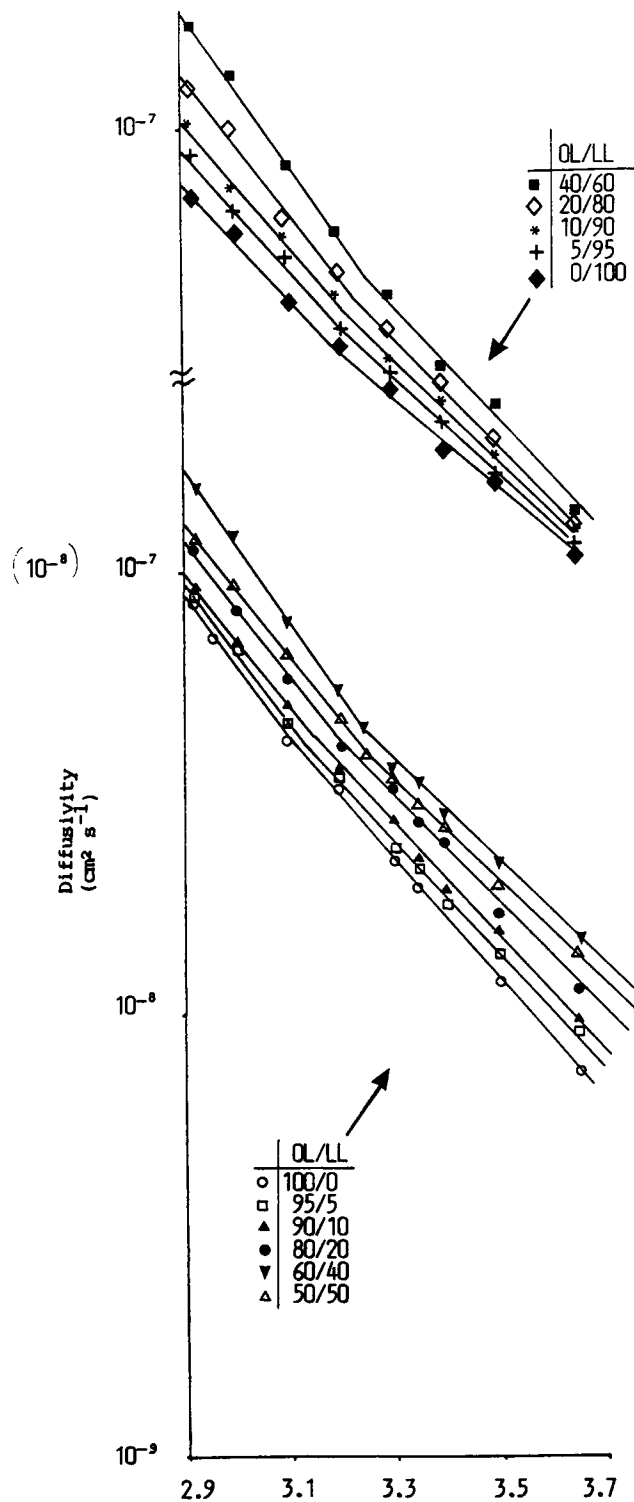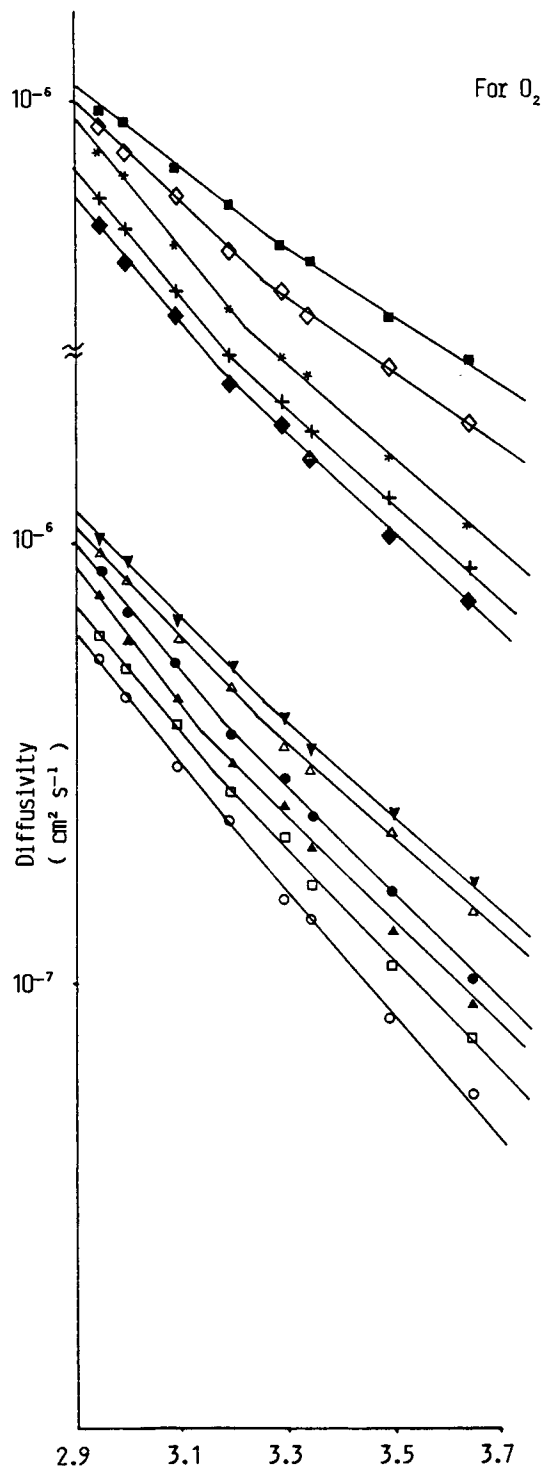
**Figure 1**   Diffusivity of N₂ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [1/T (K)].

ability coefficient vs. 1/T [K]), similar to those obtained by various workers,[13,36] produced values for the glass transition points being in agreement with those determined by thermal (DSC) and thermo-mechanical (DMTA)[34] methods of analysis (Table III).
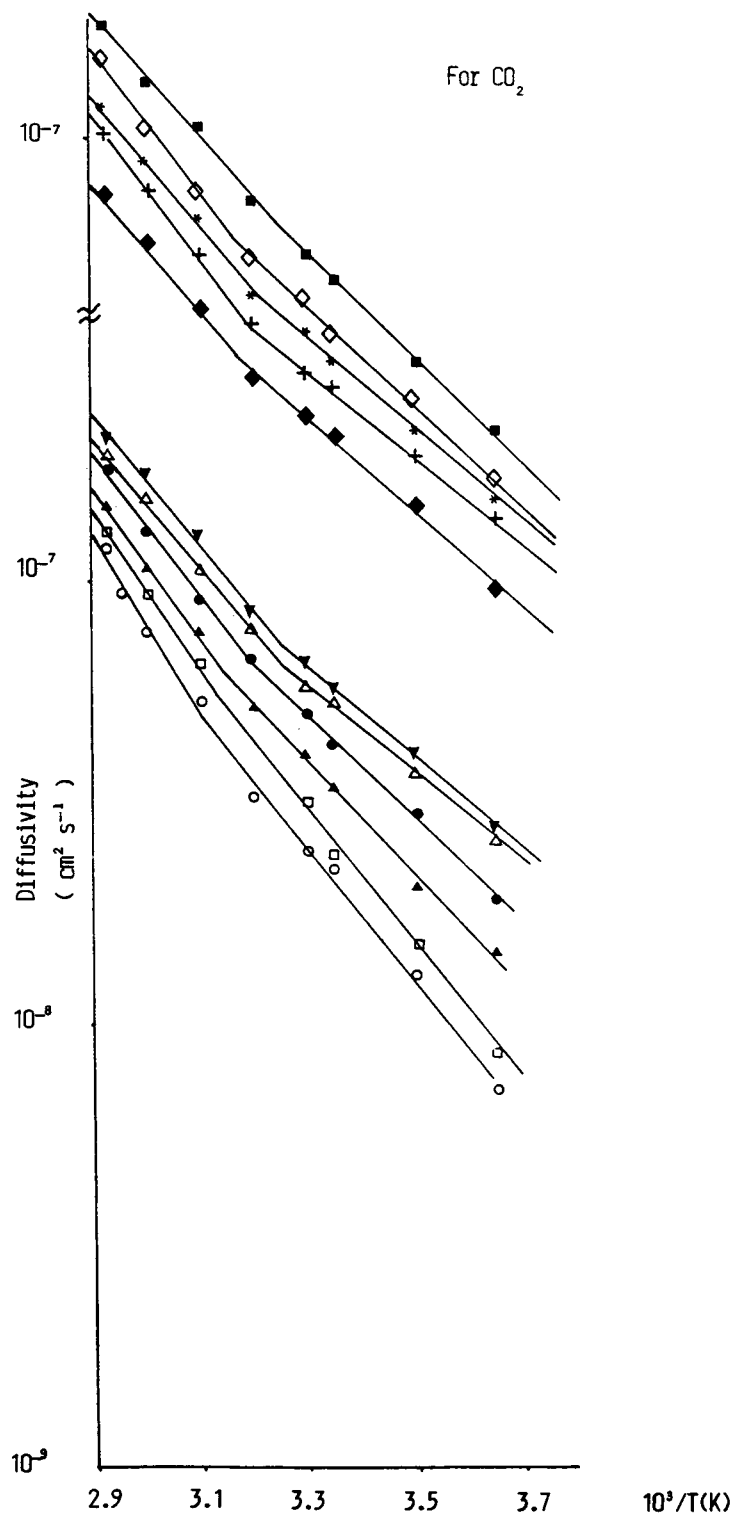
**Figure 2** Diffusivity of $CO_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [$1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

**Figure 3**   Diffusivity of $O_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [$1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.
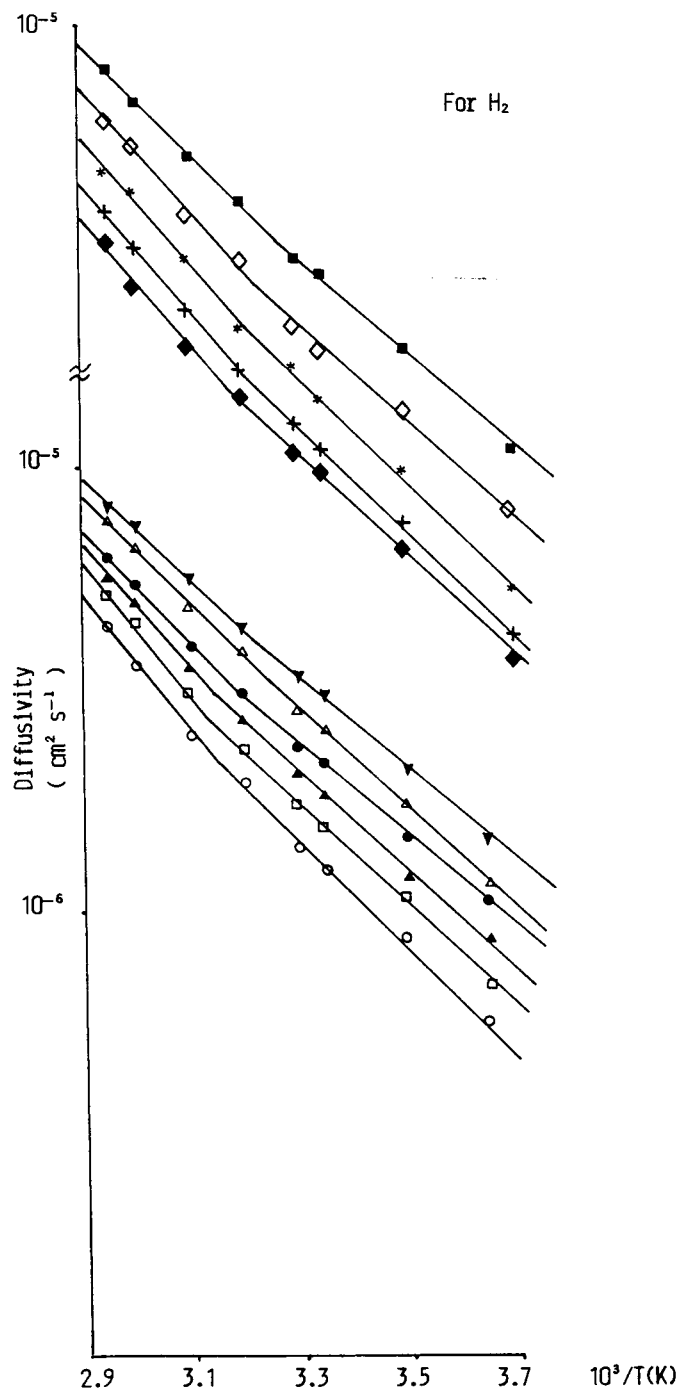
### Effect of Uniaxial Drawing on Permeability

As has already been stated in previous studies,[17,18] the diffusion/permeation coefficient decreases with

draw. The orientational and conformational changes of the polyamide chains caused by drawing are held responsible for the observed decrease in the diffusion/permeation coefficient (Figs. 13 and 14 and

**Figure 4**  Diffusivity of $H_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature $[1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

Table III). The permeation coefficient $(P_g)$ is given by the following expression:

$$P_g = S_a \times D_a/\tau \cdot \zeta \qquad (4)$$

where $D_a$ is the diffusion coefficient in the amorphous phase; $\tau$, the geometrical factor related to the length and cross section of the diffusion trace; $\zeta$, the mobility of the chain segments associated with chain linkage; $S_a$, the solubility coefficient of the small molecules in the amorphous phase; and $x$ the amorphous phase fraction.

From eq. (4) it is evident that in addition to crystallinity orientation and free volume are also important. In fact, the adsorption and absorption of
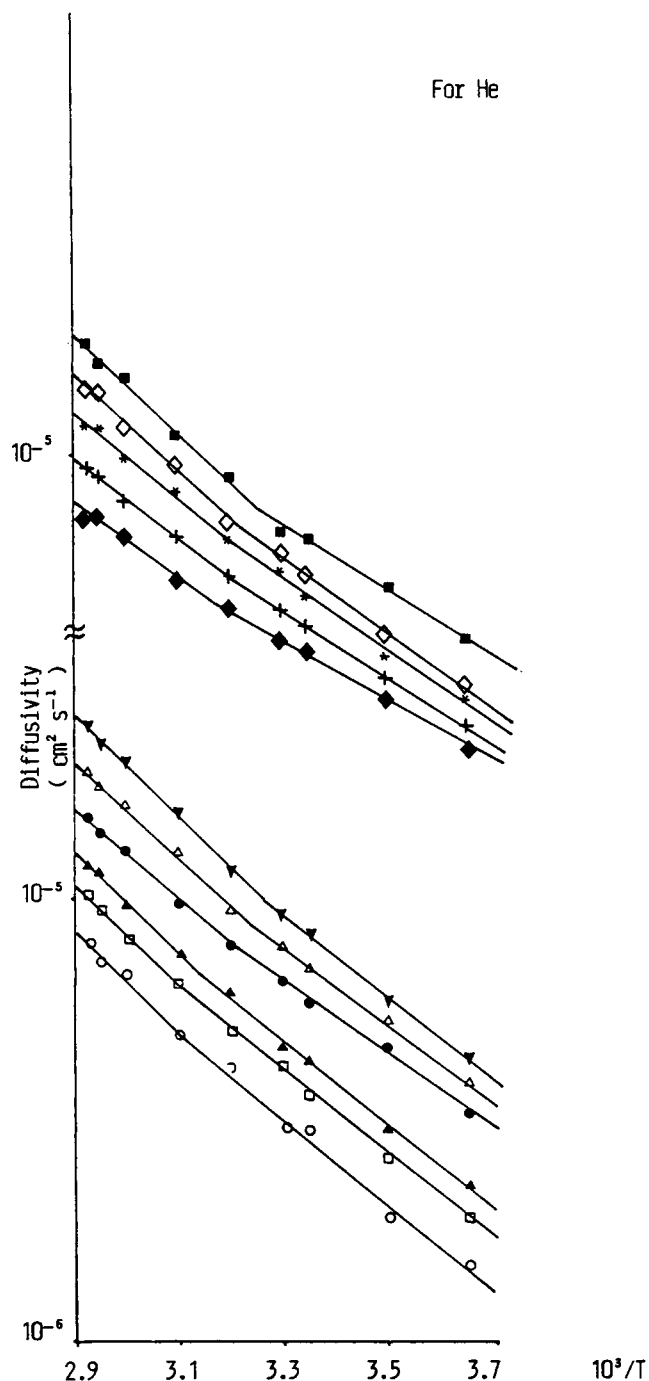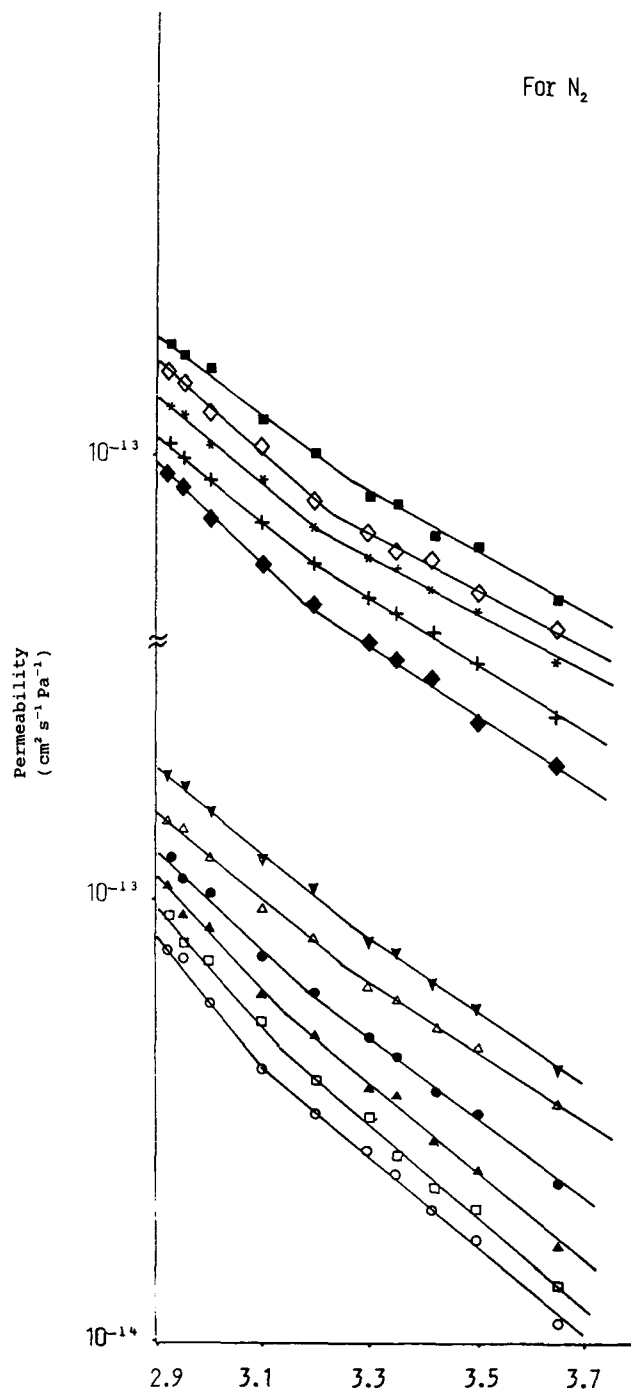
**Figure 5**   Diffusivity of He gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [1/$T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

the gas in the polymer's free volume effectively control the solubility of the gas in the polyamide films.

Despite the pronounced changes observed with minor elastic deformations, an increase in free volume produced higher $D_a$, $S_a$, and $P_g$ values (Table III and Figs. 13 and 14). Within the range of plastic

deformation, the % crystallinity drastically increased and, consequently, diffusion and permeation coefficients substantially decreased (Table III). These results agree with previous studies on the permeability of $CO_2$ in polyethylene (PE) on drawing.[17,37-39]
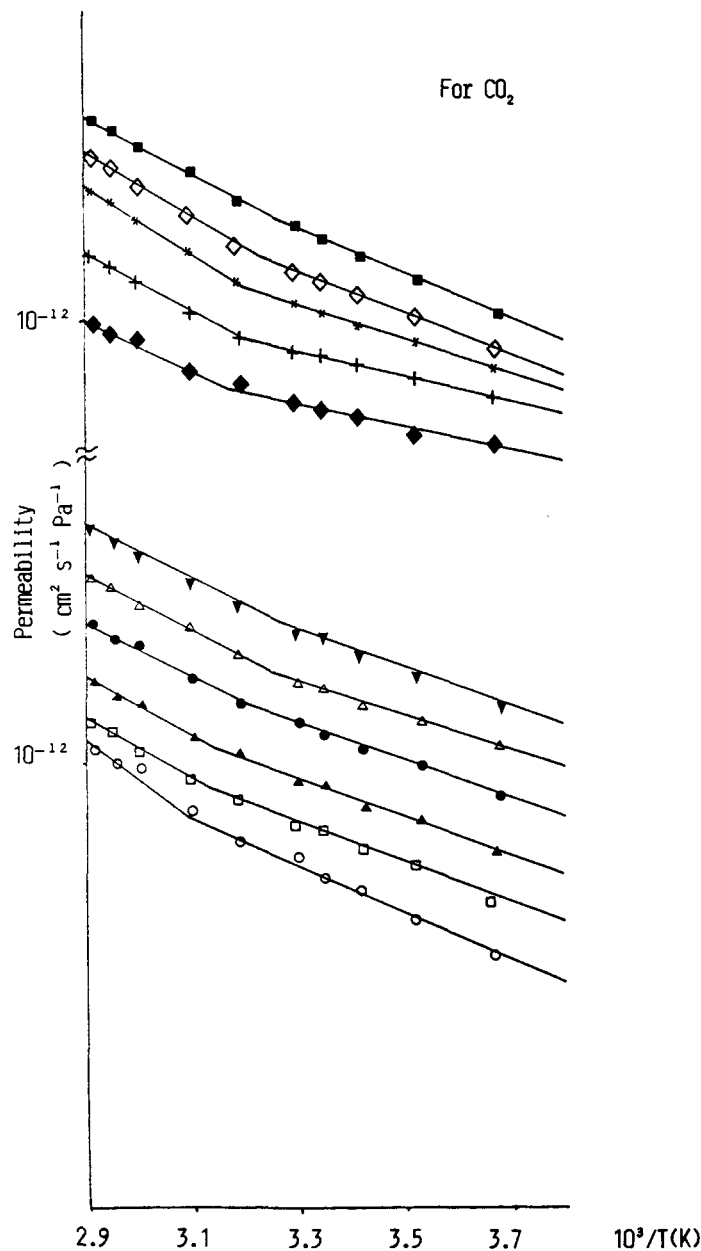
**Figure 6**   Permeability of $N_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [$1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

## Effect of Annealing on the Permeability Coefficient in Copolyamide Films

In the original polyamide samples we suspect that there were a number of intralamellar, amorphous imperfections that could be described as "holes" in the case of permeability measurements. Such a view is supported by the decrease in permeability and diffusivity both with annealing time and temperature as is obvious from Table III and Figures 13 and 14. Annealing tends to reduce considerably the number of imperfections and the % amorphous content by increasing the thickness of the lamellae.[5,15] Previous publications have shown that the lamellar thickness
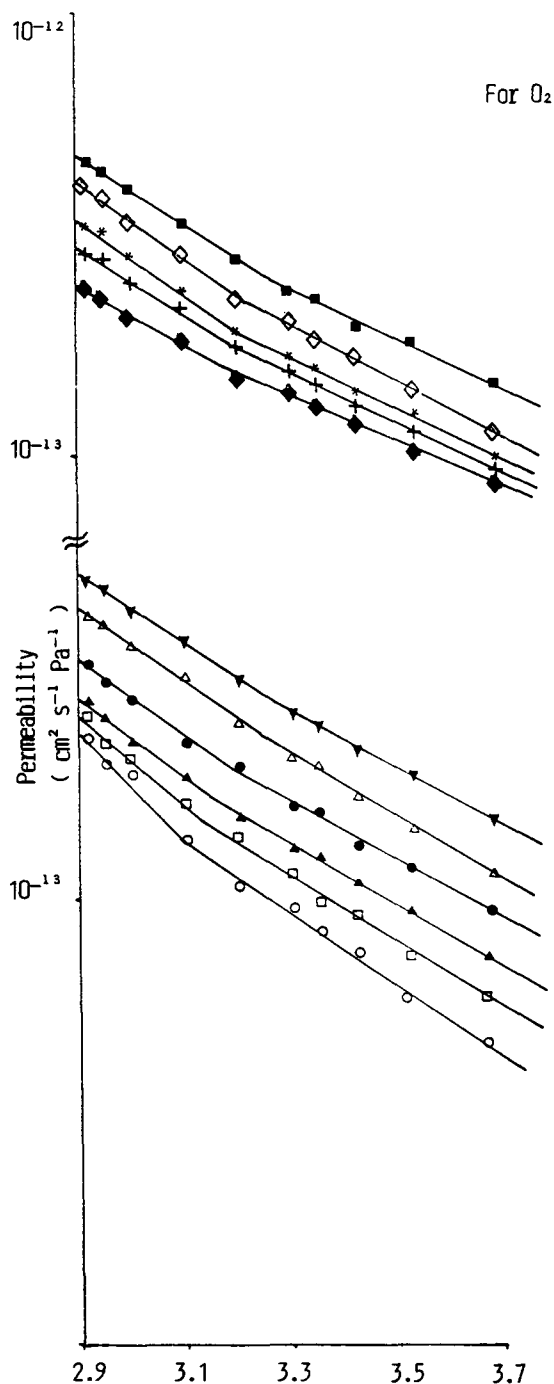
**Figure 7**  Permeability of $CO_2$ gas in copolyamide films OL/LL (0/100-100/0 mol/mol) vs. the inverse temperature [$1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

increases with the temperature of crystallization and the occurrence of heterogeneous crystallization, whereas the existence of steric hindrances reduces the chain mobility, crystal growth, and crystal perfection.[15]

### Effect of Moisture on Permeability Coefficient in Copolyamides

It is generally believed that absorbed water molecules may act as active centers for gas absorption and an increase in gas permeation could be explained in terms of a dual process consisting of solution and evaporation.[7,8,11] Absorption of water incites strong localization of the initially sorbed water over a limited number of sites, whereas higher water contents cause a expansion of the polyamide structure due to swelling of the molecular network and weakening of the inter/intramolecular forces, thereby favoring the development of potential holes. It has been shown that the higher the water content of the film, the higher the permeability [i.e., cellulosic, poly(vinyl

**Figure 8**  Permeability of $O_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature $[1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

alcohol), protein films].[13] It should be noted, however, that the permeability of a wet film is related to the solubility of the permeant gas in water. In consequence, it is desirable to know the relative humidity of the gas and its solubility in water.

It has also been found that the incorporation of wax, plasticizers, and resins induces an increase in

permeability probably due to a disruption of the ordered network. The stronger the interchain forces, the lower the permeability coefficient [i.e., poly(vinyl alcohol) has lower permeability than does polyethylene because the latter is held together only by weak van der Waal's forces]. Another form of plasticization in the film is produced by the presence
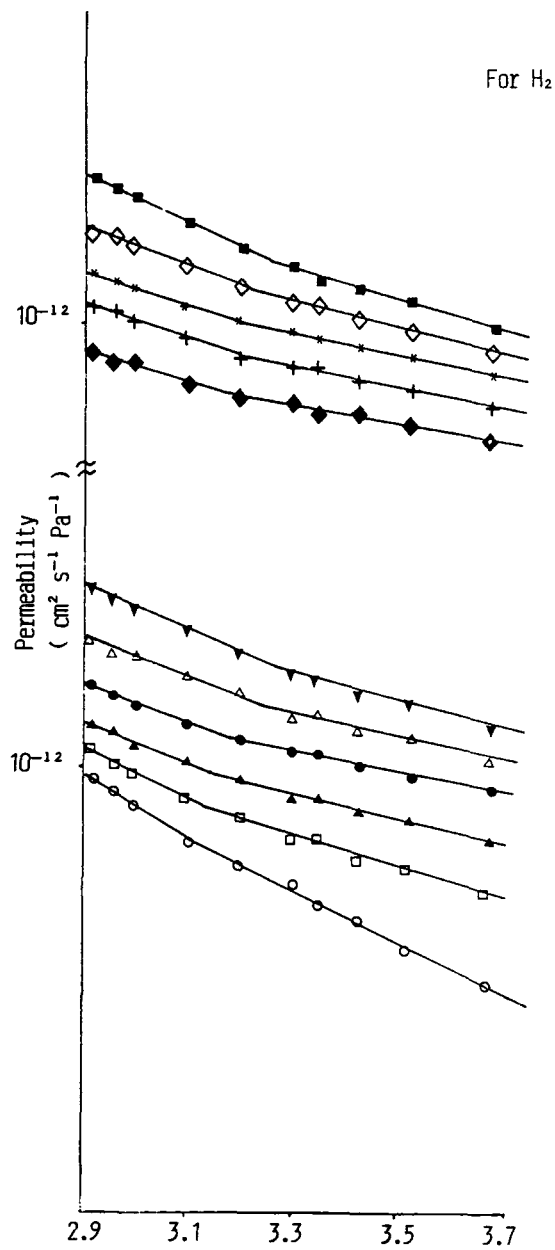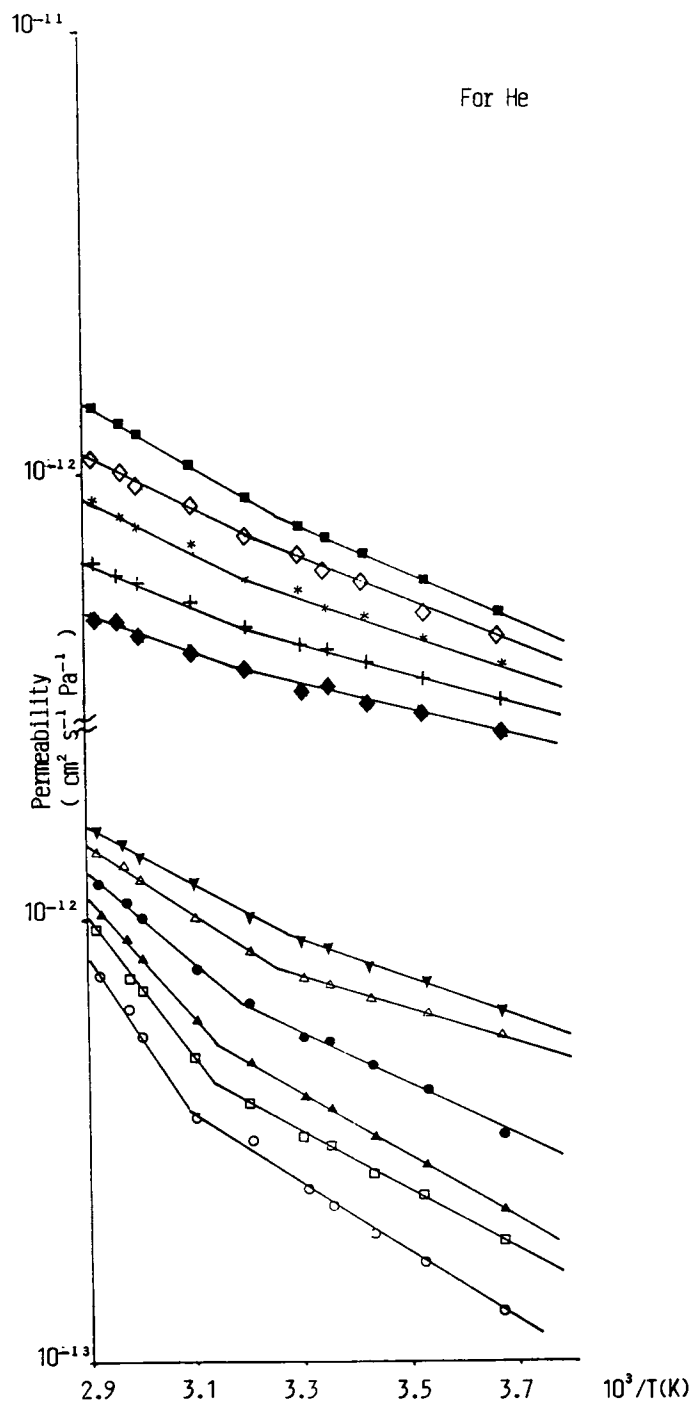
**Figure 9** Permeability of $H_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [$1/T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

of side chains that result in a disruption of polymer intermolecular forces and a consequent increase in path availability. An eightfold increase in permeability (Figs. 15 and 16 and Table IV) was observed for wet films (conditioned at 97% RH) of OL/LL copolyamides, which is in good agreement with the already-found 10-fold increase in permeability already reported for wet nylons 66/610/6 (40/30/30 weight ratio).[9] Such a substantial increase in per-

meability can be attributed to the breaking of intermolecular bonds.[9]

In an effort to provide the reader with (a) the necessary background toward the understanding of the mechanisms of the gas solubility, diffusivity, and permeability procedures in polymeric films and (b) standard values, theoretically calculated, for comparison with our experimentally found ones, it was thought that a brief physicochemical description of

**Figure 10**   Permeability of He gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature [1/$T$ (K)]. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

the above-mentioned procedures and the equations governing them is indispensable. Therefore, the following subsections will be devoted to the accomplishment of this task.

**Theoretical Calculation of Heat of Solution**

It is well known that the solubility of the gas in the polymeric film is the first of the two stages for the
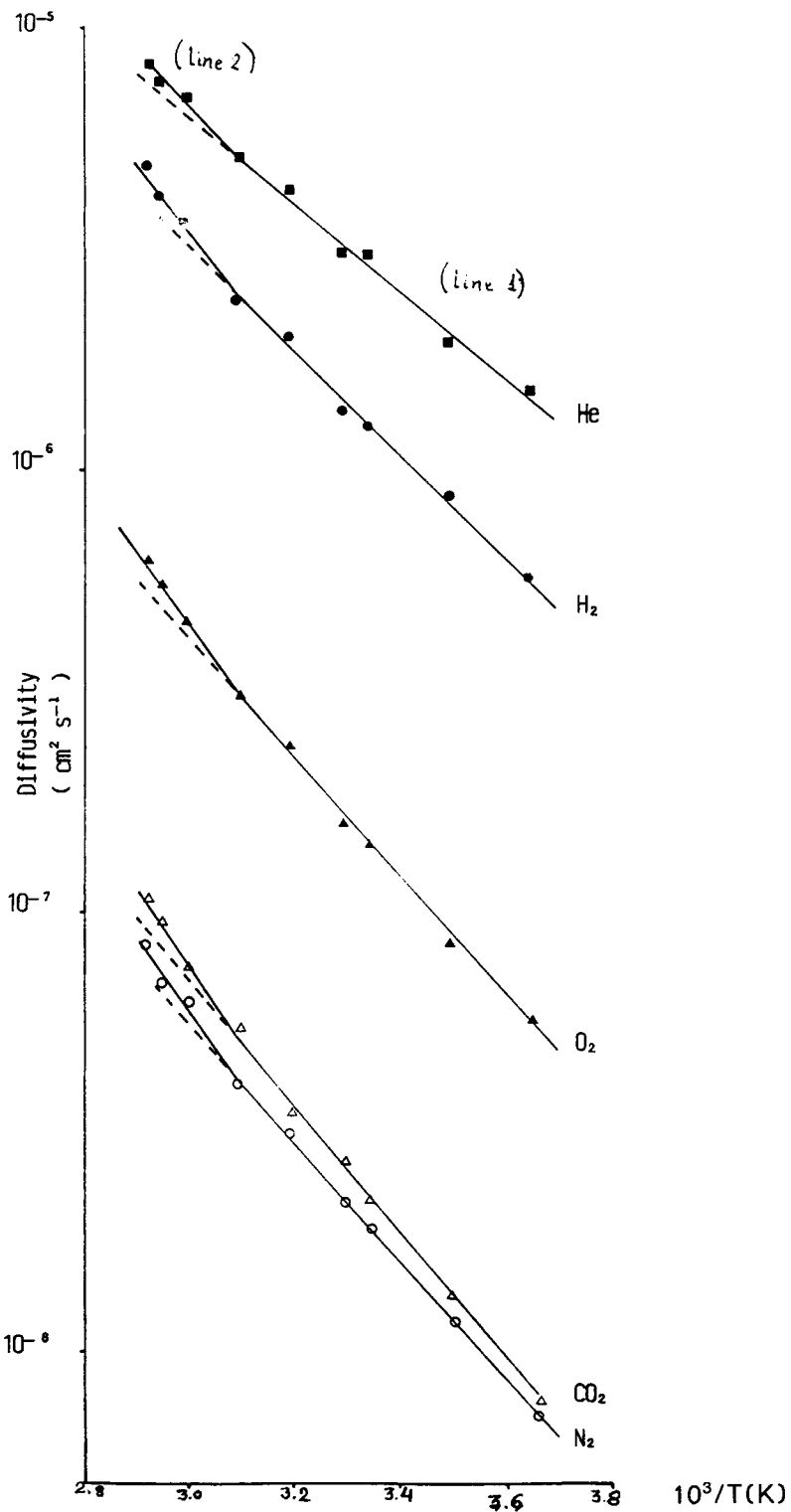
**Figure 11**   Schematic determination of $T_g$ (glass transition) from diffusivity of $N_2$, $O_2$, $CO_2$, $H_2$, and He gas in OL/LL (100/0 mol/mol) copolyamide film vs. the inverse temperature [$1/T$ (K)]. $T_g$ is defined as the intersection of the extrapolation of lines 1 and 2.
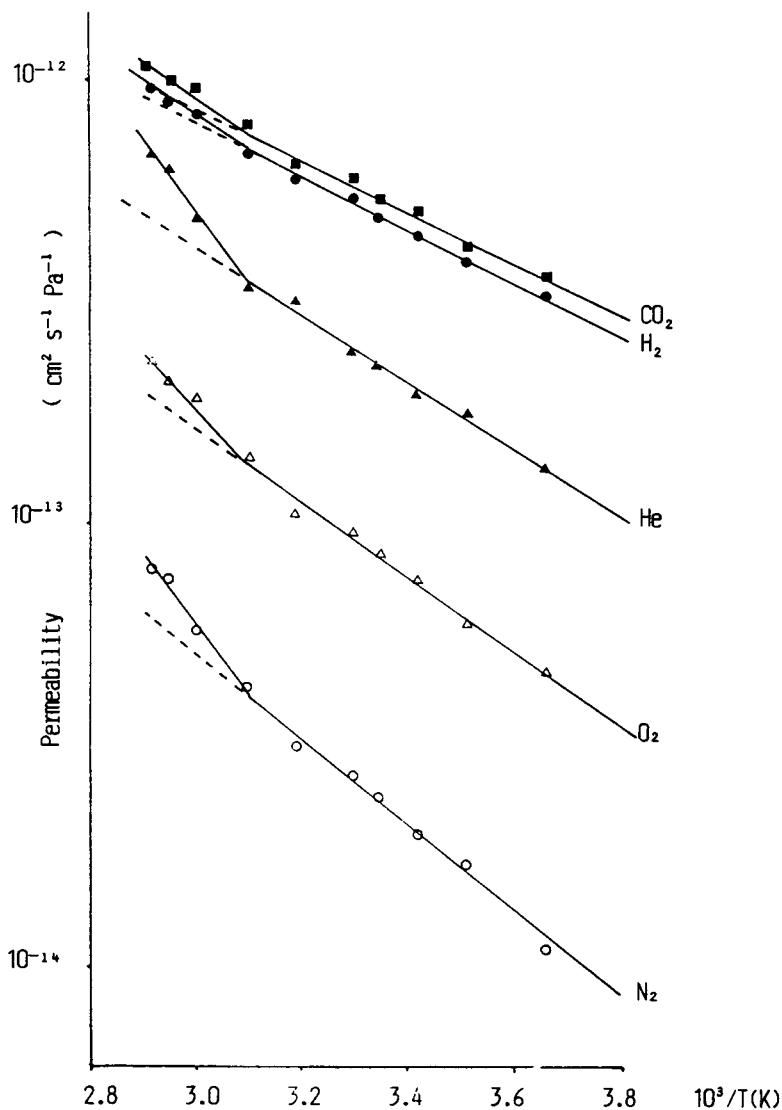
**Figure 12** Schematic determination of $T_g$ (glass transition) from permeability of $N_2$, $O_2$, $CO_2$, $H_2$, and He gas in OL/LL (100/0 mol/mol) copolyamide film vs. the inverse temperature $[1/T \text{ (K)}]$. $T_g$ is defined as in Figure 1.

accomplishment of the gas permeability procedure.[7,8] The heat of solution of the gas in the polyamide can be described with the following exponential eq. (5):

$$S = S_0 e^{-\Delta H/RT} \tag{5}$$

where $S$ is the solubility and $S_0$ is the solubility constant for a particular gas and polymer, and using eq. (3) we see that

$$S_0 = P_0/D_0 \tag{6}$$

where $\Delta H$ = heat of solution; $\Delta H = \Delta H_{cond.} + \Delta H_1$; $\Delta H_{cond.}$ = molar heat of condensation; and $\Delta H_1$ = partial molar heat of mixing of the liquefied gas with the polyamide.

According to Hildebrand,[40] the enthalpy of mixing can be calculated by the following equation:

$$\Delta \bar{H}_1 = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \tag{7}$$

where $\phi_1$, $\phi_2$ = volume fractions of polyamide and gas, and $\delta_1$, $\delta_2$ = solubility parameters of polyamide and gas.

**Table II   Glass Transition ($T_g$) Values from Permeability DSC and DMTA Measurements with the Copolyamide Composition**

| OL/LL (mol/mol) | $T_g$ (°C) Determination from | | | | |
|---|---|---|---|---|---|
| | DMTA[4] | | | DSC[3] | Permeability Measurements |
| | tan $\delta$ | log $E'$ | log $E''$ | | |
| 0/100 | 44.3 ± 0.3 | 39.9 ± 0.3 | 43.3 ± 0.4 | 42.0 | 42.7 |
| 5/95 | 42.6 ± 0.4 | 38.4 ± 0.4 | 40.9 ± 0.5 | 40.5 | 41.5 |
| 10/90 | 41.4 ± 0.4 | 36.8 ± 0.5 | 40.7 ± 0.4 | 39.0 | 40.0 |
| 20/80 | 39.5 ± 0.3 | 34.6 ± 0.4 | 35.8 ± 0.4 | 36.5 | 37.0 |
| 40/60 | 36.7 ± 0.4 | 32.1 ± 0.3 | 34.7 ± 0.4 | 34.0 | 35.2 |
| 50/50 | 36.0 ± 0.5 | 31.8 ± 0.2 | 34.0 ± 0.6 | 33.7 | 34.5 |
| 60/40 | 37.7 ± 0.6 | 33.0 ± 0.2 | 35.9 ± 0.5 | 35.0 | 35.0 |
| 80/20 | 43.4 ± 0.7 | 38.8 ± 0.3 | 40.7 ± 0.5 | 41.0 | 41.5 |
| 90/10 | 48.0 ± 0.6 | 43.9 ± 0.4 | 45.8 ± 0.4 | 45.8 | 47.0 |
| 95/5 | 48.9 ± 0.5 | 45.0 ± 0.4 | 47.0 ± 0.6 | 46.7 | 47.5 |
| 100/0 | 53.8 ± 0.6 | 49.2 ± 0.5 | 51.9 ± 0.5 | 51.1 | 51.0 |

The defining equation for the solubility parameter is

$$\delta_1 = (\delta_{d^2} + \delta_{p^2} + \delta_{h^2})^{1/2} \quad (8)$$

where $\delta_d$ = solubility parameter depending on dispersion forces; $\delta_p$ = solubility parameter depending on polar forces; and $\delta_h$ = solubility parameter depending on hydrogen bonding.

The solubility parameter components can be predicted from group contributions using the following equations:[41]

$$\delta_d = \sum F_i / V \quad (9)$$

$$\delta_p = (\sum F_{pi^2})^{1/2} / V \quad (10)$$

$$\delta_h = (\sum E_{h^2})^{1/2} / V \quad (11)$$

where $F$ = molar attraction constant; $E$ = cohesive energy; and $V$ = volume.

Introducing eq. (7) into (8),

$$\Delta \bar{H}_1 = \phi_1 \phi_2 [(\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} - \delta_g]^2 \quad (12)$$

where $\delta_g$ is the solubility parameter of the molecules in the gaseous phase:

$$\Delta \bar{H}_1 = \phi_1 \phi_2 [((\sum F_{di}/V)^2 + (\sum F_{pi}/V)^2 + (\sum E_{hi}/V)^2)^{1/2} - \delta_g]^2 \quad (13)$$

The application of eq. (13) to permanent gases has the inconvenience that the cohesive energy density (C.E.D.) cannot be calculated for these gases at room temperature. At the boiling point of He, $H_2$, $N_2$, and $O_2$, the value of $\delta_g = (E_g/V_g)^{1/2}$ amounts to 0.67, 2.5, 5.9, and 7.4, respectively.[8] However, this value decreases considerably with rising temperature because of a decrease in $E_g$ and an increase in $V_g$.

Another way of determining $H_s$ is with the aid of the equation

$$10^{-3} \Delta H_s / R = +0.05 - 0.010(\epsilon/k) \pm 1.2 \quad (14)$$

In this case,

$$\log S = -6.65 - 0.005(\epsilon/k) \pm 1.8 \quad (15)$$

where $\epsilon/k$ is the Lennard–Jones temperature (K) characteristic for each gas [i.e., $(\epsilon/k)_{He} = 10$, $(\epsilon/k)H_2 = 60$, $(\epsilon/k)N_2 = 71$, $(\epsilon/k)O_2 = 107$, and $(\epsilon/k)_{CO_2} = 195$].[40]

Equations (14) and (15) describe the glassy state and they are applicable in the case of our copolyamides, the $T_g$'s of which are within the range 38–50°C.

A theoretical calculation may be made to determine the solubility of all types of amorphous polymers as follows:
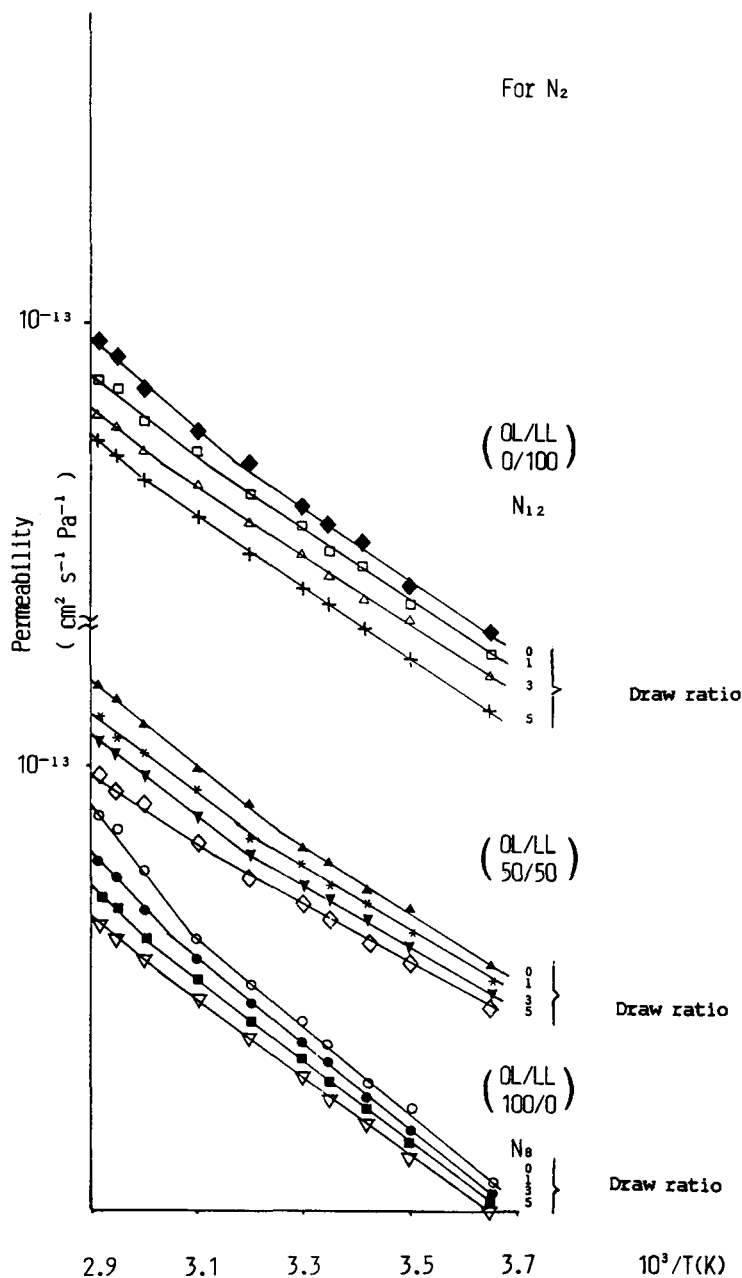
**Figure 13**   Effect of draw ratio on permeability of $N_2$ gas in copolyamide films OL/LL (0/100, 50/50, and 100/0 mol/mol) vs. the inverse temperature [1/$T$ (K)].

$$\log S(T) = \log S(298)$$

$$- 0.435(\Delta H_s/R)(1/T - 1/298) \quad (16)$$

In the case of semicrystalline films (i.e., copolyamides nylon 8/12), Michaels and Bixler[15] showed that the following equation is valid for a wide range of gases:

$$S(298) = S_a(298)(1 - X_c) \quad (17)$$

where $X_c$ = is the degree of crystallinity and $S_a$ = solubility in the amorphous state.

Therefore, e.g., (16) could be modified according to eqs. (17) and (14) or (13), respectively:

$$\log S(T) = \log[S_a(298)(1 - X_c)] - 0.435 \cdot 10^3$$

$$\times (0.05 - 0.010\epsilon/k \pm 1.2)(1/T - 1/298) \quad (18)$$
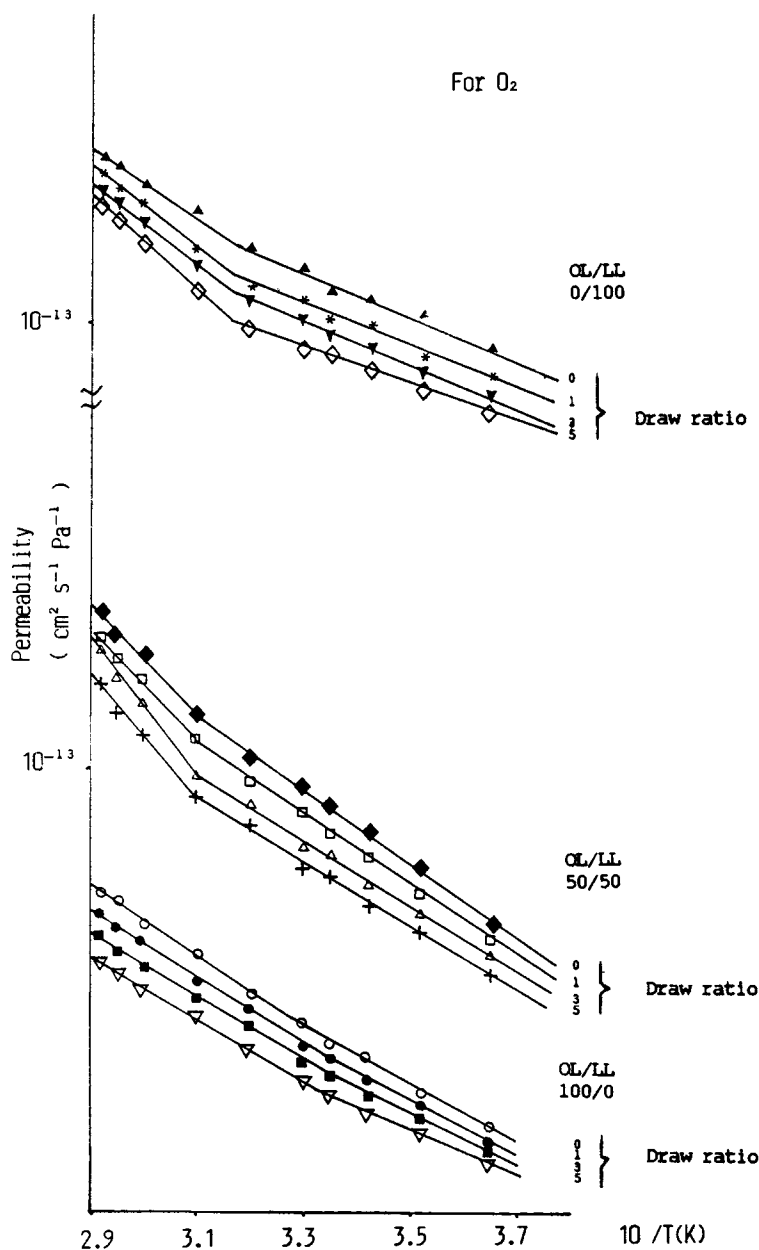
**Figure 14** Effect of draw ratio on permeability of $O_2$ gas in copolyamide films OL/LL (0/100, 50/50, and 100/0 mol/mol) vs. the inverse temperature $[1/T\,(\mathrm{K})]$.

$$\log S(T) = \log[S_a(298)(1 - X_c)] - 0.435$$

$$\times\ (\phi_1\phi_2[((\Sigma F_{di}/V)^2 + (\Sigma F_{di}/V)^2$$

$$+\ (\Sigma E_{hi}/V)^2)^{1/2} - \delta g]^2)/$$

$$R(1/T - 1/298) \quad (19)$$

The three main parameters governing the solution (sorption) process of simple gases could be concisely considered as follows: Lennard–Jones temperature of the gas $(\epsilon/k)$, the glass transition temperature

$(T_g)$, and the degree of crystallinity $(X_c)$ of the polymer. Both eqs. (18) and (19) produced results that are in satisfactory agreement with those mentioned by previous workers:[12] [0.05 − 1.71 × $10^{-5}$ cm$^3$ (STP)/cm$^3$ Pa)] (±8–12% deviation).

**Theoretical Calculation of Diffusivity in Polyamides**

Diffusivity is described by the same general exponential equation as is solubility. Therefore, the same

**Table III   Effect of Draw Ratio (0, 1, 3, and 5) on the Activation Energies of Diffusion ($E_D$) and Permeation ($E_p$) (Experimental and Calculated Values) of $N_2$ and $O_2$ Gas in Polyamide Films OL/LL (0/100, 50/50, and 100/0 mol/mol) at 25 and 60°C**

| OL/LL (mol/mol) | Draw Ratio | $E_p$ (kJ/mol) Gas | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $N_2$ | | | | $O_2$ | | | |
| | | Temperature | | | | | | | |
| | | 25°C | | 60°C | | 25°C | | 60°C | |
| | | Expt | Calcd[a] | Expt | Calcd[a] | Expt | Calcd[a] | Expt | Calcd[a] |
| 0/100 | 0 | 40.2 ± 3.2 | 36.3 | 15.2 ± 1.4 | 12.8 | 30.3 ± 2.7 | 25.3 | 13.4 ± 1.2 | 11.3 |
| | 1 | 40.9 ± 3.4 | 37.5 | 15.5 ± 1.3 | 13.4 | 31.4 ± 2.8 | 26.7 | 13.9 ± 1.2 | 11.6 |
| | 3 | 42.0 ± 3.5 | 39.4 | 16.9 ± 1.5 | 15.1 | 32.1 ± 2.9 | 27.9 | 14.2 ± 1.3 | 12.4 |
| | 5 | 43.2 ± 4.1 | 41.2 | 17.8 ± 1.4 | 16.3 | 33.0 ± 3.0 | 29.8 | 13.2 ± 1.4 | 12.6 |
| 50/50 | 0 | 35.6 ± 2.9 | 32.1 | 14.1 ± 1.3 | 12.1 | 33.4 ± 3.1 | 30.1 | 12.6 ± 1.1 | 10.0 |
| | 1 | 36.5 ± 2.8 | 33.4 | 15.3 ± 1.4 | 13.2 | 34.3 ± 3.2 | 31.5 | 12.8 ± 1.0 | 10.8 |
| | 3 | 37.1 ± 2.9 | 35.1 | 16.7 ± 1.5 | 14.1 | 35.2 ± 3.3 | 32.3 | 14.7 ± 1.2 | 11.5 |
| | 5 | 37.9 ± 3.0 | 35.7 | 16.9 ± 1.5 | 15.2 | 36.2 ± 3.2 | 33.5 | 14.8 ± 1.3 | 11.7 |
| 100/0 | 0 | 42.9 ± 3.8 | 39.2 | 16.3 ± 1.5 | 13.9 | 42.9 ± 3.9 | 39.8 | 17.9 ± 1.4 | 14.2 |
| | 1 | 43.6 ± 3.9 | 41.0 | 17.5 ± 1.6 | 14.5 | 43.6 ± 4.0 | 40.1 | 18.3 ± 1.5 | 14.9 |
| | 3 | 44.5 ± 4.1 | 42.2 | 17.9 ± 1.6 | 15.2 | 44.1 ± 4.1 | 41.4 | 18.8 ± 1.4 | 15.6 |
| | 5 | 45.2 ± 4.2 | 43.4 | 20.8 ± 1.9 | 17.6 | 45.2 ± 4.1 | 42.3 | 19.0 ± 1.6 | 16.9 |

[a] According to Van Krevelen.[41]

procedure should be followed for the calculation of diffusivity values and their activation energies.

The logarithmic expression of the Arrhenius eq. (20) governing the diffusion process is

$$D = D_0 \exp(-E_D/RT) \quad (20)$$

$$\log D = \log D_0 - E_D/RT \quad (21)$$

$$\log D(T) = \log D_0 - 435/T \cdot 10^{-3} E_D/R \quad (22)$$

In the case of semicrystalline and glassy amorphous, the following three equations are derived, respectively:

$$D = D_a(1 - X_c) \quad (23)$$

For glassy amorphous polymers:

$$\log D_0 = 10^{-3} \cdot E_D/R - 5.0 \pm 0.8 \quad (24)$$

$$\log D(T) = \log D_0 - 435/T \cdot 10^{-3} \cdot E_D/R$$

$$= -4.0 - E_D/R[0.46 \cdot 10^{-3}$$

$$+ 0.435(1/T - 1/298)] \quad (25)$$

The theoretically determined values are in agreement with the experimental ones (Table V and Figs. 1-5) although only the simplest case of ideal permeation was considered, i.e., Henry's law for sorption and Fick's first law for diffusion. Only the "permanent gases" show this ideal behavior, and in the case of polyamides, it can be assumed that no polymer-dependent interaction and no specific interaction between the penetrant molecules takes place.

**Theoretical Calculation of Permeability in Copolyamides**

The theoretical calculation of gas permeability in copolyamides can be accomplished according to two methods: First, similarly to the calculations of solubility and diffusivity and in accordance with eqs.
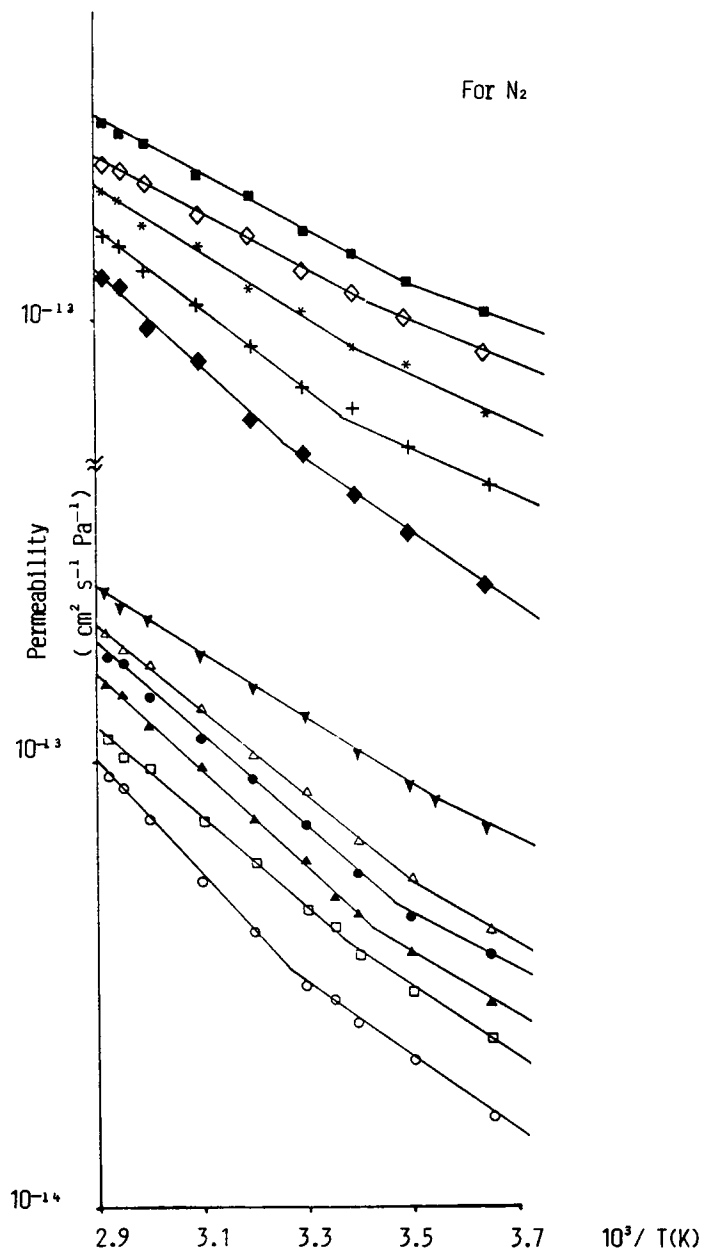
**Figure 15** Effect of conditioning (relative humidity 97%) on permeability of $N_2$ gas in copolyamide films OL/LL (0/100-100/0 mol/mol) vs. the inverse temperature $[1/T\ (\text{K})]$. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

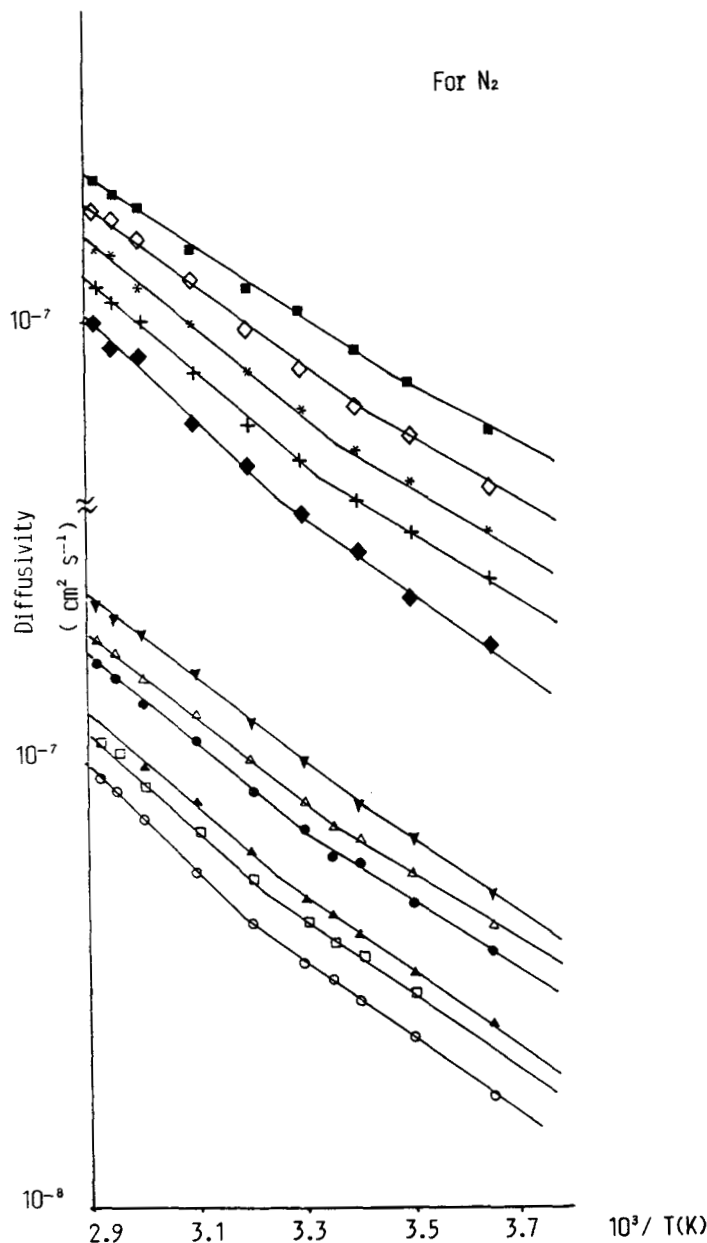(5) and (20), the logarithmic expressions of the Arrhenius equations for the permeability for glassy polymers are

$$\log P_0 = -11.25 + 10^{-3}E_p/R \pm 0.75 \quad (26)$$

$$\log P(298) = -11.25 - 0.46 \cdot 10^{-3}E_p/R \quad (27)$$

and for semicrystalline polymers,

$$P_{sc} = S_{sc}D_{sc}(1 - x_c)^2 = P_a(1 - x_c)^2 \quad (28)$$

$$\log P(T) = -11.25 - E_p/R[\,0.46 \cdot 10^{-3}$$
$$+ 0.435(1/T - 1/298)\,] \quad (29)$$

**Figure 16** Effect of conditioning (relative humidity 97%) on diffusivity of $N_2$ gas in copolyamide films OL/LL (0/100–100/0 mol/mol) vs. the inverse temperature $[1/T(K)]$. Annotation of curves according to copolyamide composition (OL/LL) as in Figure 1.

$$P_{sc} = (1 - x_c)^2 \{ -11.25 - E_p/R[0.46 \cdot 10^{-3}$$
$$+ 0.435(1/T - 1/298)] \} \quad (30)$$

The second method used for testing both our experimental results and the calculated ones on gas permeability of the copolyamides depended on an additive molar function introduced quite recently,[42] under the name permachor ($\pi$). The molar permachor ($\pi$) is defined as follows:

$$N \times \pi = \Pi = \sum_i (N_i \pi_i) \quad (31)$$

where $N$ = number of characteristic groups per structural unit and $i$ = increment of the group $i$.

The numerical value of $\pi$ being known, the permeability at room temperature can be estimated from the equation

$$P(298) = P^*(298) \exp(-S\pi) \quad (32)$$

**Table IV  Effect of Conditioning (RH 97%) on Activation Energy of Diffusion ($E_D$) and Permeation ($E_p$) of $N_2$ Gas in Polyamide Films OL/LL (0/100–100/0 mol/mol) at 25 and 60°C**

| OL/LL (mol/mol) | $E_D$ (kJ/mol) | | | | $E_p$ (kJ/mol) | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Temperature | | | | | | | |
| | 25°C | | 60°C | | 25°C | | 60°C | |
| | Calcd[a] | Expt | Calcd[a] | Expt | Calcd[a] | Expt | Calcd[a] | Expt |
| 0/100 | 37.8 | 41.4 ± 3.2 | 19.3 | 22.4 ± 1.7 | 30.3 | 35.7 ± 2.4 | 15.7 | 19.2 ± 1.7 |
| 5/95 | 36.1 | 38.3 ± 3.0 | 16.7 | 19.4 ± 1.9 | 29.4 | 32.4 ± 2.3 | 15.1 | 10.0 ± 1.8 |
| 10/90 | 34.9 | 37.1 ± 3.1 | 15.9 | 20.6 ± 1.9 | 26.5 | 31.2 ± 3.0 | 14.4 | 18.2 ± 1.6 |
| 20/80 | 33.1 | 35.2 ± 2.8 | 14.7 | 18.8 ± 1.6 | 24.9 | 30.0 ± 2.9 | 13.9 | 18.1 ± 1.5 |
| 40/60 | 32.7 | 33.6 ± 2.7 | 14.3 | 18.3 ± 1.6 | 23.4 | 28.3 ± 2.7 | 13.7 | 18.0 ± 1.5 |
| 50/50 | 27.8 | 30.4 ± 2.7 | 12.2 | 14.1 ± 1.2 | 22.1 | 25.1 ± 2.2 | 10.3 | 12.5 ± 1.1 |
| 60/40 | 35.4 | 38.0 ± 2.8 | 15.8 | 18.1 ± 1.6 | 28.5 | 31.5 ± 2.8 | 12.5 | 16.9 ± 1.3 |
| 80/20 | 32.7 | 35.2 ± 2.9 | 16.2 | 16.7 ± 1.5 | 27.3 | 30.3 ± 2.7 | 16.3 | 19.9 ± 1.4 |
| 90/10 | 29.3 | 32.2 ± 2.7 | 17.1 | 13.9 ± 1.4 | 23.4 | 27.2 ± 2.6 | 15.7 | 18.8 ± 1.5 |
| 95/5 | 25.8 | 29.9 ± 1.9 | 17.9 | 12.2 ± 1.2 | 21.5 | 25.7 ± 2.3 | 15.4 | 17.3 ± 1.5 |
| 100/0 | 26.3 | 28.5 ± 2.0 | 18.6 | 12.0 ± 1.0 | 22.1 | 26.5 ± 2.4 | 11.2 | 15.3 ± 1.3 |

[a] According to Van Krevelen.[41]

where $P(298)$ is the permeability of an arbitrary simple gas in an arbitrary polymer, $P^*(298)$ = permeability of the same gas in a chosen standard polymer (i.e., natural rubber)[42] and $S$ = a scaling factor. The logarithmic expression of (32) by substituting $\log P^*(298) = -12$ and $S = 0.122$ gives the following equation:

$$\log P(298) = -12 - 0.53\pi \qquad (33)$$

The derived eq. (33) is applicable only to amorphous polymers. In the case of semicrystalline polymers, the following expression is valid:

$$\pi_{s.c.} = \pi_a - 18 \ln a = \pi_a - 41.5 \log(1 - x_c) \qquad (34)$$

where $a$ = amorphous volume fraction and $x_c$ = crystallinity.

The theoretical calculations with the aid of eqs. (30) and (34) fall in agreement between them (±5–10% deviation) (Table VI) and also with the experimental values (Figs. 6–10 and Table VI), as was the case in solubility and diffusivity. Both equations for the glassy state (below the $T_g$) and for the semicrystalline state (above the $T_g$) proved to be applicable to OL/LL copolyamides and they also provided an indirect measurement (confirmation) of the glass transition temperature (Table II).

## Current Trends in Food Packaging and Correlation with the Present Study

Although for a long time the amorphous regions in a polyamide used to be considered responsible for the permeability of gases in polyamide films,[36,41] this assertion has been almost superseded nowadays by the conception that amorphous copolyamides, synthesized under certain circumstances, can act as very efficient gas barriers. Unfortunately, most of the work in this field is either patented[43–48] or there are only articles, not scientific, in journals of general interest.[49–53] Therefore, the synthesis of amorphous polyamides possessing very good gas barrier properties tends to become of major importance in the food-packaging industry.

## CONCLUSIONS

Although quite recently a number of publications claim that there is no real relationship as such between the crystallinity of polymer and the gas permeability (amorphous films based on aromatic polyamides proved to be extremely good barriers), in this particular study, it was shown that the low % crystallinity is of crucial importance for high permeability values and vice versa. This assertion was

**Table V  Activation Energy (x ± SD) of Diffusion ($E_D$, kJ/mol) of $N_2$, $CO_2$, $O_2$, $H_2$, and He Gases with the Molar Composition of Copolyamides (OL/LL) at 25 and 60°C**

$E_D$ (kJ/mol)

| OL/LL (mol/mol) | $N_2$ 25°C Calcd[a] | $N_2$ 25°C Expt | $N_2$ 60°C Calcd[a] | $N_2$ 60°C Expt | $CO_2$ 25°C Calcd[a] | $CO_2$ 25°C Expt | $CO_2$ 60°C Calcd[a] | $CO_2$ 60°C Expt | $O_2$ 25°C Calcd[a] | $O_2$ 25°C Expt | $O_2$ 60°C Calcd[a] | $O_2$ 60°C Expt | $H_2$ 25°C Calcd[a] | $H_2$ 25°C Expt | $H_2$ 60°C Calcd[a] | $H_2$ 60°C Expt | He 25°C Calcd[a] | He 25°C Expt | He 60°C Calcd[a] | He 60°C Expt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0/100 | 59.4 | 66.2 ± 5.1 | 24.3 | 30.8 ± 1.1 | 59.9 | 66.2 ± 6.2 | 23.7 | 29.8 ± 2.3 | 45.3 | 51.7 ± 5.0 | 22.4 | 27.5 ± 2.3 | 28.9 | 35.3 ± 3.2 | 21.3 | 27.4 ± 2.1 | 19.2 | 27.6 ± 2.4 | 18.5 | 20.2 ± 1.7 |
| 5/95 | 58.2 | 65.2 ± 5.3 | 22.3 | 28.1 ± 1.9 | 58.1 | 65.5 ± 6.3 | 22.4 | 32.1 ± 3.0 | 43.8 | 50.1 ± 4.6 | 21.0 | 26.3 ± 2.5 | 27.2 | 32.5 ± 3.0 | 19.5 | 24.3 ± 1.3 | 18.0 | 26.1 ± 2.5 | 16.5 | 19.0 ± 1.6 |
| 10/90 | 57.0 | 64.6 ± 5.2 | 20.2 | 25.7 ± 2.2 | 57.0 | 62.8 ± 6.1 | 21.2 | 27.2 ± 2.6 | 42.0 | 48.5 ± 4.5 | 19.7 | 24.7 ± 2.0 | 26.0 | 31.4 ± 3.0 | 17.8 | 22.9 ± 1.9 | 16.5 | 24.7 ± 2.2 | 14.7 | 18.8 ± 1.5 |
| 20/80 | 55.3 | 63.8 ± 5.0 | 18.8 | 23.3 ± 1.9 | 55.6 | 61.1 ± 5.8 | 20.0 | 26.6 ± 2.4 | 40.7 | 47.4 ± 4.3 | 19.8 | 24.9 ± 2.1 | 25.3 | 30.0 ± 2.9 | 16.5 | 22.0 ± 1.8 | 15.3 | 22.4 ± 2.0 | 13.4 | 18.6 ± 1.8 |
| 40/60 | 53.9 | 62.6 ± 4.9 | 16.9 | 22.4 ± 1.3 | 54.7 | 59.2 ± 5.7 | 18.7 | 24.1 ± 2.3 | 38.9 | 45.4 ± 4.2 | 18.3 | 23.5 ± 1.9 | 24.6 | 28.7 ± 2.6 | 16.0 | 22.3 ± 1.6 | 14.1 | 21.1 ± 1.9 | 11.5 | 16.4 ± 1.8 |
| 50/50 | 54.6 | 63.0 ± 5.4 | 16.8 | 22.5 ± 2.7 | 53.5 | 58.7 ± 5.6 | 18.2 | 27.0 ± 2.1 | 37.9 | 44.7 ± 4.3 | 18.0 | 23.5 ± 1.8 | 23.2 | 27.3 ± 2.4 | 15.1 | 20.8 ± 1.5 | 13.2 | 19.5 ± 1.7 | 10.3 | 13.6 ± 1.2 |
| 60/40 | 55.9 | 63.8 ± 5.2 | 17.6 | 23.7 ± 2.6 | 54.6 | 59.2 ± 5.7 | 18.5 | 23.4 ± 2.0 | 35.0 | 42.8 ± 4.0 | 16.3 | 17.4 ± 1.6 | 24.4 | 28.4 ± 2.5 | 15.7 | 21.4 ± 1.7 | 15.1 | 21.4 ± 1.6 | 10.9 | 14.9 ± 1.3 |
| 80/20 | 57.2 | 64.5 ± 4.3 | 18.9 | 25.7 ± 2.4 | 57.3 | 61.1 ± 5.6 | 18.7 | 34.1 ± 2.1 | 37.0 | 45.2 ± 4.2 | 17.5 | 20.4 ± 1.5 | 25.9 | 31.4 ± 2.3 | 16.2 | 22.5 ± 1.5 | 16.5 | 23.0 ± 1.7 | 12.3 | 17.0 ± 1.4 |
| 90/10 | 59.3 | 66.2 ± 6.0 | 20.3 | 27.3 ± 2.5 | 58.5 | 62.8 ± 6.0 | 18.9 | 23.8 ± 2.3 | 38.4 | 47.4 ± 4.3 | 18.7 | 24.2 ± 1.4 | 27.1 | 33.6 ± 3.1 | 17.4 | 25.1 ± 1.9 | 17.2 | 23.9 ± 1.8 | 14.8 | 17.8 ± 1.5 |
| 95/5 | 59.9 | 66.6 ± 5.5 | 21.4 | 26.9 ± 2.4 | 59.6 | 65.5 ± 6.1 | 19.8 | 25.2 ± 2.1 | 40.3 | 49.7 ± 4.4 | 19.5 | 24.8 ± 1.9 | 29.5 | 35.5 ± 3.2 | 19.3 | 25.2 ± 1.9 | 18.4 | 24.9 ± 1.9 | 16.3 | 19.4 ± 1.6 |
| 100/0 | 61.5 | 67.4 ± 5.2 | 22.6 | 27.8 ± 2.5 | 60.3 | 66.2 ± 6.2 | 31.4 | 27.3 ± 3.4 | 42.5 | 51.1 ± 4.6 | 19.7 | 25.0 ± 2.1 | 31.3 | 36.2 ± 3.3 | 20.9 | 25.9 ± 2.0 | 19.0 | 25.9 ± 2.1 | 17.9 | 21.6 ± 1.9 |

[a] According to eqs. (24) and (25).

## Table VI Activation Energy of Permeation ($E_p$, kJ/mol) of $N_2$, $O_2$, $CO_2$, and $H_2$ with the Molar Composition of Copolyamides (OL/LL) at 25 and 60°C

$E_p$ (kJ/mol)

| OL/LL (mol/mol) | $N_2$ 25°C Calcd[a] | $N_2$ 25°C Expt | $N_2$ 60°C Calcd[a] | $N_2$ 60°C Expt | $CO_2$ 25°C Calcd[a] | $CO_2$ 25°C Expt | $CO_2$ 60°C Calcd[a] | $CO_2$ 60°C Expt | $O_2$ 25°C Calcd[a] | $O_2$ 25°C Expt | $O_2$ 60°C Calcd[a] | $O_2$ 60°C Expt | $H_2$ 25°C Calcd[a] | $H_2$ 25°C Expt | $H_2$ 60°C Calcd[a] | $H_2$ 60°C Expt | He 25°C Calcd[a] | He 25°C Expt | He 60°C Calcd[a] | He 60°C Expt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0/100 | 35.4 | 40.2 ±3.8 | 19.9 | 24.8 ±2.0 | 16.2 | 18.1 ±1.7 | 9.8 | 12.9 ±1.1 | 28.2 | 32.9 ±3.0 | 12.3 | 14.9 ±1.3 | 17.9 | 22.1 ±2.1 | 9.3 | 12.0 ±1.8 | 17.0 | 19.2 ±1.8 | 8.3 | 10.1 ±1.0 |
| 5/95 | 32.1 | 38.1 ±3.6 | 17.4 | 20.8 ±1.8 | 14.1 | 16.1 ±1.5 | 7.9 | 10.9 ±0.9 | 26.1 | 31.7 ±2.9 | 10.4 | 13.3 ±1.2 | 15.6 | 20.8 ±2.0 | 8.0 | 10.6 ±1.0 | 13.8 | 16.4 ±1.5 | 7.2 | 7.3 ±0.6 |
| 10/90 | 30.0 | 36.2 ±3.3 | 16.2 | 20.2 ±1.9 | 11.9 | 14.6 ±1.3 | 6.8 | 10.6 ±0.8 | 23.8 | 29.9 ±2.9 | 8.9 | 13.1 ±1.1 | 14.9 | 19.0 ±1.8 | 7.2 | 9.9 ±0.8 | 11.2 | 14.9 ±1.3 | 6.4 | 6.2 ±0.5 |
| 20/80 | 28.2 | 35.4 ±3.2 | 15.1 | 20.5 ±1.8 | 10.0 | 12.3 ±1.1 | 5.9 | 10.2 ±0.8 | 20.7 | 28.0 ±2.7 | 8.2 | 12.0 ±1.1 | 13.8 | 17.6 ±1.6 | 6.4 | 7.9 ±0.6 | 10.1 | 13.9 ±1.1 | 5.5 | 5.7 ±0.4 |
| 40/60 | 26.4 | 33.6 ±3.1 | 13.9 | 17.3 ±1.6 | 8.3 | 10.4 ±0.9 | 5.0 | 10.0 ±0.9 | 18.6 | 26.2 ±2.5 | 7.3 | 11.3 ±1.0 | 12.2 | 16.2 ±1.5 | 5.1 | 5.5 ±0.4 | 9.6 | 11.5 ±1.0 | 4.9 | 6.2 ±0.6 |
| 50/50 | 26.9 | 33.8 ±3.0 | 14.6 | 17.5 ±1.7 | 6.9 | 8.3 ±0.7 | 4.7 | 9.8 ±0.8 | 17.2 | 24.5 ±2.3 | 8.0 | 13.8 ±1.1 | 11.0 | 14.8 ±1.3 | 7.2 | 11.5 ±0.9 | 8.2 | 10.0 ±0.9 | 4.7 | 8.8 ±0.7 |
| 60/40 | 27.9 | 35.7 ±3.3 | 15.4 | 17.7 ±1.5 | 9.3 | 10.2 ±1.1 | 5.3 | 8.0 ±0.6 | 18.3 | 25.1 ±2.4 | 9.1 | 14.5 ±1.2 | 12.4 | 16.4 ±1.5 | 8.5 | 12.7 ±1.1 | 9.4 | 11.9 ±1.1 | 5.8 | 7.6 ±0.6 |
| 80/20 | 29.6 | 38.2 ±3.6 | 17.6 | 16.3 ±1.4 | 10.3 | 12.0 ±1.0 | 6.5 | 9.4 ±0.7 | 19.3 | 26.9 ±2.5 | 10.2 | 14.0 ±1.3 | 13.8 | 18.7 ±1.6 | 9.7 | 15.4 ±1.3 | 10.1 | 12.8 ±1.1 | 6.8 | 5.9 ±0.5 |
| 90/10 | 31.3 | 39.7 ±3.8 | 18.5 | 19.8 ±1.8 | 11.2 | 13.2 ±1.1 | 7.4 | 11.3 ±0.9 | 20.5 | 27.0 ±2.6 | 10.9 | 14.4 ±1.2 | 15.9 | 21.4 ±1.9 | 10.8 | 18.2 ±1.5 | 11.7 | 14.2 ±1.2 | 7.3 | 6.5 ±0.6 |
| 95/5 | 34.5 | 42.3 ±4.0 | 19.7 | 19.9 ±1.8 | 12.4 | 15.0 ±1.4 | 8.6 | 11.6 ±1.0 | 22.4 | 28.5 ±2.5 | 11.9 | 17.5 ±1.5 | 18.0 | 22.3 ±1.8 | 13.2 | 18.5 ±1.6 | 12.9 | 15.3 ±1.3 | 8.6 | 7.9 ±0.7 |
| 100/0 | 37.6 | 42.9 ±4.0 | 20.8 | 20.9 ±1.3 | 14.5 | 17.1 ±1.5 | 9.3 | 11.4 ±1.1 | 25.2 | 29.6 ±2.6 | 13.4 | 18.7 ±1.6 | 20.8 | 25.5 ±2.1 | 15.0 | 21.1 ±1.9 | 14.5 | 17.2 ±1.4 | 9.7 | 12.1 ±1.1 |

[a] The average value calculated according to two methods: (a) application of eqs. (33) and (34) and (b) application of eqs. (27) and (30).
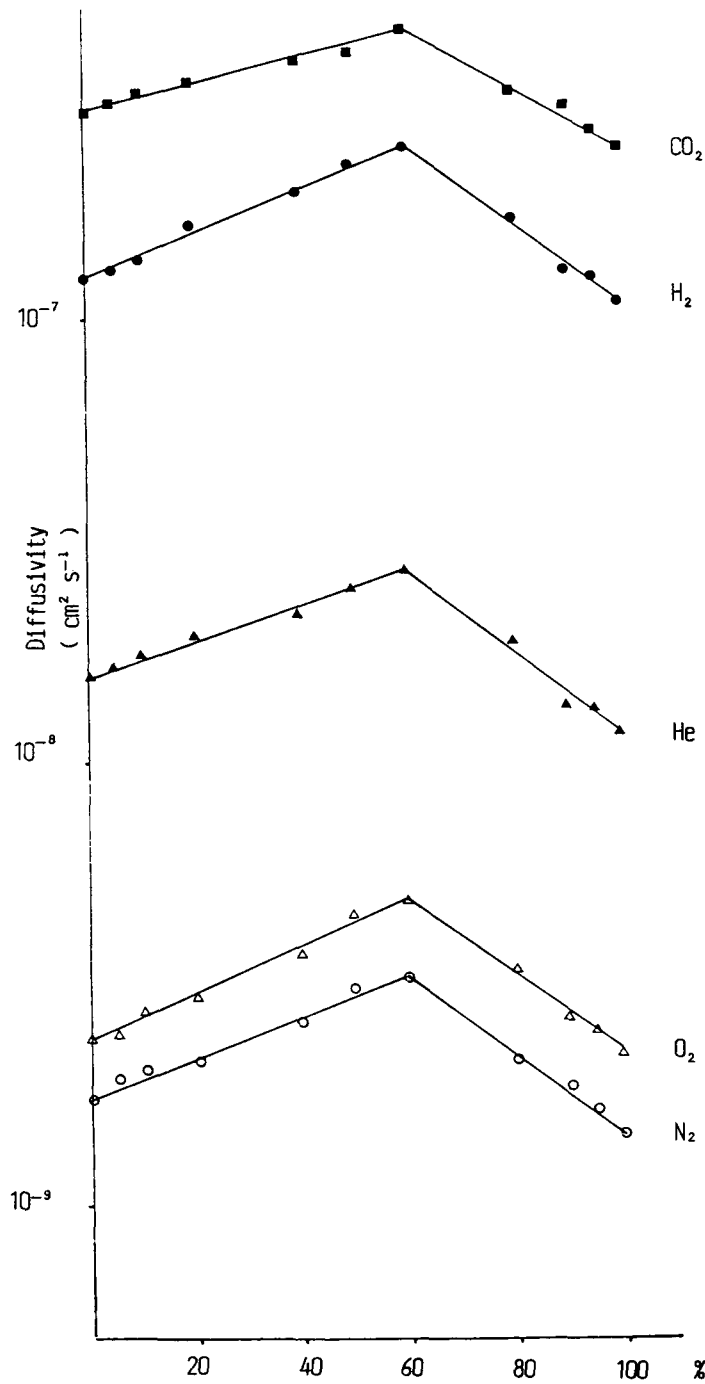
**Figure 17**   Diffusivity of $N_2$, $O_2$, He, $H_2$, and $CO_2$ gas vs. the composition of copolyamide
films OL/LL (0/100–100/0 mol/mol) at 298 K.

further confirmed by the permeability measurements carried out on uniaxially drawn copolyamide films (the higher crystallinity, the lower the permeability). An increase in the moisture content of the film proved to enhance considerably the permeability.

Finally, the abrupt change recorded in the slope of the permeability values vs. the inverse time gave values that were in agreement with those determined by measurements of the thermal properties of the copolyamides.
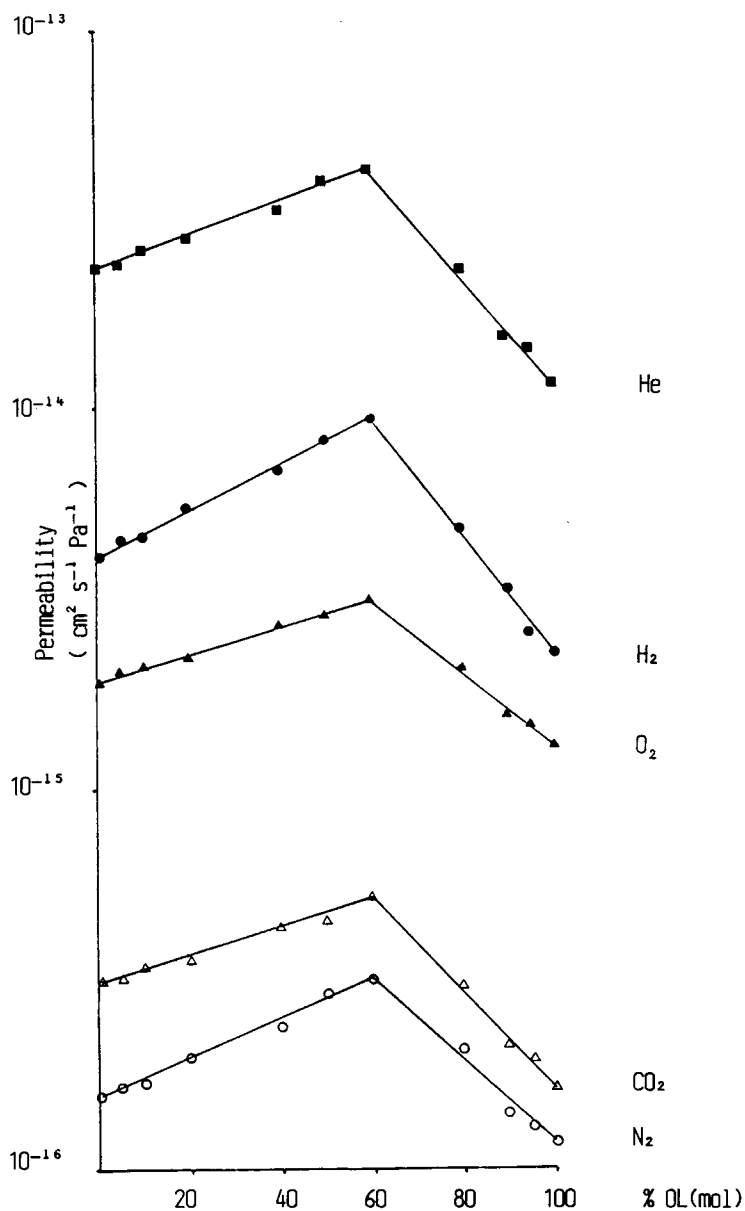
**Figure 18**   Diffusivity of $N_2$, $O_2$, He, $H_2$, and $CO_2$, gas vs. the composition of copolyamide films OL/LL (0/100–100/0 mol/mol) at 298 K.

## REFERENCES

1. A. H. Kehayoglou and I. Arvanitoyannis, *Eur. Polym. J.*, **26**, 261 (1990).
2. I. Arvanitoyannis and A. H. Kehayoglou, *Angew. Makromol. Chem.*, to appear.
3. A. H. Kehayoglou and I. Arvanitoyannis, *Polymer*, to appear.
4. I. Arvanitoyannis, A. H. Kehayoglou, and J. M. V. Blanshard, *Polym. Int.*, **29**, 107 (1992).
5. I. Arvanitoyannis and J. M. V. Blanshard, *Polym. Int.*, to appear.
6. I. Arvanitoyannis, J. M. V. Blanshard, and E. Psomiadou, to appear.
7. G. J. Amerongen, *J. Polym. Sci.*, **2**, 381 (1947).
8. G. L. Amerongen, *J. Polym. Sci.*, **5**, 307 (1949).
9. V. L. Simril and A. Herschberger, *Mod. Plast.*, **27**, 95 (1950).
10. R. Waack, N. H. Alex, H. L. Frisch, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **47**, 2524 (1955).
11. V. Stannett and M. Szwarc, *J. Polym. Sci.*, **16**, 9 (1955).
12. W. Heilman, V. Tammela, J. A. Meyer, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **48**, 821 (1956).

13. R. W. Myers, V. Tammela, V. Stannett, and M. Szwarc, *Mod. Plast. (Techn. Sect.)*, **37**, 139 (1960).

14. Von H. Braunisch and H. Lenhart, *Koll. Z.*, **177**, 24 (1961).

15. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **21**, 413 (1961).

16. A. L. Andrady and M. D. Sefcif, *J. Polym. Sci.*, **22**, 237 (1984).

17. L. H. Wang and R. S. Porter, *J. Polym. Sci.*, **22**, 1645 (1984).

18. I. Arvanitoyannis, R. Heath, and I. Embeoglou, *Polym. Int.*, **29**, 165 (1992).

19. R. M. Barrer, I. A. Barrie, and P. S.-L. Wong, *Polymer*, **9**, 609 (1968).

20. R. J. Pace and A. Datyner, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 437 (1979).

21. A. L. Andrady, M. A. Llorente, and J. E. Mark, *J. Chem. Phys.*, **72**, 2282 (1980).

22. A. L. Andrady, M. A. Llorente, and J. R. Mark, *J. Chem. Phys.*, **73**, 1439 (1980).

23. M. A. Llorente and J. E. Mark, *Macromolecules*, **13**, 681 (1980).

24. M. A. Llorente, A. L. Andrady, and J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 2263 (1980).

25. A. L. Andrady and M. D. Cefcik, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 2453 (1983).

26. S. W. Lasoski, Jr. and W. H. Cobbs, *J. Polym. Sci.*, **36**, 21 (1959).

27. W. J. Koros and D. R. Paul, *J. Polym. Sci. A-2*, **16**, 2171 (1978).

28. N. Kurosa, *Sen'l Gakkaishi*, **35**, 413 (1979).

29. P. D. Grisword, A. E. Zachariades, and R. S. Porter, in *Flow Induced Crystallization in Polymer Systems*, R. L. Miller, Ed., Gordon and Breach, New York, 1979, pp. 205–211.

30. A. E. Zachariades, E. S. Sherman, and R. S. Porter, *J. Appl. Polym. Sci.*, **24**, 2137 (1979).

31. A. E. Zachariades, E. S. Sherman, and R. S. Porter, *J. Appl. Polym. Lett. Ed.*, **17**, 255 (1979).

32. C. M. C. Kaye and T. H. Layd, *Tables of Physical and Chemical Constants*, 14th ed., Longman, London, 1973.

33. American Standard Testing Method, *Annual Book of A.S.T.M.*, 1987, Vol. 0801, D4230.

34. P. H. Hermans, D. Heinkens, and A. Weidinger, *J. Polym. Sci.*, **35**, 145 (1959).

35. American Standard Test Methods (A.S.T.M.), *Gas Transmission Rate of Plastic Film and Sheeting D1434-66*, 1966.

36. P. Meares, *J. Am. Chem. Soc.*, **76**, 3415 (1954).

37. A. S. Michaels, W. R. Vieth, and H. J. Bixler, *J. Appl. Polym. Sci.*, **3**, 2735 (1964).

38. A. S. Michaels and R. E. Parker, Jr., *J. Polym. Sci.*, **41**, 53 (1959).

39. H. Yasuda and A. Peterlin, *J. Appl. Polym. Sci.*, **18**, 531 (1974).

40. J. H. Hildebrand, *Solubility*, Reinhold, New York, 1936, pp. 30, 73.

41. D. W. Van Krevelen, *Properties of Plastics*, Elsevier, Amsterdam, 1990, pp. 189–225, 535–562.

42. M. Salame, *Polym. Eng. Sci.*, **26**, 1543 (1986).

43. H. Takida and T. Iwanami, Ger. Pat. 3,923,704 (1990) (to Nippon Synthetic Chemical Industry Ltd.; *Chem. Abstr.*, **113**(2), 7537 (1990).

44. R. B. Barbee and L. A. Minnick, U.S. Pat. 4,855,397 (1989) (to Eastman Kodak Co.); *Chem. Abstr.*, **112**(10), 78234e (1989).

45. N. Hisazumi, R. Uehara, H. Ohba, and K. Hirose, Eur. Pat. 336,680 (1989) (to Kurcha Chemical Industry Co., Ltd.); *Chem. Abstr.*, **112**(2) 8359a (1989).

46. M. Fant, S. E. Ennis, and P. Gaultam Shah, Eur. Pat. 236,099 (1987) (to W. R. Grace and Co.); *Chem. Abstr.*, **108**(18), 151754y (1987).

47. T. Negi, S. Hirofuji, N. Tanaka, and S. Kawai, Eur. Pat. 104,395 (1987) (to Curaray Co. Ltd.); *Chem. Abstr.*, **108**(8), 57525c (1987).

48. J. Davidovits and M. Lefebre, Fr. Pat. 2,116,306 (1972) (to Omnium de Prospective Industrielle); *Chem. Abstr.*, **78**(12), 73244c (1972).

49. Mitusbishi Chemical Industries Ltd., *Plast. Ind. News (Jpn.)*, **32**(4) 50 (1986).

50. E. I. Du Pont de Nemours & Co. Inc., *Packaging (USA)*, **31**(3), 72 (1986).

51. A. Kazia, *J. Plast. Film Sheet*, **1**(4), 285 (1985).

52. E. I. Du Pont de Nemours & Co. Inc., *Plast. World*, **43**(13), 66 (1985).

53. K. Bertrand, *Packing (USA)*, **31**(1), 24 (1986).